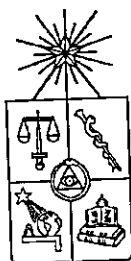


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**INDICES DE REACTIVIDAD Y
SELECTIVIDAD PARA CARACTERIZAR
MOLECULAS, CLUSTERS Y REACCIONES
QUIMICAS**

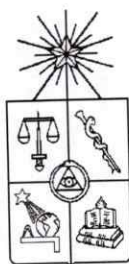
PABLO CESAR JAQUE OLMEDO

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INDICES DE REACTIVIDAD Y SELECTIVIDAD PARA
CARACTERIZAR MOLECULAS, CLUSTERS Y
REACCIONES QUIMICAS

por

Pablo César Jaque Olmedo

Tesis

entregada a la

Universidad de Chile

en cumplimiento parcial de los requisitos

para optar al grado de

Doctor en Ciencias con Mención en Química

NOVIEMBRE 2003



Director de Tesis: Dr. Alejandro Toro Labbé

UNIVERSIDAD DE CHILE
FACULTAD DE CIENCIAS



INFORME DE APROBACION
TESIS DE DOCTORADO

Se informa a la Escuela de Postgrado de la Facultad de Ciencias que la Tesis de Doctorado presentada por el Candidato:

PABLO CESAR JAQUE OLMEDO

ha sido aprobada por la comisión de evaluación de la Tesis como requisito para optar al grado de Doctor en Ciencias con Mención en Química, en el exámen de defensa de Tesis rendido el día 21 de Noviembre de 2003.

Director de Tesis:

Prof. Dr. Alejandro Toro Labbé

A handwritten signature in blue ink, appearing to be "ATL", written over a horizontal line.

Comisión Evaluadora de Tesis:

Prof. Dr. Paulo Araya F.

A handwritten signature in blue ink, appearing to be "P. Araya", written over a horizontal line.

Prof. Dr. Marcelo Campos V.

A handwritten signature in blue ink, appearing to be "M. Campos", written over a horizontal line.

Prof. Dr. Joaquín Cortés G.

A handwritten signature in blue ink, appearing to be "J. Cortés", written over a horizontal line.

Prof. Dr. Miguel Kiwi T.

A handwritten signature in blue ink, appearing to be "M. Kiwi", written over a horizontal line.

Prof. Dr. Octavio Vásquez A.

A handwritten signature in blue ink, appearing to be "O. Vásquez", written over a horizontal line.

A mis Padres
Jorge y María

“La mayoría de las ideas fundamentales de la ciencia son esencialmente sencillas y, por regla general pueden ser expresadas en un lenguaje comprensible para todos.”

Albert Einstein (1879-1955)

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Abstract

Potential energy surface is a key concept in the application of electronic structure methods to the study of molecular structure, properties and reactivities, however its determination imply a high computational cost. The aim of this work is to apply the concepts and principles based upon Density Functional Theory to the study of molecules, chemical reactions and copper clusters and to propose theoretical models of chemical reactivity from the calculation of specific portions of the potential energy surface.

It is shown that principles of chemical reactivity and descriptors based on DFT are operative for characterizing and rationalizing the electronic properties of molecular systems and reactions. The conceptual classical model in which a reaction proceeds from one energy minimum to another via an intermediate maximum, together with the Principles of Maximum Hardness and Minimum Polarizability provide the necessary elements to discuss the activation and relaxation processes in terms of the activation chemical potential and chemical hardness.

On the other hand the *Sanderson's* geometric equalization principle for electronegativity has been used to derive expressions for molecular hardness and its derivative, in this context, a new scheme for obtaining molecular properties from the isolated fragments is proposed with results that are in excellent agreement with others addition schemes.

The formation reactions of copper clusters have been studied from the available experimental data of binding energy and DFT-descriptors and very useful relationship between energy and electronic properties are proposed to characterize the growth pattern of copper clusters.

Resumen

El concepto de superficie de energía potencial es clave en la aplicación de métodos de estructura electrónica al estudio de estructuras moleculares, propiedades y reactividades, sin embargo su determinación implica un alto costo computacional. El objetivo de este trabajo es aplicar los conceptos y principios que están basados en la Teoría Funcional de la Densidad al estudio de moléculas, reacciones químicas y clusters de cobre y proponer modelos teóricos de reactividad química a partir del cálculo de porciones específicas de la superficie de energía potencial.

Es mostrado que los principios de reactividad química y descriptores basados sobre la TFD son de utilidad para caracterizar y racionalizar propiedades electrónicas de sistemas moleculares y reacciones químicas. El modelo conceptual clásico que procede a partir de un mínimo de energía a otro via un intermediario cuya energía es máxima junto a los Principios de Máxima Dureza y Mínima Polarizabilidad proveen los elementos necesarios para discutir los procesos de activación y relajación en términos de potencial químico y dureza química de activación.

Por otra parte, el principio del promedio geométrico de la electronegatividad de *Sanderson's* ha sido utilizado como base para derivar expresiones para dureza molecular y su derivada, en este contexto, se ha propuesto un nuevo esquema para obtener propiedades moleculares a partir de fragmentos aislados con resultados que están en excelente acuerdo con otros esquemas de aditividad.

Las reacciones de formación de clusters de cobre han sido estudiadas a partir de datos experimentales de energías de enlace y propiedades electrónicas y descriptores-TFD y se han propuesto relaciones entre energía y propiedades electrónicas que son de gran utilidad para caracterizar patrones de crecimiento de clusters de cobre.

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Capítulo 1

Introducción

Desde un punto de vista computacional, muchos aspectos de la química se reducen básicamente a preguntas cuyas respuestas provienen de la superficie de energía potencial (SEP), en la Figura 1 se presenta un modelo de superficie de energía como una función de la geometría molecular donde se indican algunas propiedades que son de interés para caracterizar diferentes aspectos de los sistemas moleculares, tales como, estabilidad, reactividad, selectividad, canales de reacción, propiedades eléctricas, como también información de tipo espectroscópica [1]. Sin embargo la determinación de la SEP se encuentra limitada por el número de átomos y de grados de libertad que se generan principalmente por el creciente costo computacional. Desde esta perspectiva, la comprensión de la estructura y propiedades electrónicas de sistemas moleculares permiten establecer modelos y mecanismos para representar reacciones químicas en términos de interacciones específicas, a partir de esta aproximación es posible formular modelos teóricos tanto cualitativos como semi-cuantitativos que resultan ser de bastante utilidad en la comprensión y predicción de la reactividad que presentan los sistemas moleculares evitando un estudio detallado de la SEP, o dicho de otra manera considerando solamente porciones específicas de esta.

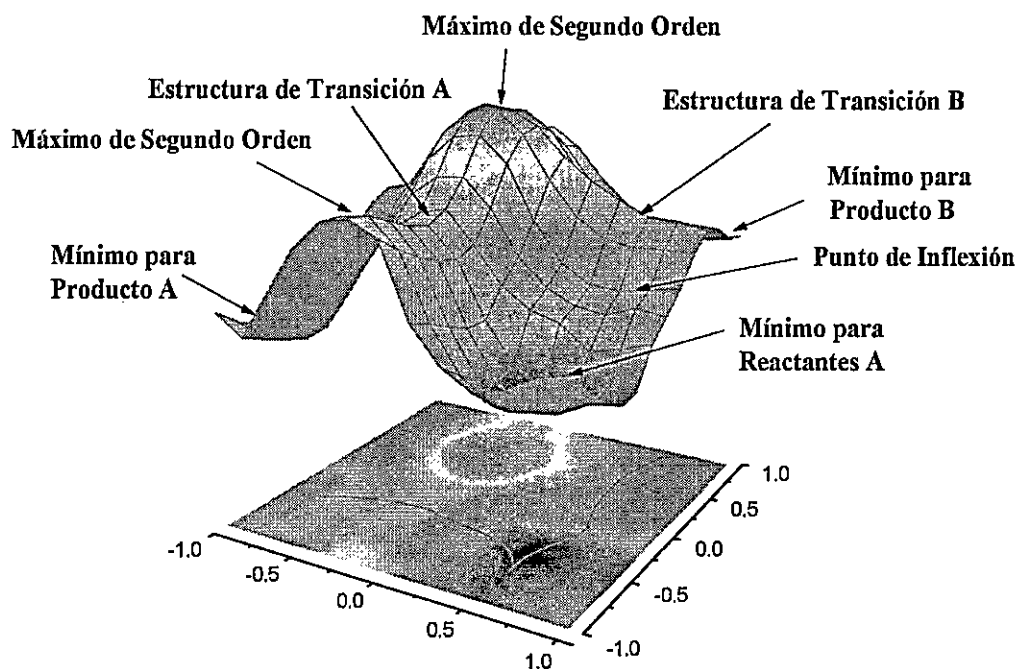


Figura 1.1: Modelo de superficie de energía potencial.

En este contexto general, la Teoría Funcional de la Densidad (TFD) [2–4] en las últimas décadas ha llamado la atención como una aproximación alternativa para la descripción mecano-cuántica de la estructura electrónica como también de la dinámica de átomos, moléculas y sólidos [5–7]. La TFD de *Hohenberg-Kohn-Sham* [3,4] se basa en la idea que la densidad electrónica ($\rho(\vec{r})$) permite la descripción completa del estado fundamental de sistemas químicos. Adicionalmente, esta teoría se ha convertido en un marco teórico útil para el desarrollo de una teoría de reactividad química, a través de la definición de cantidades de carácter global, local y no-local las que son denominadas funciones de respuestas, es decir, respuestas de propiedades de los sistemas químicos, tal como, la energía (E) o la densidad electrónica ($\rho(\vec{r})$), a estímulos externos, como por ejemplo, variaciones en el número de electrones (N) y/o en el potencial debido a los núcleos $v(\vec{r})$, permitiendo describir la química de los sistemas moleculares [2, 8–22]. La TFD ofrece un tremendo soporte conceptual de varios aspectos interpretativos de la química, esta rama de la teoría, que se concentra en la definición de conceptos y principios de relevancia química, es conocida como la TFD *Conceptual* [14, 22–27].

Dentro de este marco teórico, la energía de un sistema de N electrones sujetos a un potencial externo $v(\vec{r})$ es expresada como un funcional único de la densidad electrónica $\rho(\vec{r})$,

$$E[\rho] = \int d\vec{r} v(\vec{r}) \rho(\vec{r}) + F[\rho] \quad (1.1)$$

donde $F[\rho]$ es la funcional universal de la densidad electrónica y contiene las contribuciones de la energía cinética de los electrones ($T[\rho]$) más la de repulsión interelectrónica ($V_{ee}[\rho]$) [2,3]. La energía para un sistema con $v(\vec{r})$ fijo es estacionaria para la densidad real, la cuál se obtiene desde la solución de la ecuación de *Euler-Lagrange*:

$$\mu = \frac{\delta E[\rho]}{\delta \rho(\vec{r})} = v(\vec{r}) + \frac{\delta F[\rho]}{\delta \rho(\vec{r})}, \quad (1.2)$$

donde μ formalmente es un multiplicador de *Lagrange* que proviene de la normalización en TFD

$$\int d\vec{r} \rho(\vec{r}) = N, \quad (1.3)$$

y ha sido identificado con el potencial químico de la nube electrónica. Desde esta representación, la reactividad química se explora a través de una expansión en series de *Taylor* de la energía funcional en el contexto de cuatro representaciones basadas en transformaciones de *Legendre*, donde varias de sus derivadas se asocian a un claro significado químico [2, 27–29]. El siguiente esquema muestra todas las funciones de respuestas hasta segundo orden en el contexto de la representación para la energía de un sistema molecular en un colectivo o ensamble canónico.

$$\begin{array}{ccc}
 & E[N, v(\vec{r})] & \\
 & \swarrow \quad \searrow & \\
 \left(\frac{\partial E}{\partial N} \right)_{v(\vec{r})} = \mu & & \left(\frac{\delta E}{\delta v(\vec{r})} \right)_N = \rho(\vec{r}) \\
 \swarrow \quad \searrow & & \swarrow \quad \searrow \\
 \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(\vec{r})} = \eta & \left(\frac{\partial^2 E}{\partial N \partial v(\vec{r})} \right) = f(\vec{r}) & \left(\frac{\delta^2 E}{\delta v(\vec{r}) \delta v(\vec{r}')} \right)_N = \chi(\vec{r}, \vec{r}').
 \end{array}$$

Las primeras derivadas, definen una propiedad global μ que permite caracterizar a un sistemas como un todo, y una cantidad local $\rho(\vec{r})$ que varía desde un punto a otro en el sistema molecular. Por otra parte, a segundo orden además se define una cantidad de tipo no-local $\chi(\vec{r}, \vec{r}')$ que representa la variación o respuesta de una propiedad local en \vec{r} debido a una perturbación en \vec{r}' [12].

Conceptos y Principios Basados en la TFD.

Potencial Químico Electrónico (μ) y Electronegatividad (χ).

Para un sistema de N -partículas con energía total E y potencial externo $v(\vec{r})$, el potencial químico está definido como [8]:

$$\mu = - \left(\frac{\partial E}{\partial N} \right)_{v(\vec{r})} = -\chi, \quad (1.4)$$

nótese la analogía de esta definición con el potencial químico termodinámico. μ es una propiedad global y puede ser considerada como una medida de la tendencia de escape de los electrones del sistema en equilibrio, electrones fluirán desde regiones de alto potencial químico hacia regiones de bajo potencial químico, este flujo ocurrirá hasta que μ sea constante a través de toda la molécula ($\frac{d\mu}{dr} = 0$). Nótese que la electronegatividad es igual al negativo del potencial químico, esta igualdad conecta la TFD formal con conceptos clásicos en química. Desde esta relación es posible calcular electronegatividades para átomos, moléculas, fragmentos, *clusters*, etc. Para estimar

numéricamente esta derivada se ha hecho uso de la aproximación de diferencias finitas expresando μ en término del potencial de ionización (PI) y la afinidad electrónica (AE) [2,8], al invocar el teorema de *Koopmans* [30], se puede estimar, a partir de los valores propios de los orbitales fronteras estableciendo la siguiente fórmula operacional:

$$\mu \approx -\frac{1}{2}(PI + AE) \approx \frac{1}{2}(\varepsilon_L + \varepsilon_H). \quad (1.5)$$

En general el valor conceptual de estas funciones de respuestas se aprecia en la formulación de principios de estructura electrónica. En este caso μ y χ están directamente conectados al principio de equalización de la electronegatividad propuesto por *Sanderson* en la década del 50, este establece que *todos los átomos que constituyen una molécula tienen igual valor de electronegatividad que viene dada por el promedio geométrico de las electronegatividades de los átomos aislados* [31,32]. Este principio ha sido la base para el desarrollo de esquemas computacionales orientados a obtener cargas atómicas [33].

Concepto de Dureza Química (η). Los conceptos empíricos de dureza y blandura propuestos por *Pearson* en la década del 60 [34] permiten racionalizar reacciones de tipo ácido base, en el marco de la TDF *Parr y Pearson* [9] han definido la dureza como:

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(\vec{r})} = \frac{1}{2} \left(\frac{\partial \mu}{\partial N} \right)_{v(\vec{r})}, \quad (1.6)$$

η es una propiedad de carácter global que mide la resistencia impuesta por el sistema para cambiar su distribución electrónica, su fórmula operacional se basa en argumentos ya señalados para μ [2,9],

$$\eta \approx \frac{1}{2}(PI - AE) \approx \frac{1}{2}(\varepsilon_L - \varepsilon_H). \quad (1.7)$$

El inverso de η ha sido identificado como blandura molecular (S), y se ha mostrado empírica y formalmente que esta propiedad se conecta con la polarizabilidad del

sistema químico [35-39]

$$S = \frac{1}{\eta}. \quad (1.8)$$

Estas definiciones han permitido establecer bases formales para los principios propuestos por *Pearson*, el principio de ácidos y bases duros y blandos (HSAB) [40] y el principio de máxima dureza (PMD) [41] los cuales son importantes guías en la caracterización de la reactividad química. Mientras el primero de ellos establece que la interacción *duro-duro* y *blando-blando* es más favorable tanto desde un punto de vista termodinámico como cinético, el PMD indica que *parece ser una regla de la naturaleza que las moléculas en sus estados fundamentales tienden a ser tan duras como sea posible* [34].

Índice de Electrofilia (ω). Este índice ha sido recientemente propuesto por *Parr y col.* [20] como la capacidad de un electrófilo para estabilizar una interacción covalente debida a un máximo flujo electrónico en términos de μ y η :

$$\omega = \frac{\mu^2}{2\eta}. \quad (1.9)$$

Polarizabilidad (α). Una caracterización completa de una función de onda de N -partículas solo requiere N y $v(\vec{r})$. La respuesta del sistema es medida por χ y η en el caso que exista una perturbación en N cuando $v(\vec{r})$ se mantiene constante. Mientras que la polarizabilidad (α) de un sistema puede ser considerada como una propiedad que proporciona información de tipo global sobre el comportamiento del sistema cuando $v(\vec{r})$ es alterado a N constante. La definición de α proviene desde la expansión en serie de *Taylor* de la energía total en las componentes del campo eléctrico uniforme \vec{F} ,

$$E = E_0 + \mu_i F_i - \frac{1}{2} \alpha_{ij} F_{ij} + \dots \quad (1.10)$$

donde E_0 es la energía en ausencia de campo eléctrico, el segundo término corresponde

al momento dipolar permanente:

$$\mu_i = - \left(\frac{\partial E}{\partial \vec{F}_i} \right)_{\vec{F}=0} \quad (1.11)$$

mientras que el tensor de polarizabilidad corresponde a:

$$\alpha_{ij} = - \left(\frac{\partial^2 E}{\partial \vec{F}_i \partial \vec{F}_j} \right)_{\vec{F}=0}, \quad (1.12)$$

donde los subíndices i y j corresponden a coordenadas cartesianas x , y y z . La cantidad experimental que se obtiene es la polarizabilidad isotrópica promedio, calculada a partir de las componentes diagonales del tensor de α :

$$\langle \alpha \rangle = \frac{1}{3} \text{tr}(\alpha) = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}). \quad (1.13)$$

Sobre la base de una relación inversa entre η y α [38], *Chattaraj y Sengupta* han propuesto el principio de mínima polarizabilidad (PMP), el cual establece que *la dirección natural de evolución es hacia un estado de mínima polarizabilidad* [42]. El PMP junto al PMD son principios de estructura electrónica ampliamente aceptados, puesto que complementan el criterio de mínima energía para la estabilidad de un sistema molecular, además ha sido mostrado que un sistema molecular es más duro y menos polarizable en su estado fundamental que en algún estado excitado [43].

Función de Fukui ($f(\vec{r})$) y Blandura Local ($s(\vec{r})$). Por otra parte, las respuestas respecto al potencial externo proporcionan información de tipo local, es decir, respuestas que dependen de la posición (\vec{r}), estas son definidas como índices de selectividad. Los descriptores locales como la función de Fukui ($f(\vec{r})$) [10] y blandura local ($s(\vec{r})$) [11] son propiedades necesarias para explicar la selectividad en una molécula. La función de Fukui (FF) está definida como [10]:

$$f(\vec{r}) = \left(\frac{\delta \mu}{\delta v(\vec{r})} \right)_N = \left(\frac{\partial \rho(\vec{r})}{\partial N} \right)_{v(\vec{r})} = \left(\frac{\partial^2 E}{\partial N \partial v(\vec{r})} \right), \quad (1.14)$$

en la ausencia de relajación orbital esto se aproxima a la densidad de los orbitales moleculares de frontera (HOMO y LUMO) permitiendo hacer un puente con la teoría de orbitales de frontera desarrollada por Fukui [44, 45]. En acuerdo con la discontinuidad que presentan las respuestas respecto a N se han definido tres tipos diferentes de $f(\vec{r})$:

$$\begin{aligned} f^+(\vec{r}) &= \left(\frac{\partial \rho(\vec{r})}{\partial N} \right)_{\nu(\vec{r})}^+ \approx [\rho_{N+1}(\vec{r}) - \rho_N(\vec{r})] \approx \rho_L(\vec{r}), \\ f^-(\vec{r}) &= \left(\frac{\partial \rho(\vec{r})}{\partial N} \right)_{\nu(\vec{r})}^- \approx [\rho_N(\vec{r}) - \rho_{N-1}(\vec{r})] \approx \rho_H(\vec{r}), \\ f^o(\vec{r}) &= \frac{1}{2}[f^+(\vec{r}) + f^-(\vec{r})]. \end{aligned} \quad (1.15)$$

En un punto \vec{r} , $f^+(\vec{r})$ mide la reactividad hacia un ataque nucleofílico; $f^-(\vec{r})$ mide la reactividad hacia un ataque electrofílico y $f^o(\vec{r})$ mide la reactividad hacia un ataque radicalario. La conexión con la teoría de orbitales de fronteras se logra a través de las densidades de los orbitales fronteras $\rho_H(\vec{r})$ y $\rho_L(\vec{r})$ como lo indica la ecuación (1.15). Un valor alto para esta función en un dado sitio implicará una mayor reactividad puesto que este sitio experimentará a un mayor cambio en el potencial químico como se establece en la ecuación (1.14). La cuantificación de esta función de respuesta se logra a través de esquemas de condensación en regiones atómicas, así la función de Fukui puede ser escrita en términos de poblaciones electrónicas en un átomo [46].

$$\begin{aligned} f_k^+ &= \int_k [\rho_{N+1}(\vec{r}) - \rho_N(\vec{r})] d\vec{r} = [q_k(N+1) - q_k(N)], \\ f_k^- &= \int_k [\rho_N(\vec{r}) - \rho_{N-1}(\vec{r})] d\vec{r} = [q_k(N) - q_k(N-1)], \\ f_k^o &= \frac{1}{2}[f_k^+ + f_k^-] = \frac{1}{2}[q_k(N+1) - q_k(N-1)]. \end{aligned} \quad (1.16)$$

En el marco de la aproximación de *core congelado*, estas cantidades pueden ser condensadas considerando sólo las contribuciones de los orbitales de frontera sobre un dado átomo, conduciendo a las siguientes expresiones [47]:

$$\begin{aligned}
 f_k^+ &= \int_k \rho_L(\vec{r}) d\vec{r} = \rho_k^L, \\
 f_k^- &= \int_k \rho_H(\vec{r}) d\vec{r} = \rho_k^H, \\
 f_k^o &= \frac{1}{2}[f_k^+ + f_k^-] = \frac{1}{2}[\rho_k^L + \rho_k^H],
 \end{aligned}
 \tag{1.17}$$

donde ρ_k^L y ρ_k^H son las poblaciones electrónicas sobre el átomo k asociadas a los orbitales de fronteras LUMO y HOMO, respectivamente. La blandura local es definida en términos de la función de Fukui y la blandura global como [11]:

$$s(\vec{r}) = f(\vec{r}) \cdot S. \tag{1.18}$$

De acuerdo a esta definición se obtienen diferentes tipos de blandura local al igual que para la FF, a partir de este descriptor local es posible establecer una versión local del principio HSAB [48].

En la década del 60 *Klopman* [49] reportó un tratamiento general de reactividad química y en él mostró que las interacciones del tipo *duro-duro* son predominantemente de naturaleza iónica (o *a través del espacio*) y por lo tanto controladas por cargas mientras que las interacciones del tipo *blando-blando* son principalmente covalentes (o *a través del enlace*) y por lo tanto controlada por orbitales fronteras. En este ámbito estas cantidades electrónicas en conexión con principios de estructura electrónica resultan interesantes a la hora de analizar el sitio de ataque preferido como también el tipo de ataque por un reactivo.

Valencia Atómica (V_k) y Molecular (V_M). Los procesos químicos producen cambios en la distribución electrónica sobre diferentes regiones de la topología molecular, la FF al igual que la blandura local permiten medir esta redistribución electrónica en un dado centro atómico de una molécula. Complementario a estos índices de reactividad de sitios, la valencia atómica (V_k) es una medida de la localización de

la densidad electrónica en las regiones de enlaces asociada a un átomo:

$$V_k = \sum_{\ell \neq k} \left[\sum_{a \in k} \sum_{b \in \ell} D_{ab} D_{ba} \right], \quad (1.19)$$

donde D_{ab} son elementos de la matriz de orden de enlace [50]. V_k es entonces una medida del número de enlaces covalentes del átomo k dentro de la molécula. Los valores V_k son siempre muy cercanos al valor clásico de valencia del átomo k , con fluctuaciones desde una molécula a otra [50-52]. Las desviaciones desde el valor clásico son atribuidas al carácter iónico de los enlaces formados por átomos de diferentes electronegatividades. Siguiendo con la observación de *Klopman* [49] sobre las interacciones específicas, un centro reactivo con interacciones locales *blando-blando* debe estar asociado con un valor mínimo de V_k (una máxima desviación desde su valor clásico) mientras que para interacciones *duro-duro* un valor máximo de V_k (una mínima desviación desde su valencia clásica) es esperado. Entonces el análisis de la valencia atómica permite inferir acerca de la naturaleza de las interacciones interatómicas.

La valencia molecular (V_M) es obtenida como

$$V_M = \frac{1}{2} \sum_k V_k \quad (1.20)$$

y corresponde a una medida de los enlaces covalentes dentro de la molécula, una molécula descrita por enlaces covalentes o levemente polares en su conformación de mínima energía se espera que presente un valor máximo de V_M . En este contexto se ha propuesto el principio de máxima valencia molecular (PMVM) [51, 52].

Habiendo definido los parámetros de reactividad y selectividad, resulta interesante saber cómo estos parámetros varían durante el progreso de un proceso físico químico y cómo ellos entregan información que permiten comprender un evento químico, este es el sujeto principal de este trabajo de Tesis.

En este trabajo de Tesis, nos hemos interesado principalmente en el estudio de propiedades globales, como la energía (E) y propiedades electrónicas globales que de ella se derivan como el potencial químico electrónico y la dureza molecular. Además nos ha interesado el estudio de propiedades electrónicas locales, como la densidad electrónica ($\rho(\vec{r})$) y la función de Fukui ($f(\vec{r})$) asociada a un sitio o región de la topología molecular, que están implicadas en la selectividad que presentan los diferentes sitios de una molécula.

El estudio de estas propiedades y su nacionalización mediante reglas de reactividad química como el *Principio de Máxima Dureza*, *Principio de Mínima Polarizabilidad*, *Principio de Acidos y Bases Duros y Blandos* y el *Principio de Equalización de Sanderson* conduce a identificar los factores electrónicos que determinan las interacciones entre varios componentes de un proceso químico. En el presente trabajo de Tesis hemos abordado el estudio y caracterización de diversas estructuras y procesos químicos.

Este escrito está organizado de la siguiente manera.

En el Capítulo 2 nuestra principal motivación ha sido validar los descriptores y principios provenientes de la TFD en el contexto de su aplicación en el estudio de vibraciones moleculares y rotaciones internas en moléculas sencillas. Con la idea de analizar el rango de aplicabilidad de estos elementos hemos estudiado sistemas de una mayor complejidad como los *clusters* o cúmulos de cobre.

En el Capítulo 3 nos centramos básicamente en el estudio de reacciones químicas poniendo un mayor énfasis en la conexión de descripciones clásicas de reactividad con los descriptores de la TFD, y cómo estos modelos permiten dilucidar los mecanismos de reacción e identificar la naturaleza de las interacciones específicas responsables de las barreras de energía.

En el Capítulo 4 avalados por el poder predictivo que presentan estos elementos de análisis nos centramos en estimar estas propiedades desde fragmentos en el marco de las reacciones de formación principalmente basados en el principio de equalización de *Sanderson*.

En el Capítulo 5 en acuerdo al éxito que presentan estos elementos en la racionalización de resultados teóricos nos propusimos abordar estudios de formación de *clusters* de cobre con el objetivo principal de racionalizar resultados experimentales recientemente reportados.

Finalmente en el Capítulo 6 indicamos las principales conclusiones de este trabajo de Tesis.



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Capítulo 2

Moléculas y Clusters de Cobre: Principios de Máxima Dureza y Mínima Polarizabilidad

Resumen

En este Capítulo se entregan resultados acerca de la caracterización de estructuras químicas en términos de conceptos y principios que provienen de la TFD. Se abordarán sistemas moleculares sencillos en el contexto de vibraciones moleculares y rotaciones internas, y sistemas de una mayor complejidad como son los *clusters* de cobre. En ambos tipos de estructuras se encontró que los principios de máxima dureza y mínima polarizabilidad son reglas que complementan el criterio de mínima energía para la estabilidad molecular. Por otra parte, estos elementos teóricos permiten caracterizar y racionalizar propiedades electrónicas en *clusters* de cobre.

2.1 Introducción

Los conceptos de electronegatividad [1] y dureza molecular [2] han sido de gran utilidad e importancia en la racionalización y predicción de varios aspectos referentes al enlace químico y reactividad de moléculas. Estas cantidades electrónicas han sido definidas en el Capítulo 1. Estos dos parámetros esencialmente determinan la respuesta de un átomo o molécula al cambio en N . Por otra parte, la polarizabilidad de una especie determina la respuesta debida al cambio del campo externo a N constante. En literatura existen varios trabajos orientados a interrelacionar estos descriptores electrónicos, en este contexto, se ha establecido empíricamente una relación inversa entre dureza y polarizabilidad [3-5], y se ha determinado, que las condiciones de máxima dureza y mínima polarizabilidad se asocian a una mayor estabilidad [6-8].

En este Capítulo, nos centramos en verificar la validez de estos elementos de análisis en la caracterización de estructuras moleculares que van desde simples moléculas hasta agregados de cobre. Nuestra principal motivación, ha sido probar que los descriptores electrónicos son elementos de análisis válidos que complementan la descripción clásica de estructuras moleculares (constantes de fuerzas, energías de enlace, etc.), y que, pueden proporcionar criterios alternativos de estabilidad molecular.

La caracterización de las estructuras de moléculas simples la hemos desarrollado en el contexto de vibraciones moleculares a través del análisis a lo largo de los modos normales de vibración, y del análisis de isómeros conformacionales a lo largo de un modo torsional. Para este propósito calculamos parámetros de reactividad (χ , η y α) a través de métodos *ab initio* SCF en el contexto de vibraciones moleculares y rotaciones internas. Hemos investigado distorsiones simétricas y asimétricas en amoníaco (NH_3), sulfuro de hidrógeno (H_2S) y agua (H_2O) a lo largo de direcciones especificadas por las coordenadas de simetría vibracional. El proceso de isomerización rotacional ha sido caracterizado a lo largo del ángulo de torsión investigando los diferentes conformeros rotacionales de sistemas moleculares del tipo HXYH ($X, Y = \text{O}, \text{S}$); HXNY ($X, Y = \text{O}, \text{S}$) y etileno ($\text{CH}_2=\text{CH}_2$) [8].

La caracterización de agregados de cobre (Cu_n ; $n=1-9$) ha sido llevada a cabo a través de sus propiedades estructurales, energéticas y descriptores de reactividad (μ , η , ω y α) como función del número de átomos que forman el agregado metálico [9].

2.2 Aplicaciones

2.2.1 Detalles Computacionales

El potencial químico electrónico, la dureza molecular y la polarizabilidad son estimados a través de las fórmulas operacionales entregadas en el Capítulo 1.

Sistemas Moleculares. Potencial químico y dureza molecular fueron calculados a través de las ecuaciones (1.5) y (1.7) a partir de los valores de energías de los orbitales fronteras las que fueron obtenidas a través de cálculos *ab initio* a nivel de teoría *Hartree-Fock* y TFD mediante el modelo B3LYP [10,11], con un set de funciones bases estándar 6-311G** implementadas en el paquete de programas Gaussian 94 [12]. En adición a estos cálculos, la polarizabilidad fue estimada a través de la base de *Sadlej*, la cual es más adecuada para reproducir propiedades moleculares eléctricas [13].

clusters de Cobre. Los cálculos de estructura electrónica para *clusters* de cobre requieren el tratamiento de la correlación electrónica, en este contexto, los métodos TFD son la mejor alternativa computacional. En este estudio se utilizó el modelo híbrido B3PW91 para el funcional de intercambio (B3) [10] y correlación (PW91) [14] combinado con el esquema de potenciales de *core* efectivo (LANL2DZ) [15]. Todos los cálculos de optimización de geometrías y análisis vibracional fueron realizados en el paquete de programas Gaussian 98 [16].

2.2.2 Resultados y Discusión

2.2.2.1 Sistemas Moleculares: Modos Vibracionales

Los resultados que se discuten en los siguientes párrafos están contenidos en el artículo, referencia [8], que se adjunta en un anexo al final de esta Tesis. El procedimiento general que seguimos para caracterizar sistemas moleculares a través de sus vibraciones moleculares fue comenzar con las moléculas en sus geometrías de equilibrio y hacer pequeñas distorsiones en direcciones que están especificadas por las coordenadas de simetría vibracional. Las Figuras 2.1 y 2.2 muestran los perfiles de energía, dureza, y polarizabilidad asociada a las distorsiones asimétricas de simetría E y distorsiones simétricas de simetría A_1 para la molécula de amoníaco (NH_3 : C_{3v}), respectivamente. Las Figuras (a) y (b) están referidas a distorsiones en la longitud del enlace N-H (modo de *stretching*) mientras que (c) y (d) están referidas al ángulo de enlace H-N-H (modo de *bending*).

Para oscilaciones no totalmente simétricas, tanto, μ como el potencial promedio núcleo-electrón ($v_{ne} = \int d\vec{r} v(\vec{r}) \rho(\vec{r})$) permanecen constantes mientras que en distorsiones totalmente simétricas estas propiedades varían considerablemente a lo largo de la coordenada vibracional [17].

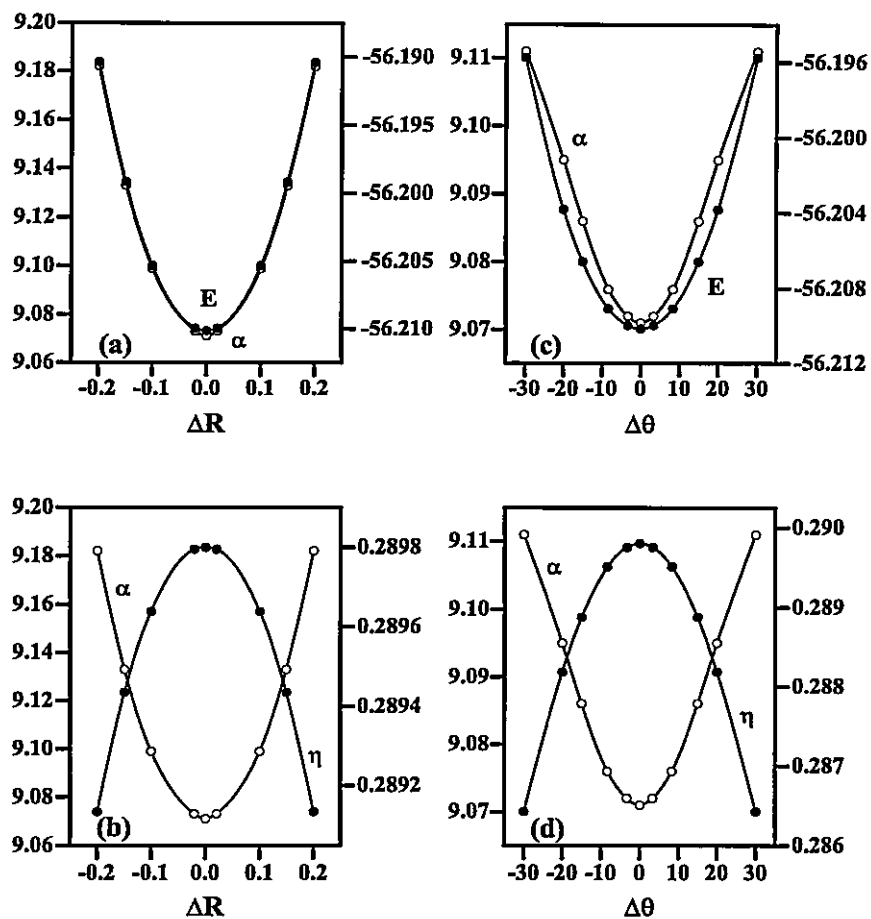


Figura 2.1: Distorsiones asimétricas de amoníaco: perfiles de energía y polarizabilidad (a), perfiles de dureza y polarizabilidad (b) para distorsiones en la distancia de enlace N-H; perfiles de energía y polarizabilidad (c), perfiles de dureza y polarizabilidad (d) para distorsiones en el ángulo de enlace H-N-H. Todos los valores están en unidades atómicas (*ua*) y fueron obtenidos mediante cálculos RHF/6-311G**.

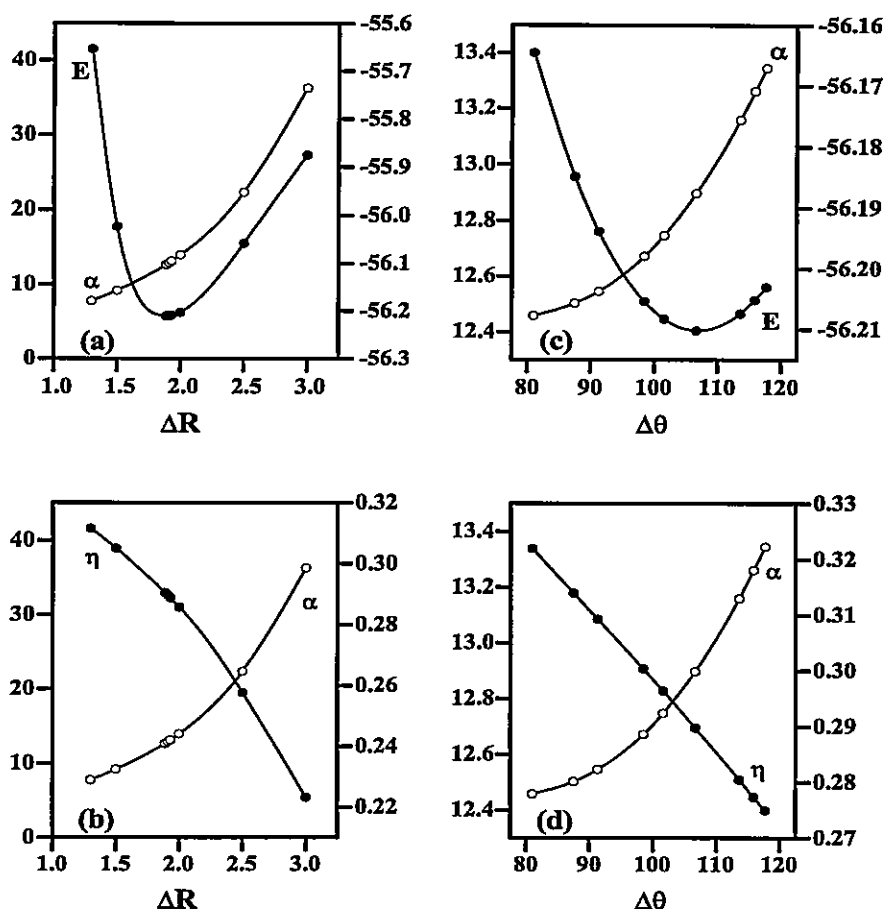


Figura 2.2: Distorsiones simétricas de amoníaco: perfiles de energía y polarizabilidad (a), dureza y polarizabilidad (b) para distorsiones en la distancia de enlace N-H; perfiles de energía y polarizabilidad (c), perfiles de dureza y polarizabilidad (d) para distorsiones en el ángulo de enlace H-N-H. Todos los valores están en *ua* y fueron obtenidos mediante cálculos RHF/6-311G**.

En las Figuras 2.1 (a) y (c) vemos que la polarizabilidad es mínima para la configuración de equilibrio (mínima energía) para modos de vibración asimétricos del tipo *stretching* y *bending*, respectivamente. Por otra parte, para estos modos normales se observa una relación inversa entre los perfiles de α y η claramente manifestada en la Figura 2.1 (b) y (d), lo cual permite demostrar de forma simultánea la validez de los principios de máxima dureza y mínima polarizabilidad en el contexto de vibraciones moleculares. Desde esta ilustración queda suficientemente claro que la configuración

de equilibrio está caracterizada por un valor máximo de η y un valor mínimo de α . Las Figuras 2.2 (a) y (c) presentan los resultados para oscilaciones totalmente simétricas, en ellas se observa que la polarizabilidad decrece a medida que los núcleos se aproximan, este proceso también es acompañado por un incremento monótono de la dureza como es señalado por las Figuras 2.2 (b) y (d). Lo interesante de este tipo de modos de vibración, es que la relación inversa entre η y α se mantiene a lo largo de la coordenada tanto en modos de *stretching* como *bending*, a pesar que la configuración de equilibrio no presenta valores extremos de estas propiedades. En estos casos, la conformación de equilibrio es determinada mas bien por el teorema electrostático de *Hellman-Feynman* [18,19] que por valores extremos de η y α , esto no necesariamente implica que el PMD y PMP estén siendo violados, el no cumplimiento de estas reglas empíricas es debido a que tanto μ como v_{ne} varían fuertemente a lo largo de ΔR y $\Delta\theta$, y por lo tanto, no existe cumplimiento con las condiciones necesarias para la validez del PMD [6].

En este contexto, hemos realizado cálculos de modos vibracionales simétricos y asimétricos tanto de *stretching* como *bending* para diversas moléculas con resultados similares a los presentados para NH_3 [8,20] éstos se encuentran en Tablas del Apéndice A de la Tesis.

2.2.2.2 Sistemas Moleculares: Rotaciones Internas

Se han caracterizado los diferentes confórmeros a lo largo del ángulo diedro para sistemas moleculares del tipo HXYH (X,Y=O,S) [8]. Los perfiles de energía, dureza y polarizabilidad para la rotación interna de H_2O_2 son presentados en la Figura 2.3. Se observa que la curva de polarizabilidad es cualitativamente similar a la curva de energía aunque la mínima polarizabilidad se encuentra levemente desplazada hacia la derecha del confórmero de mínima energía. Una situación similar se observa para los perfiles de E y η . En esta Figura se aprecia que la dureza y polarizabilidad presentan una relación inversa a lo largo del ángulo de torsión, máximos (mínimos) en el perfil de dureza corresponden a mínimos (máximos) en el perfil de polarizabilidad, una clara evidencia de la validez de ambos principios de estructura electrónica (PMD

y PMP) durante el proceso torsional. Con la idea de probar la validez de estas reglas de reactividad en el contexto del análisis conformacional se llevaron a cabo cálculos similares en otras moléculas no rígidas del tipo HXNY (X,Y=O,S) [20] y etileno [8] ($\text{CH}_2=\text{CH}_2$) observándose las mismas tendencias descritas anteriormente, sus resultados están reportados en el Apéndice B de esta Tesis.

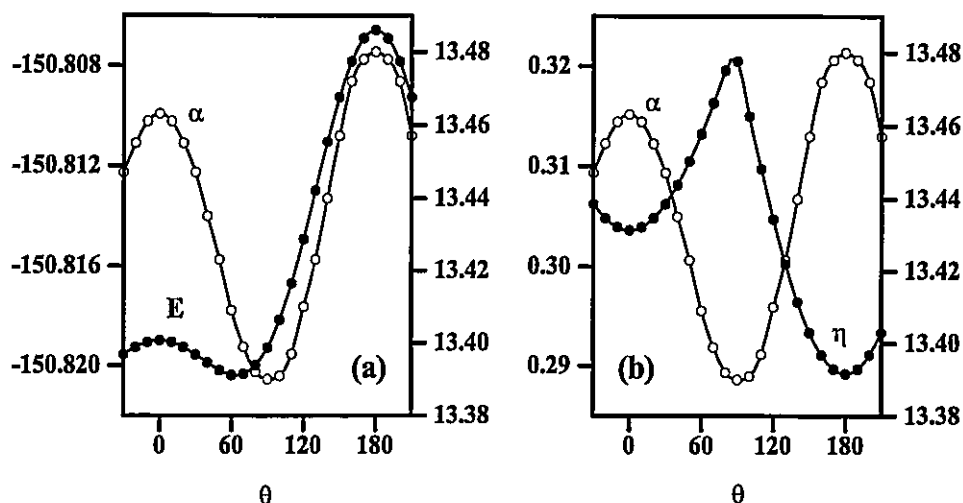


Figura 2.3: Rotación interna en H_2O_2 : perfiles de energía y polarizabilidad (a), perfiles de dureza y polarizabilidad (b). Todos los valores están en ua y fueron obtenidos mediante cálculos RHF/6-311G**.

2.2.2.3 Clusters de Cobre.

Los antecedentes que se han acumulado en literatura, y que han permitido mostrar el éxito de estos descriptores en la caracterización de moléculas nos llevaron a investigar estructuras más complejas tales como *clusters* o agregados de cobre. Estos sistemas resultan particularmente interesantes por su potencial uso en diversos procesos en ciencia de superficie, como modelos en química organometálica y electrónica a escala molecular [21–25].

El interés en el estudio de pequeños *clusters* metálicos ha crecido considerablemente en los últimos años debido al desarrollo de nuevas técnicas tanto experimentales como teóricas que han permitido caracterizar este tipo de sistemas más detalladamente.

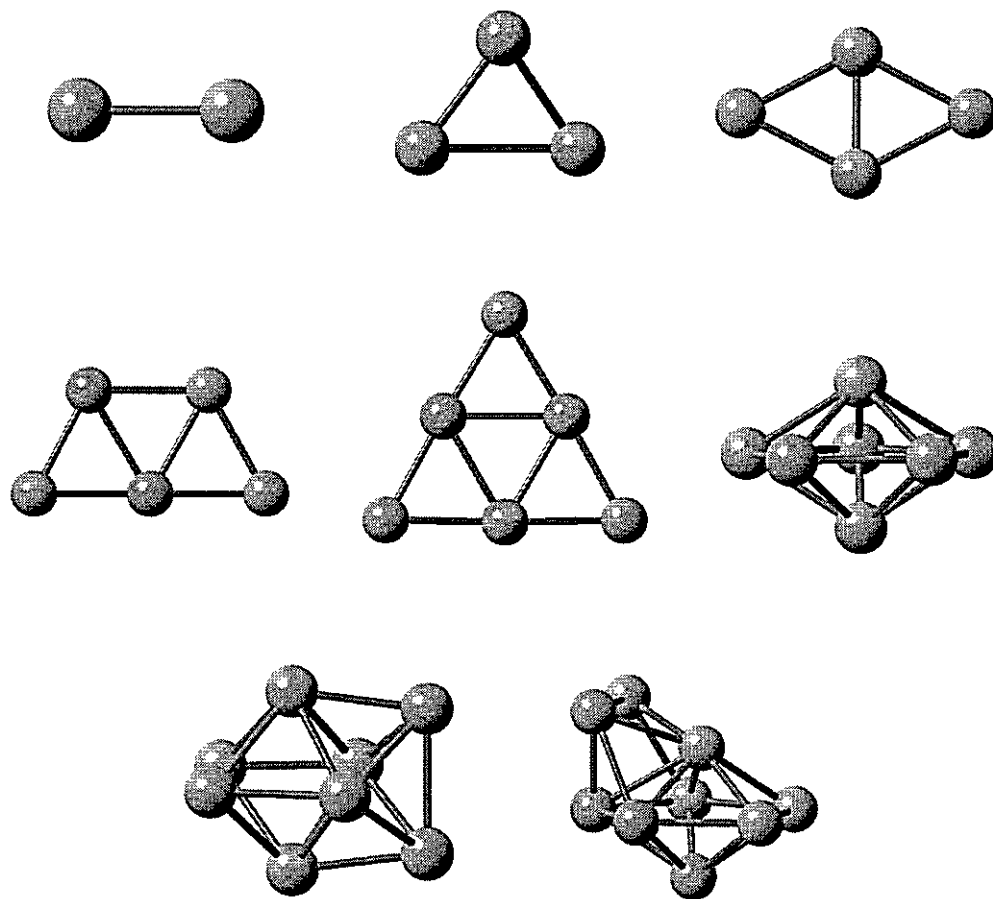


Figura 2.4: Estructuras de los estados fundamentales de *clusters* de cobre neutros, Cu_n ($n=2-9$).

La investigación en química de *clusters* ha estado dirigida al estudio de la dependencia y evolución de diferentes propiedades con el tamaño del *cluster*, y cómo estas se aproximan al valor del material (*bulk*) [26]. En general, se ha observado que las propiedades de *clusters* son muy sensibles al número de átomos, y estas pueden cambiar dramáticamente con la adición o remoción de un átomo. En este trabajo de Tesis, nos centramos en caracterizar *clusters* neutros de cobre considerando aspectos estructurales, energéticos y de reactividad mediante los mismos descriptores que han sido utilizados en la sección anterior.

| Cluster | | $\langle r_{Cu-Cu} \rangle$ | NC | ν_{max} |
|------------------|----------------|-----------------------------|------|-------------|
| Cu | | | | |
| Cu_2 | $D_{\infty h}$ | 2.254 | 1.0 | 259 |
| Cu_3 | C_{2v} | 2.447 | 2.0 | 240 |
| Cu_4 | D_{2h} | 2.418 | 2.5 | 256 |
| Cu_5 | C_{2v} | 2.429 | 2.8 | 252 |
| Cu_6 | D_{3h} | 2.431 | 3.0 | 255 |
| Cu_7 | D_{5h} | 2.500 | 4.3 | 224 |
| Cu_8 | C_{2v} | 2.501 | 4.5 | 222 |
| Cu_9 | C_s | 2.534 | 5.1 | 231 |
| exp ^a | | 2.556 | 12 | |

Tabla 2.1: Longitud de enlace promedio Cu–Cu ($\langle r_{Cu-Cu} \rangle$, Å), número de coordinación promedio (NC) y frecuencia armónica de mayor energía (ν_{max} , cm^{-1}) de Cu_n .

^a Ref. [27]

2.2.2.3.1 Clusters de Cobre: Estructura. La Figura 2.4 muestra las estructuras optimizadas de los estados fundamentales de *clusters* de cobre desde el dímero al nonámero, se puede visualizar que la dimensionalidad de estas estructuras es: $Cu_2 \rightarrow 1D$, Cu_3 a Cu_6 son estructuras **2D** mientras que desde Cu_7 a Cu_9 son sistemas **3D**. Las estructuras de agregados de cobre han sido caracterizadas a través de la distancia promedio $Cu - Cu$ ($\langle r_{Cu-Cu} \rangle$), el número de coordinación promedio (NC) y la frecuencia armónica de vibración de mayor energía (ν_{max}), todas estas cantidades están contenidas en la Tabla 2.1. La variación de $\langle r_{Cu-Cu} \rangle$ ilustrada en la Figura 2.5 muestra que están ocurriendo transiciones estructurales a medida que el tamaño del *clusters* crece, y la distancia $Cu - Cu$ en las estructuras **3D** es la que mejor se aproxima al valor experimental en el material [27]. En el NC se observa un aumento con el crecimiento del tamaño del cluster indicando que el grado de deslocalización electrónica incrementa, y por lo tanto, la fuerza de los enlaces, tal como veremos en la siguiente subsección.

Finalmente, el último descriptor estructural que se considera en este análisis también permite observar las transiciones estructurales que ocurren a medida que los *clusters* crecen, cuando se adiciona un átomo a Cu_6 la frecuencia ν_{max} claramente disminuye

por 29 cm^{-1} debido al cambio estructural desde una 2D a una conformación más compacta 3D.

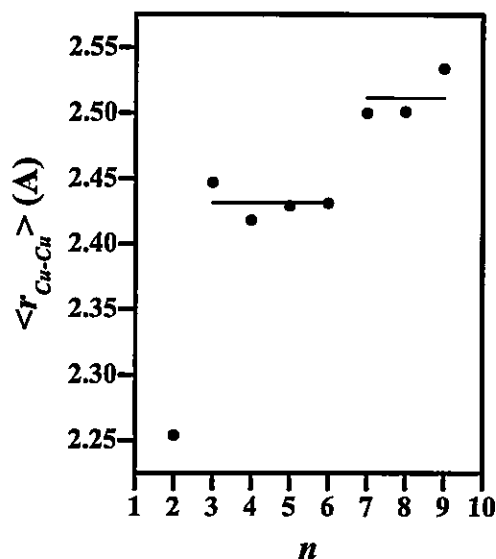


Figura 2.5: Dependencia de la longitud de enlace promedio ($\langle r_{Cu-Cu} \rangle$) con el tamaño del cluster.

2.2.2.3.2 Clusters de Cobre: Estabilidad. Energía de Enlace. La Tabla 2.2 contiene los valores de energía total junto a la energía de atomización total (BE), que ha sido calculada como:

$$BE = nE_{Cu} - E_{Cu_n}. \quad (2.1)$$

También en esta Tabla se incluyen las BE experimentales determinadas a través de experiencias de disociación inducidas por colisión (CID, *Collision Induced Dissociation*) de *clusters* aniónicos [28] y catiónicos [29]. La Figura 2.6 permite observar que nuestros resultados siguen correctamente las tendencias cualitativas y cuantitativas de los datos experimentales.

| Cu_n | $-E$ | BE | BE/n | $BE(\text{exp})^a$ | $BE(\text{exp})^b$ |
|--------|------------|---------|--------|--------------------|--------------------|
| Cu | 196.15426 | | | | |
| Cu_2 | 392.37926 | 1.9250 | 0.9625 | 2.04 ± 0.17 | 1.81 ± 0.14 |
| Cu_3 | 588.57325 | 3.0061 | 1.0020 | 3.19 ± 0.26 | 2.57 ± 0.27 |
| Cu_4 | 784.80931 | 5.2320 | 1.3080 | 5.91 ± 0.33 | 4.60 ± 0.81 |
| Cu_5 | 981.03363 | 7.1384 | 1.4277 | 7.76 ± 0.37 | 6.19 ± 1.13 |
| Cu_6 | 1177.27957 | 9.6332 | 1.6055 | 10.32 ± 0.49 | 7.99 ± 1.37 |
| Cu_7 | 1373.51538 | 11.8523 | 1.6932 | 12.98 ± 0.66 | 9.04 ± 1.58 |
| Cu_8 | 1569.76050 | 14.3247 | 1.7906 | 15.96 ± 0.75 | 11.20 ± 1.77 |
| Cu_9 | 1765.97437 | 15.9468 | 1.7719 | | 12.22 ± 1.84 |

Tabla 2.2: Energía total (ua) de la estructuras optimizadas a nivel de teoría B3PW91/LANL2DZ de *clusters* de Cu_n , ($n=1-9$); energía de atomización (BE) y energía de cohesión (BE/n) (en eV).

^a Experimentos de CID en *clusters* aniónicos Ref. [28] .

^b Experimentos de CID en *clusters* catiónicos Ref. [29].

Otra cantidad que permite analizar la estabilidad de estos sistemas, es la energía de cohesión, la cual es definida como la energía de atomización total por átomo BE/n , los resultados para esta cantidad se entregan en la Tabla 2.2 donde se compara con datos experimentales. El buen acuerdo alcanzado entre nuestros resultados teóricos determinados a través de la combinación de métodos de funcionales de la densidad con potenciales de *core* efectivo, y aquellos determinados en experimentos CID (Figura 2.6) ciertamente permite validar la metodología de cálculo empleada en la caracterización de *clusters* de cobre. Los resultados numéricos de BE y BE/n muestran un incremento con el tamaño del *cluster*, y en el caso de BE/n se observa el máximo valor en Cu_8 . Este incremento se debe a una alta deslocalización electrónica producto de una mayor coordinación de los átomos a medida que el *cluster* crece. Estas cantidades proporcionan información acerca de la fuerza de los enlaces químicos en el *cluster* determinando la estabilidad y reactividad de estos sistemas.

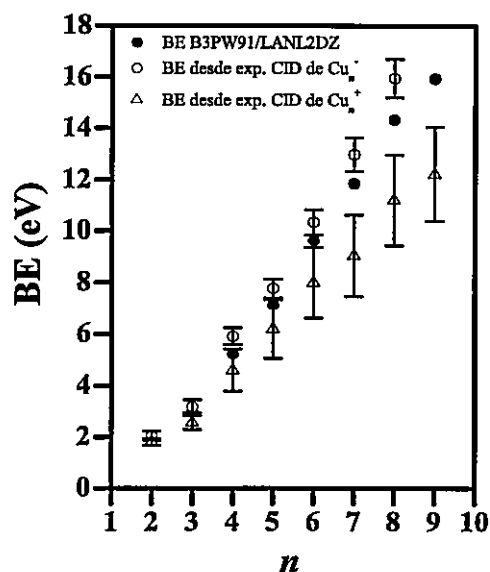


Figura 2.6: Energías de enlace experimentales (CID) y teóricas (BE) en función del tamaño del *cluster*.

Energía Relativa. Otra cantidad que proporciona información sobre la estabilidad de agregados metálicos es la energía de enlace relativa ($\Delta_2 E$):

$$\Delta_2 E = E(n+1) + E(n-1) - 2E(n), \quad (2.2)$$

esta cantidad permite estimar la estabilidad relativa de un cluster con n átomos respecto de aquellos con $(n-1)$ y $(n+1)$ átomos frente a un proceso de fragmentación ($\text{Cu}_n \rightarrow \text{Cu}_{n-1} + \text{Cu}$) y de formación ($\text{Cu}_n + \text{Cu} \rightarrow \text{Cu}_{n+1}$), respectivamente. Un alto valor en $\Delta_2 E$ indica que Cu_n es más estable que Cu_{n-1} y Cu_{n+1} . La Figura 2.7 ilustra la variación de $\Delta_2 E$ como una función del número de átomos del agregado metálico, en ella se observa un comportamiento oscilatorio al que en literatura se ha denominado como regla de alternación del tipo *par-impar*, dicho comportamiento se atribuye al cambio de multiplicidad de *spin* de los estados fundamentales a lo largo de la serie [30,31]. *Clusters* con un número par de átomos presentan máximos locales de $\Delta_2 E$ identificando a estas especies como más estables respecto a aquella con un

número impar de átomos de las cuales se espera una mayor reactividad. Este comportamiento es atribuido al tipo de configuración electrónica que presenta el estado fundamental del agregado metálico, el estado fundamental de *clusters* con n par es *singlete*, es decir, presenta una configuración del tipo capa cerrada (*closed-shell*), y como es bien sabido a este tipo de configuraciones se les asocia una estabilización extra, mientras que, el estado fundamental para agregados con n impar es del tipo *doblete*, es decir, capa abierta (*open-shell*) y por lo tanto se espera que este tipo de sistema presenten una reactividad intrínseca mayor.

Finalmente, se debe destacar que estos resultados están en acuerdo con el modelo de capas electrónicas de *jellium*, que ha sido aplicado con éxito en la caracterización de *clusters* formados por elementos monovalentes, de acuerdo a este modelo, cluster con capas electrónicas completas con 2,8,18,20,40,... electrones de valencia presentan una estabilidad en analogía a los elementos nobles de la tabla periódica. La estabilidad de *clusters* con estas características se manifiesta en el espectro de masa, *clusters* de elementos monovalentes con estos números de átomos, los cuales son denominados *números mágicos*, presentan mayor intensidad en el espectro [31].

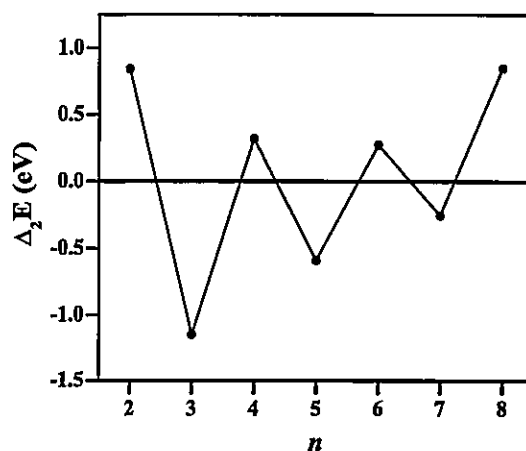


Figura 2.7: $\Delta_2 E$ en función del tamaño del *cluster*.

| Cu_n | PI | $PI(exp)$ | AE | $AE(exp)^a$ |
|--------|--------|------------------------------|--------|---------------|
| Cu | 7.6919 | 7.724 ^b | 0.6427 | 1.235 ± 0.005 |
| Cu_2 | 7.8016 | 7.9042 ± 0.0008 ^c | 0.5880 | 0.836 ± 0.006 |
| Cu_3 | 5.7700 | 5.80 ± 0.04 ^d | 0.7641 | 2.37 ± 0.01 |
| Cu_4 | 6.4682 | 7.15 ± 0.75 ^e | 1.2139 | 1.45 ± 0.05 |
| Cu_5 | 6.1618 | 6.3 ± 0.1 ^d | 1.5551 | 1.94 ± 0.05 |
| Cu_6 | 7.0573 | 7.15 ± 0.75 ^e | 0.9075 | 1.96 ± 0.05 |
| Cu_7 | 5.9678 | 6.1 ± 0.05 ^d | 1.5777 | 2.16 ± 0.1 |
| Cu_8 | 6.6353 | 7.15 ± 0.75 ^e | 1.1143 | 1.57 ± 0.05 |
| Cu_9 | 5.3376 | 5.35 ± 0.05 ^d | 0.7149 | 2.40 ± 0.05 |

Tabla 2.3: Potenciales de ionización verticales y afinidades electrónicas para Cu_n . Todos los valores están en eV.

^a Ref. [33]; ^b Ref. [34]; ^c Ref. [35]; ^d Ref. [36]; ^e Ref. [37].

2.2.2.3.3 Clusters de Cobre: Propiedades Electrónicas. En acuerdo a las fórmulas operacionales en el cálculo de μ y η es crucial una buena estimación de propiedades monoeléctricas (PI , AE). En cálculos TFD estas propiedades son muy sensibles al funcional de intercambio y correlación, en este ámbito, *De Proft y col.* [32] han aplicado varios funcionales de intercambio y correlación en el cálculo de PI y AE para sistemas atómicos y moleculares con el resultado que funcionales híbridos estiman adecuadamente estas propiedades. A la luz de este dato, hemos escogido el funcional B3PW91 para la caracterización de propiedades electrónicas de Cu_n . En la Tabla 2.3 se entregan resultados teóricos de PI y AE [9] verticales obtenidos a través de un procedimiento Δ SCF, además se incluyen datos experimentales como referencia.

Potencial de Ionización. Desde la Tabla 2.3 se observa que PI verticales varían en forma oscilatoria debido al cambio de multiplicidad de *spin* del estado fundamental, agregados con un número par de átomos presentan valores máximos de PI respecto a los sistemas vecinos (*clusters* con n impar), esta tendencia nuevamente puede ser racionalizada en términos de la configuración electrónica de estos agregados. Desde esta perspectiva, el proceso de ionización implica un mayor costo energético para remover un electrón desde un HOMO doblemente ocupado de un sistema de capa

cerrada (*clusters* con n par) que desde un orbital molecular simplemente ocupado (SOMO) de un sistema de capa abierta (*clusters* con n impar). Esta tendencia es consistente con la variación de la energía del HOMO a lo largo de la serie como se muestra en la Figura 2.8(b).

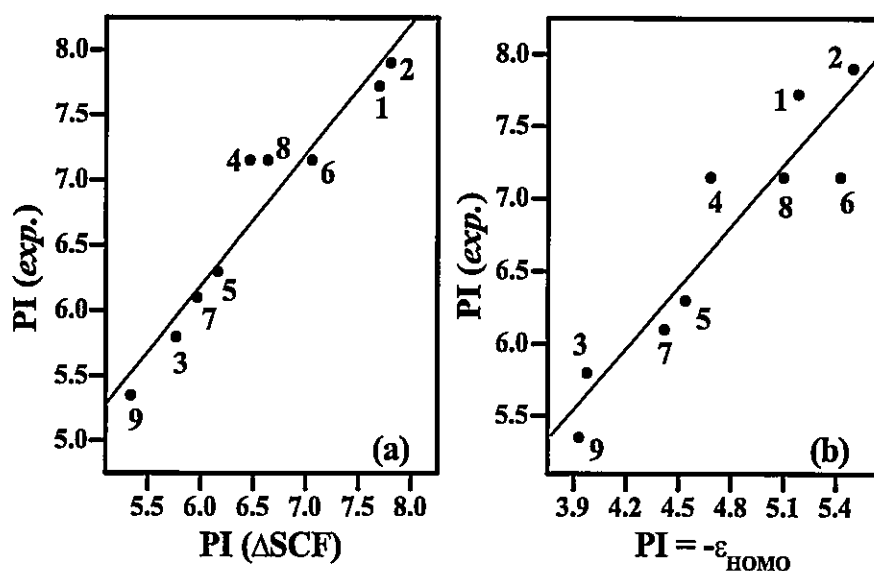


Figura 2.8: Comparación de potenciales de ionización experimentales y teóricos a lo largo de la serie Cu_n ($n=1-9$): (a) PI teóricos desde un procedimiento Δ SCF ($r=0.96$); (b) PI teóricos calculados desde la energía del HOMO mediante el teorema de *Koopmans* ($r=0.93$).

La Figura 2.8(a) indica que los resultados Δ SCF muestran un muy buen acuerdo con los datos experimentales, esto se verifica a través de un buen coeficiente de correlación ($r=0.96$). En este contexto, resulta interesante verificar la validez del teorema de *Koopmans* [38] para estimar potenciales de ionización a partir de la energía del HOMO ($PI = -\epsilon_{HOMO}$). La Figura 2.8(b) muestra una buena correlación lineal ($r=0.93$) entre potenciales de ionización experimentales y el negativo de la energía del HOMO, sin embargo, PI s obtenidos a través del teorema de *Koopmans* sistemáticamente subestiman el valor experimental. Por otra parte, es bien conocido que dentro del esquema de *Kohn-Sham* [39] la aproximación de PI por la energía del HOMO es considerado como una medida de la calidad del funcional empleado, y solamente en el

límite del funcional exacto $PI = -\varepsilon_{HOMO}$ [40]. Este satisfactorio acuerdo confirma la confiabilidad de nuestros resultados y del esquema de computo utilizado en este trabajo.

Afinidades Electrónicas. Es bien conocido que la afinidad electrónica es una propiedad considerablemente de una mayor dificultad de estimar que el potencial de ionización, básicamente debido a los siguientes aspectos: (i) el proceso de ionización es un proceso endotérmico mientras que el proceso de agregar un electrón a un sistema puede ser endotérmico o exotérmico; (ii) las afinidades electrónicas son más pequeñas en magnitud que las energías de ionización; y (iii) el electrón adicional tiende a presentar una distribución de carga mucho más difusa que en el sistema neutro o catiónico, esto hace necesario incluir funciones difusas en el set de bases atómicas empleadas en cálculos químico cuántico. Los valores de AE para *clusters* de cobre se presentan en la Tabla 2.3, y en acuerdo a estos antecedentes no se obtiene una estimación cuantitativa satisfactoria, sin embargo se obtiene de forma correcta la tendencia cualitativa, donde *clusters* con un número par de átomos presentan valores mínimos de AE respecto a *clusters* con n impar.

2.2.2.3.4 Clusters de Cobre: Descriptores de Reactividad. La cuantificación de descriptores electrónicos: potencial químico (μ), dureza molecular (η) y el índice de electrofilia ($\omega = \mu^2/2\eta$), que permiten caracterizar la reactividad de estas complejas estructuras se ha llevado a cabo a través de las fórmulas operacionales de las ecuaciones (1.5) y (1.7) utilizando propiedades monoeléctricas tanto experimentales como teóricas, y también las energías de los orbitales fronteras. La Figura 2.9 ilustra las tendencias que siguen estos descriptores respecto al tamaño del *cluster*, al igual que en otras propiedades se observa un comportamiento oscilatorio.

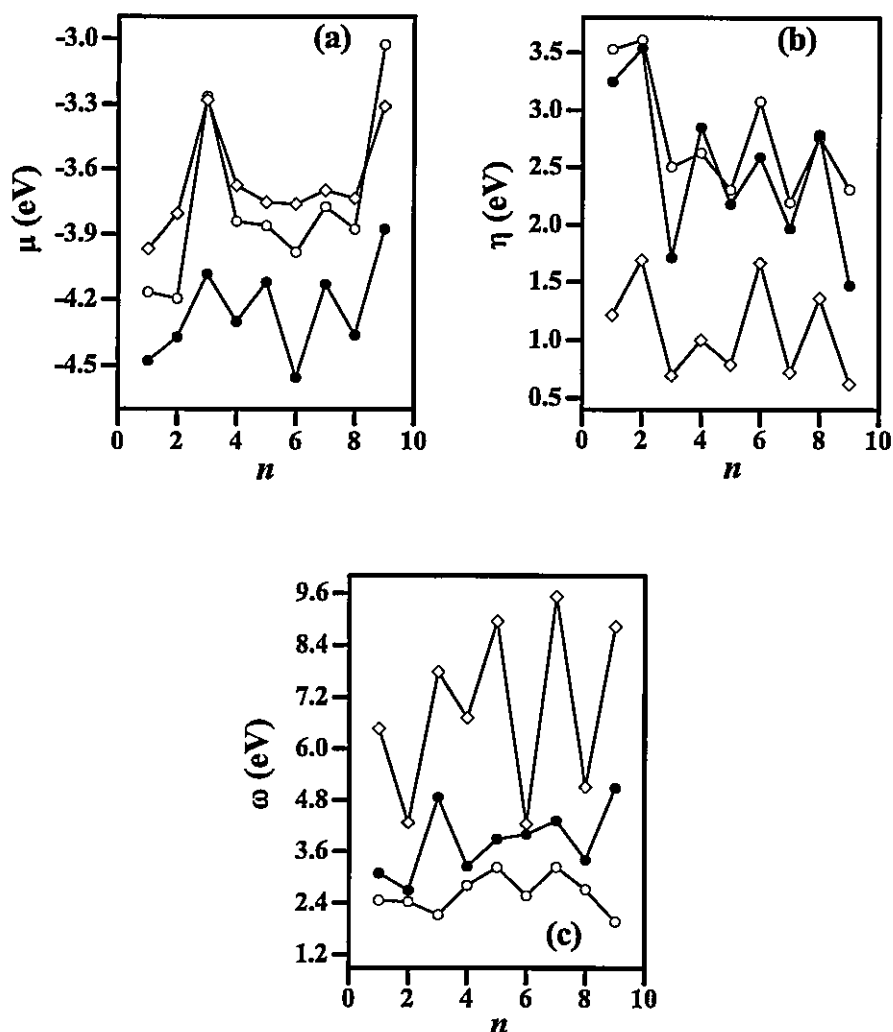


Figura 2.9: (a) Potencial químico, (b) dureza química, y (c) índice de electrofilia en función del tamaño del *cluster*. [$P^{(PI,EA)} = -\circ-$; $P^{(exp.)} = -\bullet-$; $P^{(H,L)} = -\diamond-$, $P = \mu, \eta, \omega$].

Potencial Químico: Se ha mencionado que μ es una propiedad que tiene relación con la transferencia de carga que presentan los sistemas moleculares, la Figura 2.9(a) presenta el perfil de μ a lo largo de la serie, y tal como es esperado *clusters* con n impar, se caracterizan por exhibir valores máximos de μ , es decir, este tipo de *clusters* presentan mayor tendencia a transferir carga que sistemas con un número par de átomos debido a que especies con capas electrónicas abiertas son más reactivas que

especies con capas cerradas. Particularmente Cu_3 y Cu_9 presentan valores extremos, estos *clusters* al cerrar sus capas electrónicas por pérdida de un electrón generan agregados con números mágicos de 2 y 8 electrones de valencia, respectivamente; de acuerdo con el modelo de *jellium*, los *clusters* resultantes presentaran mayor estabilidad, este resultado es consistente con lo observado en la Figura 2.7 donde Cu_2 y Cu_8 presentan máximos en $\Delta_2 E$.

Dureza Química: La Figura 2.9(b) muestra el perfil de dureza a lo largo de la serie, este sigue la misma tendencia que $\Delta_2 E$ en la Figura 2.7, y tal como es esperado η presenta máximos locales en agregados con n par, es decir *clusters* más (menos) estables son especies más (menos) duras. Estos resultados permiten confirmar que la estabilidad de los *clusters* con n par esta determinada por el cierre de la capa electrónica como una manifestación del principio de máxima dureza. Otro aspecto que merece ser destacado corresponde a la estabilidad de η respecto del tipo de aproximación que se utilice para su estimación, la Figura 2.9 muestra las mismas tendencias cualitativas para η a partir de $\{PI, AE\}$ y $\{\epsilon_H, \epsilon_L\}$. Este antecedente en conexión con el PMD sugiere que en aquellos sistemas que presenten dificultades en obtener información energética, como por ejemplo dificultades en localizar puntos estacionarios sobre la superficie de energía potencial, el conocimiento de η puede ser considerado como un camino alternativo para obtener ordenes de estabilidad [41].

Indice de Electrofilia: ω ha sido definido como la estabilización de un complejo donador-aceptor debida a un máximo flujo electrónico [42]. La evolución de esta propiedad se muestra en la Figura 2.9(c), se observa que *clusters* con n impar presentan máximos locales que se atribuyen a la alta capacidad de aceptar carga electrónica por sistemas de capa abierta.

Polarizabilidad Dipolar Eléctrica: α es una propiedad que proporciona información complementaria a μ y η ya que permite comprender el comportamiento del sistema cuando el potencial externo ($v(\vec{r})$) es alterado y el número de electrones se mantiene fijo. Esta propiedad es considerada uno de los observables más importantes

| Cu_n | $\langle \alpha \rangle$ | $\langle \alpha \rangle / n$ | $ \Delta\alpha $ |
|--------|--------------------------|------------------------------|------------------|
| Cu | 52.610 | 52.610 | 0.000 |
| Cu_2 | 77.574 | 38.787 | 30.752 |
| Cu_3 | 137.148 | 45.716 | 62.256 |
| Cu_4 | 153.948 | 38.487 | 98.882 |
| Cu_5 | 196.506 | 39.301 | 107.685 |
| Cu_6 | 221.212 | 36.869 | 107.978 |
| Cu_7 | 242.873 | 34.696 | 45.051 |
| Cu_8 | 267.640 | 33.455 | 33.946 |
| Cu_9 | 312.970 | 34.774 | 66.652 |

Tabla 2.4: Polarizabilidad dipolar promedio ($\langle \alpha \rangle$), polarizabilidad promedio por átomo ($\langle \alpha \rangle / n$), y anisotropía del tensor de polarizabilidad ($|\Delta\alpha|$) de *clusters* de cobre. Todos los valores están en *ua*.

en la comprensión de propiedades electrónicas de *clusters* metálicos [43]. La Tabla 2.4 presenta los valores promedio de polarizabilidad ($\langle \alpha \rangle$) y la polarizabilidad por átomo ($\langle \alpha \rangle / n$) calculadas al nivel B3PW91/LANL2DZ.

A pesar de no existir medidas experimentales de α en Cu_n hemos encontrado un acuerdo satisfactorio de nuestros resultados con aquellos reportados por *Calaminici y col.* [44] que provienen de cálculos mecano-cuánticos donde se han considerado todos los electrones, este resultado permite sostener que la contribución de los electrones de *core* al valor de $\langle \alpha \rangle$ es despreciable. La Figura 2.10 muestra $\langle \alpha \rangle$ y $\langle \alpha \rangle / n$ en función del tamaño del *cluster*. En la Figura 2.10(a) notamos un incremento monótonico de $\langle \alpha \rangle$ desde Cu a Cu_9 mostrando la proporcionalidad que se espera con el número total de electrones; desde la Figura 2.10(b) se observa que $\langle \alpha \rangle / n$ presenta un comportamiento que puede ser ajustado a un decaimiento exponencial de primer orden, $\langle \alpha \rangle / n = A + Be^{-Cn}$; ($A = 31.14$; $B = 28.67$; $C = 3.66$), con esta forma analítica se predice un valor de 31.14 *ua* para la polarizabilidad por átomo en el límite del *bulk* de cobre.

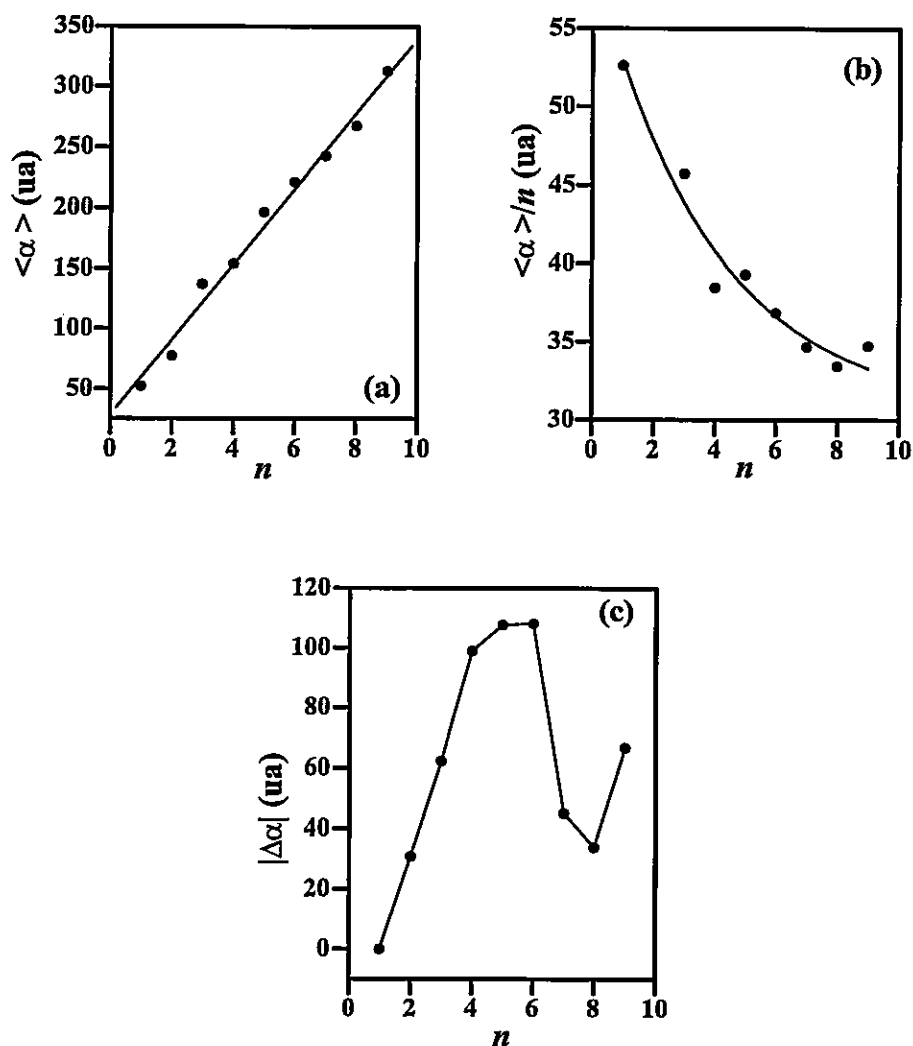


Figura 2.10: (a) Polarizabilidad calculada ($r=0.99$), (b) polarizabilidad por átomo ($r=0.96$), y (c) anisotropía de la polarizabilidad como función del tamaño del *cluster*.

La anisotropía del tensor de polarizabilidad ($|\Delta\alpha|$) proporciona información adicional sobre la forma del *cluster*, en particular la anisotropía puede ser considerada como una medida del grado de empaquetamiento de una estructura, así estructuras compactas deben presentar valores pequeños de $|\Delta\alpha|$. La anisotropía de la polarizabilidad está definida como:

$$|\Delta\alpha|^2 = \frac{3tr(\alpha)^2 - (tr\alpha)^2}{2} = \frac{1}{2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2] \quad (2.3)$$

y los resultados se incluyen en la Tabla 2.4 y se ilustran en la Figura 2.10(c). Se puede notar que a medida que el *cluster* crece $|\Delta\alpha|$ aumenta hasta Cu_6 y luego decae abruptamente en Cu_7 hasta Cu_9 pasando por un mínimo en Cu_8 , esta fuerte caída es debida básicamente al cambio estructural que ocurre desde Cu_6 (**2D**) a estructuras más compactas (**3D**). En este contexto se puede observar que $|\Delta\alpha|$ es una cantidad que es capaz de identificar las transiciones estructurales que están ocurriendo a medida que el tamaño del *cluster* crece.

Se ha hecho mención que Cu_8 presenta los valores más altos de energía de cohesión y más bajos de polarizabilidad por átomo en acuerdo al PMP. Para demostrar que se ha alcanzado consistencia entre descriptores energéticos y electrónicos, en la Figura 2.11 se presenta una buena relación lineal entre BE/n y $\langle \alpha \rangle / n$, esta relación indica que en aquellos sistemas con enlaces fuertes (o alta deslocalización electrónica) están asociados a valores mínimos de $\langle \alpha \rangle / n$ en acuerdo con el PMP, este resultado permite dejar en evidencia que la polarizabilidad es una propiedad electrónica que puede ser utilizada como un indicador de estabilidad química en el contexto de química de *clusters*.

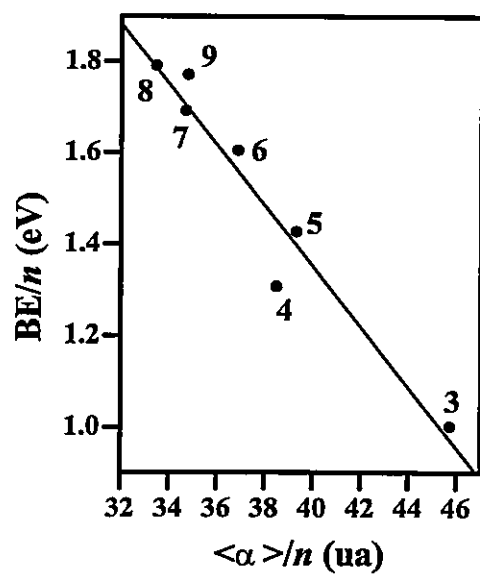


Figura 2.11: Correlación entre energía de enlace por átomo y polarizabilidad por átomo a lo largo de la serie ($n=1-9$; $r=-0.97$).

2.3 Conclusiones

- Los resultados presentados en sistemas moleculares tanto en el contexto de vibraciones moleculares como en rotaciones internas han confirmado la validez de los principios de máxima dureza y mínima polarizabilidad.
- Las moléculas en sus geometrías de equilibrio presentan valores máximos y mínimos de dureza y polarizabilidad, respectivamente; cuando se comparan a los correspondientes valores en alguna otra geometría obtenida a través de una distorsión del tipo asimétrica.
- En rotaciones internas los resultados entregados muestran que isómeros más (menos) estables están asociados con valores máximos (mínimos) de dureza y mínimos (máximos) de polarizabilidad.
- *Clusters* de cobre más estables son especies más duras y menos polarizables en acuerdo al PMD y PMP, respectivamente. Este comportamiento muestra que estas reglas funcionan en la caracterización de este tipo de sistemas, y en conjunto con el análisis de descriptores TFD eventualmente permiten obtener una mayor comprensión en procesos que están involucrados, tales como, en catálisis y reacciones de fragmentación.
- En este Capítulo se ha mostrado que conceptos provenientes de la TFD resultan ser de gran utilidad en la interpretación de resultados teóricos y experimentales en la caracterización de sistemas moleculares complementando así la información clásica que se obtiene desde la superficie de energía potencial.
- Los resultados presentados en este Capítulo sugieren que en ausencia de información de tipo energética, estos conceptos en conjunto con los principios de máxima dureza y mínima polarizabilidad pueden ser considerados como criterios alternativos que permiten caracterizar la estabilidad y reactividad de sistemas moleculares. Estos resultados permiten promover el uso de estos elementos de análisis en una variedad de dominios en química como veremos en los siguientes Capítulos.

Parte del trabajo presentado en este Capítulo ha sido publicado en los siguientes artículos:

1. Validity of the Minimum Polarizability Principle in Molecular Vibrations and Internal Rotations: An Ab Initio SCF Study.
Pratim K. Chattaraj, Patricio Fuentealba, **Pablo Jaque**, and Alejandro Toro-Labbé. *Journal of Physical Chemistry A*, 103 (1999) 9307–9312.
2. Characterization of Copper *Clusters* Through the use of Density Functional Theory Reactivity Descriptors.
Pablo Jaque and Alejandro Toro-Labbé. *Journal of Chemical Physics*, 117 (2002) 3208–3218.
3. Towards Understanding the Molecular Internal Rotations and Vibrations and Chemical Reactions Through the Profiles of Reactivity and Selectivity Indices: An Ab Initio SCF and DFT Study.
Pratim K. Chattaraj, Soledad Gutiérrez-Oliva, **Pablo Jaque** and Alejandro Toro-Labbé. *Molecular Physics*, 101 (2003) 2841–2853.
4. Polarizability of Neutral Copper *Clusters*.
Pablo Jaque and Alejandro Toro-Labbé. Manuscrito en preparación.



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Capítulo 3

Caracterización de Reacciones Químicas a partir de Conceptos Clásicos y Descriptores de Reactividad

Resumen

En este Capítulo presentaremos como los conceptos clásicos de reactividad en conexión con descriptores definidos en la TFD son elementos de análisis adecuados para caracterizar reacciones químicas. El modelo conceptual clásico, en el cual una reacción procede desde un mínimo de energía a otro pasando por un máximo, junto a los principios de máxima dureza y mínima polarizabilidad proveen los elementos necesarios para discutir los procesos de activación y relajación en términos de potencial químico y dureza molecular. Se entregan aplicaciones en reacciones torsionales y de doble transferencia protónica que validan este esquema de análisis.

3.1 Introducción

La química es la ciencia que estudia los cambios moleculares, y la comprensión de las transformaciones estructurales que acompañan la conversión de reactantes a productos es el tema central de ella. Dentro de este marco general existen muchos esfuerzos que permiten justificar teóricamente la preferencia de un camino de reacción sobre otro, la formación de solo algunos productos seleccionados entre varios posibles y elucidar los factores que gobiernan el curso de una reacción química.

En general, un proceso químico puede ser caracterizado a través de perfiles de reacción, que ilustran el cambio de las propiedades de los sistemas reactivos como una función de la coordenada de reacción (CR). Estas propiedades pueden ser de tipo global (energía, potencial químico electrónico, dureza molecular, polarizabilidad, electrofilia, valencia molecular, etc) o de carácter local (poblaciones electrónicas, funciones de Fukui, valencias atómicas, cargas atómicas, ordenes de enlaces, etc). En el contexto de la aproximación de *Born-Oppenheimer* [1], la CR representa el reordenamiento nuclear a medida que la reacción avanza, es decir, el cambio en longitudes y ángulos de enlaces durante la reacción química. Existen muchas situaciones en donde la CR puede ser una variable conformacional que conecta dos conformaciones que pueden ser consideradas como reactantes y productos de una reacción química, desafortunadamente en muchos procesos la CR es bastante compleja para su visualización.

La comprensión de la reactividad química permite predecir mecanismos de reacción y determinar como la energía de activación depende de propiedades específicas de reactantes y productos. En este contexto, la identificación de estas propiedades y aquellas asociadas al estado de transición son especialmente importantes. La TFD a través de la definición de propiedades de reactividad global y local, es una teoría adecuada para describir la reorganización electrónica que ocurre a medida que la reacción química avanza, y la nacionalización del cambio energético resultante en término de las funciones de respuestas TFD forman un conjunto de elementos teóricos de análisis que permiten caracterizar varios aspectos de un proceso químico.

Por otra parte, para caracterizar estados de transición (TS) se han definido un conjunto de herramientas conceptuales que permiten comprender su estructura y propiedades. Estas herramientas conceptuales son: (a) el postulado de *Hammond* (PH) que permite relacionar la estructura del TS con la exotermicidad de la reacción [2]; (b) el coeficiente de *Brønsted* (β) que es una medida de la localización del TS a lo largo de la CR, β es un índice que cuantifica el postulado de *Leffler* y puede ser interpretado como el grado de semejanza del TS respecto a los productos de reacción [3]; (c) la ecuación de *Marcus* que corresponde a una simple expresión que permite escribir la barrera de energía (ΔE^\ddagger) en términos de la energía de reacción (ΔE°) y de propiedades estructurales de reactantes y productos [4]; y (d) los principios de máxima dureza (PMD) [5] y mínima polarizabilidad (PMP) [6] que aseguran que los sistemas moleculares en equilibrio tienden a valores máximos de dureza y mínimos de polarizabilidad, respectivamente. La extensión de estos principios de estructura electrónica para estados de transición implica que en el TS se esperan valores mínimos de dureza y máximos de polarizabilidad. Aunque estos principios no sean ampliamente aplicables al estudio de TSs, ellos forman una base conceptual para racionalizarlos y caracterizar mecanismos de reacción.

En este Capítulo, nos concentramos en el estudio de reacciones químicas dentro del esquema de la teoría del estado de transición, en la cual reactantes (**R**) cambian a productos (**P**) pasando por un estado de transición (**TS**), estos tres estados estacionarios sobre la superficie de energía potencial (SEP) están conectados por una coordenada de reacción [7,8]. Nuestro principal interés ha sido abarcar el estudio de un proceso químico desde una nueva perspectiva, la cual consiste en lograr conectar conceptos clásicos de reactividad con descriptores de la TFD, y así generar un conjunto de elementos teóricos de análisis que permitan caracterizar diferentes aspectos (termodinámicos, cinéticos y mecanísticos) de una reacción química. En las siguientes secciones de este Capítulo se presentan aspectos teóricos y aplicaciones, particularmente hemos llevado a cabo estudios en proceso de isomerización rotacional en sistemas que presenta simetría de reflexión HXNX ($X=O,S$) [9], y reacciones de doble

transferencia protónica en complejos cíclicos enlazados por puentes de hidrógeno formados por unidades de HCX-XH (X=O,S) [9, 10].

3.2 Aspectos Teóricos

3.2.1 Procesos de Isomerización Rotacional



Figura 3.1: Esquema del proceso de isomerización rotacional.

Para una transformación rotacional *trans* \rightleftharpoons *cis* que ocurre a través de la rotación interna con respecto a un dado enlace en una molécula, la CR es el ángulo de torsión α definido como el ángulo dihedro que se indica en la Figura 3.1. En los casos que hemos considerado en este trabajo, se tienen isomerizaciones *trans* \rightleftharpoons *cis* en donde los isómeros de referencias son planares y el ángulo de torsión es medido desde el conformero *trans* ($\alpha=0$) al *cis* ($\alpha=\pi$). Se ha utilizado el siguiente modelo de potencial para describir este proceso [11–14]:

$$V(\alpha) = \frac{1}{4}K_V[1 - \cos^2(\alpha)] + \frac{1}{2}\Delta V^\circ[1 - \cos(\alpha)] \quad (3.1)$$

donde K_V es la suma de las constantes de fuerza de las conformaciones *trans* y *cis* ($K_V = k_t + k_c$) y $\Delta V^\circ = [V(\pi) - V(0)]$, es la energía de la reacción. Por otra parte, expresamos la CR en término de una coordenada de reacción reducida que esta definida entre 0 y 1, que mide el progreso de la reacción cuando va desde reactantes a productos. En el contexto de las reacciones conformacionales esta coordenada de reacción reducida ω , denominada función conformacional, está definida como:

$$\omega(\alpha) = \frac{1}{2}[1 - \cos(\alpha)], \quad (3.2)$$

en esta representación la energía potencial viene dada por:

$$V[\omega] = K_V f[\omega] + \omega \Delta V^\circ \quad (3.3)$$

con $f[\omega] = \omega(1 - \omega)$. Existen varias formas analíticas posibles para $f[\omega]$ puesto que el único requerimiento es que esta debe ser simétrica con respecto a $\omega = 1/2$.

La energía potencial es una propiedad global del sistema en estudio, por tanto, la evolución de otras propiedades de carácter global como μ y η a lo largo de ω vendrá dada por la misma forma analítica que para $V[\omega]$

$$\mu[\omega] = K_\mu f[\omega] + \omega \Delta \mu^\circ \quad (3.4)$$

$$\eta[\omega] = K_\eta f[\omega] + \omega \Delta \eta^\circ. \quad (3.5)$$

El set de parámetros $(K_\mu, \Delta \mu^\circ)$ y $(K_\eta, \Delta \eta^\circ)$ tienen el mismo significado que K_V y ΔV° en $V[\omega]$. Al considerar que V , μ y η depende de la misma función $f[\omega]$, es posible establecer relaciones analíticas entre el potencial torsional y las propiedades electrónicas, esto conduce a una descripción completa del proceso rotacional permitiendo conectar aspectos energéticos (termodinámicos) con mecanísticos. La extensión de la aplicación de este tipo de relaciones es aún materia de investigación, sin embargo se sabe que su aplicabilidad depende del grado de independencia que puedan mostrar las propiedades electrónicas respecto de la energía [10, 13, 14].

La posición del TS puede ser determinada por diferenciación de la ecuación (3.1):

$$\left(\frac{dV}{d\alpha}\right) = 0 \Rightarrow \cos(\alpha_0) = -\frac{\Delta V^\circ}{K_V} \Rightarrow \omega(\alpha_0) \equiv \beta = \frac{1}{2} + \frac{\Delta V^\circ}{2K_V} \quad (3.6)$$

donde β es el coeficiente de *Brønsted* que según el postulado de *Leffler* [3] mide el grado de semejanza del TS con respecto a los productos. Al introducir β en la ecuación (3.3) se obtiene la siguiente expresión para la barrera de energía asociada al proceso rotacional

$$V[\beta] \equiv \Delta V^\ddagger = \frac{1}{4}K_V + \frac{1}{2}\Delta V^\circ + \frac{(\Delta V^\circ)^2}{4K_V}. \quad (3.7)$$

Esta expresión es idéntica a la ecuación de *Marcus*, originalmente propuesta para caracterizar procesos de transferencia electrónica [4], en este trabajo mostraremos su utilidad en la interpretación de barreras de energía de reacciones químicas de diferentes tipos [9, 10, 13]. También se debe hacer notar la consistencia que existe entre la ecuación de *Marcus* con la definición de *Leffler* del coeficiente de *Brønsted* ($\beta = (\partial\Delta V^\ddagger/\partial\Delta V^\circ)$). Esta ecuación contiene la estructura formal necesaria para una representación analítica del postulado de *Hammond* [9, 15, 16].

3.2.2 Reacciones de Transferencia

Los resultados presentados en la sección anterior pueden ser aplicados para caracterizar estados de transición de procesos químicos más complejos, ya que una reacción química, puede ser racionalizada en términos de etapas elementales que conectan reactantes, estado de transición y productos: $\mathbf{R} \longrightarrow (\text{TS})^\ddagger \longrightarrow \mathbf{P}$. Estos estados estacionarios son conectados por una coordenada de reacción interna (IRC) que viene dada por cálculos estándar [17, 18], a lo largo del IRC es posible definir los perfiles de energía, potencial químico, dureza y polarizabilidad que permite caracterizar la reacción y las propiedades del estado de transición. Nuevamente, para caracterizar TS se ha hecho uso de la ecuación de *Marcus* y el coeficiente de *Brønsted*. Por otra parte, conociendo ΔV° y ΔV^\ddagger se puede obtener K_V que será utilizado para determinar la posición del TS a lo largo del IRC. Se debe hacer notar que para caracterizar la posición del TS se requiere una definición explícita de la coordenada de reacción, sin embargo la ecuación de *Marcus* proporciona una base analítica para obtener una mayor comprensión del TS.

3.2.3 Propiedades Electrónicas de Activación

Para reacciones isoenergéticas la ecuación de Marcus se reduce a:

$$\Delta V_0^\ddagger = \frac{1}{4}K_V \quad (3.8)$$

y el TS está localizado en el punto medio entre reactantes y productos ($\beta = 1/2$). La cantidad ΔV_0^\ddagger es equivalente a la energía de activación intrínseca de *Marcus* y corresponde a la altura de la barrera para el caso en el cual no existen fuerzas de origen energéticas (o termodinámicas) que controlen el proceso, esta cantidad debería estar relacionada a propiedades puramente electrónicas tal como el potencial químico y dureza molecular. La ecuación de *Marcus* puede ser escrita como:

$$\Delta V^\ddagger = \Delta V_0^\ddagger + \frac{1}{2}\Delta V^\circ + \frac{(\Delta V^\circ)^2}{16\Delta V_0^\ddagger}. \quad (3.9)$$

Esta expresión indica que cuando la reacción es exoenergética ($\Delta V^\circ < 0$) ΔV^\ddagger es menor que la barrera intrínseca mientras que para reacciones endoenergéticas ($\Delta V^\circ > 0$) ΔV^\ddagger es mayor que la barrera intrínseca. Como hemos mencionado la barrera intrínseca podría ser interpretada en términos de propiedades estructurales y electrónicas, a partir de nuestras investigaciones hemos sugerido que esta barrera puede ser racionalizada a través de las propiedades electrónicas μ y η [9, 10]. Hemos propuesto la siguiente expresión que relaciona ΔV_0^\ddagger con las propiedades electrónicas de activación:

$$\Delta V_0^\ddagger = \frac{1}{2}Q_\eta\Delta\mu^\ddagger + \frac{1}{2}Q_\mu\Delta\eta^\ddagger \quad (3.10)$$

donde $\Delta\mu^\ddagger \equiv [\mu(TS) - \mu(R)]$ y $\Delta\eta^\ddagger \equiv [\eta(TS) - \eta(R)]$ son el potencial químico y dureza de activación, respectivamente. Los parámetros Q_η , Q_μ han sido relacionados a la cantidad de carga electrónica transferida durante la reacción química [13, 14], estos pueden ser determinados numéricamente a través de:

$$Q_\eta = \frac{(\Delta V^\ddagger - \Delta V^\circ)}{(\Delta\mu^\ddagger - \Delta\mu^\circ)}, \quad (3.11)$$

y

$$Q_{\mu} = \frac{(\Delta V^{\ddagger} - \Delta V^{\circ})}{(\Delta \eta^{\ddagger} - \Delta \eta^{\circ})}. \quad (3.12)$$

Se debe destacar que de acuerdo a esta representación la validez del principio de máxima dureza implica una curvatura opuesta para la energía y dureza molecular, esto se debe reflejar en un valor negativo para el parámetro Q_{μ} [9, 13, 14].

3.2.4 Mecanismos de Reacción

El concepto de mecanismo de reacción está relacionado con el desplazamiento nuclear que ocurre al pasar desde reactantes a productos. Estos desplazamientos están relacionados con las fuerzas que actúan sobre el sistema para transformar reactantes en productos. Las fuerzas que actúan sobre el sistema dependen solo de la posición a lo largo de la coordenada de reacción, entonces:

$$F(\omega) = -\frac{dV}{d\omega}, \quad (3.13)$$

y suponiendo que $V(\omega)$ puede ser expresado como:

$$V(\omega) = K_V \omega(1 - \omega) + \omega \Delta V^{\circ}, \quad (3.14)$$

entonces se obtiene:

$$F(\omega) = -(K_V + \Delta V^{\circ}) + (2K_V)\omega. \quad (3.15)$$

Para obtener una descripción adecuada de toda la reacción química, es útil distinguir los diferentes procesos que tienen lugar a lo largo de la coordenada de reacción. En la región de reactantes ocurre un proceso de activación al que asociamos el trabajo de activación W_{act} :

$$W_{act} = \int_0^{\beta} F(\omega) d\omega = \Delta V^{\ddagger}, \quad (3.16)$$

en la región de productos tenemos un proceso de relajación, el trabajo (W_{rel}) asociado es:

$$W_{rel} = \int_{\beta}^1 F(\omega) d\omega = \Delta V^{\circ} - \Delta V^{\ddagger}. \quad (3.17)$$

Reacciones isoenergéticas presentan estados de transición en $\beta = 1/2$, en valor absoluto el trabajo de activación es igual al de relajación. En contraste a esto y considerando el postulado de *Hammond*, reacciones exoenergéticas están caracterizadas por estados de transición tempranos ($\beta < 1/2$) y por un trabajo de activación menor que de relajación. Finalmente, un proceso endoenergético está caracterizado a través de un TS tardío $\beta > 1/2$ y un trabajo de activación mayor que de relajación.

Es importante destacar que las expresiones anteriores permiten discutir los trabajos de activación y relajación en términos del potencial químico y la dureza molecular. Esta forma de racionalizar un evento químico permite conectar conceptos clásicos de reactividad química con descriptores de reactividad definidos desde la TFD. Para establecer esta regla cualitativa se debe asumir que la ecuación (3.10) es válida para todo ω , y se define el perfil de energía como:

$$V(\omega) = \frac{1}{2} Q_{\eta} \mu(\omega) + \frac{1}{2} Q_{\mu} \eta(\omega). \quad (3.18)$$

Consecuentemente, el concepto de fuerza aparece como dos contribuciones que están asociadas a μ y η :

$$F(\omega) = -\frac{dV}{d\omega} = -\frac{1}{2} Q_{\eta} \frac{d\mu}{d\omega} - \frac{1}{2} Q_{\mu} \frac{d\eta}{d\omega}. \quad (3.19)$$

Haciendo uso de definiciones directa y considerando que $Q_{\mu} < 0$ en cumplimiento del PMD, $F(\omega)$ puede ser dividido como:

$$F(\omega) = -F_{\mu}(\omega) + F_{\eta}(\omega). \quad (3.20)$$

Esta Expresión permite realizar un análisis cualitativo de $F(\omega)$ en término del signo que toma la fuerza a lo largo de la coordenada de reacción:

$$(0 \leq \omega < \beta) : \quad F(\omega) < 0 \quad \implies \quad F_{\mu}(\omega) > F_{\eta}(\omega) \quad (3.21)$$

entonces cuando se avanza en la CR desde reactantes al estado de transición (proceso de activación), el potencial químico controla la reacción. En el estado de transición se tiene que:

$$(\omega = \beta) : \quad F(\omega) = 0 \quad \implies \quad F_{\mu}(\omega) = F_{\eta}(\omega) \quad (3.22)$$

ambas contribuciones se cancelan. En la región que está definida desde el TS a los productos de la reacción (proceso de relajación), se tiene que:

$$(\beta < \omega \leq 1) : \quad F(\omega) > 0 \quad \implies \quad F_{\eta}(\omega) > F_{\mu}(\omega), \quad (3.23)$$

esta etapa de la reacción es controlada por la dureza molecular, el sistema se reordenará para alcanzar una configuración de máxima dureza. En resumen, este simple modelo sugiere que el proceso de activación es básicamente controlado por μ mientras que el proceso de relajación estará gobernado por η .

3.3 Aplicaciones: Isomerización Rotacional y Reacciones de Transferencia Protónica

3.3.1 Detalles Computacionales

Todos los cálculos fueron realizados al nivel de teoría RHF/6-311G** y B3LYP/6-311G** usando el programa Gaussian 94/98 [19, 20]. Los perfiles de E , μ , η , y α para procesos de isomerización rotacional en HXNX (X=O,S) se obtuvieron haciendo cálculos cada 10° a lo largo del ángulo de torsión en un intervalo de 0° a 180° mientras que para el proceso de doble transferencia protónica en dímeros de referencias (HCOOH)₂ y (HCSSH)₂, se obtuvieron a través de cálculos de puntos sencillos de las estructuras optimizadas indicadas por el procedimiento IRC.

Los descriptores electrónicos fueron obtenidos a través de las fórmulas operacionales entregadas en el Capítulo 1.

3.3.2 Isomerización Rotacional de HXNX (X=O,S)

La comprensión de procesos de isomerización rotacional que presentan los sistemas moleculares es de fundamental importancia en la optimización de propiedades biológicas, químicas y físicas. Para este propósito resulta indispensable la determinación de la estabilidad relativa de los diferentes isómeros, la identificación del mecanismo de reacción, la evaluación de las barreras de potencial y velocidades de transformación entre varias conformaciones. La metodología que fué presentada en las secciones anteriores ha sido utilizada para analizar procesos de isomerización rotacional del tipo *trans* \Rightarrow *cis* en sistemas moleculares del tipo HXNX (X=O,S), ácido nitroso (HO₁-N=O₂) y tionitroso (HS₁-N=S₂) como es ilustrado en la Figura 3.2.

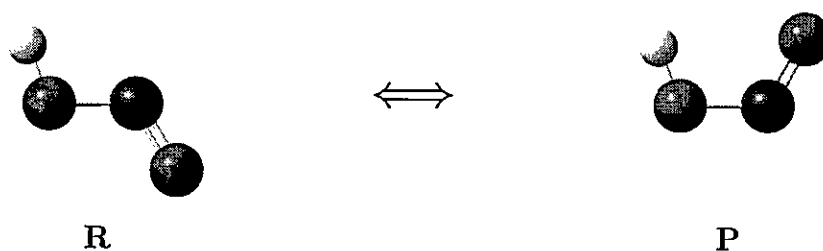


Figura 3.2: Representación de la reacción conformacional en moléculas del tipo HXNX (X=O,S).

3.3.2.1 Índices de Reactividad.

En la Tabla 3.1 se presentan los parámetros globales de reactividad (en el caso de la polarizabilidad agregamos su componente fuera del plano molecular α_{zz}) y el momento dipolar para los reactantes, estados de transición y productos asociados con el proceso de isomerización rotacional de HONO y HSNS obtenidos mediante cálculos a niveles RHF/6-311G** y B3LYP/6-311G**. En ambos casos estudiados, tanto los conformeros *trans* como *cis* corresponden a mínimos sobre la SEP y están caracterizados por la no presencia de frecuencias imaginarias (NIMAG=0). Tanto los resultados RHF como B3LYP indican que la isomerización rotacional *trans* \rightarrow *cis* es un proceso favorable desde un punto de vista termodinámico, en ambos casos el conformero *cis* es levemente más estable que el isómero *trans*, debido al puente de hidrógeno intramolecular que se forma en la conformación *cis*.

Los estados de transición tanto para HONO como HSNS están localizados próximos a 90° , y como es de esperar, son caracterizados por una frecuencia imaginaria (NIMAG=1), además de valores de máxima energía, mínima dureza y valencia molecular, que indican la validez de los principios de máxima dureza y máxima valencia molecular. La polarizabilidad promedio del TS presenta un valor máximo en el caso de HONO mientras que en HSNS presenta un valor mínimo, indicando la validez del principio de mínima polarizabilidad solamente en el proceso torsional en HONO. En este ámbito, *Ghanty y Ghosh* [21] sugieren el análisis de la componente fuera del plano molecular

| <i>HONO</i> | <i>E</i> | μ | η | $\langle \alpha \rangle$ | α_{zz} | V_M | DM |
|---------------------|-------------|---------|--------|--------------------------|---------------|--------|--------|
| trans | -204.700158 | -4.4627 | 7.7635 | 13.448 | 7.488 | 3.7597 | 2.5469 |
| ($\theta = 0$) | -205.761769 | -5.1239 | 2.6803 | 15.352 | 7.806 | 3.9783 | 2.0645 |
| TS($\theta=92.6$) | -204.682531 | -4.8028 | 7.5213 | 13.535 | 9.477 | 3.6886 | 1.8656 |
| TS($\theta=92.5$) | -205.741044 | -5.5675 | 2.4109 | 15.334 | 10.516 | 3.8779 | 1.6155 |
| cis | -204.701446 | -4.7811 | 7.9104 | 13.268 | 7.402 | 3.7497 | 1.5730 |
| ($\theta = 180$) | -205.762150 | -5.3634 | 2.7892 | 15.110 | 7.703 | 3.9815 | 1.5151 |
| <i>HSNS</i> | | | | | | | |
| trans | -850.021798 | -4.4736 | 4.8546 | 40.576 | 19.690 | 3.7540 | 1.9299 |
| ($\theta = 0$) | -851.727234 | -4.8872 | 1.3062 | 43.653 | 20.249 | 3.9734 | 2.1297 |
| TS($\theta=93.8$) | -850.001284 | -4.7539 | 4.7403 | 37.645 | 25.386 | 3.6253 | 1.7356 |
| TS($\theta=92.7$) | -851.702711 | -5.4124 | 1.1511 | 42.099 | 27.068 | 3.8109 | 1.6378 |
| cis | -850.022786 | -4.5764 | 4.8850 | 40.189 | 19.316 | 3.7627 | 2.2822 |
| ($\theta = 180$) | -851.729019 | -4.9716 | 1.3551 | 43.380 | 19.836 | 3.9993 | 2.3820 |

Tabla 3.1: Parámetros globales de reactividad de los puntos estacionarios para la reacción de isomerización de HONO y HSNS. La primera entrada de datos corresponde a resultados obtenidos mediante cálculos RHF mientras que la segunda presenta resultados TFD(B3LYP). (E , $\langle \alpha \rangle$ and α_{zz} están en ua ; μ y η en eV ; MD esta en Debye).

(α_{zz}), en ambos sistemas se observa un valor máximo de α_{zz} para el TS respecto a reactantes y productos, este resultado insinúa que el análisis de la componente perpendicular al plano molecular puede ser criterio alternativo en la aplicación del PMP.

La energía torsional y propiedades electrónicas fueron evaluadas cada 10 grados a lo largo del ángulo de torsión. La Figura 3.3 muestra los perfiles de E , μ , η , V_M y α_{zz} para HONO (a) y HSNS (b). Dentro de los resultados más relevantes se confirma la validez de principios de estructura electrónica, PMD, PMP y PMVM.

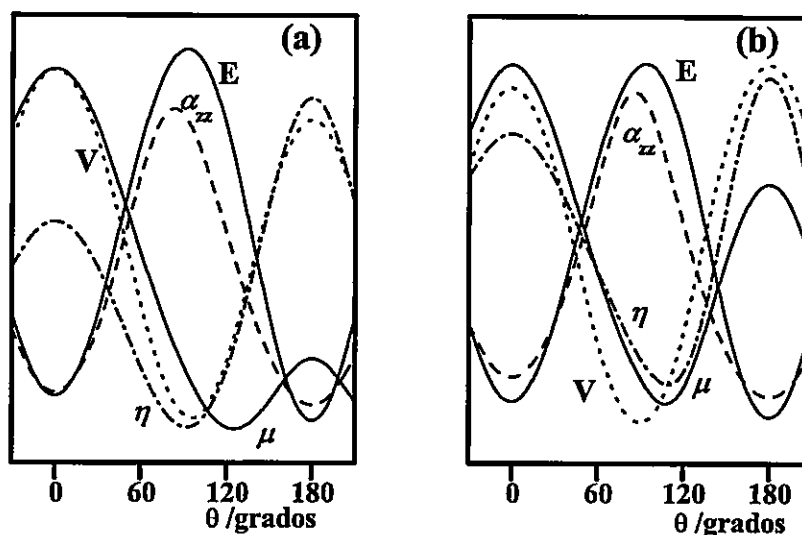


Figura 3.3: Perfiles cualitativos de propiedades globales de reactividad a lo largo del ángulo de torsión de HONO (a) y HSNS (b) obtenidos mediante cálculos RHF/6-311G**.

La Tabla 3.2 complementa estos resultados y en ella se presentan valores relativos a reactantes de diferentes propiedades ($\Delta P^\circ = [P(P) - P(R)]$ y $\Delta P^\ddagger = [P(TS) - P(R)]$, $P = V, \mu, \eta, \alpha_{zz}$) que caracterizan el proceso torsional. Se observan valores negativos para $\Delta \eta^\ddagger$ mostrando que en estos casos el PMD se cumple aún cuando μ varía a lo largo del ángulo de torsión. Por otra parte, valores positivos de $\Delta \alpha_{zz}^\ddagger$ validan el PMP. También en esta Tabla se incluye el coeficiente de *Brønsted* (β) que indica si la estructura del TS estará más próxima a las estructuras de reactantes o productos, este descriptor estructural en conjunto con ΔV° permiten clasificar a la isomerización rotacional en HONO y HSNS como reacciones tipo *Hammond*, debido a que ambos procesos son exoenergéticos ($\Delta V^\circ < 0$), lo cual implica $\beta < 0.5$, por otra parte, los productos de reacción son las especies más estables, más duros ($\Delta \eta^\circ > 0$) y menos polarizables ($\Delta \alpha_{zz}^\circ < 0$), este resultado permite mostrar consistencia entre el postulado de *Hammond* y los principios de máxima dureza y mínima polarizabilidad [22].

| <i>HONO</i> | ΔV^o | ΔV^\ddagger | $\Delta\mu^o$ | $\Delta\mu^\ddagger$ | $\Delta\eta^o$ | $\Delta\eta^\ddagger$ | $\Delta\alpha_{zz}^o$ | $\Delta\alpha_{zz}^\ddagger$ | β |
|-------------|--------------|---------------------|---------------|----------------------|----------------|-----------------------|-----------------------|------------------------------|---------|
| HF | -0.8082 | 11.0611 | -7.3424 | -7.8428 | 3.3876 | -5.5852 | -0.086 | 1.989 | 0.4912 |
| DFT | -0.2391 | 13.0051 | -5.5230 | -10.2296 | 2.5113 | -6.2125 | -0.103 | 2.710 | 0.4977 |
| <i>HSNS</i> | | | | | | | | | |
| HF | -0.6200 | 12.8728 | -2.3706 | -6.4638 | 0.7010 | -2.6358 | -0.347 | 5.696 | 0.4941 |
| DFT | -1.1201 | 15.3884 | -1.9463 | -12.1113 | 1.1277 | -3.5767 | -0.413 | 6.819 | 0.4912 |

Tabla 3.2: Propiedades de Activación de la reacción de isomerización de HONO and HSNS. Todos los valores están en *kcal/mol*.

En relación a las barreras de energía torsional se observa que sus valores están muy próximos, HSNS presenta un valor de ΔV^\ddagger levemente mayor que HONO. Este resultado permite concluir que la naturaleza física de la barrera torsional es similar en ambos procesos de isomerización, esta conclusión se verifica a partir del análisis local que veremos en los párrafos siguientes.

3.3.2.2 Indices de Selectividad

Los perfiles de índices de selectividad de sitios son presentados en la Figura 3.4. Funciones de Fukui condensadas (f_k) fueron determinadas usando la ecuación (1.17). En la mayoría de los casos, al igual que en los índices de reactividad se observan valores extremos en la cercanías o en el TS, las mismas tendencias fueron obtenidas cuando se usa la aproximación de diferencias finitas en el cálculo de funciones de Fukui (ecuación (1.16)). En relación a valencias atómicas, estas permanecen constantes a lo largo de la coordenada de reacción con la excepción de V_{O1} en HONO y V_{S1} en HSNS presentando un valor mínimo en el TS. Esta observación permite confirmar lo mencionado acerca de la similaridad de la naturaleza física de las barreras de potencial en HONO y HSNS. Las funciones de Fukui al igual que las valencias atómicas no son fuertemente dependientes del ángulo torsional, en general los patrones de reactividad tanto para ataques electrofílicos como nucleofílicos permanecen constantes. Sin embargo, las funciones de Fukui frente a un ataque electrofílico de los átomos de oxígeno presentan una mayor variación, y como es de esperar, éstas son opuestas.

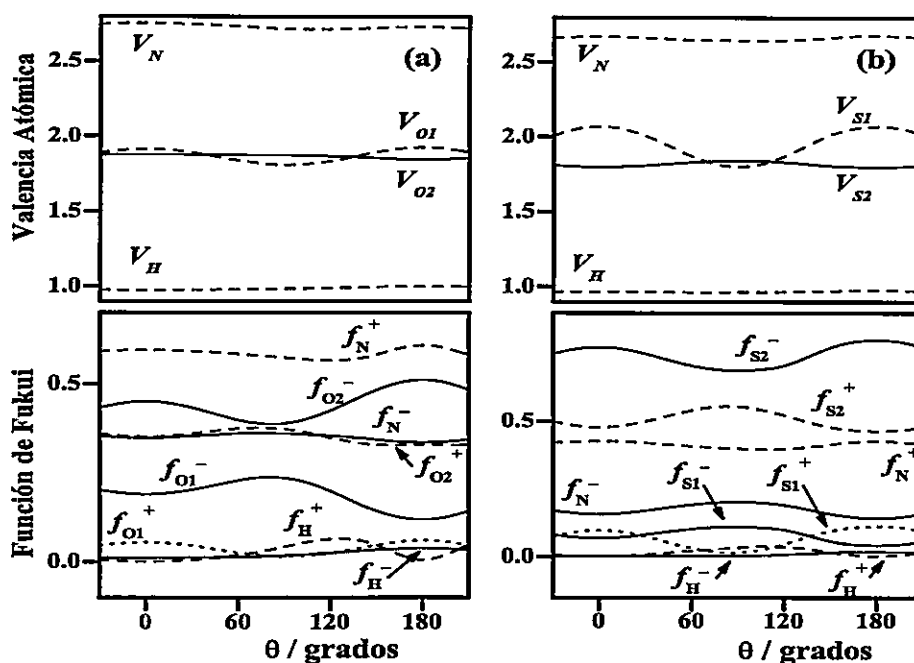


Figura 3.4: Perfiles cualitativos de propiedades locales de selectividad a lo largo del ángulo de torsión de $\text{HO}_1\text{-N=O}_2$ (a) y $\text{HS}_1\text{-N=S}_2$ (b) obtenidos mediante cálculos RHF/6-311G**.

Un resultado a destacar respecto a los perfiles de índices de selectividad es el comportamiento inverso que presenta V_{X1} con aquellos de f_{X1}^- ($V_k \propto \frac{1}{f_k}$), esta observación puede ser explicada de la siguiente manera, puesto que todos los valores de valencias atómicas son positivos, y un valor máximo de V_M implica mayor estabilidad, por lo tanto, aquellos sitios con valores altos deben ser menos reactivos (f_k pequeños) mientras que valores pequeños de V_k implica un alto valor de f_k , es decir una mayor reactividad del sitio k .

Finalmente, destacamos que los resultados obtenidos a partir de métodos TFD muestran las mismas tendencias cualitativas que aquellos obtenidos mediante cálculos RHF.

3.3.3 Reacciones de Doble Transferencia Protónica

Las reacciones de transferencia protónicas (TP) son unas de las más simples y fundamentales en química, debido a su importancia en reacciones de oxidación y reducción en muchos procesos químicos y biológicos [23, 24]. Existe un creciente interés en el estudio de propiedades intrínsecas, tanto de complejos enlazados por puentes de hidrógeno como de la dinámica de la transferencia protónica, en la literatura se han reportados numerosos estudios basados en diferentes metodologías tanto en la teoría *Hartree-Fock* como en la teoría funcional de la densidad [25–28]. Estos estudios en su mayoría considera la transferencia de un protón, las reacciones en las cuales más de un protón es transferido han sido menos estudiadas. En esta sección se presentan los resultados del estudio de la reacción de doble transferencia protónica (2TP) en complejos cíclicos enlazados por puentes de hidrógeno por combinación de unidades del tipo HCX-XH (X=O,S) ilustrado en la Figura 3.5.

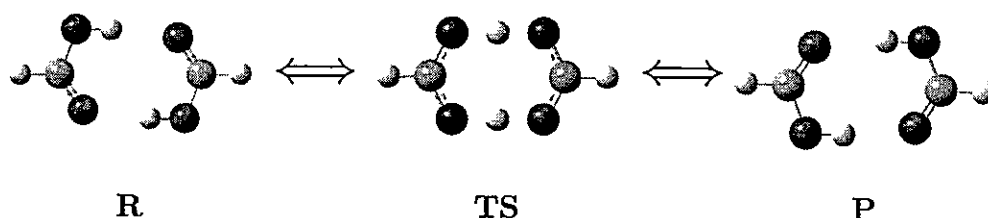


Figura 3.5: Esquema de las reacciones de doble transferencia protónica.

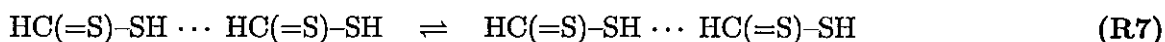
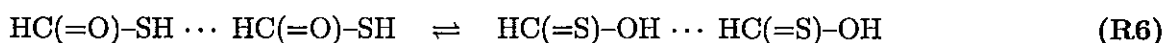
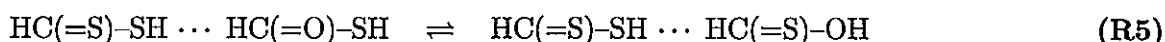
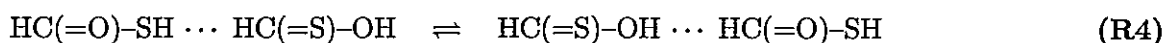
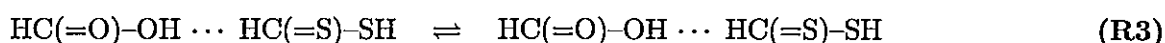
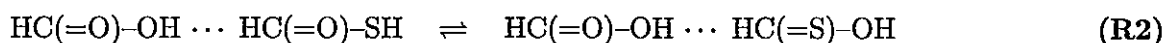
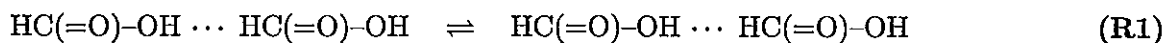
Dentro de los antecedentes bibliográficos, se encuentra que la reacción de 2TP en el dímero de ácido fórmico $[(\text{HCOOH})_2]$ ha sido estudiada extensivamente desde los puntos de vista experimental y teórico [29–33]. $[(\text{HCOOH})_2]$ ha sido utilizado como modelo para estudiar y comprender propiedades de muchos sistemas multiprotónicos de importancia química y biológica. Recientes estudios teóricos donde la principal motivación ha sido predecir estructuras de $[(\text{HCOOH})_2]$, y la SEP para el proceso 2TP, han permitido identificar el camino de mínima energía (MEP) sobre la SEP, este involucra un conjunto de desplazamientos nucleares: la transferencia es iniciada en una primera etapa por desplazamientos de átomos pesados aproximando a

las unidades monoméricas, en la vecindad del estado de transición, el MEP implica principalmente movimiento de los protones transferidos [29, 34, 35].

Otra característica interesante en procesos de TP tiene relación con la dirección del flujo de carga electrónica, la cual es opuesta al movimiento del protón [26], este antecedente sugiere que el análisis detallado de la redistribución de la carga electrónica manifestada en variaciones de descriptores electrónicos durante el proceso dinámico proporcionará los elementos necesarios para comprender el mecanismo de la reacción e identificar las interacciones específicas que gobiernan el proceso.

3.3.3.1 Reacciones de 2TP

Desde las unidades monoméricas HCX-YH ($X, Y = \text{O, S}$) es posible generar 10 estructuras bimoleculares enlazadas por hidrógeno, entre estas estructuras existen 7 posibles reacciones de doble transferencia protónica. En este estudio se ha considerado el proceso de transferencia sincrónica.



La Tabla 3.3 se presentan varias propiedades del TS para las 7 reacciones de 2TP. En primer lugar se observa que es su mayoría estas reacciones son isoenergéticas, y solo 3 reacciones son endoenergéticas, (R2), (R5) y (R6) como lo señala el valor de ΔV° en la Tabla 3.3. Las barreras de energía para las reacciones de transferencia protónica están ordenadas en el sentido que esta propiedad incrementa desde la reacción R1

| Reacción | ΔV° | ΔV^\ddagger | K_V | β | N |
|-----------|------------------|---------------------|----------|---------|-----|
| R1 | 0.0000 | 17.9311 | 71.7244 | 0.500 | 48 |
| R2 | 0.4675 | 19.9937 | 79.0370 | 0.503 | 56 |
| R3 | 0.0000 | 23.1733 | 92.6932 | 0.500 | 64 |
| R4 | 0.0000 | 25.6087 | 102.4348 | 0.500 | 64 |
| R5 | 2.2685 | 29.0499 | 111.6165 | 0.510 | 72 |
| R6 | 3.0754 | 30.4612 | 115.6122 | 0.513 | 64 |
| R7 | 0.0000 | 37.3895 | 149.5580 | 0.500 | 80 |

Tabla 3.3: Propiedades energéticas y estructurales para reacciones de 2TP obtenidas mediante cálculos RHF/6-311G**.

a la **R7**, es decir, estas reacciones definen los límites de ΔV^\ddagger para las barreras de reacciones restantes; **R1** y **R7** son reacciones de referencia debido a que ellas ocurren en dímeros de HCOOH y HCSSH. Es interesante notar que esta cantidad es proporcional al número total de electrones (N) del agregado molecular.

Utilizando los valores optimizados de ΔV^\ddagger y ΔV° en la ecuación (3.7), se determinó el valor del parámetro K_V el cual sigue la misma tendencia que ΔV^\ddagger . A través de la expresión (3.6) se obtuvo el coeficiente de *Brønsted*, que indica la posición del TS a lo largo de la coordenada de reacción. Los resultados muestran que $\beta = 0.50$ o $\beta > 0.50$ indicando que el TS se encuentra a mitad de camino entre **R** y **P** en el caso de reacciones isoenergéticas o más cerca de productos en el caso de reacciones endoenergéticas en acuerdo al postulado de *Hammond*, este resultado permite validar la ecuación (3.7) para caracterizar estados de transición asociados a reacciones de transferencia protónica.

Respecto a propiedades electrónicas, estas son entregadas en la Tabla 3.4, y se indican los valores de potencial químico, dureza molecular y polarizabilidad referidos a los

reactantes ($\Delta P^\circ = [P(P) - P(R)]$ y $\Delta P^\ddagger = [P(TS) - P(R)]$, $P = \mu, \eta, \alpha$). En el caso de procesos endoenergético se encuentra $\Delta\mu^\circ < 0$ indicando que la dirección del flujo de carga electrónica es en el sentido $\mathbf{R} \rightarrow \mathbf{P}$, la cual es opuesta al movimiento del protón. Por otra parte, se observan valores relativamente altos de $\Delta\mu^\ddagger$ que indican que el potencial químico no se mantiene constante a lo largo del proceso, este hecho es importante a la hora de discutir el principio de máxima dureza [36], en todos los casos con $\Delta V^\circ > 0$ se observa que $\Delta\eta^\circ < 0$ mostrando que reactantes son especies más duras que los productos. Por otra parte β indica que la estructura del TS es tipo producto encontrando consistencia entre el PMD ($\Delta\eta^\circ < 0$) y PH para caracterizar este tipo de procesos. Los valores de $\Delta\eta^\ddagger$ están indicando que el TS es la especie más blanda a lo largo de la coordenada de reacción. Estos resultados muestran que un máximo en energía esta asociado a un valor mínimo en dureza, lo cual permite confirmar la validez del PMD en reacciones de doble transferencia protónica. Este resultado y los presentados en procesos de isomerización rotacional son ejemplos en que el PMD se mantiene valido aún cuando el potencial químico no es constante a lo largo del IRC [10, 22].

Los valores de polarizabilidad de activación muestran que en todos los casos el estado de transición es más polarizable que los reactantes y productos indicando que el principio de mínima polarizabilidad también se cumple en este tipo de reacciones. Adicionalmente en los tres casos de reacciones endoenergéticas $\Delta\alpha^\circ > 0$ lo cual confirma que la dirección de evolución es hacia un estado de mínima energía y polarizabilidad, como es requerido por el PMP [6].

| Reacción | $\Delta\mu^\circ$ | $\Delta\mu^\ddagger$ | $\Delta\eta^\circ$ | $\Delta\eta^\ddagger$ | $\Delta\alpha^\circ$ | $\Delta\alpha^\ddagger$ |
|-----------|-------------------|----------------------|--------------------|-----------------------|----------------------|-------------------------|
| R1 | 0.0000 | -1.7633 | 0.0000 | -6.1245 | 0.0000 | 1.0890 |
| R2 | -0.5397 | 13.3471 | -22.4460 | -16.5851 | 2.0937 | 4.0350 |
| R3 | 0.0000 | 15.4995 | 0.0000 | -4.1165 | 0.0000 | 6.6230 |
| R4 | 0.0000 | 0.8848 | 0.0000 | -4.0725 | 0.0000 | 9.1603 |
| R5 | -5.8672 | 5.9613 | -2.1586 | -14.3700 | 2.1844 | 11.9334 |
| R6 | -8.2685 | -9.2056 | -27.5288 | -15.2422 | 4.2687 | 6.6884 |
| R7 | 0.0000 | -1.9327 | 0.0000 | -7.7497 | 0.0000 | 17.6313 |

Tabla 3.4: Propiedades electrónicas para reacciones de 2TP obtenidas mediante cálculos RHF/6-311G**.

3.3.3.2 Relación Entre los Procesos de Formación y 2TP

Estos procesos son secuenciales, es decir, la formación del complejo cíclico que está caracterizado por la energía de interacción $\Delta E_{hb} = E_{hb} - \sum_m^2 E_m$, donde E_{hb} es la energía del complejo bimolecular optimizado y E_m es la energía de las correspondientes especies monoméricas optimizadas, es seguida por la reacción 2TP. Aunque estos procesos parecen ser independientes uno del otro, encontramos una buena correlación entre los valores de ΔE_{hb} y ΔV^\ddagger , la Figura 3.6 indica que altas barreras de energía están asociadas con pequeñas energías de interacción, así mientras más fuerte es el enlace de hidrógeno más baja es la barrera energética para la transferencia indicando que el enlace se fortalece en la medida que los protones se encuentran dinámicamente deslocalizados.

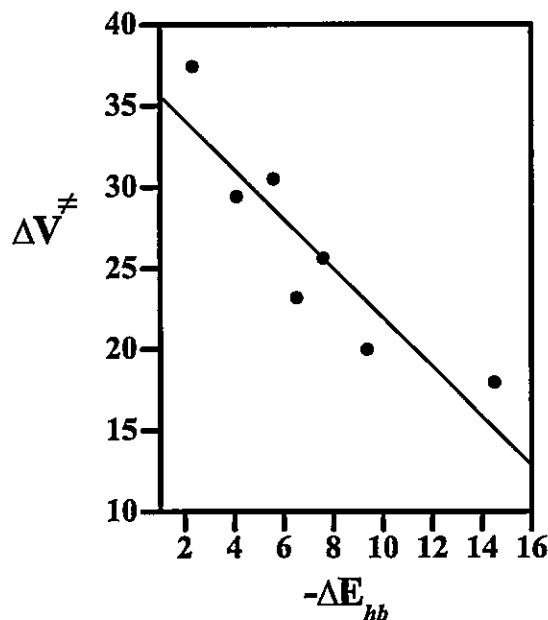


Figura 3.6: Correlación entre la barrera energética para la transferencia protónica (ΔV^\ddagger) y la energía de formación del agregado (ΔE_{hb})

3.3.3.3 Mecanismos de Reacción de 2TP

3.3.3.3.1 Perfiles de Reacción En el caso de los dímeros de referencia formados por ácidos fórmico (HCO-OH) y ditió fórmico (HCS-SH) se realizaron cálculos de estructura electrónica a lo largo del IRC con la idea de obtener los perfiles presentados en la Figura 3.7. En primer lugar notamos que en ambas reacciones μ presenta valores intermedios entre E y η , este decrece para alcanzar una región completamente plana alrededor del TS, donde tres puntos críticos pueden ser identificados, los cuales sugieren que en esta región del MEP toma lugar un mayor reordenamiento electrónico en el proceso. El peculiar comportamiento de μ confirma el mecanismo propuesto en literatura, se debe recordar que en una primera etapa la transferencia protónica es iniciada por el desplazamiento de las estructuras monoméricas para favorecer la

subsecuente transferencia de los protones, que es acompañada de una redistribución de la $\rho(\vec{r})$. Observamos que el perfil de dureza presenta un comportamiento opuesto mientras que el de polarizabilidad sigue la misma tendencia al perfil de energía, el TS está asociado a un valor mínimo de η y máximo de α indicando la validez simultánea de los principios de máxima dureza y mínima polarizabilidad.

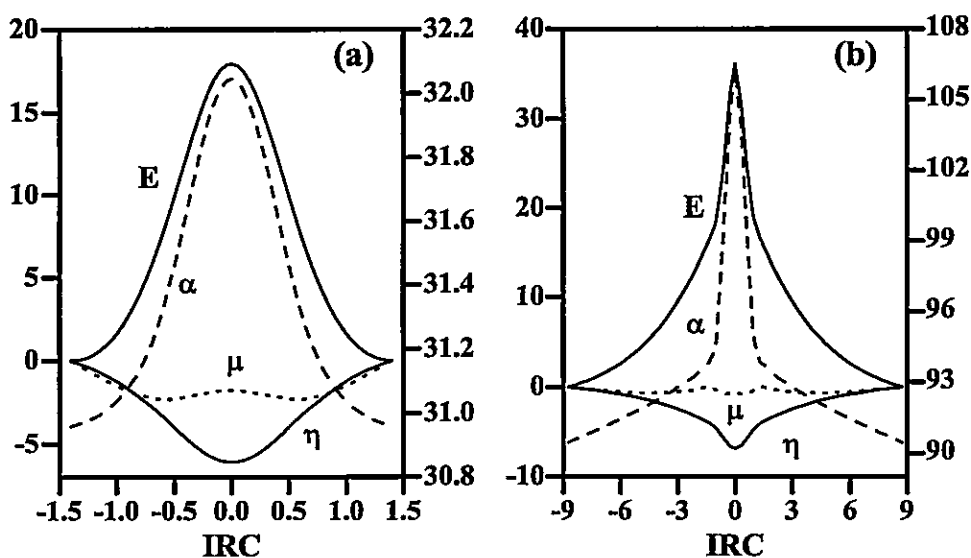


Figura 3.7: Perfiles de energía, potencial químico, dureza molecular y polarizabilidad a lo largo del IRC para la reacción de 2TP en dímeros de ácido fórmico (a) y ditiófórmico (b).

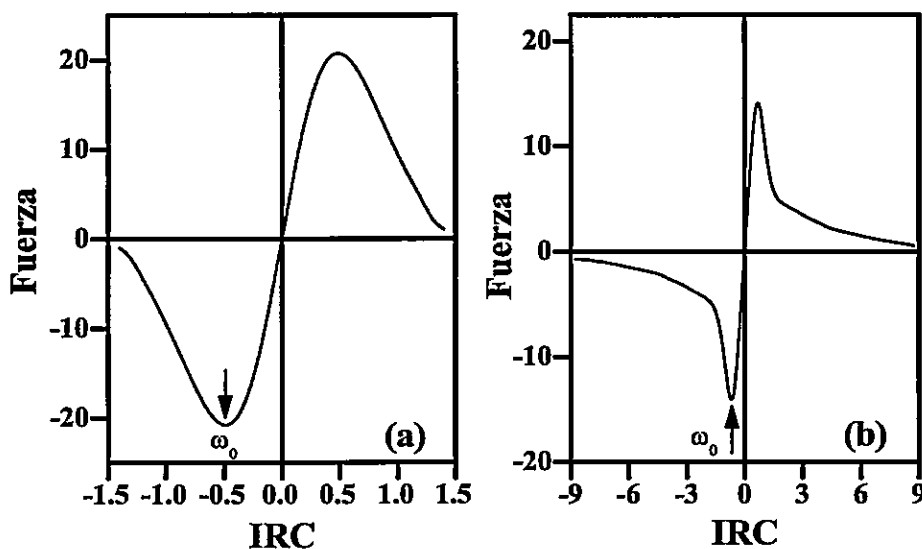


Figura 3.8: Perfiles de fuerza a lo largo del IRC para dímeros de ácido fórmico (a) y ditió fórmico (b).

3.3.3.3.2 Perfiles de Fuerza En la Figura 3.8 se muestra el perfil de fuerza determinado por diferenciación numérica del perfil de energía dado en la Figura 3.7. $F(\omega)$ es negativo en la región de reactantes y es positivo en la región de productos, este permite distinguir los diferentes procesos que toman lugar a lo largo de la coordenada de reacción. En la región de reactantes ocurre el proceso de activación para alcanzar la estructura del estado de transición mientras en la región de productos ocurre la relajación desde el TS hacia productos.

Los perfiles de fuerza presentan mínimos y máximos en las cercanías del TS, estos definen una región donde las interacciones específicas y reordenamientos intermoleculares son de naturaleza diferente a las encontradas en las vecindades de reactantes y productos. Los resultados de $F(\omega)$ sugiere que la primera etapa de la reacción

requiere una cantidad de trabajo (W_1) necesaria para traer las unidades monoméricas lo más próximas una de la otra, que es mayor al trabajo requerido para el movimiento hidrogénico (W_2). Estos trabajos son cualitativamente definidos como:

$$W_1 = \int_{-\infty}^{\omega_0} F(\omega) d\omega \quad y \quad W_2 = \int_{\omega_0}^0 F(\omega) d\omega, \quad (3.24)$$

donde ω_0 es la posición del mínimo de $F(\omega)$ como es indicado por las flechas en la Figura 3.8. Se observa que $W_1 > W_2$ indicando que la reacción es determinada por la primera etapa, es decir, el movimiento de las unidades monoméricas para obtener lo más cerca posible una de la otra en favor a permitir y asistir la posterior transferencia protónica en estos agregados moleculares.

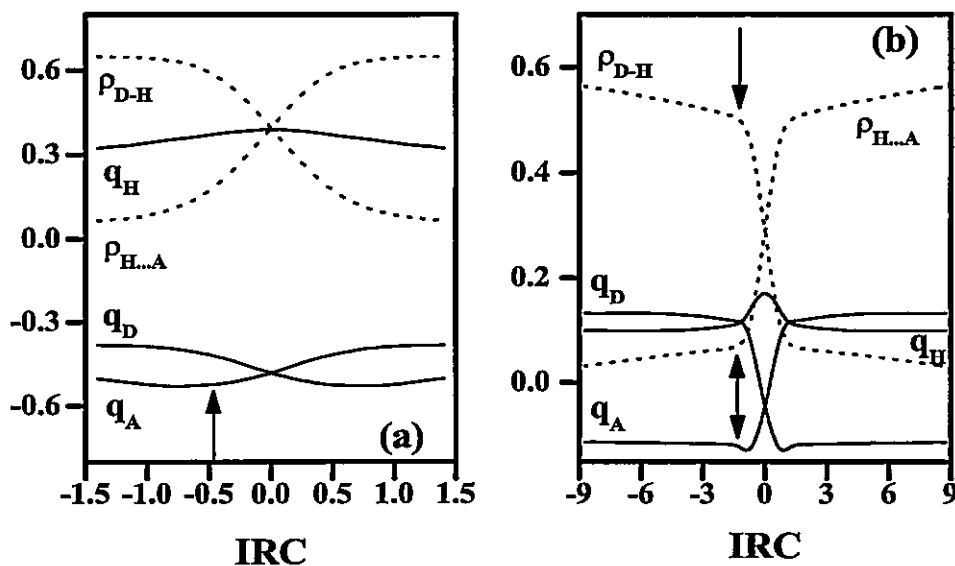


Figura 3.9: Perfiles a lo largo del IRC de poblaciones electrónicas específicas para dímeros de ácido fórmico (a) y ditiófórmico (b). ρ_{D-H} y $\rho_{H...A}$ corresponde a la población electrónica en regiones que están definidas entre el átomo de hidrógeno y los centro dador (D) y aceptor (A), respectivamente.

3.3.3.3 Naturaleza de las Barreras de Energía de 2TP Con la idea de obtener una mayor comprensión sobre el mecanismo de reacción y la naturaleza de las barreras de potencial es necesaria una caracterización cuantitativa de las poblaciones electrónicas en regiones de enlaces y centros atómicos (o fragmentos) a lo largo de la coordenada de reacción. La población de *Mulliken* [37,38] a lo largo del IRC en regiones de enlace y centros atómicos que participan directamente en la reacción es mostrada en la Figura 3.9. La evolución electrónica en regiones topológicas en enlaces (ρ_{X-H}) y enlaces de hidrógeno ($\rho_{X...H}$) siguen tendencias opuestas; cuando un protón es transferido, ρ_{X-H} decrece mientras $\rho_{X...H}$ incrementa confirmando la existencia de una transferencia de carga en la dirección opuesta al movimiento del protón. Es interesante notar que los cambios más notables en estas poblaciones ocurre después del punto ω_0 (indicados por las flechas en la Figura 3.9), es decir en la región donde ocurre la transferencia de los protones.

En el caso del dímero del ácido fórmico la carga atómica de los protones transferidos (q_H) incrementa en forma leve en el TS (Figura 3.9(a)), mientras que en el dímero del ácido ditiofórmico esta cantidad es completamente constante pero desde ω_0 esta incrementa rápidamente hasta alcanzar un valor máximo en el TS (Figura 3.9(b)). Las cargas atómicas en los átomos donores ($X-, q_D$) y aceptores ($X=, q_A$) de protones siguen una tendencia opuesta a lo largo del IRC. En el dímero de ácido fórmico son bastante similares en magnitud lo cual favorece la deslocalización de los protones entre los átomos de oxígeno, contrario a esto, en $(\text{HCSSH})_2$ se observa una diferencia mucho más marcada entre estas cantidades que está determinada incluso por el signo de las cargas atómicas indicando que interacciones electrostáticas y de polarización pueden estar jugando un rol importante en la estabilización de este sistema.

Estos resultados sugieren que la barrera de energía para la transferencia protónica en el dímero de ácido fórmico es básicamente del tipo *a través del enlace* o *controlado por orbital* en el sentido de *Klopman* mientras que en el dímero del ácido ditió fórmico es básicamente debido a interacciones electrostáticas, es decir una barrera *a través del espacio* o *controlado por cargas* en el sentido de *Klopman* [5, 39]. Cualitativamente, interacciones *a través del enlace* ocurren entre patrones que presentan poblaciones electrónicas locales similares mientras que las interacciones *a través del espacio* ocurre entre patrones que presentan poblaciones electrónicas locales completamente diferentes, y esta es la razón de porque este tipo de interacciones es comúnmente asociado a interacciones no enlazantes.

En nuestra investigación hemos mostrado como el análisis de poblaciones electrónicas y momentos dipolares ayuda a caracterizar la naturaleza de barreras de potencial [10, 40, 41]. Sin embargo, en el presente caso esto no es posible debido a que las conformaciones cíclicas de los dímeros de ácido fórmico y ditió fórmico presentan un centro de inversión a lo largo de IRC. Por lo tanto, en ausencia de momentos dipolares permanentes, en esta dirección puede ser utilizada la polarizabilidad para realizar un análisis cualitativo. La polarizabilidad de una molécula es proporcional a su tamaño o su número de electrones, la Tabla 3.4 indica que esta proporcionalidad se mantiene para la polarizabilidad de activación ($\Delta\alpha^\ddagger$). Por otra parte, desde la Tabla 3.3 es posible visualizar la proporcionalidad entre ΔV^\ddagger y N , entonces es de esperar, también encontrar una proporcionalidad a $\Delta\alpha^\ddagger$. La Figura 3.10(a) muestra una buena correlación lineal entre ΔV^\ddagger y $\Delta\alpha^\ddagger$ para los complejos identificados por su número total

de electrones (en este análisis se ha considerado un valor promedio para aquellos sistemas con $N=64$, para las reacciones (R3), (R4) y (R6)). Se observa que altas barreras están asociadas a altos valores de $\Delta\alpha^\ddagger$ confirmando que se trata de barreras del tipo *a través del espacio* mientras que barreras bajas están asociadas a pequeños valores de $\Delta\alpha^\ddagger$ indicando que son del tipo *a través del enlace*.

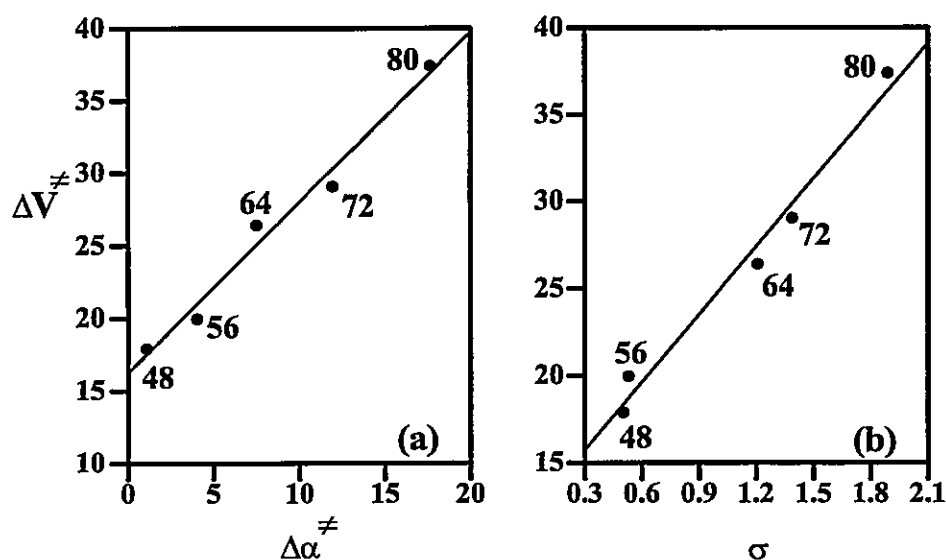


Figura 3.10: Correlación entre las barrera energética 2TP con: (a) polarizabilidad de activación y (b) el parámetro σ para el análisis HSAB local. Los diferentes complejos son identificados por su número total de electrones.

Para validar este resultado se debe considerar que las interacciones *a través del enlace* pueden ser explicadas por medio de una versión local del principio de ácidos y bases duros y blandos de *Pearson*. El principio HSAB local, permite explicar interacciones del tipo *blando-blando*, estableciendo que interacciones entre especies blandas ocurren a través de átomos que están caracterizados por una blandura similar. El principio HSAB local entrega un criterio independiente en término de interacciones específicas para caracterizar la naturaleza de barreras de potencial. *Gázquez y Méndez [42]*

han definido una cantidad que proporciona la información que se requiere para este análisis:

$$\sigma = (s_{H1}^{\circ} - s_{A1}^{\circ})^2 + (s_{H2}^{\circ} - s_{A2}^{\circ})^2 \quad (3.25)$$

donde s_X° es la blandura local del átomo X [hidrógeno (H) o el correspondiente aceptor (A)] definido desde la blandura global como $s_X^{\circ} = \rho_X S/N$. Si las interacciones específicas pueden ser explicadas en término del principio HSAB local, entonces se espera un pequeño valor de σ debido a que las blanduras de los patrones interactuantes son esperados a ser similares, esto correspondería a la parte blando con blando del HSAB. Entonces valores grandes del parámetro σ indica que la interacción es de tipo *a través del espacio*. En la Figura 3.10(b) se muestra una buena correlación entre las barreras energéticas para el proceso 2TP y el parámetro σ . Estos resultados muestran que la barrera para el dímero del ácido fórmico puede ser explicado en término del principio HSAB (σ pequeño) confirmando su naturaleza *a través del enlace*. En el caso del dímero de ácido ditiofórmico σ presenta un valor relativamente alto que permite confirmar que la barrera 2TP es principalmente de naturaleza *a través del espacio*. De acuerdo a estos resultados debe ser posible clasificar el origen físico de las barreras de energía para los sistemas remanentes como promedios de los sistemas de referencias.

3.4 Conclusiones

- Desde una perspectiva global, se ha encontrado que en procesos de isomerización rotacional en HONO y HSNS, el estado de transición presenta valores máximos de E , α_{zz} y valores mínimos de μ , η y V_M . Estas características permiten validar los principios de máxima dureza y máxima valencia molecular y el principio de mínima polarizabilidad.
- En un contexto local se ha encontrado una débil dependencia de descriptores locales en procesos de isomerización rotacional en HONO y HSNS. Sin embargo se encontró una relación inversa entre la función de Fukui y la valencia atómica que resulta útil a la hora de discutir la reactividad de sitios.
- A partir de un análisis global se han verificados los PMD y PMP en reacciones de doble transferencia protónica en sistemas del tipo $\text{HCX}-\text{YH}\cdots\text{HCX}-\text{YH}$ ($\text{X}, \text{Y} = \text{O}, \text{S}$), mientras que a partir de un análisis local ha permitido identificar las interacciones específicas que controlan el proceso logrando clasificarlas de acuerdo a su naturaleza como: *a través del enlace* o *a través del espacio*.
- En este Capítulo se ha mostrado que el estudio de descriptores electrónicos de reactividad a lo largo de la coordenada de reacción resulta de gran interés en la caracterización de mecanismos de reacción e identificación de interacciones específicas responsables del cambio químico. Los estudios descritos en este Capítulo básicamente están aludiendo a incorporar la coordenada de reacción en la formulación de una teoría de reactividad química en el contexto de la TFD. Esta idea está fundamentada en que cambios en las coordenadas internas a lo largo de la CR produce un cambio en el potencial externo $v(\vec{r})$ permitiendo caracterizar $F(\omega)$ en la ecuación (3.19) como una sumatoria de contribuciones

locales, las cuales pueden identificar regiones específicas de la topología molecular que son responsables de la activación y relajación a través de la formulación de una ley de fuerza locales, en esta dirección $F(\omega)$ puede ser descrito a través de $\left[\frac{\delta\mu}{\delta v(\vec{r})}\right]_N$ y $\left[\frac{\delta\eta}{\delta v(\vec{r})}\right]_N$ los cuáles pueden conducir a establecer nuevas reglas de reactividad local.

Parte del trabajo presentado en este Capítulo ha sido publicado en los siguientes artículos:

1. Theoretical Study of the Double Proton Transfer in the CHX-XH...CHX-XH (X=O,S) Complexes.
Pablo Jaque and Alejandro Toro-Labbé. *Journal Physical Chemistry A*, 104 (2000) 995-1003.
2. Characterization of Chemical Reactions Through Classical Concepts and DFT Descriptors.
Soledad Gutiérrez-Oliva, Pablo Jaque and Alejandro Toro-Labbé. *Review of Modern Quantum Chemistry: A Celebration of the Contributions of Robert G. Parr*. K.D. Sen Editor. Singapore (2002) 966.
3. Towards Understanding the Molecular Internal Rotations and Vibrations and Chemical Reactions Through the Profiles of Reactivity and Selectivity Indices: An Ab Initio SCF and DFT Study.
Soledad Gutiérrez-Oliva, Pablo Jaque and Alejandro Toro-Labbé. *Molecular Physics*, 101 (2003) 2841-2853.

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Capítulo 4

Reacciones de Formación:

Principio de *Sanderson*

Resumen

En este Capítulo usamos el principio de equalización de la electronegatividad de *Sanderson* para derivar expresiones para la dureza molecular (η) y su derivada (γ), éstas se utilizarán para estimar propiedades electrónicas en moléculas y agregados bimoleculares enlazados por puentes de hidrógeno a partir de valores asociados a fragmentos que participan en la formación de estas especies. En estas aplicaciones se encuentra que las condiciones de máxima dureza y mínima polarizabilidad complementan el criterio de mínima energía para la estabilidad de agregados moleculares. En la parte final de este Capítulo se propone un nuevo esquema para obtener propiedades moleculares desde fragmentos aislados que producen resultados que están es excelente acuerdo con aquellos determinados a través del esquema de *Sanderson*.

4.1 Introducción

Una reacción de formación es racionalizada como el resultado de la combinación de los fragmentos constituyentes, desde esta perspectiva, las propiedades moleculares asociadas al sistema resultante (molécula o agregado molecular) pueden ser determinadas a partir de las propiedades de los fragmentos que lo forman. Sin embargo, los principales problemas que conlleva esta aproximación en la estimación de propiedades moleculares se debe a los siguientes factores que no son considerados dentro de este esquema: el potencial de enlace, la redistribución de la densidad electrónica entre los fragmentos y la relajación estructural debida a las nuevas interacciones específicas *a través del enlace y a través del espacio* que controlan el proceso de formación. Los errores asociados al uso de fragmentos rígidos para estimar propiedades moleculares básicamente se deben a la completitud del set de funciones bases y mezclas de estados electrónicos, en este contexto, la determinación de propiedades moleculares basadas en esquemas de adición de fragmentos se espera que no sea muy exacta. Sin embargo, el uso de éstos resulta atractivo principalmente por el poder predictivo que presentan.

En este Capítulo nos centramos en el estudio de la obtención de propiedades electrónicas globales (μ , η) desde los correspondientes valores asociados a los fragmentos constituyentes a través de la aplicación del principio de equalización de la electronegatividad de *Sanderson* [1-3]. También se exploró cómo estas propiedades se conectan con las energías de enlaces en procesos de formación de moléculas y agregados enlazados por puentes de hidrógeno [4]. Consideramos la formación de cuatro moléculas del tipo HCX-YH desde especies radicalarias HCO, HCS, OH, y SH, y 10 complejos

bimoleculares cíclicos enlazados por puentes de hidrógeno del tipo HCX–YH... HCX–YH formados por combinación de especies del tipo HCX–YH (X,Y= O,S). La principal motivación para llevar a cabo este estudio fue validar el esquema de adición de *Sanderson* en el cálculo de propiedades electrónicas globales e investigar la posibilidad de discutir el reordenamiento electrónico debido al proceso de formación de enlace.

4.2 Aspectos Teóricos

4.2.1 Energía de Formación: Moléculas y Agregados Moleculares

El cambio energético debido a la formación de una molécula o agregado a partir de n_f fragmentos no enlazados está dada por:

$$\Delta E_{n_f} = E - E_{n_f}^{\circ} \quad (4.1)$$

donde E es la energía del sistema molecular optimizado que resulta de la combinación de los n_f fragmentos, y $E_{n_f}^{\circ} = \sum_x^{n_f} E_x$; E_x corresponde a la energía del fragmento x optimizado. En estas aplicaciones la energía del producto de formación se obtuvo a partir de dos fragmentos (E_2°) en el caso de moléculas del tipo HCX–YH (X,Y= O,S) mientras que en el caso de complejos bimoleculares (HCX–YH... HCX–YH; X,Y = O,S) se usaron dos (E_2°) y cuatro (E_4°) fragmentos, es decir desde dos especies moleculares (HCX–YH; X,Y= O,S) y cuatro especies radicalarias (HCX(Y) y X(Y)H; X,Y= O,S), respectivamente, como lo ilustra la Figura 4.1. Es importante destacar que tanto el error de superposición de base como las mezclas de estados electrónicos son fuentes de errores en la estimación de $\Delta E_{n_f}^{\circ}$, sin embargo la evaluación de estos

efectos escapan a los objetivos planteados en este trabajo de Tesis.

4.2.2 Principio de *Sanderson*: μ , η y γ

El principio de *Sanderson* establece que la electronegatividad ($\chi = -\mu$) de una molécula está dada por el promedio geométrico de las electronegatividades de los átomos o fragmentos aislados [1-3], así el potencial químico de un sistema molecular puede ser expresado como:

$$\mu_{n_f}^{\circ} = - \left(\prod_x^{n_f} |\mu_x^{\circ}| \right)^{1/n_f}, \quad (4.2)$$

donde μ_x° corresponde al potencial químico del fragmento x . Se debe destacar que dentro de esta aproximación mientras mayor sea el valor de n_f menos exacto es el resultado debido a que existe un mayor número de enlaces y potenciales de enlaces que no son considerados en el cálculo de $\mu_{n_f}^{\circ}$.

Para estimar la dureza molecular de forma aproximada dentro del esquema de *Sanderson* se debe considerar que el potencial químico al igual que la energía puede ser escrito como: $\mu = \mu[N, v(\vec{r})]$, la dureza se obtiene a través de la diferenciación de la ecuación (4.2) respecto a N [4-7],

$$\eta_{n_f}^{\circ} = \left(\frac{\partial \mu_{n_f}^{\circ}}{\partial N} \right)_{v(\vec{r})} = \frac{\mu_{n_f}^{\circ}}{n_f} \sum_x^{n_f} \frac{\eta_x^{\circ}}{\mu_x^{\circ}}, \quad (4.3)$$

donde η_x° corresponde a la dureza del fragmento x . La diferencia entre los valores aproximados y aquellos obtenidos para las especies moleculares estructuralmente optimizadas pueden ser atribuidas a la relajación de la densidad electrónica después del enlace químico. La cuantificación de estas diferencias resultan interesantes en la

discusión y comprensión de la $\rho(\vec{r})$ a medida que la reacción avanza en dirección de la formación de sistemas moleculares.

La dureza también puede ser escrita como: $\eta = \eta[N, v(\vec{r})]$, la derivada respecto a N a $v(\vec{r})$ constante fue definida por *Fuentealba y Parr* [8] como una propiedad de tercer-orden γ , estimaciones de esta propiedad solamente se llevó a cabo en átomos e iones resultando ser una cantidad mucho más pequeña en comparación a μ y η . En el contexto del esquema de *Sanderson* se obtiene la siguiente expresión luego de diferenciar $\eta_{n_f}^\circ$ respecto a N [4]:

$$\gamma_{n_f}^\circ = \left(\frac{\partial \eta_{n_f}^\circ}{\partial N} \right)_{v(\vec{r})} = \frac{(\eta_{n_f}^\circ)^2}{\mu_{n_f}^\circ} - \frac{\mu_{n_f}^\circ}{n_f} \sum_x^{n_f} \left(\frac{\eta_x^\circ}{\mu_x^\circ} \right)^2 + \frac{\mu_{n_f}^\circ}{n_f} \sum_x^{n_f} \frac{\gamma_x^\circ}{\mu_x^\circ}. \quad (4.4)$$

En el contexto del esquema de *Sanderson*, se ha propuesto una expresión analítica para estimar valores de γ en sistemas moleculares a partir de potenciales químicos, durezas moleculares y sus derivadas asociadas a sistemas atómicos y fragmentos moleculares.

4.3 Aplicaciones: Reacciones de Formación

4.3.1 Detalles Computacionales

El esquema de cálculo utilizado para caracterizar la estructura electrónica de moléculas y agregados enlazados por puentes de hidrógeno fue del tipo RHF con un set de funciones bases estándar 6-311G** implementado en el paquete de programas Gaussian 94 [9]. En el caso de fragmentos radicalarios se utilizó un esquema de cálculo del tipo UHF/6-311G**. Para estimar los valores de μ y η , se aplicaron las fórmulas operacionales entregadas en el Capítulo 1, en término de las energías de orbitales fronteras

| Fragmento | E | μ | η |
|-----------|-----------|---------|--------|
| CHO | -113.2802 | -0.1327 | 0.2450 |
| OH | -75.4107 | -0.1906 | 0.3153 |
| CHS | -435.9153 | -0.1492 | 0.1852 |
| SH | -398.0929 | -0.1907 | 0.1864 |

Tabla 4.1: Energía, potencial químico y dureza para las estructuras optimizadas de fragmentos radicalarios determinados a un nivel de teoría *ab initio* UHF/6-311G**. Todos los valores están en *ua*.

(ϵ_H y ϵ_L).

En la Tabla 4.1 se presentan los valores de referencia de E , μ y η para las especies radicalarias del tipo HCX y XH (X= O,S). Estos fragmentos en reacción pueden formar el siguiente conjunto de moléculas HCO-OH (**M1**), HCS-OH (**M2**), HCO-SH (**M3**) y HCS-SH (**M4**), el cambio energético y electrónico (manifestado a través de cambios en μ y η) que caracteriza este proceso está asociado principalmente a la formación de un enlace covalente que involucra a los centros atómicos C-X (X= O,S). La comparación entre los valores aproximados de $\mu_{n_f}^o$ y $\eta_{n_f}^o$ (obtenidos a partir de fragmentos rígidos) respecto aquellos obtenidos desde las estructuras optimizadas permite discutir cualitativamente el efecto del potencial de enlace sobre estos descriptores electrónicos, este aspecto será expuesto con un mayor énfasis en el siguiente Capítulo.

En relación a la formación de agregados moleculares solo fueron consideradas estructuras cíclicas de todas las posibles geometrías que se encuentran en la superficie de energía potencial. Estos agregados están estabilizados por dos enlaces de hidrógeno como se muestra en la Figura 4.1. La combinación de monómeros del tipo HCX-YH

| Sistema | | $-E$ | $-E_2^o$ | $-E_4^o$ | $-\Delta E_2$ | $-\Delta E_4$ |
|---------------|-------|-----------|-----------|-----------|---------------|---------------|
| HCOOH | (M1) | 188.8205 | 188.6910 | | 0.1295 | |
| HCSOH | (M2) | 511.4454 | 511.3260 | | 0.1194 | |
| HCOSH | (M3) | 511.4493 | 511.3731 | | 0.0762 | |
| HCSSH | (M4) | 834.0867 | 834.0082 | | 0.0785 | |
| HCOOH...HCOOH | (C1) | 377.6641 | 377.6410 | 377.3819 | 0.0231 | 0.2822 |
| HCOOH...HCSOH | (C2) | 700.2840 | 700.2659 | 700.0170 | 0.0181 | 0.2670 |
| HCSOH...HCSOH | (C3) | 1022.9027 | 1022.8908 | 1022.6520 | 0.0119 | 0.2507 |
| HCOOH...HCOSH | (C4) | 700.2847 | 700.2698 | 700.0641 | 0.0149 | 0.2206 |
| HCOOH...HCSSH | (C5) | 1022.9176 | 1022.9072 | 1022.6992 | 0.0104 | 0.2184 |
| HCOSH...HCSOH | (C6) | 1022.9068 | 1022.8947 | 1022.6992 | 0.0121 | 0.2076 |
| HCSSH...HCSOH | (C7) | 1345.5389 | 1345.5320 | 1345.3342 | 0.0069 | 0.2047 |
| HCOSH...HCOSH | (C8) | 1022.9076 | 1022.8987 | 1022.7463 | 0.0089 | 0.1613 |
| HCSSH...HCOSH | (C9) | 1345.5425 | 1345.5360 | 1345.3813 | 0.0065 | 0.1612 |
| HCSSH...HCSSH | (C10) | 1668.1770 | 1668.1733 | 1668.0164 | 0.0037 | 0.1606 |

Tabla 4.2: Energías totales y de reacción en procesos de formación de sistemas moleculares a nivel RHF/6-311G**. Todos los valores están en *ua*.

(X,Y= O,S) conduce a la formación de 10 agregados cíclicos enlazados por puentes de hidrógeno (C1 a C10). En la construcción de estos agregados se han considerado dos aproximaciones como se muestra en la Figura 4.1: (a) la formación de complejos bimoleculares desde dos moléculas neutras ($n_f = 2$) donde los valores optimizados de E , μ y η de cada unidad del tipo HCX-YH (X,Y= O,S) son utilizadas para producir E_2^o , μ_2^o y η_2^o , nótese que en estos valores no es considerado el efecto de dos enlaces de hidrógeno; y (b) la segunda aproximación establece la formación del agregado a partir de cuatro fragmentos radicalarios ($n_f = 4$), mediante los valores entregados en la Tabla 4.1 se obtiene E_4^o , μ_4^o y η_4^o , estos valores no incluyen los efectos de dos enlaces covalentes (C-X; X=O,S) y dos enlaces de hidrógeno (X-H...Y; X,Y= O,S). En la Tabla 4.2 se definen las especies bajo estudio y se entregan los valores de energías totales como las energías de formación de moléculas y de agregados ΔE_2 y ΔE_4 .

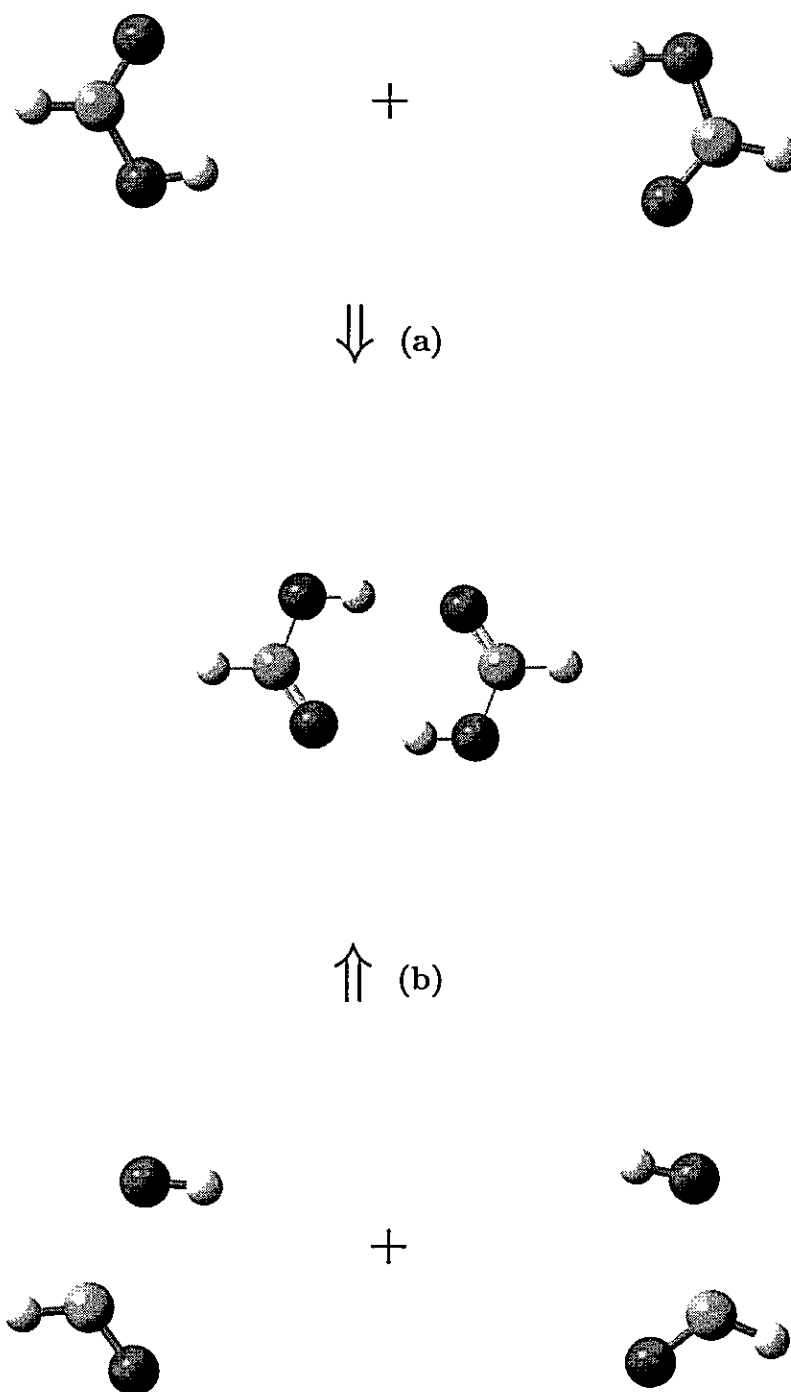


Figura 4.1: Esquema del proceso de formación de agregados bimoleculares del tipo $\text{HCX-YH} \cdots \text{HCX-YH}$ ($\text{X, Y} = \text{O, S}$) a partir de (a) 2 fragmentos moleculares del tipo HCX-YH ($\text{X, Y} = \text{O, S}$), y (b) 4 fragmentos radicalarios del tipo HCX(Y) y HY(X) ($\text{X, Y} = \text{O, S}$).

4.3.2 Resultados y Discusión

4.3.2.1 Energías de Enlaces

4.3.2.1.1 Energías de enlaces C-X (X= O,S). Los valores de energías de reacción (ΔE_{n_f}) entregados en la Tabla 4.2 indican que tanto la formación de moléculas (M1 a M4) como de agregados bimoleculares (C1 a C10) son procesos termodinámicamente favorables. Considerando los valores de ΔE_2 desde M1 a M4 permiten estimar las energías de enlaces del tipo C-X (X=O,S). El valor de ΔE_2 involucrado en la formación de M1 y M2 se identifica con la energía de un enlace simple C-O, mientras que en los procesos de formación de M3 a M4 están asociados a la formación de un enlace C-S. Los valores promedios para estas energías de enlaces fueron comparadas a valores experimentales, para el enlace C-O se determinó que $\langle \Delta E_2 \rangle_{CO} \approx 0.12 \text{ ua}$ y para el enlace C-S $\langle \Delta E_2 \rangle_{CS} \approx 0.08 \text{ ua}$, mientras que los valores experimentales son 0.13 y 0.10 ua [10], respectivamente. Aunque los valores numéricos presentan algunas variaciones, los resultados teóricos acuerdan cualitativamente con los experimentales en cuanto a que estos indican que el enlace C-O es más fuerte que el C-S.

Estos resultados son consistentes cuando se racionaliza la formación de agregados moleculares desde cuatro fragmentos radicalarios y se desprecian la interacciones por puentes de hidrógeno, así la energía de reacción (ΔE_4) puede ser escrita en términos de energías de enlaces del tipo C-X (X= O,S). Los valores de ΔE_4 entregados en la Tabla 4.2 asociados a la formación de C1, C2 y C3 fluctúan desde -0.28 ua (C1) a -0.25 ua (C3), estos pueden ser asignados a la formación de dos enlaces C-O ($\Delta E_4 \approx 2 \langle \Delta E_2 \rangle_{CO}$). Desde C4 a C7 se determina un valor promedio para ΔE_4 de -0.21 ua, este valor esta asociado principalmente a contribuciones energéticas

debido a la formación de un enlace C-O y C-S ($\Delta E_4 \approx \langle \Delta E_2 \rangle_{CO} + \langle \Delta E_2 \rangle_{CS}$). Desde C8 a C10 se encuentra que $\Delta E_4 \approx -0.16 \text{ ua}$ el cual es debido a la contribución de dos enlaces C-S ($\Delta E_4 \approx 2 \langle \Delta E_2 \rangle_{CS}$). Los resultados de energías de enlaces determinados mediante cálculos RHF/6-311G** acuerdan satisfactoriamente con datos experimentales lo cual permite validar la metodología de cálculo para caracterizar este tipo de sistemas.

4.3.2.1.2 Energías de Enlaces de Hidrógeno $H \cdots X$ ($X = O, S$). Antes de continuar con este análisis se debe hacer mención que aunque se espera que los cálculos *Hartree-Fock* no sean muy exactos al estimar energías de enlaces de hidrógeno, los resultados obtenidos en este estudio concuerdan satisfactoriamente con aquellos obtenidos mediante otros estudios teóricos [6]. En relación a datos experimentales se encuentra un buen acuerdo con la información experimental disponible, en el caso de la formación del dímero de ácido fórmico (C1) se obtiene que $\Delta E_2 = -0.0231 \text{ ua}$, valor que es comparable al experimental ($\Delta E_2 = -0.0233 \text{ ua}$) [11]. En literatura no existe información experimental acerca del sistema C10, sin embargo hay estudios en sistemas que contienen solo una unidad del tipo $S \cdots H$, el dato experimental para esta interacción es de 0.0016 ua [12] que compara con una fracción (1/2) de la cantidad entregada en la Tabla 4.2 para C10 ($\Delta E_2/2 = 0.0019 \text{ ua}$), esta asimilación es justificada considerando que C10 es estabilizado por la presencia de dos unidades $S \cdots H$.

A partir de esta partición y motivados con la idea de racionalizar las energías de enlaces de hidrógeno en la serie estudiada, se exploró la idea de estimar energías de enlaces a partir $E(H \cdots O)$ y $E(H \cdots S)$ obtenida desde C1 y C10 como $\Delta E_2/2$

| Sistema | N | $-\Delta E_2$ | $-\Delta E_2^{(a)}$ | $-\Delta E_2^{(b)}$ |
|---------|-----|---------------|---------------------|---------------------|
| C1 | 48 | 0.0231 | 0.0231 | 0.0231 |
| C2 | 56 | 0.0181 | 0.0134 | 0.0175 |
| C3 | 64 | 0.0119 | 0.0037 | 0.0119 |
| C4 | 56 | 0.0149 | 0.0231 | 0.0160 |
| C5 | 64 | 0.0104 | 0.0134 | 0.0104 |
| C6 | 64 | 0.0121 | 0.0134 | 0.0134 |
| C7 | 72 | 0.0069 | 0.0134 | 0.0078 |
| C8 | 64 | 0.0089 | 0.0231 | 0.0089 |
| C9 | 72 | 0.0065 | 0.0134 | 0.0063 |
| C10 | 80 | 0.0037 | 0.0037 | 0.0037 |

Tabla 4.3: Energías de enlaces de hidrógeno de agregados bimoleculares ($\Delta E_2 = E - E_2^0$; $\Delta E_2^{(a)} = \sum_X E(H \cdots X)$; $\Delta E_2^{(b)} = \sum_{X,Y} E(X - H \cdots Y)$). Todos los valores están en ua .

($E(H \cdots O) = \Delta E_2(C1)/2 = -0.01155 ua$; $E(H \cdots S) = \Delta E_2(C10)/2 = -0.00185 ua$). Estos valores son utilizados para estimar ΔE_2 como $\Delta E_2^{(a)} = \sum_x E(H \cdots X)$, es decir simplemente al sumar las energías de enlace $H \cdots X$ que están presentes en el agregado. Estos resultados se incluyen en la Tabla 4.3. Nótese que desde esta aproximación la estimación de $\Delta E_2^{(a)}$ no es adecuada para describir los valores de ΔE_2 para los sistemas remanentes (C2 a C9) observándose desviaciones hasta un 70% (C3).

Una aproximación considerablemente mejor a ΔE_2 puede ser obtenida al considerar además del enlace $H \cdots X$ el efecto del heteroátomo vecino, a través de la definición de la energía del fragmento $X - H \cdots Y$ ($X, Y = O, S$). Para ello se consideran cuatro dímeros (C1, C3, C8, y C10) que contienen los fragmentos deseados: $E(O - H \cdots O) = \Delta E_2(C1)/2 = -0.01155 ua$; $E(O - H \cdots S) = \Delta E_2(C3)/2 = -0.00595 ua$; $E(S - H \cdots O) = \Delta E_2(C8)/2 = -0.00445 ua$; $E(S - H \cdots S) = \Delta E_2(C10)/2 = -0.00185 ua$. Nótese que un átomo de azufre adyacente al enlace de hidrógeno lo

hace más débil que en presencia de un átomo oxígeno. A partir de esta aproximación se define $\Delta E_2^{(b)} = \sum_{X,Y} E(X - H \cdots Y)$ cuyos resultados también se incluyen en la Tabla 4.3 y se comparan a ΔE_2 y $\Delta E_2^{(a)}$. Los valores de $\Delta E_2^{(b)}$ presentan desviaciones menores respecto a los de referencia. Esto indica que el efecto del heteroátomo adyacente al enlace de hidrógeno es importante en caracterizar las energías de enlaces de hidrógeno. En resumen, a través de esta aproximación para la energía de enlace $H \cdots O$ se estima un valor de 0.0080 ± 0.0036 *ua* y para $H \cdots S$ un valor de 0.0039 ± 0.0021 *ua*, el enlace de $H \cdots O$ puede ser considerado dos veces más fuerte que el enlace $H \cdots S$.

4.3.2.1.3 Constantes de Fuerza (k) y Energías de Enlaces de Hidrógeno.

La Tabla 4.3 además de entregar los valores de energías de enlaces ΔE_2 incluye el número total de electrones N para cada sistema. Se observa que ΔE_2 decrece con N y que el enlace $H \cdots O$ es más fuerte que $H \cdots S$. La fuerza de un enlace químico es usualmente representada por la constante de fuerza (k), la cual permite caracterizar las diferentes estructuras sobre la SEP, en este contexto es de esperar que ΔE_2 este relacionada con la k asociada al par de enlaces de hidrógeno del agregado bimolecular. Se determinaron los valores de constantes de fuerzas a través de cálculos *ab initio* de frecuencias vibracionales a partir de las estructuras optimizadas de estos complejos, los resultados se entregan en la Figura 4.2(a), donde una buena correlación lineal ($r = 0.980$) puede ser observada entre ΔE_2 y k para los 10 sistemas estudiados que están identificados con el número total de electrones que presentan. Para un dado valor de N pueden asociarse a más de una estructura, así en la Tabla 4.3 se logra identificar que hay dos sistemas con 56 electrones (C2 y C4); cuatro con 64 electrones (C3, C5, C6, y C8); y dos con 72 electrones (C7 y C9), al considerar valores promedios

de sus respectivos datos de ΔE_2 y k se logra una mejor correlación ($r = 0.996$) como es ilustrado en la Figura 4.2(b), por lo tanto, las constantes de fuerzas *ab initio* son consistentes con los resultados energéticos: enlaces de hidrógeno más fuertes están asociados a un alto valor de $|\Delta E_2|$.

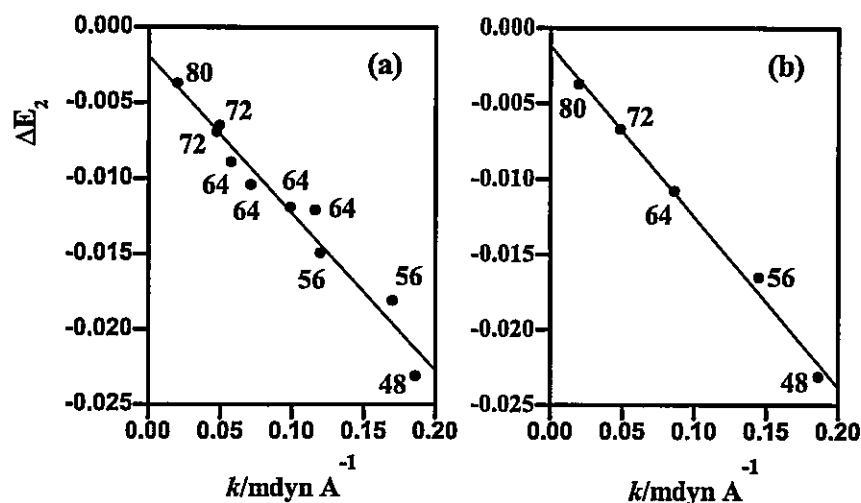


Figura 4.2: Correlación entre energías de enlaces de hidrógeno y constantes de fuerzas de agregados bimoleculares identificados por el número de electrones (a). Valores promedio de ΔE_2 y k en sistemas que presentan igual número de electrones (b).

4.3.2.2 Descriptores Electrónicos

4.3.2.2.1 Potencial Químico Electrónico. La ecuación (4.2) se ha utilizado para obtener μ en el contexto del esquema de *Sanderson*. Para el caso de moléculas (M1–M4) se requieren los datos *ab initio* (μ_x° y η_x°) para las especies radicalarias entregadas en la Tabla 4.1 ($x = \text{CHO}, \text{OH}, \text{CHS}, \text{y SH}$). Mientras que en el caso de la formación de agregados bimoleculares se han considerado dos aproximaciones; una desde dos fragmentos moleculares y otra desde cuatro especies radicalarias, los valores de $\mu_{n_f}^\circ$ están listados en la Tabla 4.4.

| Sistema | μ | μ_2° | μ_4° | η | η_2° | η_4° | γ_2° | γ_4° |
|---------|---------|---------------|---------------|--------|----------------|----------------|------------------|------------------|
| M1 | -0.1554 | -0.1590 | | 0.3138 | 0.2783 | | 0.0247 | |
| M2 | -0.1402 | -0.1686 | | 0.2206 | 0.2441 | | 0.0214 | |
| M3 | -0.1391 | -0.1591 | | 0.2608 | 0.2246 | | 0.0431 | |
| M4 | -0.1532 | -0.1687 | | 0.1996 | 0.1872 | | 0.0062 | |
| C1 | -0.1503 | -0.1554 | -0.1590 | 0.3204 | 0.3138 | 0.2783 | 0.0317 | 0.0247 |
| C2 | -0.1411 | -0.1476 | -0.1638 | 0.2251 | 0.2652 | 0.2619 | 0.0303 | 0.0269 |
| C3 | -0.1462 | -0.1402 | -0.1686 | 0.2169 | 0.2206 | 0.2441 | 0.0153 | 0.0214 |
| C4 | -0.1402 | -0.1470 | -0.1590 | 0.2609 | 0.2863 | 0.2515 | 0.0281 | 0.0380 |
| C5 | -0.1601 | -0.1543 | -0.1638 | 0.2021 | 0.2563 | 0.2342 | 0.0398 | 0.0326 |
| C6 | -0.1320 | -0.1397 | -0.1638 | 0.2215 | 0.2408 | 0.2342 | 0.0231 | 0.0326 |
| C7 | -0.1604 | -0.1466 | -0.1687 | 0.1966 | 0.2108 | 0.2157 | 0.0148 | 0.0187 |
| C8 | -0.1331 | -0.1391 | -0.1591 | 0.2607 | 0.2608 | 0.2246 | 0.0240 | 0.0431 |
| C9 | -0.1511 | -0.1460 | -0.1638 | 0.2000 | 0.2319 | 0.2065 | 0.0288 | 0.0289 |
| C10 | -0.1576 | -0.1532 | -0.1687 | 0.1965 | 0.1996 | 0.1871 | 0.0084 | 0.0064 |

Tabla 4.4: Propiedades electrónicas calculadas y estimadas de moléculas y agregados bimoleculares, μ y η fueron obtenidos mediante cálculos RHF/6-311G**, $\mu_{n_f}^\circ$, $\eta_{n_f}^\circ$, y $\gamma_{n_f}^\circ$ fueron estimados mediante las ecuaciones (4.2), (4.3), y (4.4) respectivamente. Todos los valores están en *ua*.

Nótese que las desviaciones de $\mu_{n_f}^\circ$ con respecto a los valores de referencias obtenidos desde cálculos *ab initio* son razonablemente pequeñas, sin embargo en la mayoría de los casos, μ_2° se aproxima mejor al valor de referencia que como lo hace μ_4° . Al igual que la energía el potencial químico depende del número de fragmentos empleados en el contexto del esquema de *Sanderson* [4].

4.3.2.2 Dureza Molecular. Dentro del esquema de *Sanderson* se han determinado valores de dureza molecular a partir de la ecuación (4.3), los resultados se entregan en la Tabla 4.4. Es interesante notar que la dureza puede ser estimada tanto por η_2° como η_4° , ambos valores representan una buena aproximación al valor *ab initio* de referencia. La consistencia cualitativa entre η_2° como η_4° indica que la ecuación (4.3) es una expresión confiable para estimar durezas moleculares a partir de fragmentos

rígidos.

Para estimar durezas moleculares desde fragmentos, en la literatura se han propuesto otros esquemas de adición, en este contexto, *Ghosh y col.* [13] se han basado en el promedio aritmético de la blandura molecular que puede ser escrito en término de dureza como:

$$\frac{1}{\eta^G} = \frac{1}{n_f} \sum_x^{n_f} \frac{1}{\eta_x^o}. \quad (4.5)$$

En esta línea *Datta* propone un esquema similar al propuesto por *Sanderson* para μ , es decir, expresa la dureza de un agregado como el promedio geométrico de las respectivas durezas de los fragmentos constituyentes [14],

$$\eta^D = \left(\prod_x^{n_f} \eta_x^o \right)^{1/n_f}. \quad (4.6)$$

La Tabla 4.5 lista valores de durezas obtenidas mediante diferentes tratamientos señalados por las ecuaciones (4.3), (4.5) y (4.6) considerando $n_f = 2$. Nótese el satisfactorio acuerdo entre estos valores obtenidos a partir de diferentes métodos, solo se observan pequeñas desviaciones. Estos resultados permiten atribuir una importante característica a la dureza, desde un punto de vista numérico η es una propiedad estable. Este atributo en conexión con el principio de máxima dureza (PMD) sugiere que para aquellos sistema en los cuales la energía es difícil de obtener, η puede abrir un camino alternativo para conseguir información de tipo energética [15].

| Sistema | η | η_2° | η^G | η^D |
|---------|--------|----------------|-----------|-----------|
| | | Ec. (4.3) | Ec. (4.5) | Ec. (4.6) |
| M1 | 0.3138 | 0.2783 | 0.2757 | 0.2779 |
| M2 | 0.2206 | 0.2441 | 0.2333 | 0.2417 |
| M3 | 0.2608 | 0.2246 | 0.2117 | 0.2137 |
| M4 | 0.1996 | 0.1872 | 0.1858 | 0.1858 |
| C1 | 0.3204 | 0.3138 | 0.3138 | 0.3138 |
| C2 | 0.2251 | 0.2652 | 0.2591 | 0.2631 |
| C3 | 0.2169 | 0.2206 | 0.2206 | 0.2206 |
| C4 | 0.2609 | 0.2863 | 0.2849 | 0.2861 |
| C5 | 0.2021 | 0.2563 | 0.2440 | 0.2503 |
| C6 | 0.2215 | 0.2408 | 0.2390 | 0.2399 |
| C7 | 0.1966 | 0.2108 | 0.2096 | 0.2098 |
| C8 | 0.2607 | 0.2608 | 0.2608 | 0.2608 |
| C9 | 0.2000 | 0.2319 | 0.2261 | 0.2282 |
| C10 | 0.1965 | 0.1996 | 0.1996 | 0.1996 |

Tabla 4.5: Comparación de valores de durezas determinados a través de diferentes métodos. η es el valor *ab initio* de referencia; las ecuaciones (4.3), (4.5) y (4.6) son aplicadas con $n_f = 2$. Todos los valores están en *ua*.

4.3.2.2.3 Relación entre Energía y Dureza. La conexión entre energía y dureza a través del PMD estimula a investigar la relación entre las energías de formación ΔE_2 y ΔE_4 para los complejos bimoleculares y las correspondientes durezas η_2° y η_4° determinados a través de la ecuación (4.3). Los gráficos (a) y (b) de la Figura 4.3 muestran correlaciones lineales entre ΔE_{n_f} y $\eta_{n_f}^\circ$ para los agregados identificados por su número total de electrones. Estas correlaciones son mejoradas cuando se utilizan valores promedios como se muestra en las Figuras 4.3 (c) y (d). En acuerdo a la predicción del PMD se observa que el agregado más estable es la especie más dura.

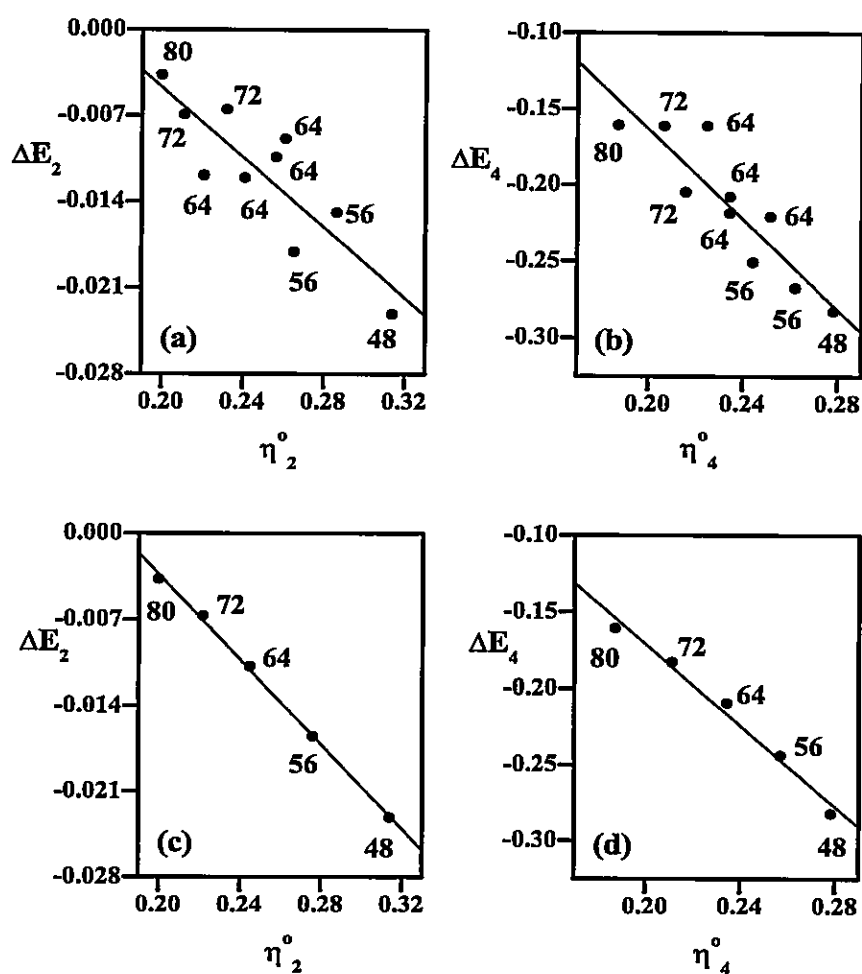


Figura 4.3: Correlación entre energías de enlaces y durezas de los productos determinados a partir de la aproximación de *Sanderson* con (a) $n_f = 2$ y (b) $n_f = 4$. (c) y (d) considera los valores promedios para sistemas que tienen igual número de electrones en los paneles (a) y (b).

La conexión entre propiedades electrónicas y energía de reacción permiten obtener un cuadro más completo de algún evento químico, esto ha sido sujeto del presente trabajo de Tesis. En este contexto, *Pearson* propuso un método empírico para clasificar el orden de ácidos y bases en término de sus durezas [16]. Más recientemente *Gázquez* propuso una expresión para la energía de enlace en término de los potenciales químicos, las durezas y las funciones de Fukui condensadas de las especies

aisladas [17]. En la búsqueda de relacionar las energías de enlaces de hidrógeno y las propiedades electrónicas de las especies aisladas, se examinó la expresión propuesta por *Gázquez* resultando que ésta sobre-estima las energías de enlaces de hidrógeno aunque indica correctamente que la principal contribución a la energía de enlace es debida al cambio en la dureza del sistema.

Para finalizar esta discusión, es interesante notar que las Figuras 4.2 y 4.3 sugieren que la dureza de los agregados está relacionada con las constantes de fuerza. La Figura 4.4 corrobora esta relación a través de una buena correlación lineal entre estas propiedades, mientras más fuerte es el enlace formado más duro es el complejo. Este resultado confirma la proporcionalidad directa entre dureza y constantes de fuerzas, como fuera apuntado por *Arulmozhiraja y Kolandaivel* [18], por otra parte estos autores y los resultados presentados en este sección sugieren que la dureza química es una cantidad bastante adecuada en describir la estabilidad química, que algún otro descriptor proveniente de la TFD.

4.3.2.2.4 Polarizabilidad de Sistemas con Enlaces de Hidrógeno. En general se ha observado que las condiciones de máxima dureza y mínima polarizabilidad complementan el criterio de mínima energía para la estabilidad molecular como es sugerido por el PMD [19] y el PMP [20, 21]. En este contexto, la Tabla 4.6 entrega valores de polarizabilidad (α) determinados mediante cálculos *ab initio* para moléculas (M1-M4) y agregados bimoleculares (C1-C10), también se listan valores de α para agregados obtenidos a través de la simple adición de polarizabilidades asociadas a las unidades monoméricas constituyentes (α_2^0).

| Sistema | N | α | α_2^o | $\Delta\alpha_2$ | $\Delta\bar{\alpha}_2$ |
|---------|-----|----------|--------------|------------------|------------------------|
| M1 | 24 | 15.1733 | | | |
| M2 | 32 | 28.2873 | | | |
| M3 | 32 | 27.7830 | | | |
| M4 | 40 | 43.4183 | | | |
| C1 | 48 | 30.9583 | 30.3466 | 0.6117 | 15.7850 |
| C2 | 56 | 45.7427 | 43.4606 | 2.2821 | 24.0124 |
| C3 | 64 | 60.5700 | 56.5746 | 3.9954 | 32.2827 |
| C4 | 56 | 43.6490 | 42.9563 | 0.6927 | 22.1709 |
| C5 | 64 | 60.9957 | 58.5916 | 2.4041 | 31.6999 |
| C6 | 64 | 58.0750 | 56.0703 | 2.0047 | 30.0399 |
| C7 | 72 | 75.0847 | 71.7056 | 3.3791 | 39.2319 |
| C8 | 64 | 56.3013 | 55.5660 | 0.7353 | 28.5183 |
| C9 | 72 | 72.9003 | 71.2013 | 1.6990 | 37.2997 |
| C10 | 80 | 88.6140 | 86.8366 | 1.7774 | 45.1957 |

Tabla 4.6: Polarizabilidades calculadas y estimadas para moléculas y agregados bimoleculares. Todos los valores están en ua .

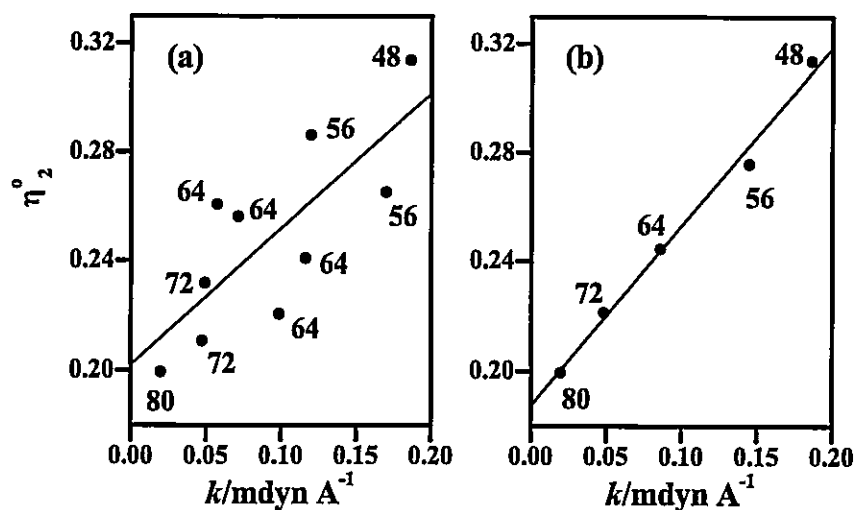


Figura 4.4: (a) Correlación entre durezas y constantes de fuerzas de agregados bimoleculares. (b) Correlación entre η_n^o versus k usando valores promedios para sistemas que presentan igual número de electrones.

Desde la Tabla 4.6 se observa el excelente acuerdo entre α_2° y los valores de referencia. Este resultado sugiere que la polarizabilidad de un sistema compuesto se puede aproximar a la suma de los n_f valores de polarizabilidades de las unidades que forman el agregado

$$\alpha_{n_f}^\circ = \sum_x^{n_f} \alpha_x^\circ, \quad (4.7)$$

donde α_x° corresponde a la polarizabilidad de los monómeros.

La adición de electrones a un sistema molecular incrementa su polarizabilidad debido a que esta propiedad es proporcional a N , esta proporcionalidad es confirmada en agregados enlazados por puentes de hidrógeno (ver Tabla 4.6). Por otra parte, como ha sido señalado las energías de enlaces de hidrógeno también muestran dependencia con N , por lo tanto se debe esperar que ΔE_2 este conectado con la polarizabilidad a través de N . Sin embargo la Figura 4.5(a) muestra un gráfico con bastante dispersión entre los valores de ΔE_2 y la polarizabilidad de reacción $\Delta\alpha_2$, que se define como la diferencia entre α de producto y de reactantes: $\Delta\alpha_2 = \alpha - \sum_x^{n_f} \alpha_x^\circ$ (estos valores están en la Tabla 4.6). La consistencia esperada se logra cuando la polarizabilidad de reactantes es definida como un promedio aritmético de las polarizabilidades de los monómeros, se define la polarizabilidad de reacción como $\Delta\bar{\alpha}_2 = \alpha - (\sum_x \alpha_x)/2$, estos valores están listados en la Tabla 4.6. La Figura 4.5(b) muestra una buena correlación lineal donde es claro que las energías de reacción más bajas están asociadas a polarizabilidades de reacción también más bajas. Este resultado alude a la posibilidad de extender la validez del PMP en comparaciones de energías y polarizabilidades relativas [4, 22]. Adicionalmente se encontró que ΔE_2 se correlaciona de forma lineal con la polarizabilidad de productos (α_2°) como lo ilustra la Figura 4.5(c). En resumen se ha encontrado que el producto de reacción más estable corresponde a la especie

más dura y menos polarizable.

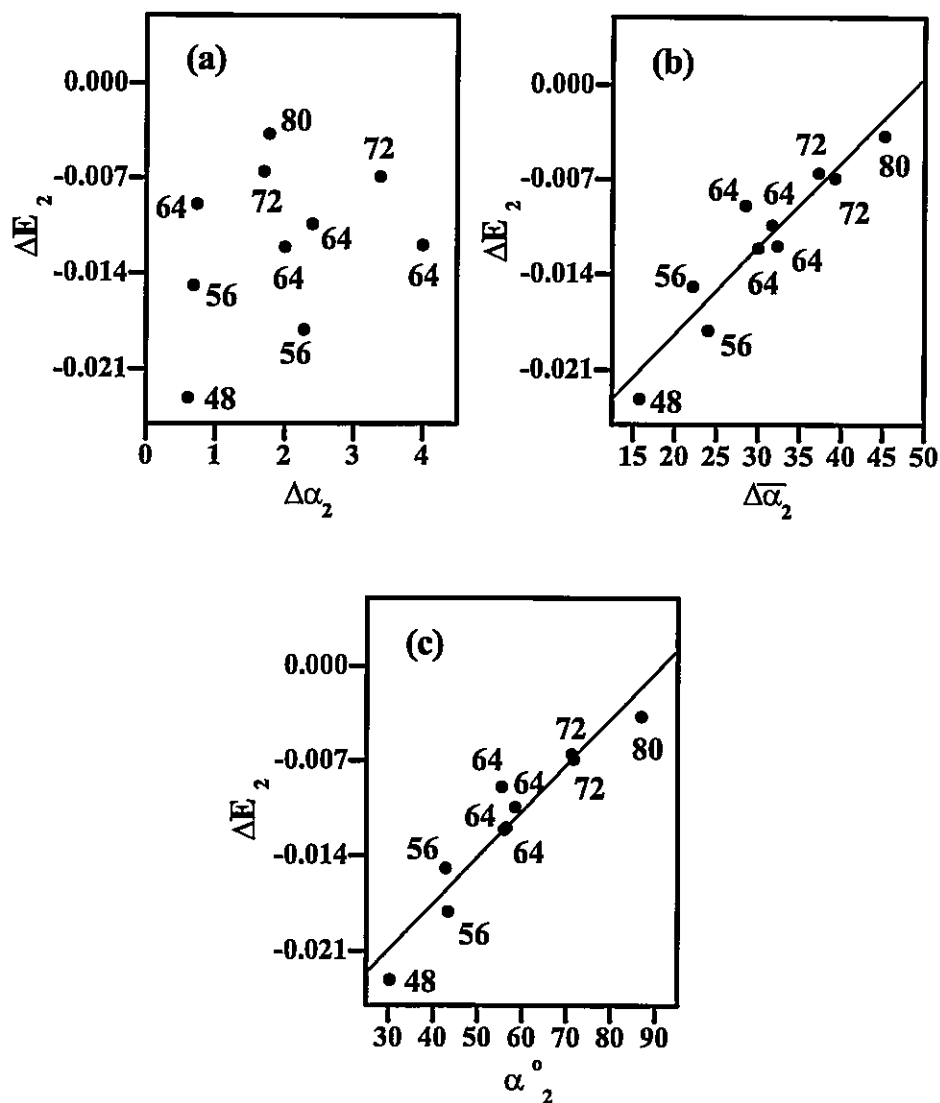


Figura 4.5: Representación de las energías de reacción con: (a) la polarizabilidad de reacción definida como $\Delta\alpha_2 = \alpha(\text{producto}) - \sum_x \alpha_x^\circ$, (b) la polarizabilidad de reacción definida como $\Delta\bar{\alpha}_2 = \alpha(\text{producto}) - (\sum_x \alpha_x^\circ)/n_f$, y (c) la polarizabilidad de los agregados bimoleculares mediante la ecuación (4.7). Todos los valores están en *ua*.

4.3.2.2.5 Derivada de la Dureza, γ . Se ha reconocido a la dureza molecular como una propiedad para caracterizar procesos químicos, por tanto es necesario conocer como esta propiedad cambia con el número de electrones y el potencial externo. La cantidad γ mide el cambio de η con N . Se utilizó la ecuación (4.4) para evaluar esta propiedad. Nótese que a partir de esta expresión se requiere de valores de γ_x° de los fragmentos aislados, estos fueron estimados a partir de la siguiente fórmula aproximada [8].

$$\gamma_x^\circ \approx \left[\frac{\varepsilon_L}{\varepsilon_H - 3\varepsilon_H} \right]_x^\circ \eta_x^\circ. \quad (4.8)$$

Los valores de γ_2° y γ_4° son entregados en Tabla 4.4 de donde se observan que ellos son muy pequeños y positivos al igual que el estudio en átomos e iones realizado por *Fuentealba y Parr* [8].

4.3.2.2.6 Nuevo Esquema de Aditividad para μ y η . Se finaliza este Capítulo, con la discusión acerca de la variación de $\mu_{n_f}^\circ$ respecto al cambio en $v(\vec{r})$. El potencial químico al igual que la energía es una función de N y un funcional de $v(\vec{r})$ la diferenciación respecto a $v(\vec{r})$ conduce a:

$$F_{n_f}^\circ = \int \left(\frac{\delta \mu_{n_f}^\circ}{\delta v(\vec{r})} \right) d\vec{r} \approx \frac{\mu_{n_f}^\circ}{n_f} \sum_x^{n_f} \left(\frac{f_x^\circ}{\mu_x^\circ} \right) \quad (4.9)$$

donde $F_{n_f}^\circ$ es una cantidad adimensional que contiene la información acerca de las reactividades de los fragmentos a través de la función de Fukui condensada f_x° . A partir de un análisis dimensional se propone que el potencial químico para un sistema compuesto por n_f fragmentos puede estar definido como:

$$\frac{1}{\mu'_{n_f}} = \sum_x^{n_f} \left(\frac{f_x^\circ}{\mu_x^\circ} \right). \quad (4.10)$$

En aplicaciones numéricas de esta nueva aproximación se requiere de una fórmula operacional para f_x° , en esta dirección, se considera como punto de partida la aproximación de densidad local (LDA) donde la función de Fukui radial puede ser aproximada como

$$f(\vec{r}) = \frac{\rho(\vec{r})}{N} \quad (4.11)$$

al integrar en el volumen del fragmento x , se obtiene la siguiente expresión para la función de Fukui condensada en x

$$f_x^\circ = \frac{N_x}{N} \quad (4.12)$$

donde $N = \sum_x N_x$, y corresponde al número total de electrones en el agregado y N_x es el número de electrones en el fragmento x . Lo interesante de la expresión (4.10) es que la función de Fukui definida a través de la ecuación (4.12) juega más bien un rol de factor de ponderación que de parámetro de reactividad. Se determinaron potenciales químico de los 10 agregados cíclicos mediante este nuevo esquema a partir de dos fragmentos rígidos, los resultados muestran un muy buen acuerdo con aquellos determinados mediante la ecuación (4.2), esto se puede verificar en la Figura 4.6. Más aún, los valores obtenidos con este nuevo esquema se aproximan mejor a los valores *ab initio* de referencia que aquellos determinados por la ecuación (4.2).

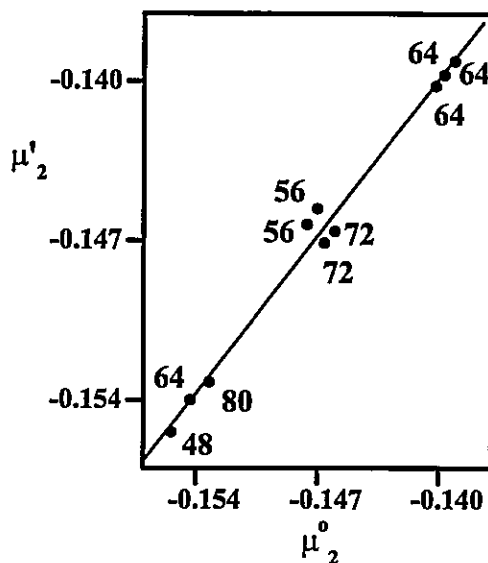


Figura 4.6: Comparación de potenciales químicos determinados a través de las ecuaciones (4.2) y (4.10). Todos los valores están en ua .

La caracterización de derivadas de la ecuación (4.10) es directa. En esta nueva formulación la dureza esta dada por

$$\eta'_{n_f} = \left(\frac{\partial \mu'_{n_f}}{\partial N} \right)_{v(\vec{r})} = (\mu'_{n_f})^2 \sum_x^{n_f} \frac{1}{(\mu_x^o)^2} [f_x^o \eta_x^o - h_x^o \mu_x^o], \quad (4.13)$$

donde h_x^o es una medida de la fluctuación de la dureza química debido al cambio en el potencial externo. Alternativamente, a través de la relación de Maxwell, h_x^o puede ser considerada como la respuesta de la función de Fukui a un cambio en el número total de electrones.

$$h_x^o = \left(\frac{\delta \eta_x^o}{\delta v(\vec{r})} \right)_N = \left(\frac{\partial f_x^o}{\partial N} \right)_{v(\vec{r})}. \quad (4.14)$$

Parr y col recientemente han definido el índice de electrofilia como $\omega = \mu^2/2\eta$ [23].

| Sistema | η | η_2° Ec.(2) | η'_2 Ec.(13) | η'_2 Ec.(13) | η^G Ec.(5) | η^D Ec.(6) |
|---------------|--------|----------------------------|----------------------|----------------------|--------------------|--------------------|
| HCOOH...HCOOH | 0.3204 | 0.3138 | 0.3138 | 0.3204 | 0.3138 | 0.3138 |
| HCOOH...HCSOH | 0.2251 | 0.2652 | 0.2565 | 0.2575 | 0.2591 | 0.2631 |
| HCSOH...HCSOH | 0.2169 | 0.2206 | 0.2206 | 0.2169 | 0.2206 | 0.2206 |
| HCOOH...HCOSH | 0.2609 | 0.2863 | 0.2813 | 0.2842 | 0.2849 | 0.2861 |
| HCOOH...HCSSH | 0.2021 | 0.2563 | 0.2416 | 0.2433 | 0.2440 | 0.2503 |
| HCOSH...HCSOH | 0.2215 | 0.2408 | 0.2407 | 0.2388 | 0.2390 | 0.2399 |
| HCSSH...HCSOH | 0.1966 | 0.2108 | 0.2102 | 0.2067 | 0.2096 | 0.2098 |
| HCOSH...HCOSH | 0.2607 | 0.2608 | 0.2608 | 0.2607 | 0.2608 | 0.2608 |
| HCSSH...HCOSH | 0.2000 | 0.2319 | 0.2303 | 0.2288 | 0.2261 | 0.2282 |
| HCSSH...HCSSH | 0.1965 | 0.1996 | 0.1996 | 0.1965 | 0.1996 | 0.1996 |

Tabla 4.7: Comparación de durezas moleculares de agregados bimoleculares determinadas a partir de diferentes esquemas de adición. Todos los valores están en *ua*.

En analogía a esta definición dentro del esquema presentado, el inverso de ω

$$\frac{\eta'_{n_f}}{(\mu'_{n_f})^2} = \sum_x^{n_f} \frac{1}{(\mu_x^{\circ})^2} [f_x^{\circ} \eta_x^{\circ} - h_x^{\circ} \mu_x^{\circ}]. \quad (4.15)$$

al contener propiedades locales y globales puede ser el punto de partida para la formulación de métodos que permitan la caracterización de conceptos de reactividad y selectividad en una perspectiva unificada.

La Tabla 4.7 entrega valores de durezas determinadas a través de los diferentes esquemas a partir de $n_f = 2$. La segunda columna de esta Tabla contiene los valores de referencia (η) mientras que la tercera columna lista los valores obtenidos mediante la ecuación (4.2), las dos columnas siguientes contienen aquellos determinados a través de la ecuación (4.13), en la primera de ellas se asume un valor de $h_x^{\circ} = 0$ mientras que la segunda considera valores de h_x° determinados a partir de los dímeros (C1,

C3, C8, y C10), a estas columnas les siguen valores ya incluidos en la Tabla 4.5. En general se observa que los valores provenientes de este nuevo esquema de aditividad se aproximan mejor a los de referencias, este hecho se debe básicamente a que este nuevo método incorpora un factor de peso de los diferentes fragmentos a través de f_x° y h_x° [7, 24].

En este contexto, como un comentario final se puede decir que mejores aproximaciones a f_x° y h_x° puede enriquecer la calidad de predicción de propiedades globales de agregados a partir de aquellas desde los fragmentos constituyentes. Por otra parte la caracterización de propiedades de TS usando estos esquemas bajo algunas restricciones impuestas por modelos de reactividad como por ejemplo el principio de máxima dureza, parece ser un interesante tópico en investigaciones futuras.

4.4 Conclusiones

- Se ha hecho uso del principio de equalización de la electronegatividad de *Sanderson* para estimar la primera (μ), segunda (η) y tercera (γ) derivada de la energía respecto al número de electrones.
- Los resultados obtenidos muestran que, el principio de equalización de la electronegatividad de *Sanderson* es adecuado para predecir propiedades electrónicas.
- Se han determinado valores numéricos para la propiedad de tercer orden γ , en magnitud estos son muy pequeños y positivos en acuerdo con comportamientos esperados.
- Los resultados para energía de enlaces obtenidos a nivel RHF/6-311G** están en satisfactorio acuerdo con datos experimentales disponibles.
- Se ha encontrado que los principios de máxima dureza y mínima polarizabilidad se cumplen en el contexto de formación de moléculas y agregados bimoleculares.
- Finalmente, se ha propuesto un nuevo esquema para obtener propiedades moleculares a partir de fragmentos aislados. En esta nueva aproximación propiedades globales y locales juegan roles equivalentes, los cuales pueden conducir a métodos para caracterizar simultáneamente los conceptos de reactividad y selectividad en procesos químicos.

Parte del trabajo presentado en este Capítulo ha sido publicado en los siguientes artículos:

1. Using Sanderson's Principle to Estimate Global Electronic Properties and Bond Energies of Hydrogen-Bonded Complexes.

Soledad Gutiérrez-Oliva, **Pablo Jaque** and Alejandro Toro-Labbé. *Journal of Physical Chemistry*, 104 (2000), 8955-8964.

2. Characterization of Chemical Reactions Through Classical Concepts and DFT Descriptors.

Soledad Gutiérrez-Oliva, **Pablo Jaque** and Alejandro Toro-Labbé. *Review of Modern Quantum Chemistry: A Celebration of the Contributions of Robert G. Parr*. K.D. Sen Editor. Singapore (2002) 966.

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Capítulo 5

Formación de *Clusters* de Cobre: Datos Experimentales de Energías de Enlaces y Descriptores de Reactividad

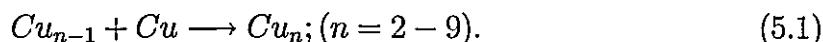
Resumen

En este Capítulo se estudia y racionaliza la formación de *clusters* de cobre desde el dímero al nonámero usando la información experimental disponible de energías de enlace y propiedades electrónicas. A partir de este estudio se ha determinado que reacciones de crecimiento por un átomo es principalmente controlada por variaciones en la dureza química. Finalmente se propone una expresión analítica para la energía de enlace como una función del tamaño del *clusters* que ha sido utilizada para predecir patrones de crecimiento de *clusters* de cobre.

5.1 Introducción

Un interesante tópico en ciencia de *clusters* es el estudio de la evolución de las propiedades con el tamaño del *cluster* cuando se incrementa el número de átomos constituyentes. *Clusters* de cobre neutros con un número par de átomos son sistemas de tipo capa cerrada (*closed-shell*) mientras que aquellos con un número impar de átomos son sistemas de tipo capa abierta (*open-shell*) [1-5]. En investigaciones acerca de propiedades, tales como, potenciales de ionización, afinidades electrónicas, energías de enlace, y estudios de reactividades sobre *clusters* de cobre se ha encontrado un comportamiento típico que en literatura ha sido bautizado como regla de alternación del tipo *par-impar* [6-9].

En este Capítulo nos concentramos en el estudio de la reacción de formación de Cu_n desde un nuevo punto de vista que permite comprender el proceso de crecimiento a partir de un análisis detallado de las energías de enlaces, la reacción en estudio es:



Esta aproximación consiste en racionalizar datos experimentales disponibles de energías de enlace [10,11] a través del uso de descriptores de reactividad (μ , η , y ω) obtenidos a partir de datos experimentales de potenciales de ionización [12-16] y afinidades electrónicas [17]. Mediante esta aproximación se espera establecer correlaciones entre energías de enlaces y propiedades electrónicas [18] que sean útiles en la comprensión de la reacción de formación de *clusters* de cobre y proporcionar nuevos elementos para racionalizar reacciones de crecimiento de *clusters* metálicos [19].

5.2 Aspectos Teóricos

5.2.1 Reacciones de Formación de *Clusters* de Cobre

El proceso indicado por la ecuación (5.1) se caracteriza a través del cambio global de energía que corresponde a la energía de enlace $Cu_{n-1} - Cu$:

$$\Delta E = E(P) - [E(R1) + E(R2)], \quad (5.2)$$

con $P = Cu_n$, $R1 = Cu_{n-1}$ y $R2 = Cu$. Este proceso también se puede racionalizar en término del cambio electrónico asociado al proceso, que se manifestará como variaciones en μ y η , en este contexto se define la siguiente cantidad para caracterizar dicho cambio:

$$\Delta\Omega = \Omega(P) - \mathcal{S}\{\Omega(R)\}, \quad \Omega = \mu, \eta, \quad (5.3)$$

donde la cantidad $\mathcal{S}\{\Omega(R)\} \equiv \Omega_S(R)$ corresponde al valor de la propiedad asociado a los reactantes $R1$ y $R2$, para estimar este valor se ha hecho uso del promedio de *Sanderson* presentado en el Capítulo anterior. El promedio de *Sanderson* para el potencial químico de reactantes está dado por el promedio geométrico de los potenciales químicos de $R1$ y $R2$:

$$\mathcal{S}\{\mu\} = - [\mu_{R1} \cdot \mu_{R2}]^{1/2} \equiv \mu_S. \quad (5.4)$$

La dureza promedio de *Sanderson* se obtiene mediante diferenciación de $\mathcal{S}\{\mu\}$ con respecto a N



$$\mathcal{S}\{\eta\} = \left(\frac{\partial \mu_S}{\partial N} \right)_{v(\vec{r})} = \frac{\mu_S}{2} \left[\left(\frac{\eta}{\mu} \right)_{R1} + \left(\frac{\eta}{\mu} \right)_{R2} \right] \equiv \eta_S, \quad (5.5)$$

la diferencia entre los valores promedios ($\mathcal{S}\{\mu\}$ y $\mathcal{S}\{\eta\}$) respecto a los valores obtenidos a partir de las fórmulas operacionales entregadas en el Capítulo 1 pueden ser atribuidas a la relajación de la densidad electrónica después del enlace, la cuantificación de estas diferencias contribuyen en la comprensión del reordenamiento de la densidad electrónica a medida que la reacción química ocurre [20, 21].

5.3 Resultados y Discusión

5.3.1 Energías de Enlace, Potenciales de Ionización y Afinidades Electrónicas

En la Tabla 5.1 se presentan los valores de energías de enlaces de *clusters* de cobre neutros (Cu_n) recientemente reportados por *Spasov y col.* [10] e *Ingólfsson y col* [11]. Estos autores han realizados experimentos de disociación inducida por colisión (*Collision-Induced Dissociation*, CID) para estudiar aspectos de estabilidad y canales de fragmentación en *clusters* de cobre catiónicos y aniónicos, respectivamente. Los datos experimentales de energías de enlaces para sistemas neutros $Cu - Cu_{n-1}$ son obtenidos a partir de un ciclo termodinámico aplicando la información de las energías de disociación por pérdida de un átomo conseguidas a partir de mediciones CID junto a valores de afinidades electrónicas en el caso de *clusters* aniónicos y potenciales de ionización para *clusters* catiónicos. En el presente análisis se considera el valor promedio que también se entrega en la Tabla 5.1.

| Cu_n | $-\Delta E(exp)^a$ | $-\Delta E(exp)^b$ | $-\Delta E$ |
|--------|--------------------|--------------------|-----------------|
| Cu_2 | 2.04 ± 0.17 | 1.81 ± 0.14 | 1.93 ± 0.11 |
| Cu_3 | 1.15 ± 0.20 | 0.76 ± 0.23 | 0.96 ± 0.15 |
| Cu_4 | 2.72 ± 0.20 | 2.03 ± 0.76 | 2.38 ± 0.39 |
| Cu_5 | 1.85 ± 0.17 | 1.59 ± 0.78 | 1.72 ± 0.40 |
| Cu_6 | 2.56 ± 0.32 | 1.80 ± 0.77 | 2.18 ± 0.42 |
| Cu_7 | 2.66 ± 0.44 | 1.05 ± 0.79 | 1.86 ± 0.45 |
| Cu_8 | 2.98 ± 0.35 | 2.16 ± 0.79 | 2.57 ± 0.43 |
| Cu_9 | | 1.02 ± 0.50 | 1.02 ± 0.50 |

Tabla 5.1: Valores experimentales de energías de enlaces para Cu_n ($n=2-9$). Todos los valores están en eV.

^a Experimentos de CID en *clusters* aniónicos Ref. [10].

^b Experimentos de CID en *clusters* catiónicos Ref. [11].

La energía de enlace (ΔE) presenta un comportamiento oscilatorio donde *clusters* con un número par de átomos presentan valores más altos que aquellos sistemas con un número impar de átomos constituyentes, es decir, enlaces químicos en *clusters* con n par son más fuertes que en *clusters* con n impar. Visto desde otra perspectiva, se espera que en procesos de fragmentación ($Cu_n \rightarrow Cu + Cu_{n-1}$), *clusters* con un número par de átomos son más estables que *clusters* con números impares, esto se explica a partir de las siguientes consideraciones, *clusters* con n par presentan configuraciones electrónicas *closed-shell* y como es bien sabido este tipo de configuraciones vienen acompañadas con una estabilización extra, mientras que *clusters* con un número impar de átomos presentan configuraciones del tipo *open-shell*, la que hace a estos sistemas mucho más reactivos como se ha observado en recientes estudios de reactividad frente a NO [7] y O_2 [6]. Por otra parte, en el límite de *clusters* muy grandes la energía de enlace se aproxima al negativo de la energía de vaporización del sólido, el valor experimental para esta propiedad es de 3.50 eV y ésta se utilizará como valor de referencia en las discusiones siguientes [22].

| Cu_n | PI | AE^a |
|--------|-----------------------|-------------------|
| Cu | 7.724^b | 1.235 ± 0.005 |
| Cu_2 | 7.9042 ± 0.0008^c | 0.836 ± 0.006 |
| Cu_3 | 5.80 ± 0.04^d | 2.37 ± 0.01 |
| Cu_4 | 7.15 ± 0.75^e | 1.45 ± 0.05 |
| Cu_5 | 6.3 ± 0.1^d | 1.94 ± 0.05 |
| Cu_6 | 7.15 ± 0.75^e | 1.96 ± 0.05 |
| Cu_7 | 6.1 ± 0.05^d | 2.16 ± 0.1 |
| Cu_8 | 7.15 ± 0.75^e | 1.57 ± 0.05 |
| Cu_9 | 5.35 ± 0.05^d | 2.40 ± 0.05 |

Tabla 5.2: Valores experimentales de potenciales de ionización y afinidades electrónicas para Cu_n ($n=1-9$). Todos los valores están en eV.

^a Ref. [17]; ^b Ref. [12]; ^c Ref. [13]; ^d Ref. [14]; ^e Ref. [16].

Los valores experimentales de potenciales de ionización (PI) y afinidades electrónicas (AE) reportadas en literatura para *clusters* de cobre son entregados en la Tabla 5.2. Nótese que en ambas propiedades se observa nuevamente el patrón oscilatorio que se atribuye al cambio de multiplicidad de *spin* de los estados fundamentales, Cu_n con n par presenta valores más altos y bajos de PI y AE , respectivamente, en comparación a sus vecinos del tipo Cu_{n-1} y Cu_{n+1} . El proceso de ionización resulta ser de mayor dificultad cuando se remueve un electrón a partir de un orbital molecular de más alta energía (HOMO) doblemente ocupado correspondiente a una configuración *closed-shell* que a partir de un orbital molecular simplemente ocupado (SOMO) de una configuración *open-shell*. En contraste a esto, el proceso de adjuntar un electrón será más favorable en *clusters* con n impar, ya que el electrón ocupará un orbital semi ocupado (SOMO), como se corrobora a partir de altos valores de AE en este tipo de sistemas.

5.3.1.1 Dependencia de PI y AE con el Tamaño del *Cluster*

Clusters metálicos son agregados que tienen propiedades que se diferencian a las de un átomo o sólido, en este contexto, estos sistemas pueden ser vistos como *clusters* infinitamente pequeños e infinitamente grandes. Se analizó la evolución de PI y AE con el tamaño del *cluster*, ambas propiedades convergen a la función trabajo (Φ) en el límite como $n \rightarrow \infty$, es decir, al valor en cobre policristalino de $\Phi = 4.65$ eV [23]. En este ámbito se ha propuesto que la evolución de una propiedad P , tal como PI y AE , como una función del número de átomos n puede ser descrito a través de la siguiente forma analítica [24]:

$$P(n) = P(\infty) + A \cdot n^{-1/3}, \quad (5.6)$$

donde $P(\infty)$ corresponde al valor de la propiedad en el límite del *bulk*. La Figura 5.1 presenta los valores de PI y AE en función del tamaño del *cluster*, las líneas rectas son referencias que están definidas a partir de las siguientes condiciones de bordes:

$$n^{-1/3} = \begin{cases} 0 \implies n \rightarrow \infty, \text{ límite bulk} \implies AE = PI = \Phi = 4.65 \text{ eV} \\ 1 \implies n = 1, \text{ límite atómico} \implies AE = 1.24 \text{ eV}; PI = 7.72 \text{ eV} \end{cases}$$

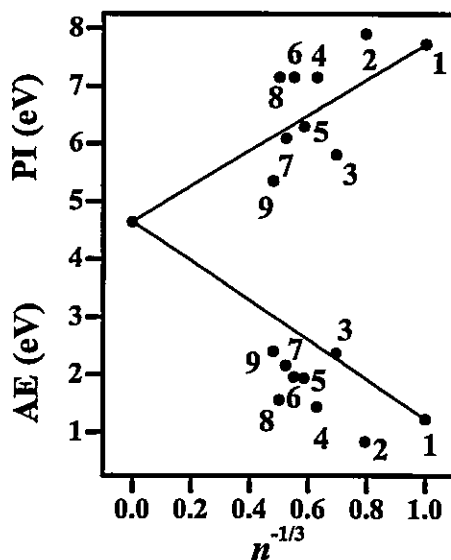


Figura 5.1: Valores experimentales de PI y AE para Cu_n como una función del tamaño del *cluster*. Todos los valores están en eV.

Nótese que todos los *clusters* a excepción de Cu_3 presentan valores de AE más bajos que los esperados a partir de la línea de referencia. Por otra parte, los valores de PI de *clusters* con número par e impar presentan comportamientos diferentes respecto a la línea de referencia, sistemas con n par presentan valores más altos mientras que sistemas con n impar presentan valores más bajos que los que predice la línea de referencia. Esta observación permite concluir que el comportamiento oscilatorio característico *impar-par* de propiedades electrónicas que dependen de PI y AE se debe al comportamiento del potencial de ionización.

5.3.2 Propiedades Electrónicas Globales

Usando los valores de PI y AE entregados en la Tabla 5.2 en las fórmulas operacionales definidas en el Capítulo 1, se obtienen los valores del potencial químico,

| Cu_n | μ | μ_S | η | η_S | ω | ω_S |
|--------|----------------------|---------|---------------------|----------|---------------------|------------|
| Cu | -4.4795 ± 0.0050 | | 3.2445 ± 0.0050 | | 3.0923 ± 0.0068 | |
| Cu_2 | -4.3701 ± 0.0061 | -4.4795 | 3.5341 ± 0.0061 | 3.2445 | 2.7019 ± 0.0071 | 3.0923 |
| Cu_3 | -4.0850 ± 0.0412 | -4.4245 | 1.7150 ± 0.0412 | 3.3914 | 4.8651 ± 0.1359 | 2.8862 |
| Cu_4 | -4.3000 ± 0.7517 | -4.2777 | 2.8500 ± 0.7517 | 2.4471 | 3.2439 ± 1.1727 | 3.7389 |
| Cu_5 | -4.1200 ± 0.1118 | -4.3888 | 2.1800 ± 0.1118 | 3.0438 | 3.8932 ± 0.2494 | 3.1641 |
| Cu_6 | -4.5550 ± 0.7517 | -4.2960 | 2.5950 ± 0.7517 | 2.6924 | 3.9977 ± 1.4871 | 3.4274 |
| Cu_7 | -4.1300 ± 0.1118 | -4.5171 | 1.9700 ± 0.1118 | 2.9226 | 4.3292 ± 0.2964 | 3.4908 |
| Cu_8 | -4.3600 ± 0.7517 | -4.3012 | 2.7900 ± 0.7517 | 2.5835 | 3.4067 ± 1.2379 | 3.5805 |
| Cu_9 | -3.8750 ± 0.0707 | -4.4193 | 1.4750 ± 0.0707 | 3.0145 | 5.0900 ± 0.2771 | 3.2394 |

Tabla 5.3: Potencial químico, dureza química e índice de electrofilia para Cu_n ($n=1-9$). Todos los valores están en eV.

dureza molecular y el índice de electrofilia para *clusters* de cobre, estos resultados se listan en la Tabla 5.3. En esta Tabla también se incluyen los valores obtenidos a través de los promedios de *Sanderson* aplicando las ecuaciones (5.4) y (5.5) mediante los correspondientes valores de μ y η de las especies en reacción Cu_{n-1} y Cu . Estos valores promedios producen $\omega_S = \mu_S^2/2\eta_S$. Nótese que todos estos descriptores presentan el patrón característico *par-impar* observados en otras propiedades, nuevamente esto se atribuye al cambio de multiplicidad de *spin* de los estados fundamentales a lo largo de la serie.

5.3.2.1 Potencial Químico y Transferencia de Carga.

Cuando dos sistemas entran en interacción ocurre un proceso de transferencia de carga desde un sistema con mayor μ al sistema con menor valor de μ . A partir de la Tabla 5.3 se observa que *clusters* con n impar (sistemas *open-shell*) presentan valores más alto de μ respecto a sistemas con n par, esto indica que sistemas *open-shell* tienen una mayor tendencia a transferir carga que aquellos sistemas cuyas configuraciones son del tipo *closed-shell*.

En el contexto del proceso de formación de moléculas y agregados, cuando dos componentes (en este caso Cu_{n-1} y Cu) comienzan a interactuar, sus potenciales químicos tienden a un único valor mediante un proceso de equalización del potencial químico que determina la dirección de la transferencia de carga, en todos los casos esta dirección es desde Cu_{n-1} a Cu , la única excepción a esta regla ocurre en la formación de Cu_7 . Para estimar la transferencia de carga (ΔN) involucrada en un proceso de formación de una molécula o agregado a partir de dos fragmentos, utilizamos la siguiente expresión [25]:

$$\Delta N = \frac{(\mu_x - \mu_y)}{2(\eta_x + \eta_y)} \quad (5.7)$$

con x y y representando a los diferentes fragmentos involucrados en el proceso de formación. Los valores de ΔN se entregan en la Tabla 5.4 como también sus dos contribuciones. Es interesante notar que en general ΔN es una cantidad pequeña aunque en la formación de *clusters* con n par es mayor debido al bajo valor asociado al término de dureza, ya que, la diferencia de potenciales químicos ($|\mu_x - \mu_y|$) es casi constante a lo largo de la serie, los valores promedios son 0.37 eV y 0.12 eV para *clusters* con n par e impar, respectivamente, estos valores muestran una pequeña dispersión. Mientras que el factor $2(\eta_x + \eta_y)$ presenta una diferencia mucho más marcada en la formación de *clusters* con n par o impar, los valores promedios de esta cantidad son 11.04 eV para el caso de n par y 12.37 eV para el caso de *clusters* con n impar. Esto indica que la formación de enlaces fuertes en *clusters* pares es caracterizado por una mayor transferencia de carga electrónica entre los reactantes (Cu y Cu_{n-1}) hasta que los potenciales químicos son equalizados.

| Cu_n | $ \mu_x - \mu_y $ | $2(\eta_x + \eta_y)$ | ΔN | $\Delta N_{max} = -(\mu/\eta)$ |
|--------|-------------------|----------------------|------------|--------------------------------|
| Cu | | | | 1.3806 |
| Cu_2 | 0.0000 | 12.9780 | 0.0000 | 1.2366 |
| Cu_3 | 0.1094 | 13.5572 | 0.0081 | 2.3819 |
| Cu_4 | 0.3945 | 9.9190 | 0.0398 | 1.5088 |
| Cu_5 | 0.1795 | 12.1890 | 0.0147 | 1.8899 |
| Cu_6 | 0.3595 | 10.8490 | 0.0331 | 1.7553 |
| Cu_7 | -0.0755 | 11.6790 | -0.0065 | 2.0965 |
| Cu_8 | 0.3495 | 10.4290 | 0.0335 | 1.5627 |
| Cu_9 | 0.1195 | 12.0690 | 0.0099 | 2.6271 |

Tabla 5.4: Estimación de la transferencia de carga electrónica (ΔN) asociada a la formación de *clusters* neutros de cobre y sus contribuciones en términos de $(|\mu_x - \mu_y|)$ and $(\eta_x + \eta_y)$. Máxima carga electrónica (ΔN_{max}) que puede ser adquirida por *clusters* de cobre.

La Figura 5.2 (a) muestra los valores de μ y η desde el sistema atómico hasta el metal. A partir de esta ilustración se puede notar una débil dependencia de μ con el tamaño del *clusters*, el valor promedio de μ es muy cercano al valor en el límite del sólido, es decir, al negativo de la función trabajo (Φ), esto es un indicativo que enlaces químicos en *clusters* de Cu son similares a aquellos en el metal, esta observación esta en acuerdo con recientes trabajos sobre análisis topológicos de la densidad electrónica para cobre en un empaquetamiento cúbico centrado en las caras (fcc) [26] y *clusters* de cobre [27]. Estos resultados además validan el uso de *clusters* metálicos en catálisis heterogénea como modelos adecuados. Es interesante destacar en la Figura 5.2 (a) que Cu_3 y Cu_9 presentan los valores más altos de μ a lo largo de la serie, esto puede ser explicado, en término, de la capacidad de estos sistemas a perder un electrón para cerrar sus capas electrónicas conduciendo a sistemas con 2 y 8 electrones de valencia, respectivamente, en concordancia a los *números mágicos* (NM) en el contexto del modelo de *jellium*, tal capacidad a perder un electrón se ve reflejado en los bajos valores de potenciales de ionización de Cu_3 y Cu_9 (ver Tabla 5.2). Por otra parte, estos sistemas presentan los valores más altos de afinidades electrónicas mostrando su

capacidad para ganar un electrón, sin embargo este proceso de adjuntar un electrón no cumple con los requerimientos de estabilidad extra asociada a sistemas *closed-shell* en el modelo de *jellium*.

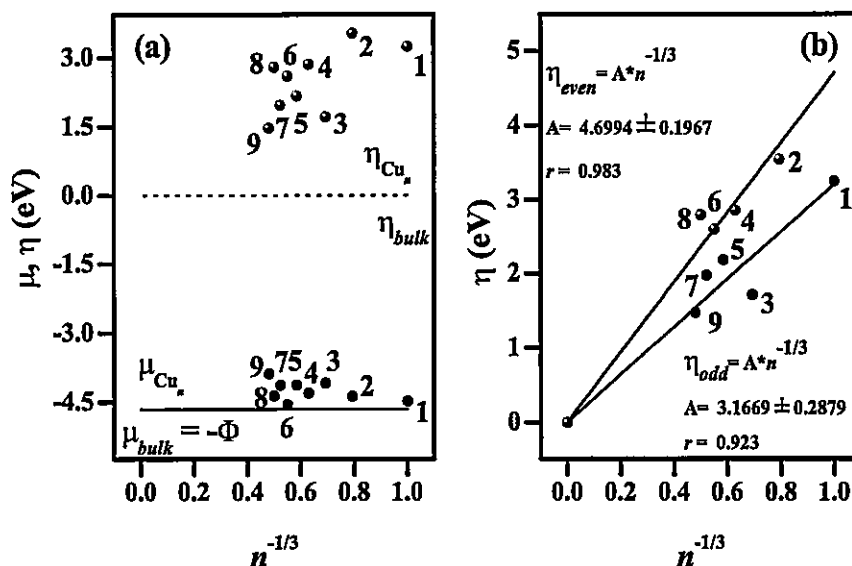


Figura 5.2: (a) Valores experimentales de μ y η y (b) dependencia de η como una función del tamaño del *cluster*.

5.3.2.2 Dureza Química

Esta propiedad se ha establecido como una cantidad electrónica que en muchos casos puede ser utilizada como criterio de estabilidad a través del PMD. A partir de la Tabla 5.3 se observa que *clusters* con n pares son más duros que sistemas con n impares, η sigue un comportamiento opuesto al de ΔE lo cual permite verificar que el PMD es válido en este tipo de proceso.

La Figura 5.2(a) muestra que la dureza química presenta una dependencia mucho

más fuerte con el tamaño del *cluster* en comparación a μ . Cu_n con n pares son en promedio 0.83 eV (19.14 kcal/mol) más duros que *clusters* impar numerados, esto sugiere que η es una propiedad que controla las reacciones de formación de *clusters* de cobre [19]. Aplicando la expresión (5.6) con la siguiente condición de borde: $\eta_{bulk} = 0$; se obtiene una expresión analítica que permite racionalizar la evolución de la dureza química sobre el crecimiento de los *clusters*: $\eta(n) = 3.8064 \cdot n^{-1/3}$ ($r = 0.84$). Al tratar de forma independientes *clusters* con números impares y pares se observa que las correlaciones mejoran, $r = 0.97$ y 0.98 respectivamente. Para trazar las líneas de referencias en la Figura 5.2(b) se utilizó este resultado de donde además se observa que $\left(\frac{d\eta}{d(n^{-1/3})}\right)_{even} > \left(\frac{d\eta}{d(n^{-1/3})}\right)_{odd}$, que puede ser considerado como una evidencia independiente que el PMD se mantiene en el proceso de crecimiento de *clusters* de cobre, y *clusters* con n par son más duros que aquellos con n impar.

5.3.2.3 Índice de Electrofilia

En acuerdo a las discusiones realizadas para μ y η se comenta la tendencia observada para ω (ver Tabla 5.3). En Cu_n el comportamiento de ω es principalmente debido al término 2η , ya que μ permanece constante a lo largo de la serie, *clusters* con n impar son considerablemente más blandos que aquellos con n par, esto conduce a observar valores máximos de ω en este tipo de sistemas.

La cuantificación de la máxima carga electrónica que puede ser adquirida por un sistema hasta que este alcance una energía de estabilización, $\Delta E = -\omega$, viene dado por $\Delta N_{max} = -(\mu/\eta)$, los valores para esta cantidad son también entregados en la Tabla 5.4. Nótese que *clusters* con n impar adquirirán más carga hasta saturación electrónica que *clusters* con n par que son *clusters* más estables. En resumen el poder

electrofilico presentado por *clusters* con n impar es debido básicamente a pequeños valores de η , este resultado esta en acuerdo con la capacidad esperada por *clusters* impares para alcanzar una configuración electrónica del tipo *closed-shell* a través de aceptar carga electrónica desde sus alrededores o medio en el cual el sistema se encuentra inmerso.

5.3.2.4 Efectos de Relajación

Las diferencias entre la propiedad estimada mediante el promedio de *Sanderson* respecto a los valores determinados a partir de *PI* y *AE* permiten cuantificar el efecto de la relajación y redistribución de la densidad electrónica que surge de las nuevas interacciones enlazantes entre Cu_{n-1} y Cu . Nótese que a partir de los valores entregados en la Tabla 5.3, los valores de μ_S son cercanos a los valores obtenidos mediante propiedades monoeléctricas (*PI* y *AE*), esto se debe al hecho que Cu_n proviene del resultado de combinación de sistemas ($Cu_{n-1} + Cu$) con valores de μ muy similares. En contraste a esto, comparaciones de η_S y η indican que la formación de *clusters* impares es acompañada por reordenamientos estructurales más fuertes que *clusters* par numerados. Estos resultados confirman la siguiente idea, la estabilidad de *clusters* pares es determinada por estructuras electrónicas *closed-shell* como una manifestación del principio de máxima dureza [1, 28, 29].

5.3.3 Racionalización de las reacciones de crecimiento en una representación $\{\mu, \eta, E\}$

La conexión entre energía y descriptores electrónicos es de considerable interés teórico puesto que el cambio en propiedades electrónicas tiene relación con los mecanismos de reacción, así la relación entre energía y propiedades electrónicas permite conectar

los aspectos energéticos y mecánicos asociados a un proceso de formación, en la literatura existen algunos interesantes y útiles intentos que relacionan los descriptores electrónicos a la energía de reacción [21, 30, 31]. En este contexto, *Gázquez y col.* lograron establecer una relación entre energía y diferencias de durezas mientras que en nuestras investigaciones [21, 30] hemos propuesto que diferentes aspectos de un evento químico son descritos en una representación donde el potencial químico y dureza molecular son consideradas como variables independientes. En este contexto, se propone escribir la energía como: $E \equiv E[\mu, \eta]$, con una diferencial total:

$$dE = Q_{\eta}d\mu + Q_{\mu}d\eta \quad (5.8)$$

donde

$$Q_{\eta} = \left(\frac{\partial E}{\partial \mu} \right)_{\eta}; \quad Q_{\mu} = \left(\frac{\partial E}{\partial \eta} \right)_{\mu}. \quad (5.9)$$

Los parámetros Q_{η} y Q_{μ} están relacionados a la redistribución de carga entre los átomos en la molécula durante la reacción química. Por lo tanto dentro de este modelo y en el contexto de las reacciones de crecimientos de *clusters* por la adición de un átomo es posible de escribir la energía de enlace (ΔE) en término de dos contribuciones: ΔE_{η} y ΔE_{μ} , donde el índice está indicando que la dureza o el potencial químico se mantiene constante durante el proceso:

$$\Delta E = \Delta E_{\eta} + \Delta E_{\mu}, \quad (5.10)$$

cada una de las contribuciones pueden ser escritas como:

$$\Delta E_{\eta} = \Delta E_{\eta}^{\circ} + Q_{\eta}\Delta\mu \quad (5.11)$$

y

$$\Delta E_{\mu} = \Delta E_{\mu}^{\circ} + Q_{\mu} \Delta \eta. \quad (5.12)$$

Donde ΔE_{η}° , ΔE_{μ}° , Q_{η} and Q_{μ} son parámetros determinados a través de procedimientos de ajustes lineales. Es interesante destacar que dentro de esta estructura formal el cambio energético puede ser escrito a través de las ecuaciones (5.11) y (5.12), las que dependen de solo dos parámetros cada una, cuando el proceso químico es principalmente controlado por μ y η , respectivamente. Al combinar estas expresiones se otorga una descripción más adecuada en el caso que ambas propiedades gobiernen el cambio químico. Por otra parte, nótese que una condición necesaria en dirección a que el principio de máxima dureza se cumpla es que Q_{μ} adquiera valores negativos, ya que un decrecimiento en ΔE_{μ} (mayor estabilidad) debería ser acompañado por un incremento del valor de $\Delta \eta$.

Mediante la Figura 5.2(a) se establece que μ permanece constante desde un *clusters* a otro y a partir de esta misma Figura es evidente que la dureza controla el proceso de formación, así la ecuación (5.12) permite racionalizar este proceso. En la Figura 5.3 se presenta ΔE versus $\Delta \eta$, de donde se observa una relación inversa entre estas propiedades como lo establece el PMD, mediante un procedimiento de ajuste lineal se determina los siguientes valores para $Q_{\mu} = -0.514$ y $\Delta E_{\mu}^{\circ} = -1.881$ eV. Por lo tanto, es posible estimar de forma confiable energías de enlaces de *clusters* solamente a partir de valores de PI y AE a través del uso del modelo propuesto que solo depende de dos parámetros. Esto permite concluir que la dureza es una propiedad clave que controla la reacción de formación, mientras que el potencial químico no juega un rol importante en reacciones de crecimiento de *clusters* de cobre.

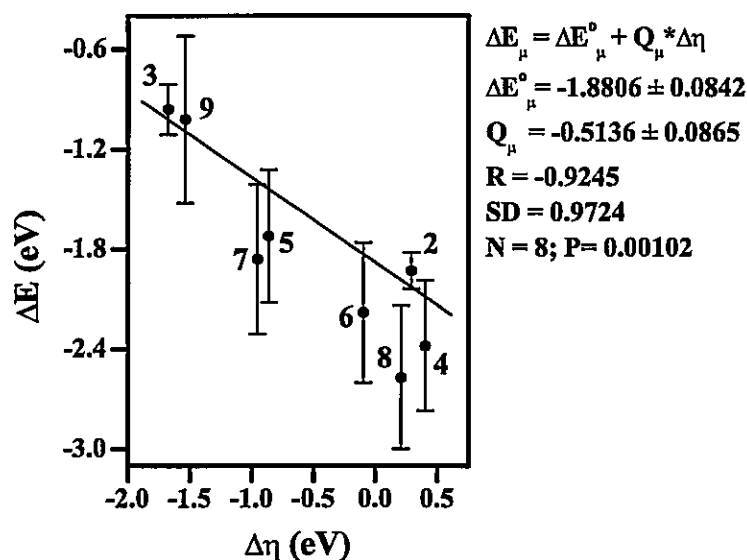


Figura 5.3: Relación entre energía de enlace y variación de dureza química en reacciones de crecimiento de Cu_n .

5.3.4 Modelo para la Energía de Enlace

Los resultados presentados en párrafos anteriores permiten caracterizar la energía de enlace como una función del tamaño del *cluster* mediante la introducción de la dependencia que se ha establecido entre η y n (Figura 5.2 (b)) y combinando las ecuaciones (5.6) y (5.12) además del hecho que $\Delta E_{\mu}^0 \sim \frac{\Delta E_{bulk}^0}{2}$, al conectar estos elementos conduce a:

$$\Delta E(n) \cong \frac{\Delta E_{bulk}^0}{2} \pm \frac{3}{2} Q_{\mu} n^{-1/3}, \quad (5.13)$$

el signo del segundo término de la ecuación (5.13) depende si se forma un cluster con un número par (+) o impar (-) de átomos. En la Figura 5.4 se presenta la

evolución de la energía de enlace con n obtenida a través de esta expresión, nótese el comportamiento oscilatorio esperado que permite extrapolar a sistemas mucho más complejos. Nuevamente se destaca que esta simple expresión depende solo de dos parámetros, los cuales son determinados a partir de datos experimentales de *clusters* pequeños, y que es capaz de producir las tendencias correctas y semicuantitativa en la región de *clusters* más grandes y en el límite del *bulk*. Adicionalmente, cuando $n \rightarrow \infty$ es $\Delta E(n) \rightarrow \frac{\Delta E_{bulk}^0}{2}$ (-1.88 eV) que se aproxima a la mitad del negativo de la energía de vaporización experimental del *bulk* de cobre (-3.50 eV), esta diferencia puede ser atribuida a la simplicidad del modelo propuesto y a efectos de relajación estructural que no han sido considerados dentro de esta aproximación. Sin embargo, los valores de energías de enlaces obtenidos para los sistemas de referencias ($Cu_n; n = 2 - 9$) están en satisfactorio acuerdo a los valores experimentales entregados en la Tabla 5.1 lo cual permite validar la extrapolación cualitativa presentada en la Figura 5.4. Finalmente, se debe hacer notar que la racionalización de energías de enlaces experimentales logradas a través de las expresiones (5.12) y (5.13) abre un nuevo camino para estimar la energía involucrada en procesos de formación cuando solo las propiedades electrónicas están disponibles.

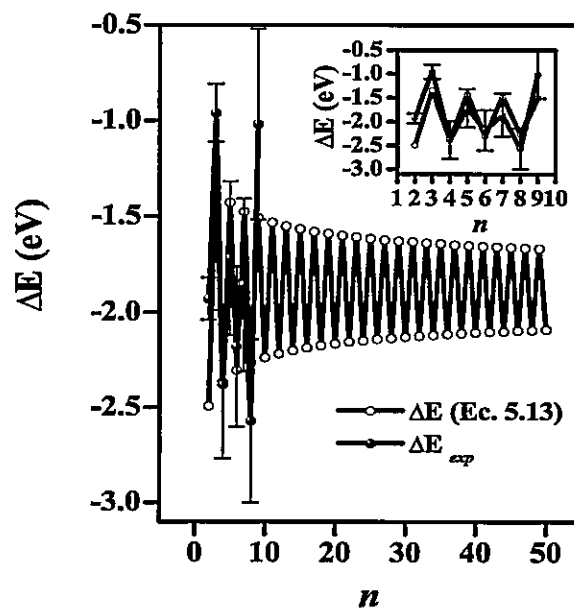


Figura 5.4: Energía de enlace como una función del tamaño del *cluster* predicha por la Ec. (5.13). El extracto de esta Figura permite comparar con valores experimentales entregados en la Tabla 5.1.

5.4 Conclusiones

- En este Capítulo se ha caracterizado y racionalizado el crecimiento de *clusters* neutros de cobre a partir de la información experimental disponible de energías de enlaces, potenciales de ionización y afinidades electrónicas. Se ha mostrado que el comportamiento oscilatorio *par-impar* que exhiben los descriptores electrónicos que dependen de *PI* y *AE* se debe principalmente a fluctuaciones en el potencial de ionización.
- Se ha encontrado que las reacciones de crecimiento de *clusters* de cobre por adición sistemática de un átomo son gobernadas principalmente por variaciones en la dureza química. Mientras que el potencial químico es independiente del tamaño del *clusters* y muy similar al valor del *bulk*, esto indica que la naturaleza de los enlaces químicos no cambian considerablemente cuando se va desde sistemas discretos al sólido, esto permite validar el uso de estos sistemas en procesos complejos, tales como, en procesos de catálisis heterogénea.
- Se ha logrado proponer relaciones analíticas entre energía y propiedades electrónicas que hacen posible estimar energías de enlace de *clusters* a partir de sus propiedades monoeléctricas (*PI* y *AE*; Ec. (5.12)) y/o tamaño del *clusters* (Ec. (5.13)). Aunque el modelo no es cuantitativo para predecir el valor de energía de enlace del *bulk*, se obtiene un acuerdo satisfactorio en las regiones de tamaño pequeño a medio donde ΔE varía fuertemente.

- Estas herramientas teóricas han mostrado ser muy útiles en el estudio de sistemas que presentan una mayor complejidad y que están involucrados en el marco de la físico química de superficies, el trabajo presentado en este Capítulo puede ser considerado como base para explorar procesos que son un desafío para la química computacional y así proponer nuevos modelos teóricos en esta área de investigación.

Parte del trabajo presentado en este Capítulo ha sido publicado en los siguientes artículos:

1. Characterization of Copper *Clusters* Through the use of Density Functional Theory Reactivity Descriptors.

Pablo Jaque and Alejandro Toro-Labbé. *Journal of Chemical Physics*, 117 (2002) 3208–3218.

2. The Formation of Neutral Copper *Clusters* From Experimental Binding Energies and Reactivity Descriptors.

Pablo Jaque and Alejandro Toro-Labbé. *Journal of Physical Chemistry B*, (2003) en prensa.

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Conclusiones Generales

- En este trabajo de Tesis hemos probado la capacidad de análisis de los descriptores (μ , η , ω , $f(\vec{r})$, $s(\vec{r})$,...) y principios (PMD, PMP, HSAB) definidos en la Teoría Funcional de la Densidad en la caracterización de moléculas, reacciones químicas y clusters de cobre.
- Hemos mostrado que conceptos provenientes de la TFD resultan ser de gran utilidad en la interpretación de resultados teóricos y experimentales para caracterizar sistemas moleculares complementando la información clásica que se obtiene desde la superficie de energía potencial. Los resultados presentados en esta Tesis sugieren que en ausencia de información de tipo energética, estos conceptos junto a los principios de máxima dureza y mínima polarizabilidad pueden ser considerados como criterios alternativos, que permiten caracterizar la estabilidad y reactividad intrínseca de especies moleculares, en condiciones de equilibrio como en reacción. Por otra parte estos resultados promueven el uso de estos elementos de análisis en una variedad de dominios en química que participen especies de naturaleza orgánica como inorgánica.
- En el contexto de reacciones químicas hemos mostrado que en la formulación de una teoría de reactividad química en el marco de la TFD se hace necesario incorporar de forma explícita la coordenada de reacción, ya que esto permitiría

caracterizar mecanismos de reacción como también identificar las interacciones específicas que controlan el evento químico.

- Por otra parte hemos propuesto un nuevo esquema de adición para obtener propiedades moleculares a partir de fragmentos aislados. En esta nueva aproximación, propiedades globales y locales juegan roles equivalentes, que pueden conducir a proponer metodologías que permitan caracterizar simultáneamente los conceptos de reactividad y selectividad en procesos químicos.
- El trabajo presentado en esta Tesis puede ser considerado como una plataforma para explorar procesos de una mayor complejidad que permitan proponer nuevo modelos teóricos en esta área de investigación.

Anexos

Apéndice A

Vibraciones Moleculares

| Molécula | $-E^a$ | η^a | α^b |
|--|------------------------|--------------|----------------|
| H ₂ S (C _{2v}) | | | |
| <i>Stretching</i> Asimétrico (B ₂) | | | |
| $\delta^c = 0.0$ | 398.701237(399.421642) | 0.258(0.142) | 23.715(25.138) |
| $\delta = \pm 0.05$ | 398.698494(399.419017) | 0.256(0.136) | 23.749(25.161) |
| $\delta = \pm 0.1$ | 398.690108(399.411001) | 0.252(0.130) | 23.850(25.233) |
| $\delta = \pm 0.2$ | 398.654109(399.376504) | 0.243(0.118) | 24.257(25.250) |
| <i>Stretching</i> Simétrico (A ₁) | | | |
| $\delta = -0.1$ | 398.688228(399.405988) | 0.265(0.151) | 22.125(23.544) |
| $\delta = -0.05$ | 398.698241(399.417162) | 0.262(0.147) | 22.886(24.315) |
| $\delta = 0.0$ | 398.701237(399.421642) | 0.258(0.142) | 23.715(25.138) |
| $\delta = +0.05$ | 398.698752(399.420927) | 0.254(0.136) | 24.616(26.014) |
| $\delta = +0.1$ | 398.692011(399.416226) | 0.250(0.130) | 25.594(26.942) |
| <i>Bending</i> (A ₁) | | | |
| 84.21 | 398.698100(399.419734) | 0.259(0.137) | 23.636(25.029) |
| 89.21 | 398.700460(399.421378) | 0.259(0.139) | 23.664(25.073) |
| 94.21 ^d | 398.701237(399.421642) | 0.258(0.142) | 23.715(25.138) |
| 99.21 | 398.700465(399.420562) | 0.257(0.140) | 23.786(25.222) |
| 104.21 | 398.698189(399.418181) | 0.256(0.137) | 23.879(25.327) |

Tabla A.1: Energía Total (E), Dureza Molecular (η) y Polarizabilidad (α) obtenidas a través de cálculos *Hartree-Fock* (TFD/B3LYP) para modos vibracionales en H₂S. Todos los valores están en *ua*. ^a Cálculos con bases 6-311G** y ^b con bases de *Sadlej*. ^c denota que la distorsión es en Å. ^d valores en la geometría de equilibrio.

| Molécula | $-E^a$ | η^a | α^b |
|--|----------------------|------------------|----------------|
| H₂O (C_{2v}) | | | |
| <i>Stretching</i> Asimétrico (B ₂) | | | |
| $\delta^c = 0.0$ | 76.047012(76.446574) | 0.32665(0.16680) | 8.297(9.712) |
| $\delta = \pm 0.05$ | 76.045417(76.445003) | 0.32654(0.16654) | 8.303(9.716) |
| $\delta = \pm 0.1$ | 76.040607(76.440268) | 0.32621(0.16581) | 8.322(9.727) |
| $\delta = \pm 0.2$ | 76.020607(76.420579) | 0.32491(0.16300) | 8.396(9.769) |
| $\delta = \pm 0.3$ | 75.984459(76.384983) | 0.32279(0.15855) | 8.519(9.840) |
| <i>Stretching</i> Simétrico (A ₁) | | | |
| $\delta = -0.3$ | 75.963429(76.351460) | 0.34316(0.18664) | 6.659(7.874) |
| $\delta = -0.2$ | 76.014620(76.406131) | 0.33759(0.18032) | 7.152(8.442) |
| $\delta = -0.1$ | 76.039885(76.435254) | 0.33211(0.17371) | 7.694(9.053) |
| $\delta = -0.05$ | 76.045325(76.442748) | 0.32938(0.17030) | 7.987(9.376) |
| $\delta = 0.0$ | 76.047012(76.446574) | 0.32665(0.16680) | 8.297(9.712) |
| $\delta = +0.05$ | 76.045542(76.447316) | 0.32392(0.16322) | 8.625(10.061) |
| $\delta = +0.1$ | 76.041464(76.445512) | 0.32119(0.15958) | 8.970(10.423) |
| $\delta = +0.2$ | 76.027167(76.435959) | 0.31574(0.15211) | 9.723(11.187) |
| $\delta = +0.2$ | 76.006909(76.420672) | 0.31026(0.14446) | 10.568(12.007) |
| <i>Bending</i> (A ₁) | | | |
| 86.20 | 76.036097(76.437182) | 0.32678(0.16605) | 8.225(9.574) |
| 89.98 | 76.040093(76.440761) | 0.32691(0.16640) | 8.233(9.592) |
| 97.18 | 76.045107(76.445129) | 0.32695(0.16679) | 8.257(9.640) |
| 100.30 | 76.046285(76.446096) | 0.32688(0.16685) | 8.271(9.665) |
| 105.38 ^d | 76.047012(76.446574) | 0.32665(0.16680) | 8.297(9.712) |
| 110.46 | 76.046370(76.445809) | 0.32627(0.16656) | 8.330(9.767) |
| 113.58 | 76.045353(76.444777) | 0.32595(0.16633) | 8.352(9.804) |
| 120.78 | 76.041395(76.440968) | 0.32500(0.16552) | 8.412(9.898) |
| 124.56 | 76.038530(76.438280) | 0.32437(0.16496) | 8.447(9.952) |

Tabla A.2: Energía Total (E), Dureza Molecular (η) y Polarizabilidad (α) obtenidas a través de cálculos *Hartree-Fock* (TFD/B3LYP) para modos vibracionales en H₂O. Todos los valores están en *ua*. ^a Cálculos con bases 6-311G** y ^b con bases de *Sadlej*. ^c denota que la distorsión es en Å. ^d valores en la geometría de equilibrio.

Apéndice B

Rotaciones Internas

| Isómero | $-E^a$ | η^a | α^b |
|--|------------------------|--------------|----------------|
| <i>cis</i> -HSOH | 473.531796(474.614686) | 0.232(0.093) | 26.860(29.027) |
| <i>gauche</i> -HSOH | 473.542668(474.626130) | 0.243(0.110) | 26.672(28.799) |
| <i>trans</i> -HSOH | 473.535313(474.618957) | 0.229(0.093) | 27.036(29.164) |
| <i>cis</i> -HSSH | 796.217610(797.619719) | 0.206(0.082) | 43.848(45.779) |
| <i>gauche</i> -HSSH | 796.230201(797.631886) | 0.234(0.108) | 43.194(45.291) |
| <i>trans</i> -HSSH | 796.221192(797.623560) | 0.206(0.081) | 43.980(45.876) |
| <i>planar</i> -C ₂ H ₄ | 78.054725(78.613656) | 0.273(0.143) | 27.276(27.667) |
| 90°-C ₂ H ₄ | 77.882949(78.463019) | 0.150(0.030) | 35.111(36.812) |

Tabla B.1: Energía Total (E), Dureza Molecular (η) y Polarizabilidad (α) obtenidas a través de cálculos *Hartree-Fock* (TFD/B3LYP) para isómeros conformacionales. Todos los valores están en *ua*. ^a Cálculos con bases 6-311G** y ^b con bases de *Sadlej*.

Apéndice C

Publicaciones

El trabajo presentado en esta Tesis ha generado la siguiente lista de publicaciones científicas.

1. Validity of the Minimum Polarizability Principle in Molecular Vibrations and Internal Rotations: An Ab Initio SCF Study.
Pratim K. Chattaraj, Patricio Fuentealba, **Pablo Jaque**, and Alejandro Toro-Labbé. *Journal of Physical Chemistry A*, 103 (1999) 9307–9312.
2. Theoretical Study of the Double Proton Transfer in the CHX-XH...CHX-XH (X=O,S) Complexes.
Pablo Jaque and Alejandro Toro-Labbé. *Journal Physical Chemistry A*, 104 (2000) 995-1003.
3. Using Sanderson's Principle to Estimate Global Electronic Properties and Bond Energies of Hydrogen-Bonded Complexes. Soledad Gutiérrez-Oliva, **Pablo Jaque** and Alejandro Toro-Labbé. *Journal of Physical Chemistry*, 104 (2000), 8955-8964.

4. Characterization of Chemical Reactions Through Classical Concepts and DFT Descriptors.
Soledad Gutiérrez-Oliva, **Pablo Jaque** and Alejandro Toro-Labbé. *Review of Modern Quantum Chemistry: A Celebration of the Contributions of Robert G. Parr*. K.D. Sen Editor. Singapore (2002) 966.
5. Characterization of Copper Clusters Through the use of Density Functional Theory Reactivity Descriptors.
Pablo Jaque and Alejandro Toro-Labbé. *Journal of Chemical Physics*, 117 (2002) 3208–3218.
6. Towards Understanding the Molecular Internal Rotations and Vibrations and Chemical Reactions Through the Profiles of Reactivity and Selectivity Indices: An Ab Initio SCF and DFT Study.
Pratim K. Chattaraj, Soledad Gutiérrez-Oliva, **Pablo Jaque** and Alejandro Toro-Labbé. *Molecular Physics*, 101 (2003) 2841–2853.
7. The Formation of Neutral Copper Clusters From Experimental Binding Energies and Reactivity Descriptors.
Pablo Jaque and Alejandro Toro-Labbé. *Journal of Physical Chemistry B*, (2003), en prensa.
8. Polarizability of Neutral Copper Clusters.
Pablo Jaque and Alejandro Toro-Labbé. Manuscrito en redacción.

Validity of the Minimum Polarizability Principle in Molecular Vibrations and Internal Rotations: An *ab Initio* SCF Study

Pratim K. Chattaraj,[†] Patricio Fuentealba,[‡] Pablo Jaque,[§] and Alejandro Toro-Labbé^{*,§}

Department of Chemistry, Indian Institute of Technology, Kharagpur, 721 302, India, Departamento de Física, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago, Chile, and Departamento de Química Física, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Correo 22, Santiago, Chile

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Molecular vibrations in ammonia (NH₃) and hydrogen sulfide (H₂S), and internal rotations in hydrogen peroxide (HOOH), hydrogen thioperoxide (HSOH), hydrogen persulfide (HSSH), and ethylene (C₂H₄) are studied using *ab initio* SCF methods at the Hartree–Fock level using a standard Pople 6-311G** basis set. Polarizability values are calculated using both Pople's and Sadlej's basis sets. Any nontotally symmetric distortion in bond length or bond angle along the vibrational symmetry coordinates of a molecule around its equilibrium geometry decreases the equilibrium hardness value and increases the equilibrium polarizability value. During rotational isomerization the minimum energy conformation corresponds to the maximum hardness and minimum polarizability values and the maximum energy conformation corresponds to the minimum hardness and maximum polarizability values. Density functional calculations confirm these observed trends. In general we have found that the conditions of maximum hardness and minimum polarizability complement the minimum energy criterion for molecular stability.

1. Introduction

Popular qualitative chemical concepts like electronegativity^{1,2} (χ) and hardness (η)^{3,4} are rigorously defined within density functional theory (DFT).^{5,6} For an N -particle system with total energy E and external potential $v(\vec{r})$ they are defined as follows:^{7,8}

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(\vec{r})} \quad (1)$$

and

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(\vec{r})} \quad (2)$$

In eq 1 μ is the electronic chemical potential which is the Lagrange multiplier associated with the normalization constraint of DFT.^{5,6}

These quantities are better appreciated through the related electronic structure principles. Sanderson's electronegativity equalization principle⁹ states that "all the constituent atoms in a molecule have the same electronegativity value given by the geometric mean of the electronegativities of the pertinent isolated atoms". Pearson proposed two hardness-related principles, viz., the hard–soft acids and bases (HSAB) principle^{3,4,8,9} and the maximum hardness principle (MHP).^{4,10,11} While the former states^{3,4,8} that "hard likes hard and soft likes soft", the statement^{4,10} of the latter is "there seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible".

Complete characterization of an N -particle wave function needs only N and $v(\vec{r})$. The response of the system is measured by χ and η when N is varied for a fixed $v(\vec{r})$. However, the polarizability (α) of the system may be used in understanding the behavior of the system for changing $v(\vec{r})$ at constant N . On the basis of an inverse relationship¹² between η and α , Chattaraj and Sengupta¹³ have proposed a minimum polarizability principle (MPP) which states that "the natural direction of evolution of any system is toward a state of minimum polarizability". It has also been shown¹⁴ that "a system is harder and less polarizable in its ground state than in any of its excited states".

In the present paper we verify whether the MPP is valid when a molecule undergoes vibration or internal rotation. For this purpose we compute various reactivity parameters, viz., χ , η , and α , using *ab initio* SCF methods in the context of molecular vibration and internal rotation. Symmetric and asymmetric distortions of ammonia and hydrogen sulfide along the directions specified by vibrational symmetry coordinates are taken from Pearson and Palke¹⁵ and Chattaraj et al.,¹⁶ respectively. The rotational isomerization of HOOH, HSOH, and HSSH is taken as given by Toro-Labbé and coworkers.¹⁷ Along the torsional angle these molecules present the interesting feature of having a single well at the nonplanar *gauche* conformation with two energy barriers at the planar *cis* and *trans* conformations. We also test the validity of the MPP in the case of the rotation of planar ethylene¹⁸ and in a few intermolecular double proton transfer reactions.¹⁹

2. Details of Computation

The chemical potential and the hardness are calculated as the following approximate versions of eqs 1 and 2:

$$\mu = \frac{1}{2}(\epsilon_L + \epsilon_H) \quad (3)$$

[†] Indian Institute of Technology.

[‡] Universidad de Chile.

[§] Pontificia Universidad Católica de Chile.

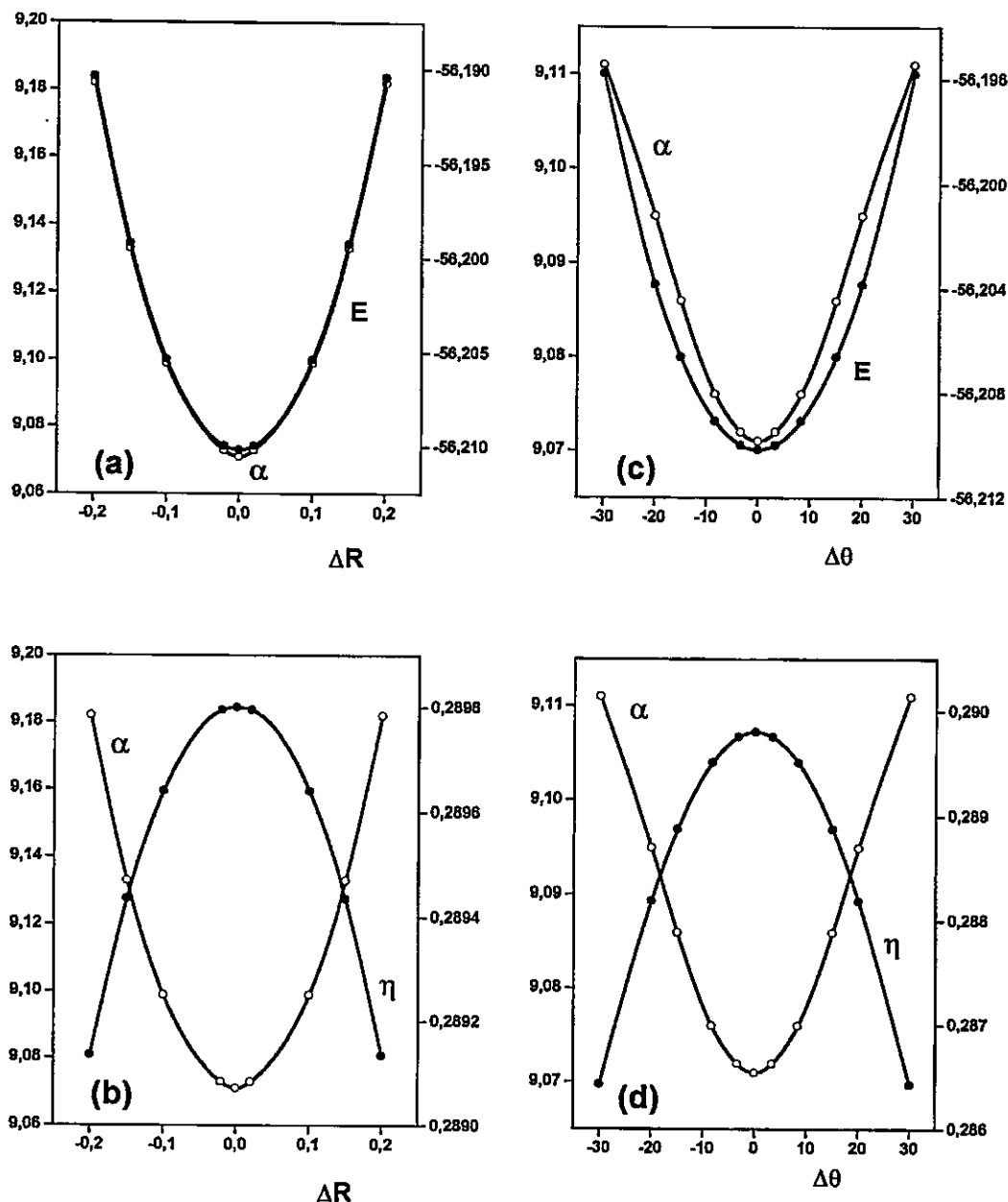


Figure 1. Asymmetric distortions of ammonia: (a) profiles of energy and polarizability and (b) profiles of hardness and polarizability for distortion in the N–H bond distance; (c) profiles of energy and polarizability and (d) profiles of hardness and polarizability for distortion in the HNH bond angle. All values are in atomic units; the left axis bears the polarizability values (open circles).

and

$$\eta = \frac{1}{2}(\epsilon_L - \epsilon_H) \quad (4)$$

where ϵ_L and ϵ_H are the lowest unoccupied and highest occupied molecular orbital energies, respectively. The energy, μ , and η were obtained through SCF ab initio calculations at the Hartree–Fock (HF) level with the Pople 6-311G** basis set using the Gaussian 94 package.²⁰ In addition to the calculations with the Pople basis set, the polarizability was calculated using the more adequate Sadlej basis set²¹ that is designed to reproduce molecular electric properties, especially polarizabilities. These calculations were complemented with the use of the B3LYP model within the frame of DFT.²²

3. Results and Discussion

Figures 1 and 2 depict the profiles of energy, hardness, and polarizability associated with the asymmetric distortions of E

symmetry and the symmetric distortions of A_1 symmetry for ammonia,¹⁵ respectively. In both figures parts a and b refer to the distortions in bond length (ΔR) while parts c and d refer to the distortions in bond angle ($\Delta\theta$). Unless otherwise specified all quantities are in atomic units. For the non totally symmetric distortions μ and electron–nuclear attraction potential (v_{en}) remain constant for small changes, in the Pearson–Palke sense.¹⁵ However, neither of them remain constant for the totally symmetric distortions. In Figure 1a,c we see that the polarizability is minimum for the equilibrium configuration (energy is minimum) for the asymmetric stretching and bending modes, respectively. For these two modes the beautiful mirror-image relationship between α and η profiles is clearly manifested in Figure 1b,d demonstrating the simultaneous validity of the MHP and the MPP in the context of molecular vibration since the equilibrium configuration is associated with the largest η and the smallest α values. As analyzed by Pearson and Palke,¹⁵ the hardness increases monotonically as the nuclei approach each

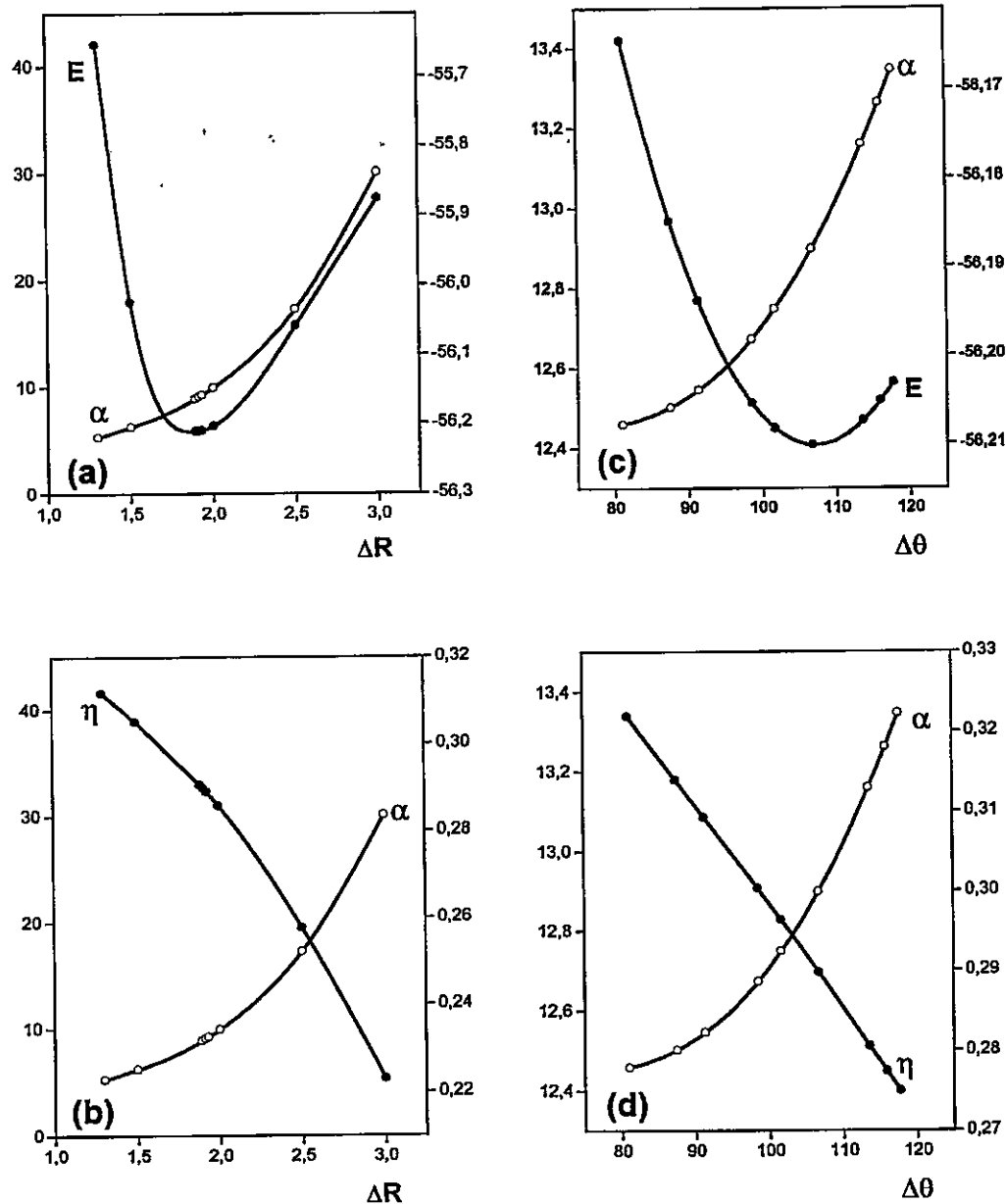


Figure 2. Symmetric distortions of ammonia: (a) profiles of energy and polarizability and (b) profiles of hardness and polarizability for distortion in the N–H bond distance; (c) profiles of energy and polarizability and (d) profiles of hardness and polarizability for distortion in the HNH bond angle. All values are in atomic units; the left axis bears the polarizability values (open circles).

other during the totally symmetric oscillation. In the present work (Figure 2a,c) it is shown that the polarizability also keeps on decreasing for such a distortion as the nuclei come closer to each other. An inverse relationship between α and η for the symmetric stretching and bending modes is transparent in parts b and d, respectively, of Figure 2. Calculation of polarizability using Pople's (α_{Pople}) and Sadlej's (α_{Sadlej}) basis sets shows the same qualitative trends for the asymmetric stretching in ammonia as is transparent in Figure 3a, which depicts the linear relationship between two sets of α values. In general the α_{Sadlej} values are larger than the α_{Pople} values. Since the α_{Pople} values do not reproduce the expected trend (decrease with an increase in HNH bond angle) for symmetric distortions of HNH bond angle in ammonia, in Figure 2c,d we present the α_{Sadlej} values. On the other hand, we have performed DFT/B3LYP calculations within the same scheme of Pople and Sadlej basis sets for energy, hardness, and polarizability. The results reproduce the same trends given in Figures 1 and 2. As an illustration of this

observation, we display in Figure 3b the linear correspondence between the polarizability values for the asymmetric stretch of the Hartree–Fock and density functional calculations. We note that the DFT polarizability values are larger than the HF ones. This situation is encountered in all remaining normal modes of NH_3 .

With the purpose of throwing more light on the applicability of these principles, we have performed similar calculations (HF and DFT) for the symmetric and asymmetric stretchings as well as the bending mode of H_2S . The results are quoted in Table 1. As for ammonia we find that the asymmetric distortions display opposite trends for α and η showing the simultaneous validity of the MHP and the MPP in the context of molecular vibration. In contrast to this for symmetric distortions neither α nor η is an extremum at the equilibrium geometry and both attain their extremum value when the atoms are closest.

Profiles of energy, hardness, and polarizability for the internal rotation of H_2O_2 are presented in Figure 4. It is clear (Figure

TABLE 1: Total Energy (E), Hardness (η), and Polarizability (α) Values Obtained through Hartree-Fock (DFT/B3LYP) Calculations for H₂S and Rotational Isomers of HSOH, HSSH, and C₂H₄ (All Values in au)

| molecule | $-E$ | η | α^a |
|--|---------------------------|---------------|-----------------|
| H ₂ S | | | |
| asym stretch | | | |
| $\delta^b = 0.0$ | 398.701 237 (399.421 642) | 0.258 (0.142) | 23.715 (25.138) |
| $\delta = \pm 0.05$ | 398.698 494 (399.419 017) | 0.256 (0.136) | 23.749 (25.161) |
| $\delta = \pm 0.1$ | 398.690 108 (399.411 001) | 0.252 (0.130) | 23.850 (25.233) |
| $\delta = \pm 0.2$ | 398.654 109 (399.376 504) | 0.243 (0.118) | 24.257 (25.250) |
| sym stretch | | | |
| $\delta = -0.1$ | 398.688 228 (399.405 988) | 0.265 (0.151) | 22.125 (23.544) |
| $\delta = -0.05$ | 398.698 241 (399.417 162) | 0.262 (0.147) | 22.886 (24.315) |
| $\delta = 0.0$ | 398.701 237 (399.421 642) | 0.258 (0.142) | 23.715 (25.138) |
| $\delta = +0.05$ | 398.698 752 (399.420 927) | 0.254 (0.136) | 24.616 (26.014) |
| $\delta = +0.1$ | 398.692 011 (399.416 226) | 0.250 (0.130) | 25.594 (26.942) |
| HSH bending | | | |
| 84.21 | 398.698 100 (399.419 734) | 0.259 (0.137) | 23.636 (25.029) |
| 89.21 | 398.700 460 (399.421 378) | 0.259 (0.139) | 23.664 (25.073) |
| 94.21 ^c | 398.701 237 (399.421 642) | 0.258 (0.142) | 23.715 (25.138) |
| 99.21 | 398.700 465 (399.420 562) | 0.257 (0.140) | 23.786 (25.222) |
| 104.21 | 398.698 189 (399.418 181) | 0.256 (0.137) | 23.879 (25.327) |
| <i>cis</i> -HSOH | 473.531 796 (474.614 686) | 0.232 (0.093) | 26.860 (29.027) |
| <i>gauche</i> -HSOH | 473.542 668 (474.626 130) | 0.243 (0.110) | 26.672 (28.799) |
| <i>trans</i> -HSOH | 473.535 313 (474.618 957) | 0.229 (0.093) | 27.036 (29.164) |
| <i>cis</i> -HSSH | 796.217 610 (797.619 719) | 0.206 (0.082) | 43.848 (45.779) |
| <i>gauche</i> -HSSH | 796.230 201 (797.631 886) | 0.234 (0.108) | 43.194 (45.291) |
| <i>trans</i> -HSSH | 796.221 192 (797.623 560) | 0.206 (0.081) | 43.980 (45.876) |
| <i>planar</i> -C ₂ H ₄ | 78.054 725 (78.613 656) | 0.273 (0.143) | 27.276 (27.667) |
| 90°-C ₂ H ₄ | 77.882 949 (78.463 019) | 0.150 (0.030) | 35.111 (36.812) |

^a Calculated using the Sadlej basis set. ^b δ denotes the amount of distortion in Å. ^c Equilibrium value.

4a) that the polarizability curve more or less mimicks the corresponding energy curve as a function of the torsional angle (ω). The polarizability minimum is slightly shifted toward the right. A similar behavior was observed¹⁷ for this molecule when E and η profiles were compared. Figure 4 demonstrates that the hardness and the polarizability (α_{Sadlej}) bear a mirror-image relationship. The α_{Pople} values keep on decreasing. It appears that Sadlej's basis set is more appropriate than Pople's one for the polarizability calculation whereas the latter works better for the calculation of energy and hardness. A maximum (minimum) in the hardness profile corresponds to a minimum (maximum) in the polarizability profile, a clear vindication of the validity of both the MHP and the MPP during molecular internal rotation. We have obtained the same trends from density functional calculations.

Further tests of the validity of the MHP and the MPP in the context of internal rotation were carried out by performing similar calculations on HSOH, HSSH, and ethylene. The energy, hardness, and polarizability values for the relevant isomers of these molecules are also quoted in Table 1. In all three cases we observe the same trends already described for hydrogen peroxide in that the stable conformations are associated with minimum values of α and maximum values of η . Moreover, we note in comparing HF with DFT calculations that in the present cases the validity of the MHP and the MPP is confirmed independent of the method of calculation.

The implication of the MPP during chemical reactions is being studied by us at present. However, it is worth to mention that results on different double proton transfer reactions are confirming the simultaneous validity of the MHP and the MPP.¹⁹ As illustrative examples, in Table 2 we display values of energy, hardness, and polarizability for the fully optimized structures of reactants (R), products (P), and transition states (TS) of four double proton transfer reactions. The numbers were obtained through ab initio calculations at the Hartree-Fock level and using the standard 6-311G** basis set. Note that, in the first three reactions, reactants and products are the same species, the

TABLE 2: Hartree-Fock 6-311G Values of Energy, Hardness, and Polarizability for the Stable Conformations and Transition States (TS) of Double Proton Transfer Reactions (All Values in au)**

| reaction | $-E$ | η | α |
|--------------------|--------------|--------|----------|
| HCO-OH...HCO-OH | | | |
| R | 377.664 112 | 0.320 | 30.958 |
| TS | 377.635 537 | 0.311 | 32.047 |
| P | 377.664 112 | 0.320 | 30.958 |
| HCO-OH...HCS-SH | | | |
| R | 1022.917 548 | 0.202 | 60.996 |
| TS | 1022.880 619 | 0.196 | 67.619 |
| P | 1022.917 548 | 0.202 | 60.996 |
| HCS-SH...HCS-SH | | | |
| R | 1668.176 971 | 0.197 | 88.614 |
| TS | 1668.117 387 | 0.184 | 106.245 |
| P | 1668.176 971 | 0.197 | 88.614 |
| HCS-SH...HC(=O)-SH | | | |
| R | 1345.542 487 | 0.200 | 72.900 |
| TS | 1345.496 193 | 0.177 | 84.834 |
| HCS-SH...HC(=S)-OH | | | |
| R | 1345.538 872 | 0.197 | 75.085 |

reaction is isoenergetic, and the TS is a planar symmetric structure. The fourth reaction is endoenergetic and the transition state, although planar, is not symmetric. In all cases the results show that the most favorable direction of evolution of these reactions is toward the state where the polarizability and energy are minima and the hardness is a maximum.

4. Concluding Remarks

Ab initio SCF studies on representative systems undergoing molecular vibrations, internal rotations, and chemical reactions have confirmed the validity of the maximum hardness and minimum polarizability principles for these processes. The molecule at the equilibrium geometry possesses the maximum hardness and the minimum polarizability values when compared with the corresponding values for any other geometry obtained through a non totally symmetric distortion. In internal rotation processes we have found that the most (least) stable isomer is associated with the maximum (minimum) hardness value and

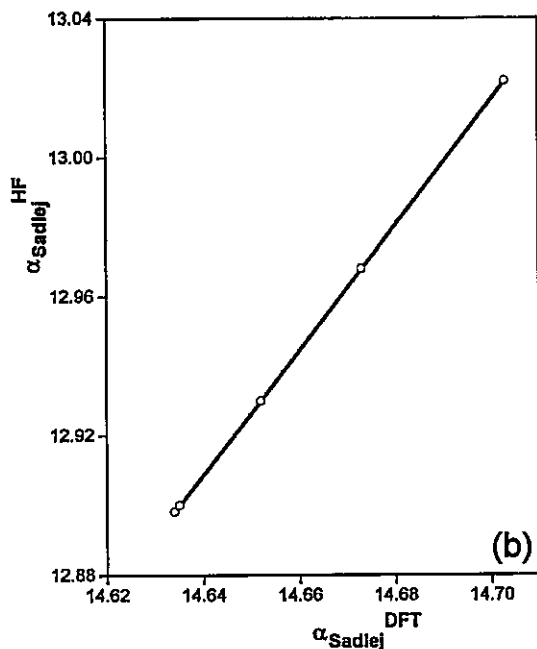
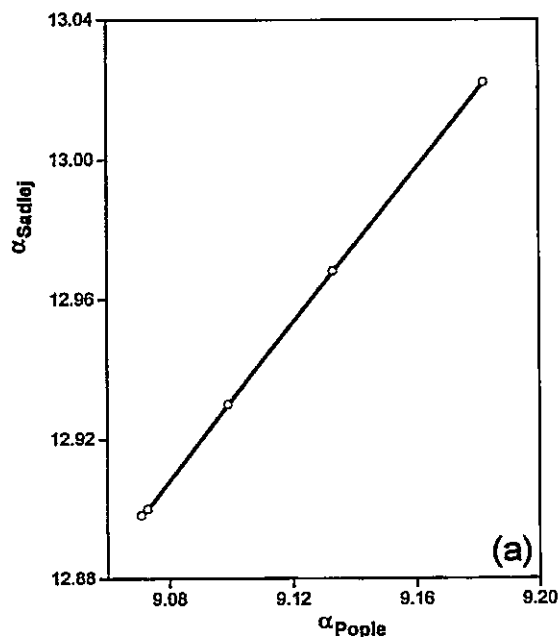


Figure 3. Asymmetric stretching of ammonia: (a) comparison of the Pople and Sadlej polarizabilities and (b) comparison of Hartree-Fock and DFT results.

the minimum (maximum) polarizability value. The double proton transfer reactions that we have reviewed in this paper tend to go in the direction that produces the less polarizable and hardest species.

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References and Notes

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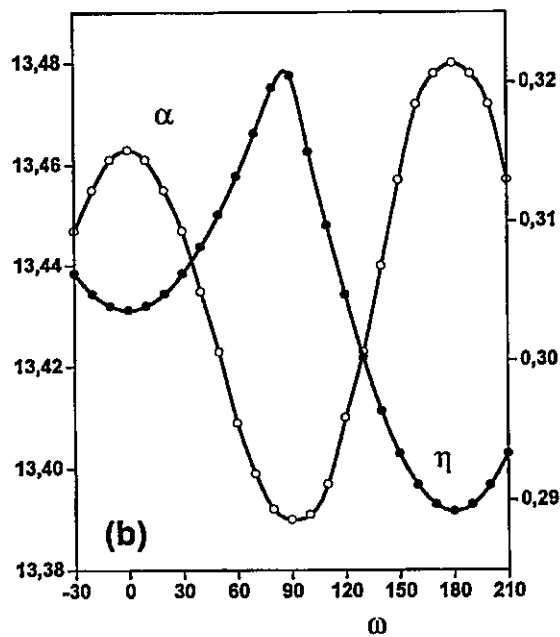
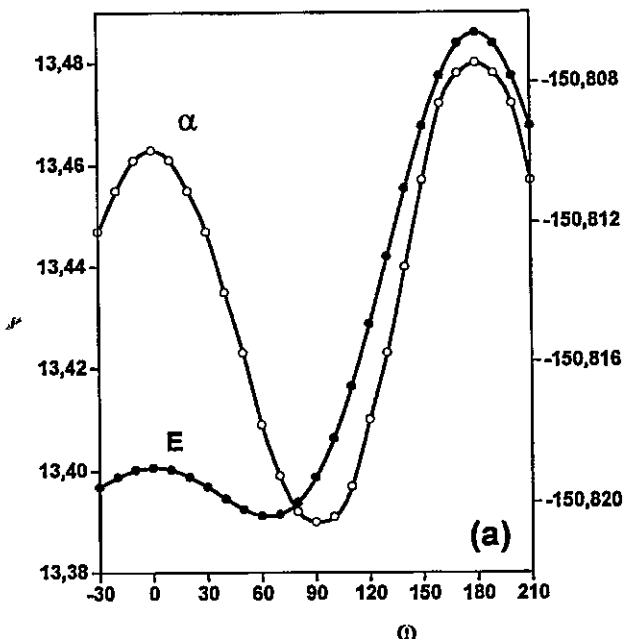


Figure 4. Internal rotation in H_2O_2 : (a) profiles of energy and polarizability and (b) profiles of hardness and polarizability. All values are in atomic units; the left axis bears the polarizability values (open circles).

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Theoretical Study of the Double Proton Transfer in the CHX–XH···CHX–XH (X = O, S) Complexes

Pablo Jaque and Alejandro Toro-Labbé*,†

Departamento de Química Física, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Correo 22, Santiago, Chile

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A theoretical study of double-proton-transfer processes in bimolecular complexes formed by combinations of molecules of the type CHX–XH (X = O, S) is reported. The reactions are rationalized in terms of the energy, chemical potential, and hardness of hydrogen-bonded and isolated species. Sanderson's rule to determine molecular chemical potential and hardness from the values of the constituent fragments is used to characterize the relaxation effects due to hydrogen bonding. In ten formation and seven double-proton transfer processes studied here, the principles of maximum hardness and minimum polarizability are verified. The mechanism for double proton transfer has been analyzed through the force acting on the system to bring reactants into products and the corresponding energy barriers have been qualitatively classified according to its *through bond* or *through space* nature.

1. Introduction

Proton transfer (PT) is one of the simplest and fundamental reactions in chemistry; because it is important in oxidation–reduction reactions in many chemical and biological process, it has been studied extensively.^{1–3} There is a growing interest in the study of intrinsic properties of both, the H-bonded complexes and the dynamic of the transfer itself, the literature accumulated over the years includes studies based on different ab initio methodologies such as Hartree–Fock (HF) and density functional calculations.^{4–11} Most PT studies concerns transfer of a single proton during the reaction, processes in which more than one proton is transferred have been less studied. In this paper we are concerned with the formation of ten cyclic bimolecular complexes formed by combinations of CHX–XH (X = O, S) species and the subsequent double proton transfer (2PT) reactions.

The double proton transfer in formic acid dimer [(HCOOH)₂] has been extensively studied from both experimental and theoretical viewpoints;^{11–25} it is well-known that it forms strong enough hydrogen bonds so that it is fairly easy to measure their infrared and Raman frequencies.^{13–15,17,18} (HCOOH)₂ has been used as a model to study key properties of many chemically and biologically important multiproton-transfer systems. On the basic units CHX–XH (X = O, S) that form the complexes in which we are interested here, there are many theoretical and spectroscopic studies of their molecular structure, electronic properties, barriers to internal rotation around the C–X bond, etc.^{26–28} The geometrical change of the monomeric units on complexation and the associated energetic stabilization due to formation of hydrogen bonds have also received attention.^{16,22,23} Recently, many theoretical studies at various levels of theory have been carried out to predict the structures of the formic acid dimer and the potential energy surface (PES) for the 2PT process. The minimum energy path (MEP) on PES involves a complex set of nuclear displacements: the transfer is initiated by the displacement of heavy atoms bringing the monomer units

closer to each other, near the barrier for transfer; at the vicinity of the transition state (TS), the MEP becomes mostly due to hydrogenic motion as the protons are transferred.^{19–23} Another interesting feature encountered in PT processes is that electronic charge flows in a direction which is opposite to that of the proton motion, so monitoring the redistribution of electron charges during the dynamical process may give insight about the reaction mechanisms.

In this context, a chemical reaction can be seen as resulting from redistribution of electron density among the atoms in a molecule. Density functional theory (DFT)^{29–34} is quite well suited to describe such electronic reorganization processes; it has provided definitions for the chemical potential (μ), molecular hardness (η) and softness ($S = 1/\eta$). The chemical potential characterizes the escaping tendency of electrons from the equilibrium systems while η and S can be seen as a resistance and capacity to charge transfer, respectively. The study of the profiles of μ and η along a reaction coordinate has been shown to be useful in rationalizing different aspects of the progress of chemical reactions, in particular those related to the characterization of transition states.^{35–39}

On the other hand, a major focus of attention in the application of DFT to chemical reactivity is the principle of maximum hardness (PMH) that asserts that molecular systems at equilibrium tend to states of highest hardness;^{32,40–42} therefore, the PMH can also be helpful in identifying transition states where minimum values of η are expected.³⁷ Rationalizing the transition states through the PMH leads to establish a bridge connecting electronic and energetic properties, i.e., reaction mechanisms and thermodynamics.³⁹ This is of considerable theoretical interest since it complements the well-known relationships between kinetic and thermodynamics.⁴³ Along with this, Chattaraj et al. have proposed a minimum polarizability principle (MPP) which states that the natural direction of evolution of any system is toward a state of minimum polarizability.^{44,45} In general the conditions of maximum hardness and minimum polarizability complement the minimum energy

† E-mail: atola@puc.cl.

criterion for molecular stability, and they are criteria that we will use to characterize our systems.

In this paper we investigate the formation of 10 bimolecular complexes from the combination of basic units of the type CHX–XH (X = O, S). Then we focus our attention to the study of synchronous 2PT processes occurring in cyclic complexes. Formation and proton-transfer processes are discussed and analyzed in terms of the change in energy, chemical potential, hardness, and polarizability (α). Characterization of various properties of the transition states of 2PT reactions allows one to identify the specific interactions stabilizing the complexes and helps determine the physical nature of the energy barrier for the simultaneous transfer of two protons.

2. Theory

General Definitions. Within the framework of DFT, the chemical potential and hardness for an N -particle system with total energy E and external potential $v(\vec{r})$ are defined as follows:^{30,33}

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{v(\vec{r})} = -\chi \quad (1)$$

and

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(\vec{r})} = \frac{1}{2} \left(\frac{\partial \mu}{\partial N} \right)_{v(\vec{r})} \quad (2)$$

As pointed out in eq 1, μ is the negative of the electronegativity χ and it is the Lagrange multiplier associated with the normalization constraint of DFT.³³ In most numerical applications, μ and η are calculated from the knowledge of ionization potential (I) and electron affinities (A), the following approximate versions of eqs 1 and 2 based upon a three-points finite difference approximation and the Koopmans theorem are widely used:³³

$$\mu \approx -\frac{1}{2}(I + A) = \frac{1}{2}(\epsilon_L + \epsilon_H) \quad (3)$$

and

$$\eta \approx \frac{1}{2}(I - A) = \frac{1}{2}(\epsilon_L - \epsilon_H) \quad (4)$$

where ϵ_H and ϵ_L are the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively. In this paper μ and η are calculated using the expressions involving the molecular orbital energies.

Formation of the Hydrogen Bonded Complex. The formation energy of the hydrogen bonded (hb) species is given by

$$\Delta E_{\text{hb}} = E_{\text{hb}} - \sum_m^2 E_m \quad (5)$$

where E_{hb} is the energy of the fully optimized hydrogen bonded complex and E_m is the energy of the corresponding fully optimized monomeric species. Although the basis set superposition error (BSSE) may be important in the calculation of the formation energies,⁴⁶ it is beyond the scope of this paper. Our main goal here is to discuss the validity of Sanderson's addition scheme⁴⁷ in the determination of molecular electronic properties from the corresponding values associated with their nonbonded

TABLE 1: Energy, Chemical Potential, Hardness and Polarizability Values for the Fully Optimized Structures of Monomeric Units^a

| molecule | E | μ | η | α |
|-----------|-------------|---------|--------|----------|
| HC(=O)–OH | –188.820525 | –0.1554 | 0.3138 | 15.1733 |
| HC(=S)–OH | –511.445375 | –0.1402 | 0.2206 | 28.2873 |
| HC(=O)–SH | –511.449325 | –0.1391 | 0.2608 | 27.7830 |
| HC(=S)–SH | –834.086649 | –0.1532 | 0.1996 | 43.4183 |

^a All values are in au.

fragments and to investigate whether this approach can be used to discuss reordering of the electronic density due to the bonding process.

To relate the molecular chemical potential to those of the constituent atoms, Sanderson proposed the electronegativity equalization principle, which states that all the constituent atoms (or fragments) in a molecule have the same electronegativity value given by the geometric mean of the electronegativity of the pertinent isolated atoms (or fragments).⁴⁷ In terms of the chemical potential we have

$$\mu^\circ = - \left(\prod_x^{n_f} |\mu_x^\circ| \right)^{1/n_f} \quad (6)$$

where n_f is the number of nonbonded fragments used to form the whole molecule and μ_x° is the chemical potential of fragment x . In this paper $n_f = 2$ and the nonbonded fragments are the monomeric units that form the hydrogen-bonded complex, so μ° is expected to give an approximation to the chemical potential of the complex that is in turn determined using the supermolecule approach. We define the associated hardness differentiating μ° with respect to the total number of electrons N :

$$\eta^\circ = \left(\frac{d\mu^\circ}{dN} \right)_{v(\vec{r})} = \frac{\mu^\circ}{n_f} \sum_x \frac{\eta_x^\circ}{\mu_x^\circ} \quad (7)$$

with η_x° being the hardness of fragment x . This is in fact an extension of the Sanderson's principle to hardness.⁴⁸ The difference between these approximate values with respect to the actual values should be attributed to relaxation of the electron density after bonding, quantification of this difference may help understand the reordering of the electron density as the reaction takes place.

Characterization of Transition States of 2PT Reactions. We will rationalize a 2PT process as a chemical reaction of the type $\mathbf{R} \rightarrow (\mathbf{TS})^\ddagger \rightarrow \mathbf{P}$ where reactants (\mathbf{R}) transition states (\mathbf{TS}) and products (\mathbf{P}) are connected by an intrinsic internal reaction coordinate (IRC), through this defining the profiles of energy, chemical potential, hardness, and polarizability^{39,45} that allows one to characterize the properties of the transition state. To rationalize the energy of the TS we use the Marcus equation that was originally proposed to characterize electron-transfer processes and later on used for interpretation of different kinds of chemical reactions.^{36–39,50} Thus the energy barrier ΔE^\ddagger for a 2PT process is assumed to be given by

$$\Delta E^\ddagger = \frac{1}{4}K + \frac{1}{2}\Delta E^\circ + \frac{(\Delta E^\circ)^2}{4K} \quad (8)$$

with K being a parameter that is an intrinsic property of the reaction, $\Delta E^\circ \equiv [E(\mathbf{P}) - E(\mathbf{R})]$ is the energy difference between reactants and products; $\Delta E^\ddagger \equiv [E(\mathbf{TS}) - E(\mathbf{R})]$ is the barrier height measured from the reactants. From the knowledge of ΔE°

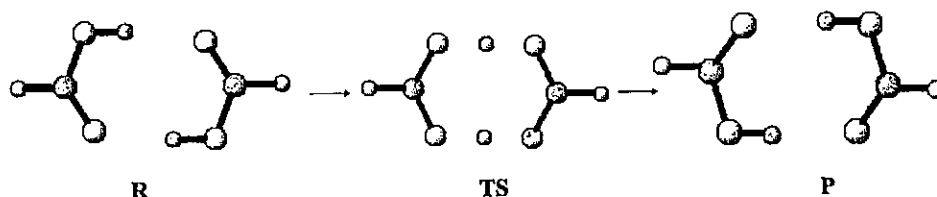


Figure 1. Schematic reaction diagram for double-proton transfer.

TABLE 2: Reference Energy (E) of the 10 Fully Optimized Bimolecular Complexes; Formation Energy (ΔE_{hb}), Chemical Potential, and Hardness from the RHF Calculation (μ, η) and from Sanderson's Rule (μ°, η°)^a

| complex | E | ΔE_{hb} | μ | μ° | η | η° |
|----------------------------|--------------|------------------------|---------|-------------|--------|--------------|
| HC(=O)-OH...HC(=O)-OH (1) | -377.664112 | -0.0231 | -0.1503 | -0.1554 | 0.3204 | 0.3138 |
| HC(=O)-OH...HC(=O)-SH (2) | -700.284742 | -0.0149 | -0.1402 | -0.1470 | 0.2609 | 0.2863 |
| HC(=O)-OH...HC(=S)-OH (3) | -700.283997 | -0.0181 | -0.1411 | -0.1476 | 0.2251 | 0.2652 |
| HC(=O)-OH...HC(=S)-SH (4) | -1022.917548 | -0.0104 | -0.1601 | -0.1543 | 0.2021 | 0.2563 |
| HC(=O)-SH...HC(=O)-SH (5) | -1022.907575 | -0.0089 | -0.1331 | -0.1391 | 0.2607 | 0.2608 |
| HC(=S)-OH...HC(=S)-OH (6) | -1022.902674 | -0.0119 | -0.1462 | -0.1402 | 0.2169 | 0.2206 |
| HC(=O)-SH...HC(=S)-OH (7) | -1022.906790 | -0.0121 | -0.1320 | -0.1397 | 0.2215 | 0.2408 |
| HC(=S)-SH...HC(=O)-SH (8) | -1345.542487 | -0.0065 | -0.1511 | -0.1460 | 0.2000 | 0.2319 |
| HC(=S)-SH...HC(=S)-OH (9) | -1345.538872 | -0.0069 | -0.1604 | -0.1466 | 0.1966 | 0.2108 |
| HC(=S)-SH...HC(=S)-SH (10) | -1668.176971 | -0.0037 | -0.1576 | -0.1532 | 0.1965 | 0.1996 |

^a All values are in au.

and ΔE^\ddagger we can obtain the parameter K that in turn we use to determine the position of the TS along the IRC. Indeed the position of the TS with respect to reactants and products is obtained through the Brønsted coefficient β that was originally defined by Leffler as⁵¹

$$\beta = \left(\frac{\partial \Delta E^\ddagger}{\partial \Delta E^\circ} \right) \Rightarrow \beta = \frac{1}{2} + \frac{\Delta E^\circ}{2K} \quad (9)$$

where β takes values between zero and one, being one-half in the case of isoenergetic reactions ($\Delta E^\circ = 0$). This equation is in fact a quantitative statement of the Hammond Postulate⁵² since if $\Delta E^\circ > 0$ (endothermic reaction) then $\beta > 1/2$ and the TS is closer to products, whereas if $\Delta E^\circ < 0$ (exothermic reaction) then $\beta < 1/2$ and the TS is closer to reactants. Note that to characterize the position of the TSs we do not need an explicit definition of the reaction coordinate, β being a relative index representing the degree of resemblance of the transition state with respect to the products.

Recently we have proposed the following expression for the energy barrier in terms of the electronic properties μ and η ³⁹

$$\Delta E^\ddagger = \frac{1}{2} Q_\eta \Delta \mu^\ddagger + \frac{1}{2} Q_\mu \Delta \eta^\ddagger \quad (10)$$

where $\Delta \mu^\ddagger \equiv [\mu(\text{TS}) - \mu(\text{R})]$ and $\Delta \eta^\ddagger \equiv [\eta(\text{TS}) - \eta(\text{R})]$ and Q_η, Q_μ are parameters that have been related to the amount of electronic charge transferred during the chemical reaction. These parameters can be determined numerically as³⁹

$$Q_\eta = \frac{(\Delta E^\ddagger - \Delta E^\circ)}{(\Delta \mu^\ddagger - \Delta \mu^\circ)} \quad (11)$$

and

$$Q_\mu = \frac{(\Delta E^\ddagger - \Delta E^\circ)}{(\Delta \eta^\ddagger - \Delta \eta^\circ)} \quad (12)$$

The validity of the principle of maximum hardness leads to opposite curvature for the energy and hardness; this leads to a negative Q_μ .^{38,39} It is important to mention that eq 10 is valid when $\Delta E^\circ = 0$ although it remains to a good approximation valid for $\Delta E^\circ \neq 0$ provided that the parameters Q_η and Q_μ be

well defined. Equation 10 is in fact a particular case of

$$E(\omega) = \frac{1}{2} Q_\eta \mu(\omega) + \frac{1}{2} Q_\mu \eta(\omega) \quad (13)$$

that for a reaction coordinate ω is a unique expression accounting for the μ and η dependence of E for isoenergetic reactions. In cases where it is not possible to define independently the parameters Q_μ and Q_η , we will use the approximation $Q_\mu = -Q_\eta^2$ that results as a consequence of the PMH and from the dimensional analysis of eq 10 in consistency with the Parr and Pearson's expression for the energy of an atom in a molecule with constant external potential.³⁰

3. Results and Discussion

Computational Details. All calculations were performed at the restricted Hartree-Fock (RHF) level of theory with the standard 6-31G** basis set using the Gaussian 94 package.⁵³ The profiles of E, μ, η , and α for double proton transfer in two reference systems, namely, formic acid and dithioformic acid dimers, were obtained through single points calculations of the fully optimized structures indicated by the IRC procedure. The electronic chemical potential and molecular hardness have been calculated by applying eqs 3 and 4, respectively.

Formation Reactions. Among the various bimolecular structures that are possible, we will review here only cyclic complexes where double proton transfer is possible as indicated in Figure 1. Pair combinations of monomeric units of formic (HCO-OH), dithioformic (HCS-SH), thiol-formic (HCO-SH), and thione-formic (HCS-OH) acids, leads to four dimers among the ten cyclic bimolecular complexes that will be studied here. In Table 1 we display reference values of energy, chemical potential, and hardness together with the polarizability of the different monomeric units. Formation of the complex from two isolated units involves a change in the total energy of the system together with the reordering of the electronic density favoring the stabilizing hydrogen bonds interactions. The effect of the bonding potential is apparent when comparing the change in energy, chemical potential and hardness. Table 2 displays the total energy for the hydrogen-bonded complexes together with their formation energy and electronic properties μ and η obtained from the ab initio calculations and from Sanderson's rule (eqs 6 and 7).

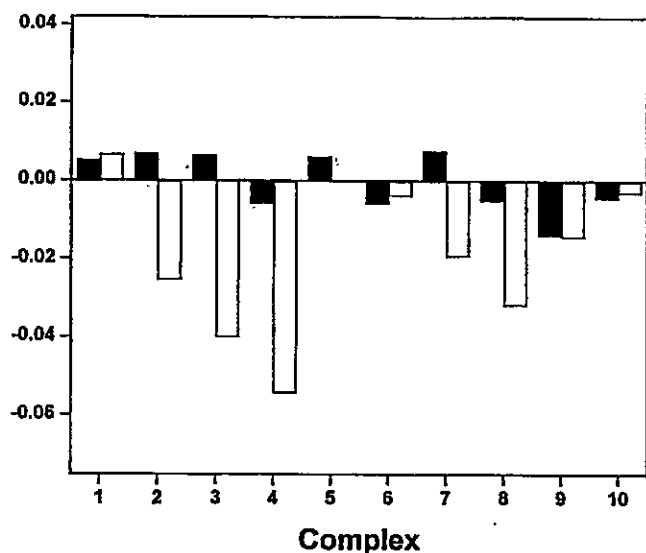


Figure 2. Deviation of the Sanderson's chemical potential (black bars) and hardness (white bars) with respect to the calculated ab initio supermolecule values of 10 bimolecular complexes labeled as in Table 2. All values are in au.

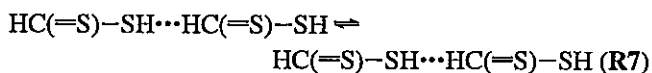
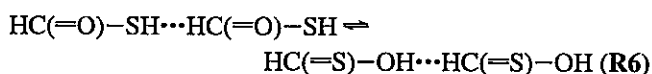
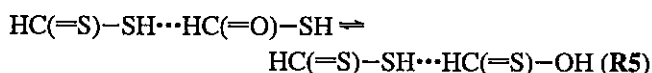
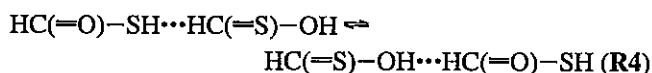
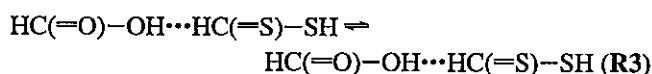
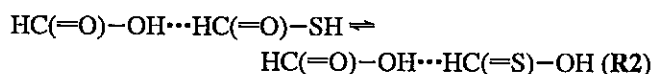
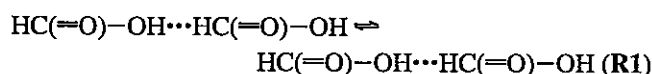
We first note that all ΔE_{hb} values fall within the energy interval defined by the dimerization energy of the reference dimers 1 and 10. In all cases formation of the bimolecular complex is a favorable process leading to complex species in which the strength of the hydrogen bonds can be qualitatively determined from the dimerization energies, the larger is the absolute value of ΔE_{hb} the stronger are the hydrogen bonds stabilizing the complex. It appears that the bond strengths are ordered as $O-H\cdots O > O-H\cdots S > S-H\cdots O > S-H\cdots S$. This observation will be discussed later in connection with the barriers for proton transfer. On the other hand, the values of μ° and η° are reasonably close to the corresponding calculated values with quite small deviations $\Delta\mu = (\mu - \mu^\circ)$ and $\Delta\eta = (\eta - \eta^\circ)$ as it is apparent in Figure 2. It is interesting to mention here that numerical values of hardness calculated from eq 7 compares satisfactorily with values determined from others treatments.^{54,55} For instance, we have estimated the hardness from the arithmetic average principle for softness [$S^\circ = (\sum_x S_x^\circ)/n$; $\eta^\circ = 1/S^\circ$]⁵⁴ and the geometric mean principle for the hardness [$\eta^\circ = (\prod_x \eta_x^\circ)^{1/n}$]⁵⁵ obtaining results that are very close to our η° displayed in Table 2, the maximum deviation detected was about 5%. Our results concerning this point indicate that there is no a dramatic reordering of the electronic density on complexation and that Sanderson's rule is adequate for predicting both μ and η of the composite system. Unfortunately we have found no evidence of direct correlation between ΔE_{hb} , which contains the relaxation energy when the dimer species is formed, and $\Delta\mu$ and $\Delta\eta$, which must include at least some extent of the effect of redistribution of the electronic density.

TABLE 3: Reaction Properties for Double Proton Transfer^a

| reactions | ΔE° | ΔE^\ddagger | K | β | $\Delta\mu^\circ$ | $\Delta\mu^\ddagger$ | $\Delta\eta^\circ$ | $\Delta\eta^\ddagger$ | $\Delta\alpha^\circ$ | $\Delta\alpha^\ddagger$ | Q_η | Q_μ |
|-----------|------------------|---------------------|----------|---------|-------------------|----------------------|--------------------|-----------------------|----------------------|-------------------------|----------|---------|
| R1 | 0.0 | 17.9311 | 71.7244 | 0.500 | 0.0 | -1.7633 | 0.0 | -6.1245 | 0.0 | 1.0890 | -10.1690 | -2.9278 |
| R2 | 0.4675 | 19.9937 | 79.0370 | 0.503 | -0.5397 | 13.3471 | -22.4460 | -16.5851 | 2.0937 | 4.0350 | -2.0064 | -4.0257 |
| R3 | 0.0 | 23.1733 | 92.6932 | 0.500 | 0.0 | 15.4995 | 0.0 | -4.1165 | 0.0 | 6.6230 | 1.4951 | -5.6294 |
| R4 | 0.0 | 25.6087 | 102.4348 | 0.500 | 0.0 | 0.8848 | 0.0 | -4.0725 | 0.0 | 9.1603 | 28.9429 | -6.2882 |
| R5 | 2.2685 | 29.0499 | 111.6165 | 0.510 | -5.8672 | 5.9613 | -2.1586 | -14.3700 | 2.1844 | 11.9334 | -2.2288 | -4.9677 |
| R6 | 3.0754 | 30.4612 | 115.6122 | 0.513 | -8.2329 | -9.2056 | -27.5288 | -15.2422 | 4.2687 | 6.6884 | -1.7199 | -2.9582 |
| R7 | 0.0 | 37.3895 | 149.5580 | 0.500 | 0.0 | -1.9327 | 0.0 | -7.7497 | 0.0 | 17.6313 | -19.3457 | -4.8246 |

^a E , μ , and η are in kcal/mol; α is in au.

2PT Reactions. From the monomeric units it is possible to generate ten bimolecular hydrogen bonded structures, among them there are seven nonredundant double proton-transfer reactions:



In Table 3 we display various TS properties of the seven 2PT reactions. We first note that most reactions are isoenergetic and thus $\Delta E^\circ = 0$. There are only three endoenergetic reactions **R2**, **R5**, and **R6** as indicated in the table. The barrier for proton transfer appear to be ordered increasingly from reaction **R1** to reaction **R7**; it is interesting to note that ΔE^\ddagger exhibits a nice proportionality with the total number of electrons of the bimolecular complex (N), as shown in Figure 3a. Note that since there are three complexes with $N = 64$ in Figure 3a we display the corresponding average value of ΔE^\ddagger .

Using the optimized values of ΔE^\ddagger and ΔE° in eq 8 we have determined the K parameters that are quoted in Table 3 with the result that they are ordered as the energy barriers. Now we use eq 9 to determine the Brønsted coefficient that, as already mentioned, indicates the position of the TS along the reaction coordinate relative to reactants and products. The results of $\beta = 0.50$ or $\beta > 0.50$ show that the TS are either at midway between **R** and **P** if the reaction is isoenergetic or closer to the products if the reaction is of the endoenergetic type; this is in agreement with the Hammond postulate⁵² and validates the use of eq 8 in the characterization of transition states.

Also quoted in Table 3 are values of chemical potential, hardness and polarizability. Note that all values are defined with respect to the reactants. For endoenergetic reactions we find that $\Delta\mu^\circ < 0$ indicating that electronic charge flows in the direction **R** \rightarrow **P**, opposite of the direction of the proton transfer. On the other hand, relatively high values of $\Delta\mu^\ddagger$ show that the chemical potential is far from being constant, this fact is

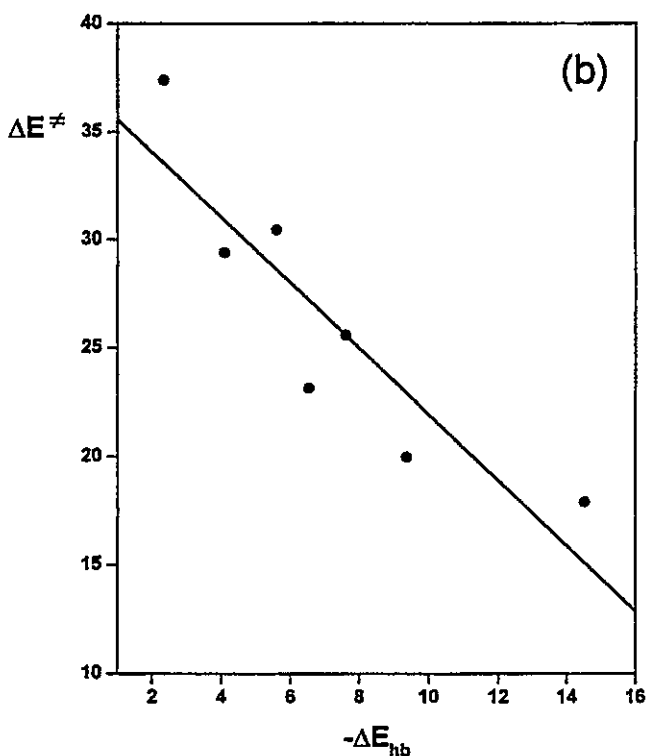
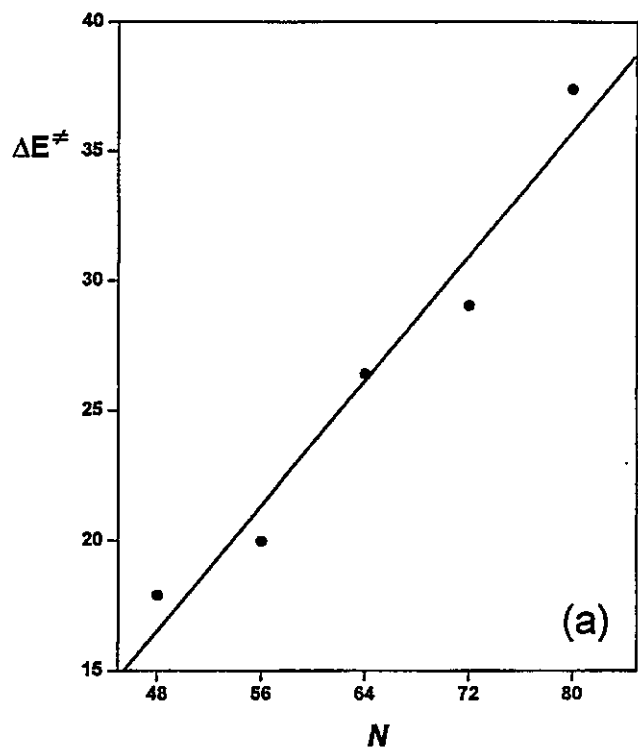


Figure 3. Correlation between the barrier to proton transfer (in kcal/mol) with: (a) the total number of electrons of the complex and (b) the formation energy (in kcal/mol).

important when discussing the principle of maximum hardness. In all cases with $\Delta E^\circ > 0$ we see that $\Delta\eta^\circ < 0$ showing that reactants are harder than the products, the hardest species corresponds to the most stable one, as expected from the PMH. Also $\Delta\eta^\ddagger < 0$ is indicating that the TS is the softest species along the reaction coordinate. These results show that a maximum in energy corresponds to a minimum value of hardness, confirming the validity of the PMH in double-proton transfer reactions. This is new evidence that the PMH holds

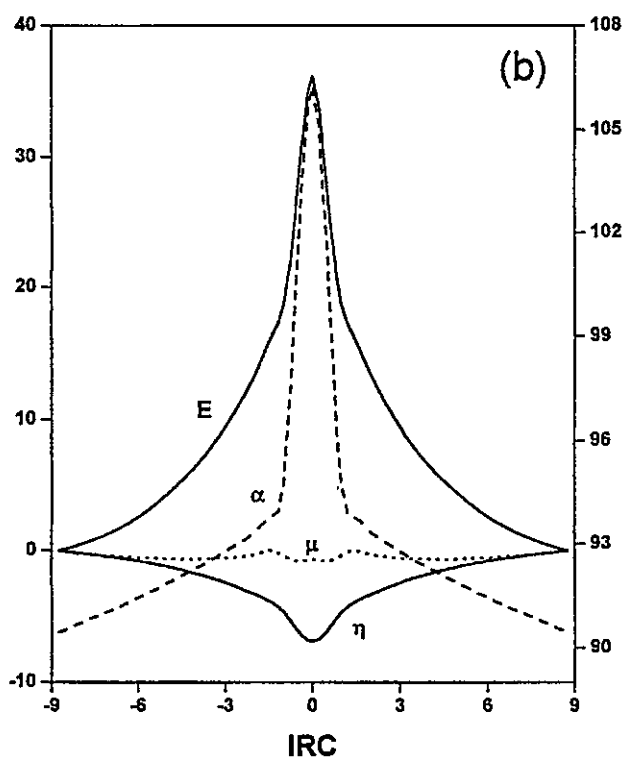
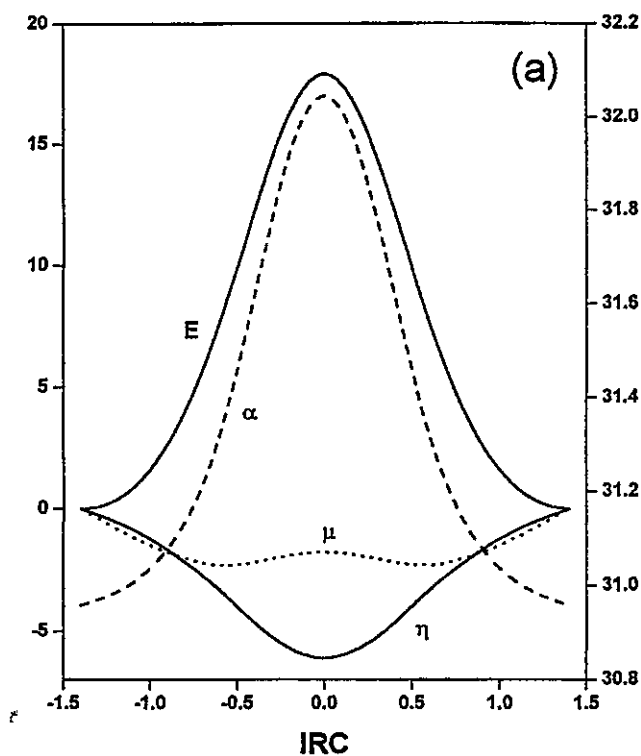


Figure 4. Energy, chemical potential, hardness and polarizability profiles along the IRC for the double-proton transfer of (a) formic acid dimer and (b) dithioformic acid dimer. E , μ , and η are in kcal/mol. The right axis bears the polarizability values in au.

even though the chemical potential is not constant along the IRC, a condition originally imposed to prove this principle.^{32,40-42}

Within the frame of DFT, a complete characterization of an N -particle wave function needs only N and the external potential $v(\vec{r})$. The response of the system to any external perturbation is measured by μ and η when N is varied for a fixed $v(\vec{r})$ as indicated by eqs 1 and 2. Complementary to this, the polarizability may be used in understanding the behavior of the system

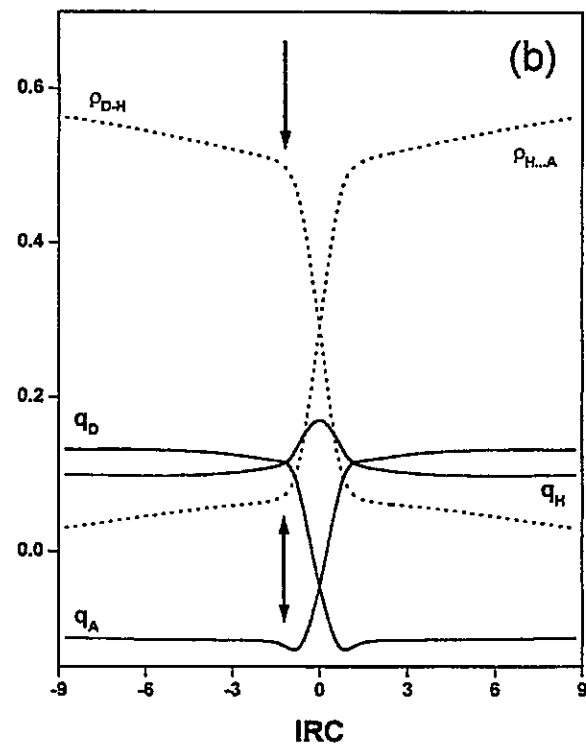
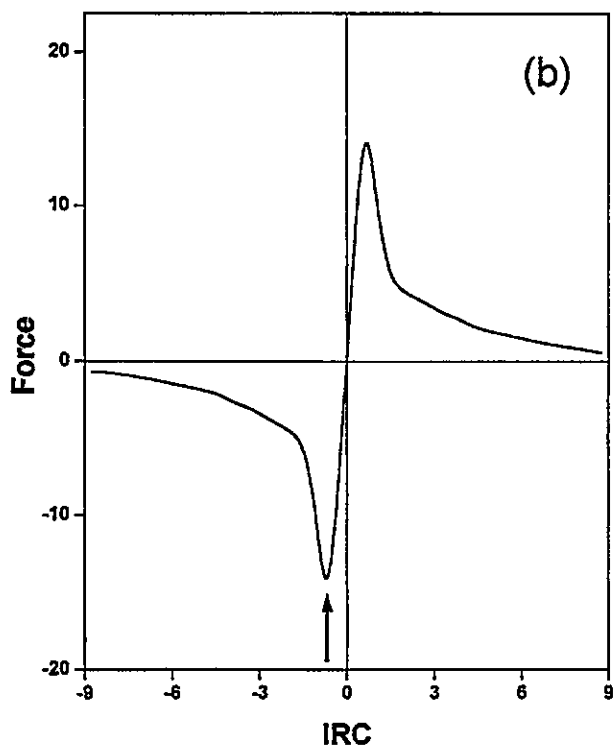
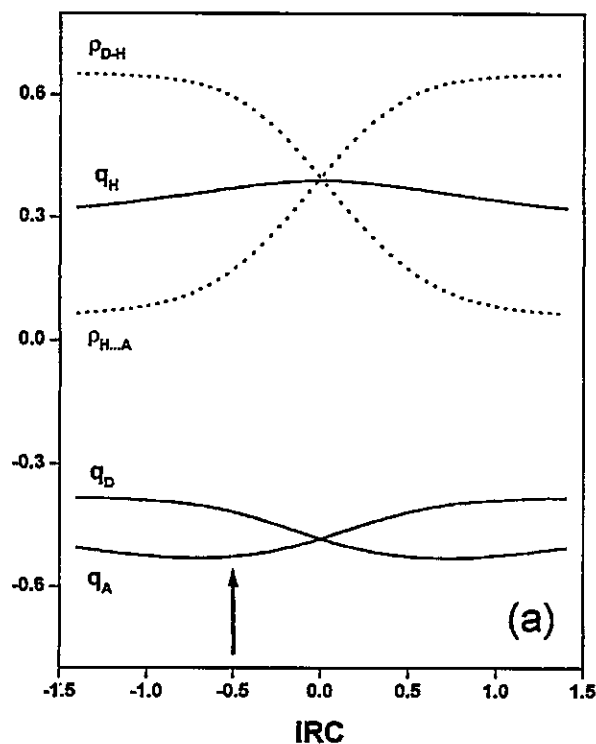
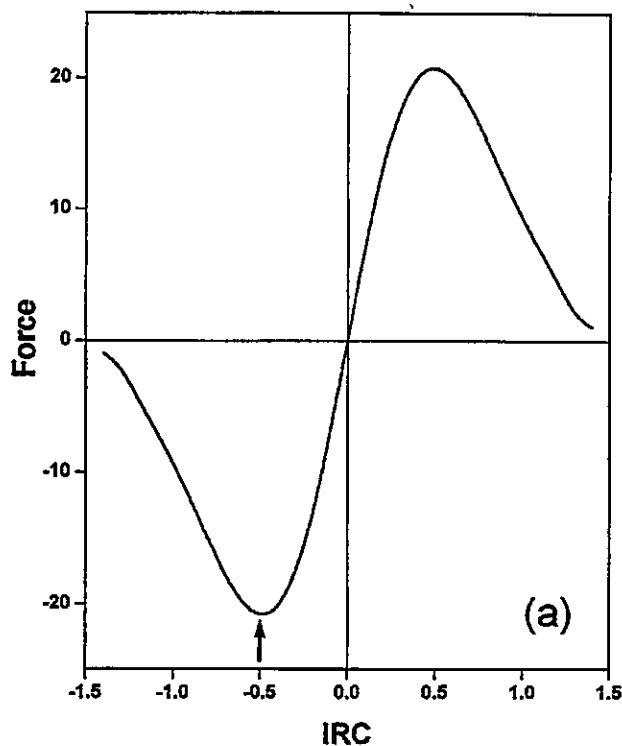


Figure 5. Profiles of the force along the IRC for (a) formic acid dimer and (b) dithioformic acid dimer. The arrows indicate the position ω_0 (see the text for details).

for changing $\nu(\vec{r})$ at constant N . Our results for α show that in all cases the transition state is more polarizable than the reactants showing that the minimum polarizability principle (MPP) is also satisfied in these reactions. Furthermore in all three endoenergetic reactions $\Delta\alpha^\circ > 0$ confirming that the direction of evolution of these systems is toward the state of minimum energy and polarizability, as required by the MPP.⁴⁵

We have defined the transition state in terms of its energy, chemical potential, and hardness, all related by eq 10 through

Figure 6. Profiles along the IRC of specific electronic populations of (a) formic acid dimer and (b) dithioformic acid dimer. ρ_{D-H} and $\rho_{H...A}$ states the population associated with the hydrogen donor (D) and acceptor (A) regions. The arrows indicate the position ω_0 (see the text).

the parameters Q_η and Q_μ that are determined from eqs 11 and 12 and displayed in Table 3. For the endoenergetic reactions (reactions **R2**, **R5**, and **R6**) the use of eqs 11 and 12 leads to results that violate the condition that Q_μ should be negative to comply with the PMH. So in these three reactions we have assumed that $Q_\mu = -Q_\eta^2$ as suggested from the exact definitions of μ and η and the dimensional analysis of eq 10 in consistency with the Parr and Pearson expression for the energy

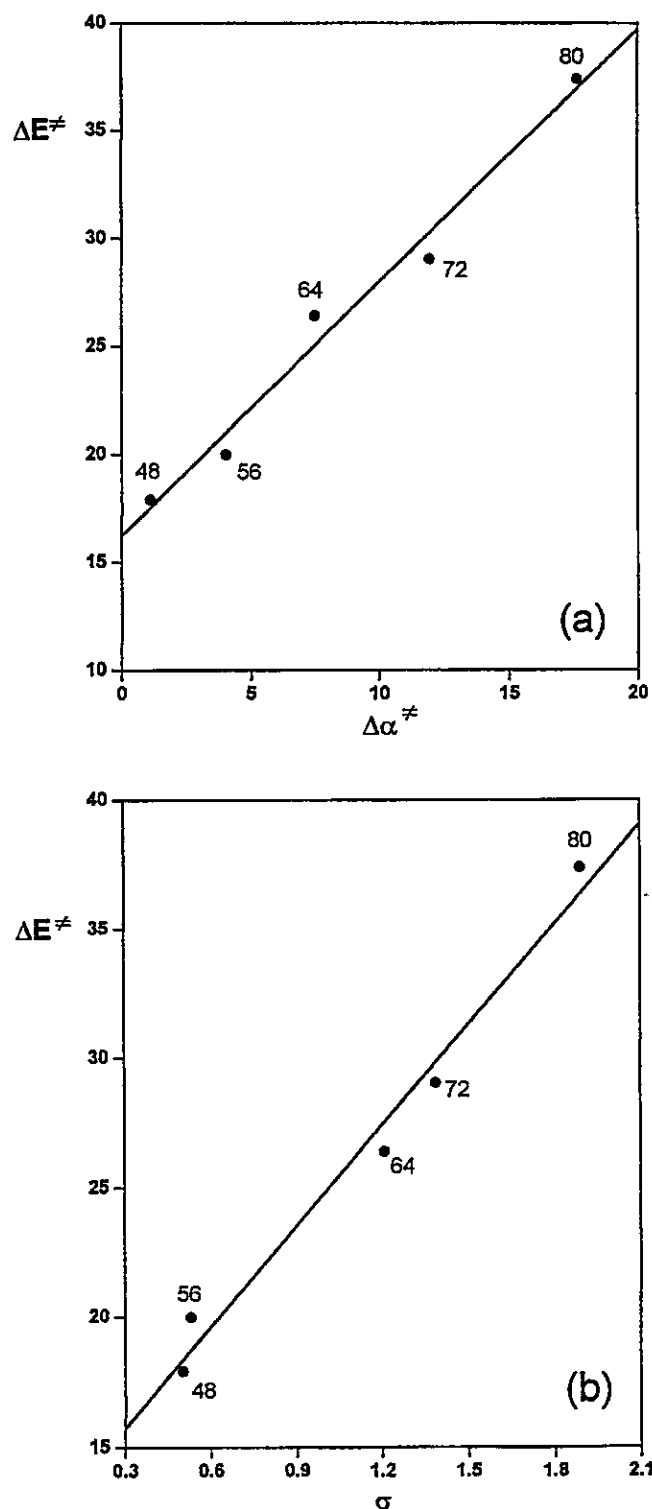


Figure 7. Correlation between the 2PT barrier (in kcal/mol) with: (a) the activation polarizability (in au) and (b) the HSAB parameter σ for the different complexes identified by their total number of electrons.

of an atom in a molecule.³⁰ The resulting set of parameters that connect the properties of transition states are also included in Table 3. It is important to mention that eq 10 has been used to rationalize the activation energy of different kind of processes,^{38,56} for example, for internal rotation and inversion reactions we have reported values of Q_μ going from -0.90 to -0.30 .^{38,56} In electrophilic aromatic substitutions processes, Zhou and Parr⁵⁷ have found proportionality between ΔE^\ddagger and $\Delta\eta^\ddagger$; their proportionality parameter was equal to -2 , a value within the order of Q_μ 's quoted in Table 3.

Relation Between Formation and 2PT Processes. We are dealing here with two different processes that take place sequentially; formation of the hydrogen-bonded cyclic complex followed by double-proton transfer. Although these processes seems to be independent to each other, we have found a fairly good linear correlation between the values of ΔE^\ddagger and ΔE_{hb} , as shown in Figure 3b. Large barriers to proton transfer are associated with a small complexation energy, so the stronger is the hydrogen bond, the lower is the barrier to proton transfer indicating that enhanced binding may occur when the protons gets dynamically delocalized. On the other hand, it is interesting to mention that the constant factor of the approximate linear equation relating ΔE^\ddagger and ΔE_{hb} is 37.072 kcal/mol which is very close to the 2PT barrier of the dithioformic acid dimer (37.390 kcal/mol). This result suggests that within an acceptable error marge all barriers of this series of bimolecular complexes can be written in terms of this reference value.

2PT Reaction Mechanism. In the case of the dimers formed by formic and dithioformic acids we have performed single-point calculations along the reaction coordinate to obtain the profiles of energy, chemical potential, hardness, and polarizability displayed in Figure 4. We first note in both reactions μ presents intermediate values between E and η . As can be seen, the profiles of μ decreases to reach a quite flat region around the TS, where three critical points can be perceived. The peculiar behavior of μ might be confirming the mechanism proposed in which the proton transfer is initiated by the displacement of the whole monomeric structures to favor the subsequent proton transfer. The profiles of η and α indicate the simultaneous validity of the principles of maximum hardness and minimum polarizability. We see that the hardness profiles present opposite behavior with respect to the energy whereas the polarizability profiles show maximum values at the TS's. Transition state structures are therefore characterized through a maximum value of energy and polarizability and a minimum value of hardness, as required by the PMH and MPP.

The concept of reaction mechanism is related to the notion of molecular structure in that any reactive process can be represented by nuclear displacements of the molecular system in going from the reactants to the products. These displacements are related with the forces acting on the system to bring reactants into products: this force depends only on the position along the reaction coordinate and from eq 13; it is given by³⁹

$$F(\omega) = -\frac{dE}{d\omega} = -\frac{1}{2}Q_\eta\frac{d\mu}{d\omega} - \frac{1}{2}Q_\mu\frac{d\eta}{d\omega} \quad (14)$$

expression that will be used only for qualitative purposes. In Figure 5 we display the force profiles determined by numeric differentiation of the energy profiles given in Figure 4. Note that $F(\omega)$ is negative in the reactants region and it is positive in the products region, allowing us to distinguish the different processes taking place along the reaction coordinate. Within the reactants region an activation process is taking place to attain the TS whereas in the product region we have a relaxation process from the TS. Now we use eq 14 for a qualitative rationalization of this observation: it indicates that activation processes are driven by the chemical potential term [$F(\omega) < 0 \Rightarrow Q_\eta d\mu/d\omega > |Q_\mu| d\eta/d\omega$], whereas the relaxation process is driven by the hardness term [$F(\omega) > 0 \Rightarrow Q_\eta d\mu/d\omega < |Q_\mu| d\eta/d\omega$].³⁹

The profiles of the force present a minimum and a maximum around the TS, and this may be defining a region where the specific interactions and intermolecular reordering is of different nature than those encountered at the vicinity of reactants and

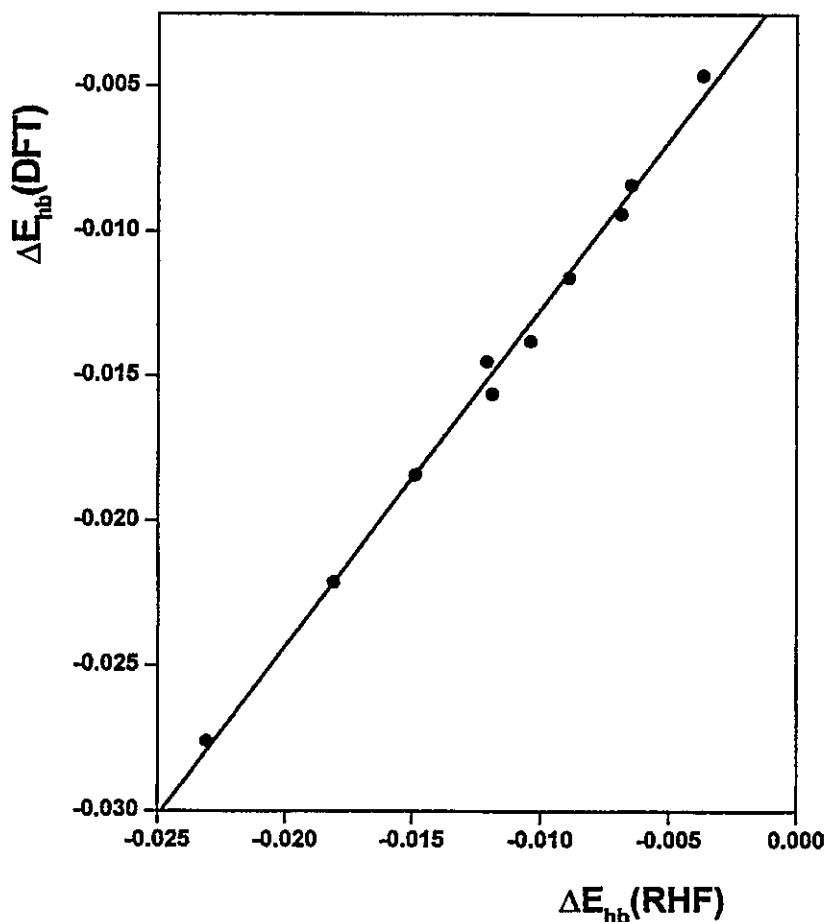


Figure 8. Comparison of DFT and RHF formation energy for the series of 10 bimolecular hydrogen-bonded complexes. All values are in au.

products, as already suggested from the peculiar profiles of the chemical potential (μ has at least three critical point at the vicinity of the TS). The results for F and μ suggest that the first step of the reaction requires an amount of work (W_1) necessary to bring the monomeric units closer to each other that is larger than the work (W_2) required for the hydrogenic motion. The associated works are qualitatively defined as $W_1 = \int_{-\infty}^{\omega_0} F(\omega) d\omega$ and $W_2 = \int_{\omega_0}^0 F(\omega) d\omega$, with ω_0 the position of the minimum of $F(\omega)$, as indicated by the arrows in Figure 5 where it is apparent that $W_1 > W_2$ indicating that the overall reaction is determined by the first step, i.e., the motion of monomeric units to get closer to each other in order to allow the proton transfer.

Nature of 2PT Potential Barriers. To get more insight on the reaction mechanisms and the nature of potential barriers, a quantitative characterization of the electronic population in bond regions and atomic (or fragments) centers along the reaction coordinate is necessary. The Mulliken population in relevant bond regions and atomic centers along the IRC are displayed in Figure 6. The evolution of the electronic populations in bond ($\rho_{\text{X-H}}$) and hydrogen bond ($\rho_{\text{X}\cdots\text{H}}$) topological regions follow opposite trends; when a proton is transferred, $\rho_{\text{X-H}}$ decreases whereas $\rho_{\text{X}\cdots\text{H}}$ increases, indicating that there is a charge transfer in the opposite direction to the proton motion. It is interesting to note that the most noticeable changes in these populations occurs after the point ω_0 (indicated by the arrows on the figures), in the region where the process is mainly proton transfer. On the other hand, in formic acid dimer the proton charge increases slightly even at the TS as shown in Figure 6a, whereas in the dithioformic dimer this quantity is quite constant but from ω_0 it suddenly increases to attain a maximum at the TS (Figure

6b). The atomic population in proton donor (X-H) and proton acceptor (=X) atoms in formic acid dimer are quite close to each other favoring delocalization of the protons among the oxygens. In the case of $(\text{HCSSH})_2$ the situation is opposite, here the difference of electronic population of donor and acceptor atoms is much more marked indicating that electrostatic and polarization interactions may be playing an important role in stabilizing the complex.

The above results suggest that the barrier for proton transfer in the formic acid dimer is roughly of *through bond* nature whereas that of dithioformic acid dimer is basically due electrostatic interactions, a *through space* barrier. Qualitatively, *through bond* interactions occur among partners that present similar local electronic population whereas *through space* interactions occurs among partners presenting quite different local electronic populations, and this is the reason this later interaction is commonly associated to non-bonded interactions. Recently we have shown that the analysis of the electronic populations and dipole moments helps characterize the nature of potential barriers.⁵⁶ In the present case however this is not possible because formic acid and dithioformic acid dimers have inversion centers and therefore their dipole moments are equal to zero all along the IRC. In the absence of permanent dipole moments we can use the polarizability to perform the qualitative analysis we require. The polarizability of a molecule is proportional to its size or to its number of electrons; Table 3 indicates that this proportionality also holds for the difference $\Delta\alpha^\ddagger$ (but not for $\Delta\alpha^0$). On the other hand, Figure 3a indicates that ΔE^\ddagger is proportional to N , so we expect it to be also proportional to $\Delta\alpha^\ddagger$. Figure 7a shows a good linear correlation between ΔE^\ddagger and $\Delta\alpha^\ddagger$ for the complexes identified by their total

number of electrons (for $N = 64$ we have used the average values of the properties of reactions R3, R4, and R6). We see that high barriers are associated to high values of $\Delta\alpha^\ddagger$ indicating that they are mostly of *through space* nature whereas low barriers are associated to low $\Delta\alpha^\ddagger$ values indicating that their nature is mostly of the *through bond* type.

Through bond interactions can be explained by means of the local version of the well-known Pearson's hard-soft acid-base (HSAB) principle.⁵⁸ The local HSAB principle, invoked to explain soft-soft interactions,⁵⁹⁻⁶¹ states that the interaction between two species occurs through atoms having nearly equal softness. The local HSAB principle provide an independent criterium in terms of specific interactions proton acceptor to characterize the nature of potential barriers. Gazquez and Mendez⁵⁹ have defined a quantity which provides the information we need:

$$\sigma = (S_{\text{HI}}^{\circ} - S_{\text{A1}}^{\circ})^2 + (S_{\text{H2}}^{\circ} - S_{\text{A2}}^{\circ})^2 \quad (15)$$

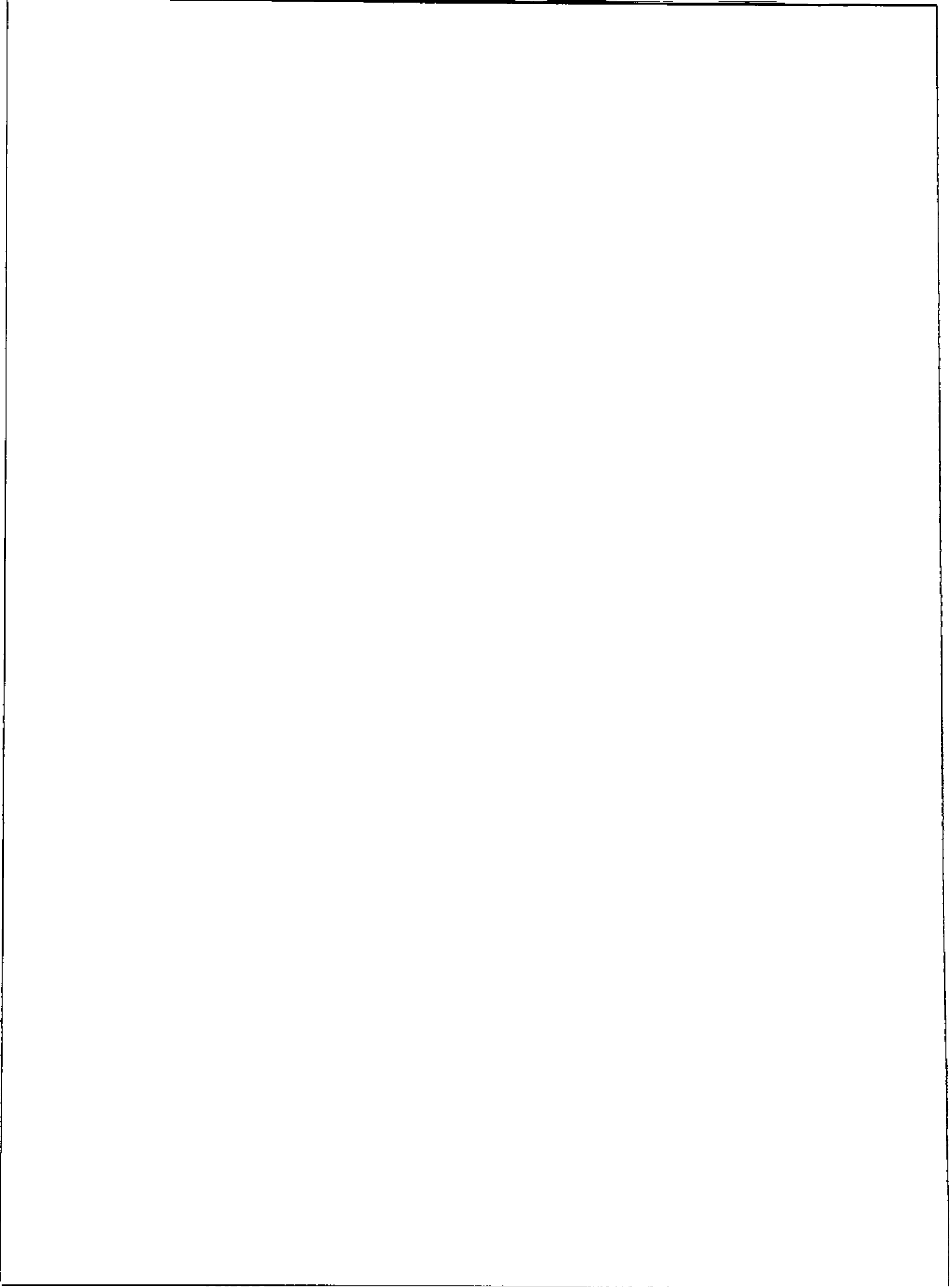
where S_X° is the local softness of the atom X [hydrogen (H) or the corresponding acceptor (A)] defined from the global softness as $S_X^{\circ} = \rho_X S/N$. If the specific interactions can be explained in terms of the local HSAB principle, then σ should be small because the softness of the interacting partners are expected to be close to each other (the *soft likes soft* part of the HSAB). So large values of σ indicate that the interaction is more of the *through space* type. In Figure 7b we display a nice correlation between the 2PT barrier and the σ parameter. The result shows that the barrier for formic acid dimer can be explained in terms of the HSAB principle (small σ) confirming its *through bond* nature. Dithioformic acid dimer is the opposite, it present a relatively large value of σ confirming that its 2PT barrier is mainly of *through space* nature. It should be possible to classify the physical origin of the barriers for proton transfer of the five remaining systems as weighted averages of these two extrema.

DFT Calculations. Finally, with the purpose to validate our results we have performed DFT/B3LYP⁶² calculations using the RHF optimized molecular structures to determine formation energies. The results reproduce the same trends of the Hartree-Fock calculations as illustrated in Figure 8 that shows a beautiful linear correspondence between the DFT and RHF results.

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Using Sanderson's Principle to Estimate Global Electronic Properties and Bond Energies of Hydrogen-Bonded Complexes

Soledad Gutiérrez-Oliva, Pablo Jaque, and Alejandro Toro-Labbé*

Departamento de Química Física, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Correo 22, Santiago, Chile

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In this paper, we use Sanderson's geometric mean equalization principle for electronegativity (χ) to derive expressions for molecular hardness (η) and its derivative (γ) that are used to estimate the electronic properties of 14 molecules and bimolecular hydrogen-bonded complexes. Beyond the determination of electronic properties, it is shown that Sanderson's scheme can be very useful as a method for rationalizing chemical reactions when both N and ν change. We have found that the conditions of maximum hardness and minimum polarizability complement the minimum energy criterion for stability of molecular aggregates. Finally, we propose a new scheme for obtaining molecular properties from the isolated fragments that produces results that are in excellent agreement with those determined through Sanderson's scheme.

1. Introduction

A formation reaction results from the combination of constituent fragments. The resulting system, a molecule or an aggregate, presents properties that, in many cases, can be rationalized in terms of the properties of the isolated constituent fragments. The main problem that arises when using this approximation to estimate molecular properties is that the bonding potential and redistribution of the electron density among the fragments are not considered, and structural relaxation due to new specific through-bond and through-space interactions is not allowed within this scheme. In fact, the approach of using the properties of rigid isolated fragments to estimate the corresponding properties of a system made up of these fragments entails errors such as the completeness of the basis sets and the mixing of electronic states. The effects of such errors are not considered at all in fragment addition schemes, and therefore, the quantities determined in this way are not expected to be very accurate. However, the use of addition rules to estimate global properties of composite systems is attractive mainly because they may be useful in predicting qualitative features. In this paper, we investigate whether one can safely estimate global molecular properties from the corresponding values associated with the constituent fragments through the application of Sanderson's principle of electronegativity equalization.^{1–3} Also, we explore how these electronic properties can be related to bond energies involved in molecule and aggregate formation processes.

Within the frame of density functional theory (DFT),^{4–6} a complete characterization of an N -particle wave function requires knowledge of only N and the external potential $\nu(\vec{r})$. The response of the system to any external perturbation is measured by the electronic chemical potential (μ) and the hardness (η) when N is varied for a fixed $\nu(\vec{r})$. Complementary to this, the polarizability (α) can be used in understanding the behavior of the system for changing $\nu(\vec{r})$ at constant N .⁷ In DFT,

μ is the Lagrange multiplier associated with the normalization constraint that the electron density integrates to N ; the association with classical structural chemistry is achieved by the identification of μ as the negative of the electronegativity (χ). Definitions of χ (or μ) and η were given by Parr et al.⁸ and Parr and Pearson,⁹ respectively. Chemical potential (electronegativity) and hardness are global electronic properties that are implicated in the reactivity of molecular systems, and they are well-established quantities that have evoked considerable research activity in the last years.^{10–14}

The product of a chemical reaction can be seen as resulting from the combination and redistribution of atom's or fragment's electron densities, giving rise to a new electronic distribution from which the electronic properties of the new molecule or aggregate are derived. It is well-known by now that molecular electron densities exhibit local topological features that makes it possible to recognize atomic or fragment shapes within the molecule.^{15–17} In this context, it is important to characterize the effect of combination and redistribution of electron densities on global electronic properties that have been defined as the response of the system to external perturbations.

To relate the molecular electronegativity to those of the constituent atoms or fragments, Sanderson proposed a geometric mean equalization principle, that defines the molecular electronegativity as the geometric mean of the electronegativities of the constituent atoms or fragments.^{1–3} In recent papers, we have extended this approach to estimate molecular hardness from the corresponding property of the constituent atoms or fragments.^{18,19} In this paper, we go further by estimating for the first time numerical values of γ [$\gamma \equiv (\partial\eta/\partial N)_\nu$] in molecules, obtaining expressions for η and γ from the geometric mean of χ (or μ), and then investigating how these properties, together with the polarizability α , might be related to the energy of conventional and hydrogen bonds.

This study concerns the formation of four molecules of the type H X –YH from radicals HCO, HCS, OH, and SH and 10 cyclic hydrogen-bonded bimolecular complexes of the type H CX –YH...H CY –XH formed by combinations of the H CX –

* Author to whom correspondence should be addressed. E-mail: atola@puc.cl.

YH species (X, Y = O, S). Our main goal in this paper is to discuss the validity of Sanderson's addition scheme and to investigate whether this approach can be used to discuss reordering of electronic density due to the bonding process.

2. Theoretical Background

Within the framework of DFT, the chemical potential and hardness for an N -particle system with total energy E and external potential $v(\vec{r})$ are defined as follows:⁴⁻⁶

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{v(\vec{r})} = -\chi \quad (1)$$

and

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial^2 N} \right)_{v(\vec{r})} = \frac{1}{2} \left(\frac{\partial \mu}{\partial N} \right)_{v(\vec{r})} \quad (2)$$

In numerical applications, μ and η are calculated through the following approximate versions of eqs 1 and 2, based upon the finite-difference approximation and Koopman's theorem:⁵

$$\mu \approx -\frac{1}{2}(I + A) \approx \frac{1}{2}(\epsilon_L + \epsilon_H) \quad (3)$$

and

$$\eta \approx \frac{1}{2}(I - A) \approx \frac{1}{2}(\epsilon_L - \epsilon_H) \quad (4)$$

where I is the ionization potential, A is the electron affinity, and ϵ_H and ϵ_L are the energies of the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO), respectively. In this paper, μ and η will be calculated using the MO energies.

The energy involved in forming a molecule or aggregate from n_f non-bonded constituent fragments is given by

$$\Delta E_{n_f} = E - E_{n_f}^0 \quad (5)$$

where E is the energy of the fully optimized resulting molecule or aggregate and $E_{n_f}^0 = \sum_x^{n_f} E_x$, with E_x the energy of the fragment x duly optimized. Note that, in our applications, the energy of the bimolecular complexes can be estimated from the energy of two (E_2^0) and four (E_4^0) fragments. It is important to point out here that both basis set superposition and the mixing of electronic states are source of errors in the estimation of ΔE_{n_f} ; however, attempts to evaluate them are beyond the scope of this paper.

Sanderson's equalization principle states that the electronegativity of a molecule is given by the geometric mean of the electronegativities of the isolated atoms (or fragments)¹⁻³

$$\mu_{n_f}^0 = - \left(\prod_x^{n_f} |\mu_x^0| \right)^{1/n_f} \quad (6)$$

where μ_x^0 is the chemical potential of fragment x . Note that the larger the value of n_f , the less accurate the result because of the number of bonds and bonding potentials not being considered in the calculations of $\mu_{n_f}^0$.

Within this scheme, the hardness is obtained by differentiating $\mu_{n_f}^0$ with respect to N ,^{18,19} thus obtaining

$$\eta_{n_f}^0 = \left(\frac{\partial \mu_{n_f}^0}{\partial N} \right)_{v(\vec{r})} = \frac{\mu_{n_f}^0}{n_f} \sum_x \frac{\eta_x^0}{\mu_x^0} \quad (7)$$

η_x^0 is the hardness of fragment x . The difference between the approximate values ($\mu_{n_f}^0$ and $\eta_{n_f}^0$) and the actual values obtained using eqs 3 and 4 from the ab initio calculations (μ and η) can be attributed to relaxation of the electron density after bonding. Quantification of this difference may help in developing an understanding of the reordering of the electron density as the reaction takes place.

The derivative of the hardness with respect to N at constant external potential was defined previously as the third-order property γ ; it was numerically studied only in atoms and atomic ions with the result that, in most cases, it is smaller than μ and η .²⁰ Within the Sanderson scheme, we obtain from eq 7

$$\gamma_{n_f}^0 = \left(\frac{\partial \eta_{n_f}^0}{\partial N} \right)_{v(\vec{r})} = \frac{(\eta_{n_f}^0)^2}{\mu_{n_f}^0} - \frac{\mu_{n_f}^0}{n_f} \sum_x \left(\frac{\eta_x^0}{\mu_x^0} \right)^2 + \frac{\mu_{n_f}^0}{n_f} \sum_x \frac{\gamma_x^0}{\mu_x^0} \quad (8)$$

This provides an analytic expression to estimate γ from atomic (or fragment) chemical potentials and hardnesses. Notice that $\eta_{n_f}^0$ and $\gamma_{n_f}^0$ have been defined by dropping, from the original definitions, the numerical factors $1/2$ and $1/3$, respectively.

3. Computational Methods

Although restricted Hartree-Fock (RHF) calculations are not expected to give accurate hydrogen-bond energies, it has been recently shown that they are highly consistent with DFT/B3LYP results.¹⁹ Therefore, all calculations were performed at the RHF level of theory with the standard 6-311G** basis set using the Gaussian 94 package.²¹ Radical fragments were calculated using the UHF theory. The electronic chemical potential and molecular hardness have been calculated by applying eqs 3 and 4, respectively, with ϵ_H and ϵ_L obtained from the RHF/UHF calculations of the fully optimized species.

In Table 1, we display reference values of energy, chemical potential, and hardness of the initial isolated radical species HCO and XH (X = O, S). Formation of molecules HCO-OH (M1), HCS-OH (M2), HCO-SH (M3), and HCS-SH (M4) from the two constituent radicals involves a change in energy and electronic properties mainly due to formation of a covalent C-X bond (X = O, S). Thus, in comparing $\mu_{n_f}^0$ and $\eta_{n_f}^0$ with respect to the actual values of μ and η determined from ab initio calculations on the fully optimized molecule, we will obtain, as a qualitative result, the effect of the bonding potential on these specific electronic properties.

Among many possible bimolecular structures, we will review here only cyclic complexes that are stabilized by two hydrogen bonds.¹⁹ Combinations of monomeric units of formic (HCO-OH), thione-formic (HCS-OH), thiol-formic (HCO-SH), and dithioformic (HCS-SH) acids leads to 10 cyclic bimolecular complexes, C1-C10 (see Table 2). To build them, two approaches have been considered: (a) formation from two neutral molecules ($n_f = 2$) where the ab initio optimized values of E , μ , and η of each HCO-XH (X, Y = O, S) species are used to produce E_2^0 , μ_2^0 , and η_2^0 (note that these quantities do not contain the hydrogen-bonds potentials); and (b) formation from four isolated radical fragments ($n_f = 4$). The latter approach leads to E_4^0 , μ_4^0 , and η_4^0 values in which the effect of two covalent and two hydrogen-bond potentials are not included. In Table 2, we define the species under study and quote the values of $E_{n_f}^0$, together with the reaction energies ΔE_2 and ΔE_4 ,

TABLE 1: Energy, Chemical Potential, and Hardness for the Fully Optimized Radical Structures Determined at the Ab Initio UHF/6-311G Level^a**

| fragment | E | μ | η |
|----------|-----------|---------|--------|
| CHO | -113.2802 | -0.1327 | 0.2450 |
| OH | -75.4107 | -0.1906 | 0.3153 |
| CHS | -435.9153 | -0.1492 | 0.1852 |
| SH | -398.0929 | -0.1907 | 0.1864 |

^a All values are in atomic units.

which should be proportional to the bond energies involved in forming the molecules and aggregates.

4. Results and Discussion

Estimating C–X Bond Energies. We note in Table 2 that all ΔE_{n_f} values are negative, indicating that formation of molecules (M1–M4) and bimolecular complexes (C1–C10) are favorable processes. Note that, in formation reactions, $E_{n_f}^o$ and E are the total energies of reactants and products, respectively. For our purposes, the most relevant feature appearing in the formation energy of M1 and M2 is that their ΔE_2 values can be identified with the energy of a single C–O bond, the average value determined from Table 2 being $\langle \Delta E_2 \rangle_{CO} \approx 0.12$ au. Note that the average value of the experimental C–O bond energy has been estimated to be 0.13 au,²² in reasonable agreement with our estimate. In the formation of M3 and M4, $-\Delta E_2$ is mainly attributed to formation of a single C–S bond, for which the average experimental bond energy is 0.10 au;²² our estimation is $\langle \Delta E_2 \rangle_{CS} \approx 0.08$ au. Although the numerical values may differ to some extent, our results show that the C–O bond is correctly estimated as being stronger than the C–S bond by about 0.04 au, in qualitative agreement with the experimental data.²²

When the complexes are formed from four isolated fragments ($n_f = 4$), the reaction energies can be related to the energies of the bonds being formed. Table 2 shows that, in C1, C2, and C3, the ΔE_4 values goes from -0.28 au (C1) up to -0.25 au (C3); these values correspond to the approximate contribution of the two C–O bonds being formed ($\Delta E_4 \approx 2\langle \Delta E_2 \rangle_{CO}$). In C4–C7, we find that the average value of ΔE_4 is 0.21 au, with quite a small dispersion. This can be associated with the energetic contribution due to formation of one C–O and one C–S bond ($\Delta E_4 \approx \langle \Delta E_2 \rangle_{CO} + \langle \Delta E_2 \rangle_{CS}$). In C8–C10, we find that $\Delta E_4 \approx -0.16$ au, which is the energetic contribution due to formation of two C–S bonds ($\Delta E_4 \approx 2\langle \Delta E_2 \rangle_{CS}$).

Estimating Hydrogen-Bond Energies. It is important to mention that, although Hartree–Fock calculations are not expected to be very accurate in estimating hydrogen-bond energies, our ΔE_2 values follow the correct qualitative trend and compare satisfactorily well with other theoretical estimates.²³ Recent DFT/B3LYP calculations on the complexes we are discussing here led to hydrogen-bond energies that are in very good agreement with the HF results (see Figure 8 of ref 19). Concerning the comparison with experimental data, we note that our energies quantitatively match the available experimental data. For example, $\Delta E_2 = -0.0233$ au for C1²⁴ (compared with $\Delta E_2 = -0.0231$ au from Table 2), and the energy of a single hydrogen bond in C10 was measured to be 0.0016 au,²⁵ which is very close to one-half of our ΔE_2 value given in Table 2 ($\Delta E_2/2 = 0.0019$ au), where the factor $1/2$ is introduced for proper comparison as C10 contains two hydrogen bonds. This latter result suggests that hydrogen-bond energies for the series of systems we are studying here might be rationalized in terms of the sum of individual H-bond energies present in the complex.

To explore this idea, we use the ΔE_2 values for the dimers C1 and C10, which present only H \cdots O or H \cdots S bonds, as reference values defining the energy of the respective bonds: i.e., $E(\text{H}\cdots\text{O}) = \Delta E_2(\text{C1})/2 = -0.01155$ au and $E(\text{H}\cdots\text{S}) = \Delta E_2(\text{C10})/2 = -0.00185$ au. Using these values, we approximate the ΔE_2 values for the remaining eight complexes as $\Delta E_2^{(a)} = \sum_X E(\text{H}\cdots\text{X})$, simply the sum of energies of H-bonds present in the system. The results are included in Table 3. We note that this estimation of ΔE_2 is rather crude, exhibiting considerable errors that go up to 70% (C3). Thus, the rough estimation of the H-bond energies from the reference systems C1 and C10 is not accurate enough to get an adequate description of the remaining ΔE_2 values.

A considerably better approach to ΔE_2 can be obtained if we consider not only the corresponding H-bonds but also the effect that the neighboring heteroatom may have, thus defining the energy of fragments X–H \cdots Y (X, Y = O, S). To do so, we use as a reference four dimers (C1, C3, C8, and C10) that present the desired fragments: $E(\text{OH}\cdots\text{O}) = \Delta E_2(\text{C1})/2 = -0.01155$ au; $E(\text{OH}\cdots\text{S}) = \Delta E_2(\text{C3})/2 = -0.00595$ au; $E(\text{SH}\cdots\text{O}) = \Delta E_2(\text{C8})/2 = -0.00445$ au; and $E(\text{SH}\cdots\text{S}) = \Delta E_2(\text{C10})/2 = -0.00185$ au. Note that the presence of a sulfur atom adjacent to the H-bond makes the H-bond weaker than it would be in the presence of oxygen. Now we define $\Delta E_2^{(b)} = \sum_{X,Y} E(\text{XH}\cdots\text{Y})$; the results are shown in Table 3 and compared with ΔE_2 and $\Delta E_2^{(a)}$. It can be seen that the deviations with respect to the calculated ΔE_2 values are now very small; they go up to 0.82 kcal/mol in C6 (the larger deviation of $\Delta E_2^{(a)}$ with respect to ΔE_2 was found in C8 and was 8.91 kcal/mol). This indicates that the effect of the heteroatom adjacent to the H-bond is very important in characterizing the different H-bond energies. In summary, we estimate the H \cdots O bond energy to be 0.0080 ± 0.0036 au and the H \cdots S bond energy to be 0.0039 ± 0.0021 au, the H \cdots O bond being about twice as strong as the H \cdots S bond.

Force Constants and Hydrogen-Bond Energies. In bimolecular systems when the energy is estimated using $n_f = 2$, the quantity $\Delta E_2 = E - E_2^o$ gives an estimate of the hydrogen-bond energies, because the larger ΔE_2 is, the stronger the pair of hydrogen bonds being formed is expected to be. Table 3 shows that the bond energy decreases with the number of electrons and that the O \cdots H bonds are stronger than the S \cdots H bonds. The strength of a chemical bond is usually represented by its force constant; in our case, we expect ΔE_2 to be related with the force constants k associated with the pair of hydrogen bonds of the complex. These force constant values have been determined through ab initio frequency calculations on the optimized structure of the complexes, and the results are displayed in Figure 1a, where a good linear correlation can be observed between ΔE_2 and k for the 10 complexes identified by their total number of electrons, the correlation factor being 0.980. Because there are four systems having 64 electrons (C3, C5, C6, and C8), two with 72 electrons (C7 and C9), and two with 56 electrons (C2 and C4), we plot the average of their ΔE_2 and k values, obtaining an enhanced correlation, as is apparent in Figure 1b ($R = 0.996$). Thus, the ab initio force constants are consistent with expectations based on the energetic results: the stronger the hydrogen bond, the higher its $|\Delta E_2|$ value.

Chemical Potential. Equation 6 has been used to obtain the chemical potential within Sanderson's scheme. The estimates for M1–M4 require the ab initio data (μ_x and η_x) for the isolated radicals $x = \text{CHO}$, OH, CHS, and SH that are quoted in Table

TABLE 2: Total and Reaction Energies of Molecular Systems and Formation Processes^a

| system | | $-E$ | $-E_2^o$ | $-E_4^o$ | $-\Delta E_2$ | $-\Delta E_4$ |
|---------------|-------|-----------|-----------|-----------|---------------|---------------|
| HCOOH | (M1) | 188.8205 | 188.6910 | | 0.1295 | |
| HCSOH | (M2) | 511.4454 | 511.3260 | | 0.1194 | |
| HCOSH | (M3) | 511.4493 | 511.3731 | | 0.0762 | |
| HCSSH | (M4) | 834.0867 | 834.0082 | | 0.0785 | |
| HCOOH...HCOOH | (C1) | 377.6641 | 377.6410 | 377.3819 | 0.0231 | 0.2822 |
| HCOOH...HCSOH | (C2) | 700.2840 | 700.2659 | 700.0170 | 0.0181 | 0.2670 |
| HCSOH...HCSOH | (C3) | 1022.9027 | 1022.8908 | 1022.6520 | 0.0119 | 0.2507 |
| HCOOH...HCOSH | (C4) | 700.2847 | 700.2698 | 700.0641 | 0.0149 | 0.2206 |
| HCOOH...HCSSH | (C5) | 1022.9176 | 1022.9072 | 1022.6992 | 0.0104 | 0.2184 |
| HCOSH...HCSOH | (C6) | 1022.9068 | 1022.8947 | 1022.6992 | 0.0121 | 0.2076 |
| HCSSH...HCSOH | (C7) | 1345.5389 | 1345.5320 | 1345.3342 | 0.0069 | 0.2047 |
| HCOSH...HCOSH | (C8) | 1022.9076 | 1022.8987 | 1022.7463 | 0.0089 | 0.1613 |
| HCSSH...HCOSH | (C9) | 1345.5425 | 1345.5360 | 1345.3813 | 0.0065 | 0.1612 |
| HCSSH...HCSSH | (C10) | 1668.1770 | 1668.1733 | 1668.0164 | 0.0037 | 0.1606 |

^a All values are in atomic units.**TABLE 3: Double Hydrogen-Bond Energies of Bimolecular Aggregates^a**

| complex | N | $-\Delta E_2$ | $-\Delta E_2^{(a)}$ | $-\Delta E_2^{(b)}$ |
|---------|-----|---------------|---------------------|---------------------|
| C1 | 48 | 0.0231 | 0.0231 | 0.0231 |
| C2 | 56 | 0.0181 | 0.0134 | 0.0175 |
| C3 | 64 | 0.0119 | 0.0037 | 0.0119 |
| C4 | 56 | 0.0149 | 0.0231 | 0.0160 |
| C5 | 64 | 0.0104 | 0.0134 | 0.0104 |
| C6 | 64 | 0.0121 | 0.0134 | 0.0134 |
| C7 | 72 | 0.0069 | 0.0134 | 0.0078 |
| C8 | 64 | 0.0089 | 0.0231 | 0.0089 |
| C9 | 72 | 0.0065 | 0.0134 | 0.0063 |
| C10 | 80 | 0.0037 | 0.0037 | 0.0037 |

^a All values are in atomic units.

1. The effect of relaxation and redistribution of the electronic density on the chemical potential due to formation of covalent and hydrogen bonds can be quantitatively characterized by the numerical values of $\mu_{n_i}^o$ with reference to the calculated chemical potential; numerical values are listed in Table 4. We note that the deviations of $\mu_{n_i}^o$ with respect to the reference ab initio values are reasonably small; in most cases, μ_2^o approaches the reference value better than μ_4^o does. As for the energy, the chemical potential seems to be quite dependent on the number of fragments used.

When two fragments are brought into contact, electrons will flow from the one of higher chemical potential to that of lower μ , the amount of flowing charge being proportional to the difference in the chemical potentials of the fragments.⁸ A qualitative estimation of the charge transfer (ΔN) involved in the formation process of a two-fragment reaction can be determined through the following expression:^{5,8,10,12}

$$\Delta N = \frac{1}{2} \frac{(\mu_x - \mu_y)}{(\eta_x + \eta_y)} \quad (9)$$

with x and y representing the different fragments used in the formation of the desired product. The values of ΔN are quoted in Table 5, where it is interesting to note that reactions involving formation of covalent bonds are accompanied with high positive values of ΔN whereas, in bimolecular complex formation, we find smaller values of ΔN . According to eq 9, the amount of charge (δN_{n_i}) that is not relaxed in the formation process from the rigid fragments must be proportional to $\Delta \mu_{n_i} = (\mu - \mu_{n_i}^o)$. Thus, we simply define $\delta N_{n_i} \equiv \Delta \mu_{n_i}$ and quote its values in Table 5. It is interesting to note, for bimolecular complexes, that formation from four fragments in most cases implies higher values of this index than formation from two

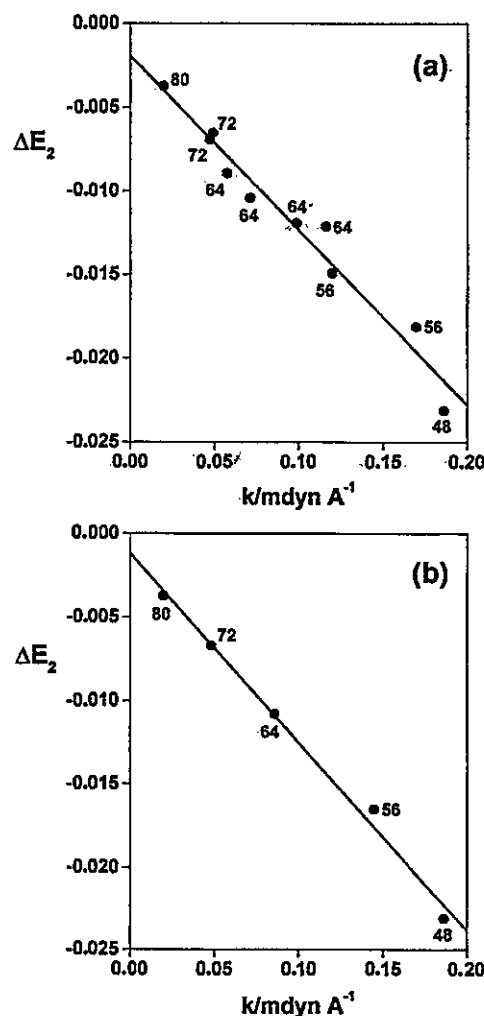


Figure 1. (a) Correlation between hydrogen-bond energies and H-bond force constants of bimolecular aggregates identified by their number of electrons. (b) Same as in panel a but using the average values of ΔE_2 and k in systems presenting the same number of electrons.

fragments, thereby implying that reordering of the electron density becomes increasingly important with the number of fragments.

Molecular Hardness. Within Sanderson's scheme, we have determined the molecular hardness using eq 7; the results that are quoted in Table 4 must be compared with the reference ab initio values also included in the table. It is interesting to note that hardness can be approached using either η_2^o or η_4^o , depending on the specific system, both approaches represent

TABLE 4: Calculated and Estimated Electronic Properties of Isolated Molecules and Molecular Aggregates^a

| system | μ | μ_2^0 | μ_4^0 | η | η_2^0 | η_4^0 | γ_2^0 | γ_4^0 |
|--------|---------|-----------|-----------|--------|------------|------------|--------------|--------------|
| M1 | -0.1554 | -0.1590 | | 0.3138 | 0.2783 | | 0.0247 | |
| M2 | -0.1402 | -0.1686 | | 0.2206 | 0.2441 | | 0.0214 | |
| M3 | -0.1391 | -0.1591 | | 0.2608 | 0.2246 | | 0.0431 | |
| M4 | -0.1532 | -0.1687 | | 0.1996 | 0.1872 | | 0.0062 | |
| C1 | -0.1503 | -0.1554 | -0.1590 | 0.3204 | 0.3138 | 0.2783 | 0.0317 | 0.0247 |
| C2 | -0.1411 | -0.1476 | -0.1638 | 0.2251 | 0.2652 | 0.2619 | 0.0303 | 0.0269 |
| C3 | -0.1462 | -0.1402 | -0.1686 | 0.2169 | 0.2206 | 0.2441 | 0.0153 | 0.0214 |
| C4 | -0.1402 | -0.1470 | -0.1590 | 0.2609 | 0.2863 | 0.2515 | 0.0281 | 0.0380 |
| C5 | -0.1601 | -0.1543 | -0.1638 | 0.2021 | 0.2563 | 0.2342 | 0.0398 | 0.0326 |
| C6 | -0.1320 | -0.1397 | -0.1638 | 0.2215 | 0.2408 | 0.2342 | 0.0231 | 0.0326 |
| C7 | -0.1604 | -0.1466 | -0.1687 | 0.1966 | 0.2108 | 0.2157 | 0.0148 | 0.0187 |
| C8 | -0.1331 | -0.1391 | -0.1591 | 0.2607 | 0.2608 | 0.2246 | 0.0240 | 0.0431 |
| C9 | -0.1511 | -0.1460 | -0.1638 | 0.2000 | 0.2319 | 0.2065 | 0.0288 | 0.0289 |
| C10 | -0.1576 | -0.1532 | -0.1687 | 0.1965 | 0.1996 | 0.1871 | 0.0084 | 0.0064 |

^a All values are in atomic units.TABLE 5: Estimation of Charge Transfer (ΔN) in Formation of Molecular Systems and Bimolecular Complexes

| system | ΔN | δN_2 | δN_4 |
|--------|------------|--------------|--------------|
| M1 | 0.0516 | 0.0036 | |
| M2 | 0.0414 | 0.0284 | |
| M3 | 0.0672 | 0.0200 | |
| M4 | 0.0558 | 0.0155 | |
| C1 | 0.0 | 0.0051 | 0.0087 |
| C2 | -0.0142 | 0.0065 | 0.0227 |
| C3 | 0.0 | -0.0060 | 0.0224 |
| C4 | -0.0142 | 0.0068 | 0.0188 |
| C5 | -0.0021 | -0.0058 | 0.0037 |
| C6 | 0.0011 | 0.0077 | 0.0318 |
| C7 | -0.0155 | -0.0138 | 0.0083 |
| C8 | 0.0 | 0.0060 | 0.0260 |
| C9 | -0.0153 | -0.0051 | 0.0127 |
| C10 | 0.0 | -0.0044 | 0.0111 |

TABLE 6: Comparison of Hardness Determined through Different Methods^a

| system | η^b | eq 7 ^c | ref 26 | ref 27 |
|--------|----------|-------------------|--------|--------|
| M1 | 0.3138 | 0.2783 | 0.2757 | 0.2779 |
| M2 | 0.2206 | 0.2441 | 0.2333 | 0.2417 |
| M3 | 0.2608 | 0.2246 | 0.2117 | 0.2137 |
| M4 | 0.1996 | 0.1872 | 0.1858 | 0.1858 |
| C1 | 0.3204 | 0.3138 | 0.3138 | 0.3138 |
| C2 | 0.2251 | 0.2652 | 0.2591 | 0.2631 |
| C3 | 0.2169 | 0.2206 | 0.2206 | 0.2206 |
| C4 | 0.2609 | 0.2863 | 0.2849 | 0.2861 |
| C5 | 0.2021 | 0.2563 | 0.2440 | 0.2503 |
| C6 | 0.2215 | 0.2408 | 0.2390 | 0.2399 |
| C7 | 0.1966 | 0.2108 | 0.2096 | 0.2098 |
| C8 | 0.2607 | 0.2608 | 0.2608 | 0.2608 |
| C9 | 0.2000 | 0.2319 | 0.2261 | 0.2282 |
| C10 | 0.1965 | 0.1996 | 0.1996 | 0.1996 |

^a All values are in atomic units. ^b η is the reference ab initio value. ^c Equation 7 is used with $n_t = 2$.

good approximations of the actual ab initio result. Qualitative consistency between η_2^0 or η_4^0 indicates that eq 7 is a reliable expression for estimating molecular hardness. There are a few different ways to estimate η from fragment values: the arithmetic average for softness²⁶ ($S = 1/\eta$) and the geometric mean principle for hardness²⁷ are among the most relevant treatments for determining hardnesses. In Table 6, we compare the numerical values of η calculated using eq 7 with values determined using the above-mentioned treatments. We note that the comparison is quite satisfactory, with only very small deviations among the values obtained through the different methods being observed. This result adds evidence for an important feature of hardness: it is a quite stable property. This attribute, in combination with the principle of maximum hardness (PMH),²⁸⁻³⁰ which states that molecular systems at equilibrium tend to states of highest hardness, suggest that, for

systems in which the energy is difficult to obtain, knowledge of η may open the way for obtaining energetic information.¹⁸

Relation between Energy and Hardness. The connection between energy and hardness through the PMH prompted us to investigate the relation between the formation energies ΔE_2 and ΔE_4 of the bimolecular complexes and the corresponding hardnesses η_2^0 and η_4^0 , determined using eq 7. Panels a and b of Figure 2 show good linear correlations between ΔE_{n_t} and $\eta_{n_t}^0$ for the complexes identified by their total number of electrons. These correlations are substantially improved when we use the average value of the properties of complexes with the same number of electrons ($N = 56, 64,$ and 72), as shown in Figure 2c,d. As dictated by the PMH, we see that the more stable the complex is, the harder it appears to be.

There have been few interesting and useful attempts to relate electronic properties to reaction energies.^{14,31,32} Pearson³¹ proposed an empirical method for ranking the order of Lewis acids and bases in terms of their hardness at their reaction sites. More recently, Gázquez³² proposed an expression for the bond energy in terms of the chemical potential, the hardnesses, and the condensed Fukui functions of the isolated species. In our search for a relation between the hydrogen-bond energies and the electronic properties of the isolated species, we have tested the Gázquez expression with the result that it overestimates the H-bond energies although it indicates correctly that the main contribution to the bond energy comes from the change in the hardness of the system.

To close this discussion, it is interesting to note that the analysis of Figures 1 and 2 suggests that hardness and the H-bond force constants must be related. In Figure 3, we show the nice linear relations connecting these properties. It can be seen that the stronger the bond being formed, the harder the complex. This result confirms the fact that there is direct proportionality between hardness and force constants, as correctly pointed out recently by Arulmozhiraja and Kolan-daivel.³³

Polarizability of Hydrogen-Bonded Systems. Along with the PMH, Chattaraj et al. have proposed a minimum polarizability principle (MPP), which states that the natural direction of evolution of any system is toward a state of minimum polarizability.³⁴ In general, the conditions of maximum hardness and minimum polarizability complement the minimum energy criterion for molecular stability.³⁵ The polarizability of the isolated molecules and those of the hydrogen-bonded systems determined through the ab initio calculations are quoted in Table 7, together with the best approach to the polarizability of the hydrogen-bonded systems: the simple addition of the polariz-

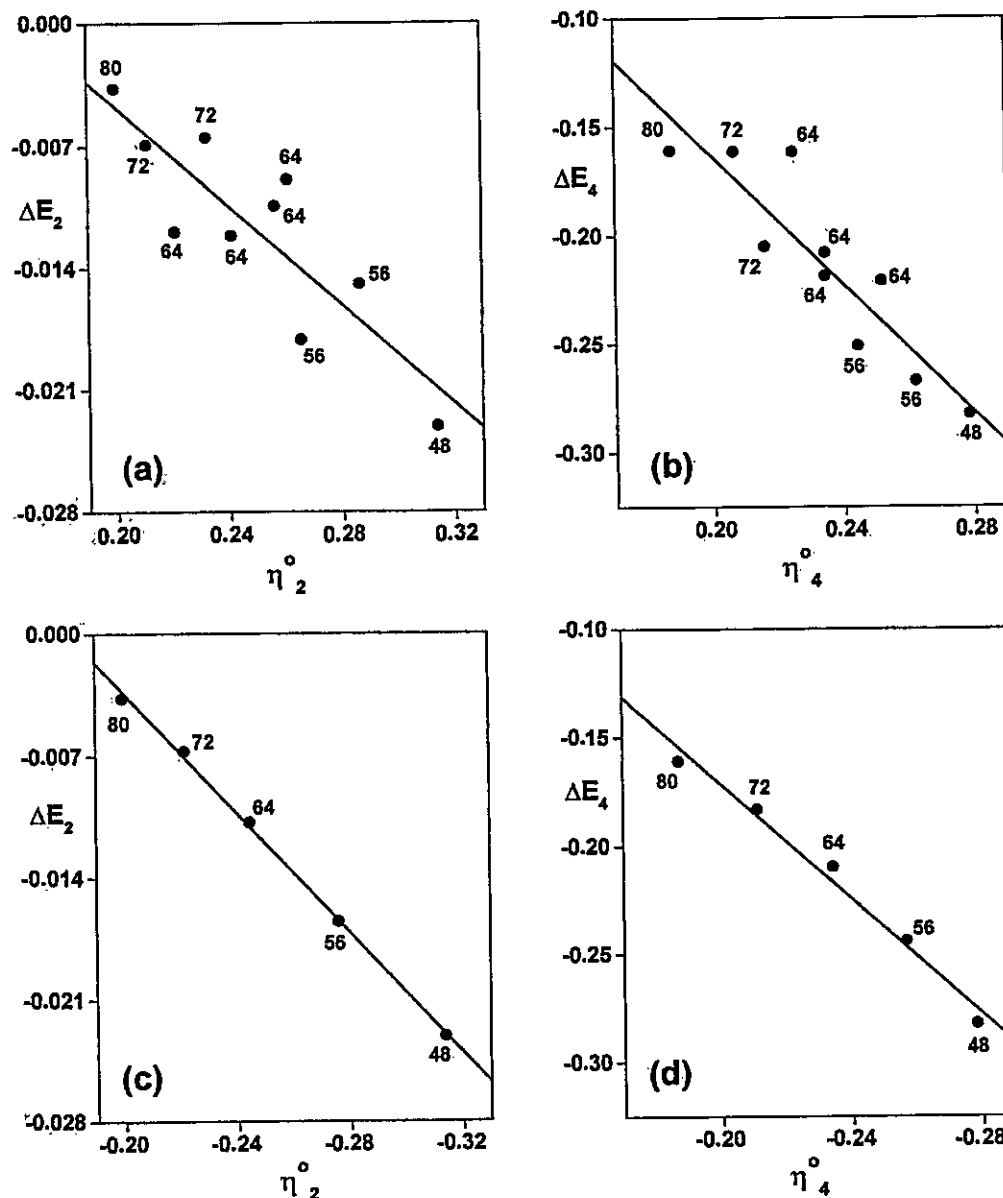


Figure 2. Correlation between bond energy and hardness of the product determined from the Sanderson approximation with (a) $n_r = 2$ and (b) $n_r = 4$. (c) and (d) Same as in panels a and b but using the average values in systems presenting the same number of electrons.

abilities of the constituent monomeric units (α_x^o , the fourth column of Table 7). Figure 4a shows the excellent quality of this approach. Our results suggest that the polarizability of a composite system is given by the sum of the n_r individual polarizabilities

$$\alpha_{n_r}^o = \sum_x^{n_r} \alpha_x^o \quad (10)$$

where α_x^o stands for the polarizabilities of the monomeric units. The above expression is not an attempt to define an addition scheme for polarizabilities; it simply comes from the empirical observation of the present results.

Adding electrons to a system will increase its polarizability because α is proportional to N ; our results concerning the hydrogen-bonded complexes confirm this proportionality, as shown in Figure 4b. On the other hand, we have shown recently¹⁹ that the H-bond energy is proportional to N ; therefore, one should expect ΔE_2 be related to the polarizability. However, Figure 5a shows a very scattered plot of ΔE_2 against the reaction

polarizability $\Delta\alpha_2$ (fifth column in Table 7), where this latter quantity is defined as the difference between the polarizabilities of the product (the H-bonded system) and reactants (the sum of monomeric units). The expected consistency in our results is achieved when the polarizability of the reactants is defined as the arithmetic mean of the polarizabilities of the monomeric units, thus defining the reaction polarizability as $\Delta\bar{\alpha}_2 = \alpha - (\sum_x \alpha_x)/2$, which is given in Table 7. Figure 5b shows a quite good linear correlation in which it is apparent that the lower the reaction energy, the lower the reaction polarizability. This result suggests the possibility of extending the validity of the MPP to allow for comparisons of relative energies and polarizabilities. Furthermore, ΔE_2 displays a linear correlation with the polarizability of the product, as shown in Figure 5c. In summary, the more stable the product species, the harder and less polarizable it was found to be.

We have mentioned that the polarizability can be used to understand the behavior of the system when the external potential is changed at constant N .⁷ Formally, the chemical potential is a function of N and a functional of the external

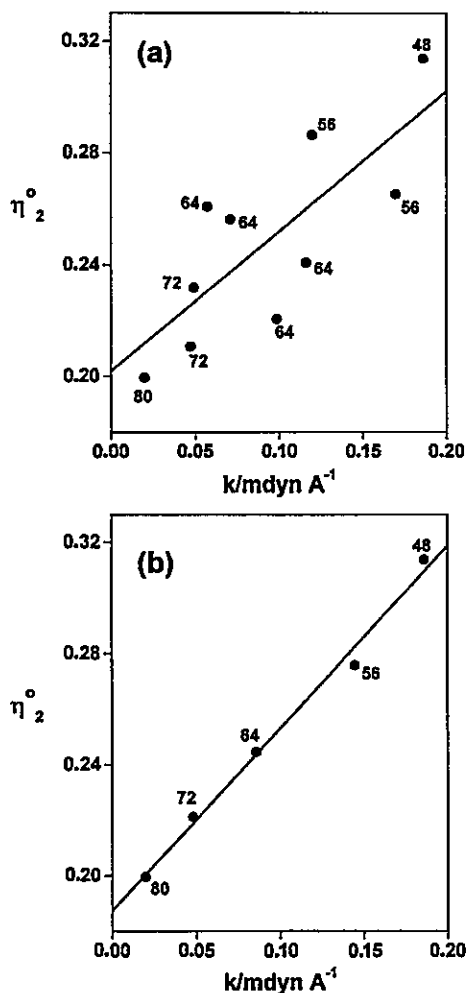


Figure 3. (a) Correlation between hardness and H-bond force constants of bimolecular aggregates. (b) Same as in panel a but using the average values in systems presenting the same number of electrons.

TABLE 7: Calculated and Estimated Polarizabilities of Isolated Molecules and Molecular Aggregates^a

| system | N | α | α_2° | $\Delta\alpha_2$ | $\Delta\bar{\alpha}_2$ |
|--------|-----|----------|------------------|------------------|------------------------|
| M1 | 24 | 15.1733 | | | |
| M2 | 32 | 28.2873 | | | |
| M3 | 32 | 27.7830 | | | |
| M4 | 40 | 43.4183 | | | |
| C1 | 48 | 30.9583 | 30.3466 | 0.6117 | 15.7850 |
| C2 | 56 | 45.7427 | 43.4606 | 2.2821 | 24.0124 |
| C3 | 64 | 60.5700 | 56.5746 | 3.9954 | 32.2827 |
| C4 | 56 | 43.6490 | 42.9563 | 0.6927 | 22.1709 |
| C5 | 64 | 60.9957 | 58.5916 | 2.4041 | 31.6999 |
| C6 | 64 | 58.0750 | 56.0703 | 2.0047 | 30.0399 |
| C7 | 72 | 75.0847 | 71.7056 | 3.3791 | 39.2319 |
| C8 | 64 | 56.3013 | 55.5660 | 0.7353 | 28.5183 |
| C9 | 72 | 72.9003 | 71.2013 | 1.6990 | 37.2997 |
| C10 | 80 | 88.6140 | 86.8366 | 1.7774 | 45.1957 |

^a All values are in atomic units.

potential $v(\vec{r})$, so we can write $\mu \equiv \mu[N, v(\vec{r})]$. To relate the change of the external potential to the reaction polarizability, we differentiate eq 6 with respect to $v(\vec{r})$, thus defining the quantity $F_{n_i}^\circ$.

$$F_{n_i}^\circ \equiv \left(\frac{\delta \mu_{n_i}^\circ}{\delta v} \right)_N \approx \frac{\mu_{n_i}^\circ}{n_i} \Delta v \sum_x \left(\frac{f_x^\circ}{\mu_x^\circ} \right) \quad (11)$$

Because the formal definition of $F_{n_i}^\circ$ is analogous to the Fukui function used to quantify the reactivity of specific sites on a

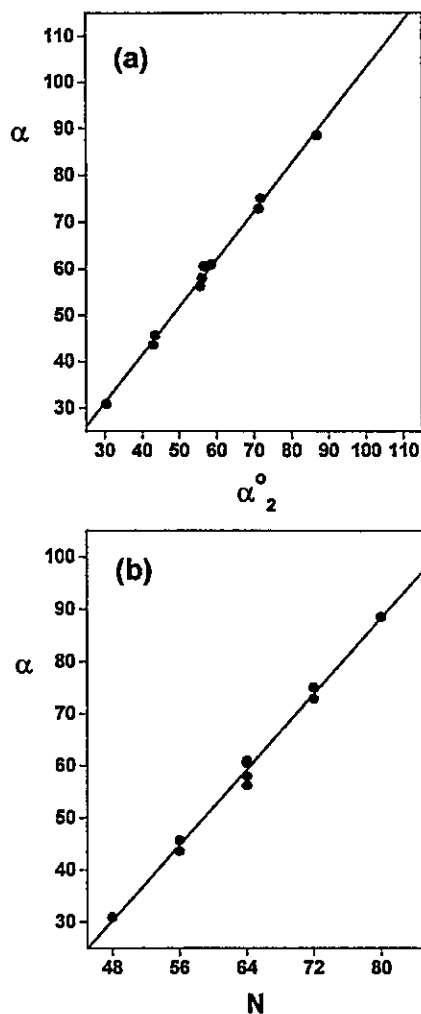


Figure 4. (a) Comparison of the calculated polarizability of the hydrogen-bonded complexes with the estimation of eq 10. (b) Characterization of the calculated polarizability with the total number of electrons of the H-bonded complexes.

given molecule and because it contains information on the overall change from reactants to products through Δv , we call it the Reaction Fukui Function (RFF). It can be seen from eq 11 that $F_{n_i}^\circ$ is a global property that contains the fragment reactivities through the Fukui functions $f_x^\circ = (\delta \mu_x^\circ / \delta v)_N$. Therefore, we expect $F_{n_i}^\circ$ to be a property measuring the global reactivity of the system.

We have determined numerical values of RFF approaching Δv by the electron-nuclei potential (V_{ne}) obtained from the ab initio calculations; in fact, we have used $\Delta v = [V_{ne}(\text{product}) - \sum V_{ne}(\text{reactants})]$. The f_x° values were approximated as N_x/N , with N_x being the number of electrons of fragment x and N the total number of electrons of the composite system such that $\sum_x N_x = N$. In Figure 6a, we show that the RFF is linearly related to the reaction energy, indicating that the RFF may be a measure of the exothermicity of the reaction: the lower ΔE_2 , the higher the RFF value. On the other hand, Figure 6b indicates that the RFF is related to the reaction polarizability through a very good straight line. This result shows that the polarizability is the right response of the system when the external potential is changed, and it emphasizes the usefulness of determining accurate values for this property. On the other hand, it is clear that the whole procedure based upon Sanderson's scheme is a powerful tool for characterizing chemical reactions when both N and v change.

The Hardness Derivative. Hardness is now recognized as an important property for characterizing chemical processes, so

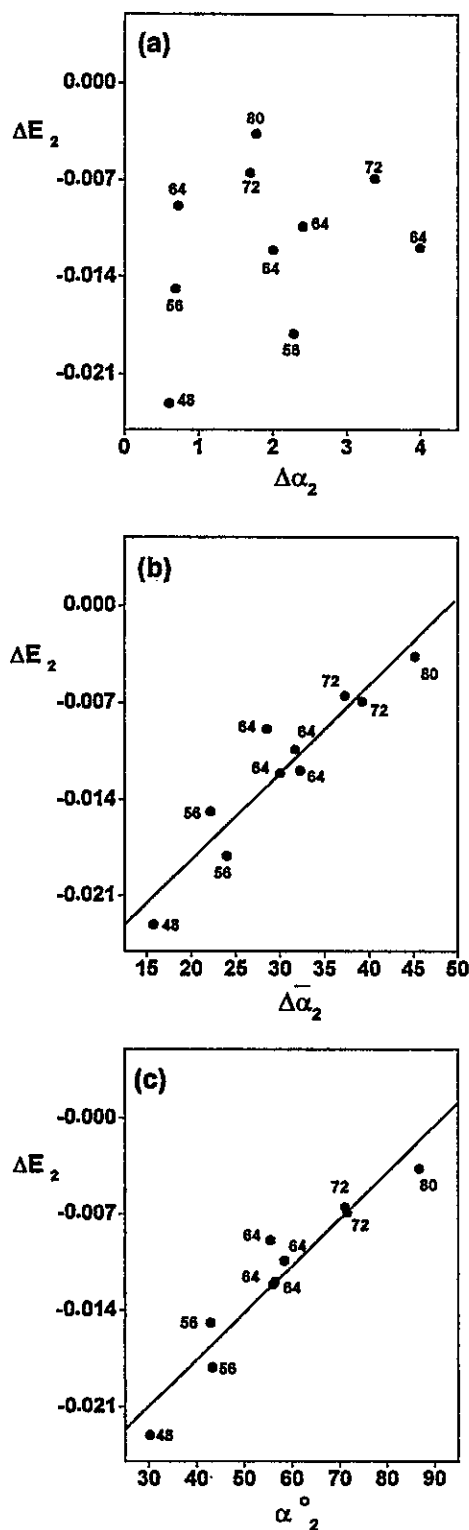


Figure 5. Representation of reaction energies ΔE_2 against (a) the reaction polarizability defined as $\Delta\alpha = \alpha(\text{product}) - \sum_x \alpha_x$, (b) the reaction polarizability defined as $\Delta\bar{\alpha} = \alpha(\text{product}) - (\sum_x \alpha_x)/n_t$, and (c) the polarizability of the bimolecular complex from eq 10. All values are in atomic units.

it is necessary to know how it changes with the number of electrons and the external potential. The quantity γ measures the change of η with N . We have used eq 8 to estimate numerical values of this property. We first note that to evaluate the third term of eq 8, we need the values of γ_x° of the isolated fragments; these were estimated from the following approximate formula proposed by Fuentealba and Parr:²⁰

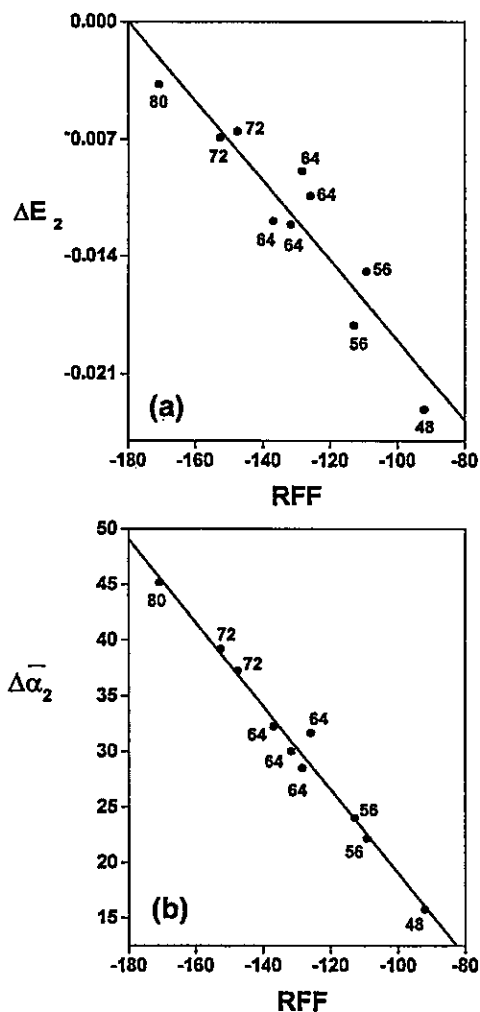


Figure 6. Characterization of the reaction Fukui function (RFF) with (a) the reaction energy and (b) the reaction polarizability. All values are in atomic units.

$$\gamma_x^\circ \approx \left[\frac{\epsilon_L}{\epsilon_L - 3\epsilon_{H,x}} \right]^\circ \eta_x^\circ \quad (12)$$

Equation 8 shows a quite complex dependence of γ with respect to η that is far from being linear, as indicated by eq 12. The validity of this latter equation and its consistency with Sanderson's scheme has been tested by calculating η and γ using eqs 7 and 8 to check their possible linear relation. Values of γ_2° and γ_4° for the 14 compounds we are studying here are quoted in Table 4. We note that, in all cases, they are positive and very small. The linear dependence between γ and η could not be obtained, as is apparent in Figure 7a,b. These results are in agreement with expectations based on the very definition of γ .²⁰ When the atomic data of Fuentealba and Parr²⁰ are used to build the properties of the bimolecular complexes, thus producing η_{10}° and γ_{10}° from the 10 constituent atoms, we obtain negative values of γ and linear behavior with η , as shown in Figure 7c. It should be noted that because there are systems presenting the same atomic composition, their values of η_{10}° and γ_{10}° are the same. Thus, in Figure 7c, the systems have been ordered in terms of their total number of electrons.

A New Additivity Scheme for μ and η . In this section, we propose a new additivity scheme for the chemical potential and hardness that is based upon dimensional analysis of eq 11, which shows that it is possible to define the inverse of the chemical potential of a composite system as

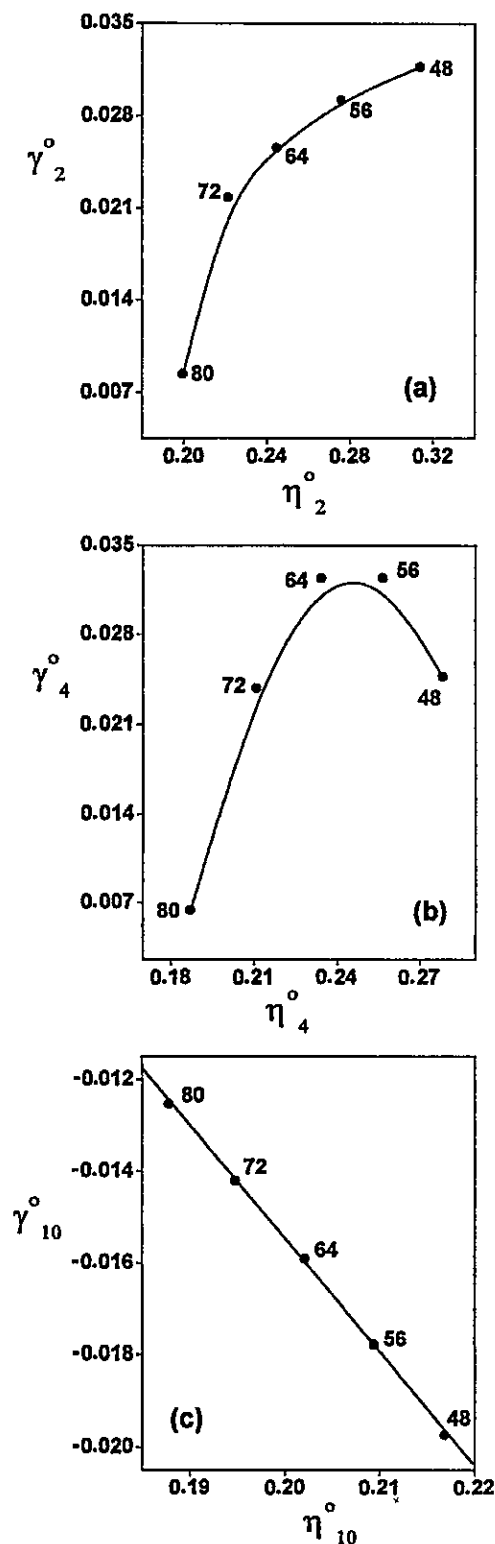


Figure 7. Relationship between $\eta_{n_f}^\circ$ and $\gamma_{n_f}^\circ$ of the H-bonded systems ordered in terms of their total number of electrons: (a) $n_f = 2$, (b) $n_f = 4$, and (c) $n_f = 10$ (from atomic data in ref 20). All values are in atomic units.

$$\frac{1}{\mu'_{n_f}} \approx \sum_x \left(\frac{f_x^\circ}{\mu_x^\circ} \right) \quad (13)$$

Determination of the chemical potential of a composite system from the properties of the isolated fragments by means of eq 13 produces results that are in very good agreement with those determined using eq 6. This can be verified in Figure 8, where

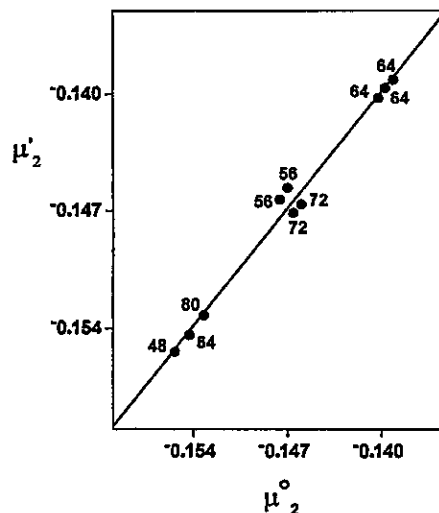


Figure 8. Comparison of chemical potentials determined through eqs 6 and 13. All values are in atomic units.

we compare both approaches for estimating the chemical potential of the 10 bimolecular complexes using $n_f = 2$. Moreover, we have verified that, in all cases studied here, μ'_{n_f} provides a better approach to the reference ab initio value than does $\mu_{n_f}^\circ$ determined from eq 6; this was verified for $n_f = 2, 4$, and 10. These results show that eq 13 represents a valid alternative to the original Sanderson's formulation. It is interesting to note that this new expression contains the electronic population of the isolated fragment, a local quantity, together with the chemical potential, a global property of the fragment.

Characterization of higher-order derivatives of eq 13 is straightforward. In the new framework the hardness is given by

$$\eta'_{n_f} = \left(\frac{\partial \mu'_{n_f}}{\partial N} \right)_{v(\bar{r})} = (\mu'_{n_f})^2 \sum_x \frac{1}{(\mu_x^\circ)^2} [f_x^\circ \eta_x^\circ - h_x^\circ \mu_x^\circ] \quad (14)$$

where h_x° is a measure of the fluctuation of the chemical hardness due to a change in the external potential. Alternatively, through the Maxwell relation, h_x° can be seen as the response of the Fukui function to a change in the total number of electrons.

$$h_x^\circ = \left(\frac{\partial \eta_x^\circ}{\partial v} \right)_N = \left(\frac{\partial f_x^\circ}{\partial N} \right)_v \quad (15)$$

Recently, Parr et al.³⁶ have defined the electrophilicity index as $W = \mu^2/2\eta$. In analogy with this definition, we can define a nucleophilicity index from eq 14 as

$$\frac{\eta'_{n_f}}{(\mu'_{n_f})^2} = \sum_x \frac{1}{(\mu_x^\circ)^2} [f_x^\circ \eta_x^\circ - h_x^\circ \mu_x^\circ] \quad (16)$$

which is a positive defined quantity. The above set of equations containing local and global properties opens a method for characterizing the reactivity and selectivity concepts in an unified perspective.

5. Concluding Remarks

We have used Sanderson's Principle to estimate the first, second, and third derivative of the energy with respect to the total number of electrons. The results for μ'_{n_f} and η'_{n_f} show that,

in the cases treated here, Sanderson's geometric mean equalization principle is adequate for predicting these electronic properties of composite systems. Numerical values for the third-order property, γ , were found to be very small and positive, in agreement with the expected behavior.

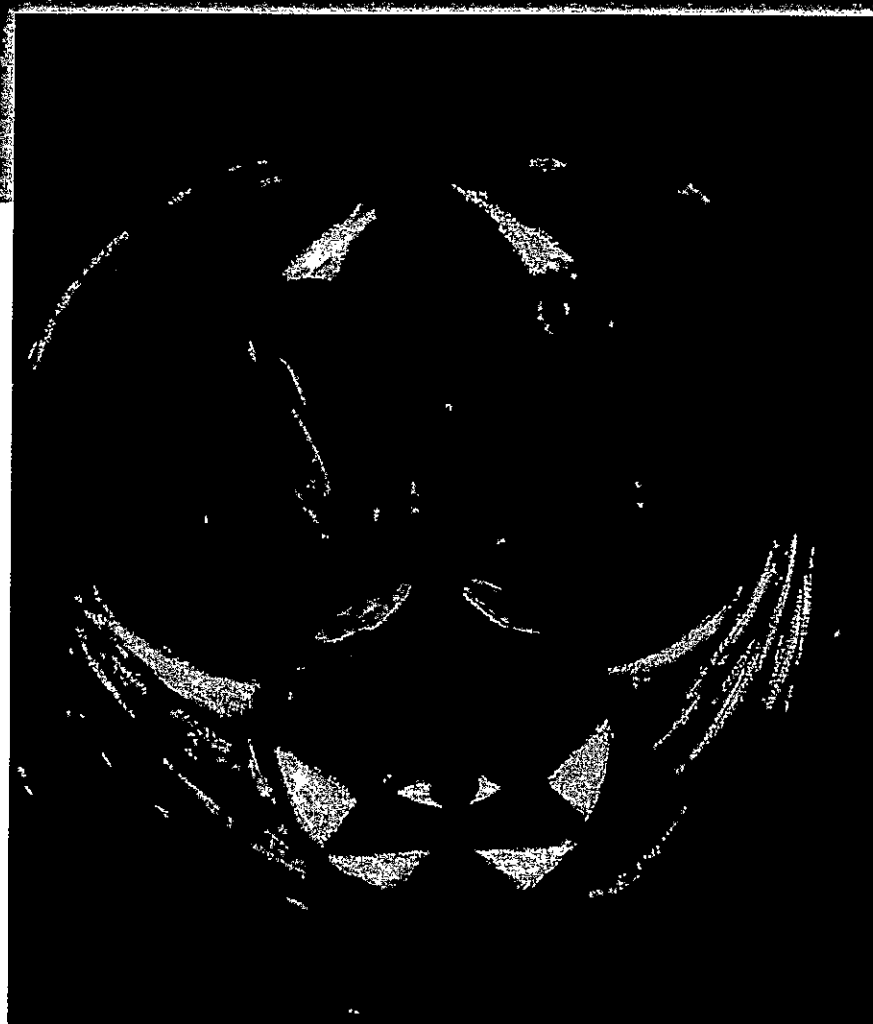
Numerical results for bond energies at the RHF/6-311G** level were qualitatively satisfactory and quantitatively in agreement with the available bond-energy data. We have found that principles of maximum hardness and minimum polarizability are operative for rationalizing the formation of molecules and bimolecular aggregates. Sanderson's scheme has been shown to be very useful not only in determining electronic properties but also in rationalizing chemical reactions when both N and ν change. Finally, we have proposed a new scheme for obtaining molecular properties from the isolated fragments with quite encouraging results for chemical potentials. In this approach, local and global properties play equivalent roles, which may lead to methods for simultaneously characterizing the reactivity and selectivity concepts in chemical processes.

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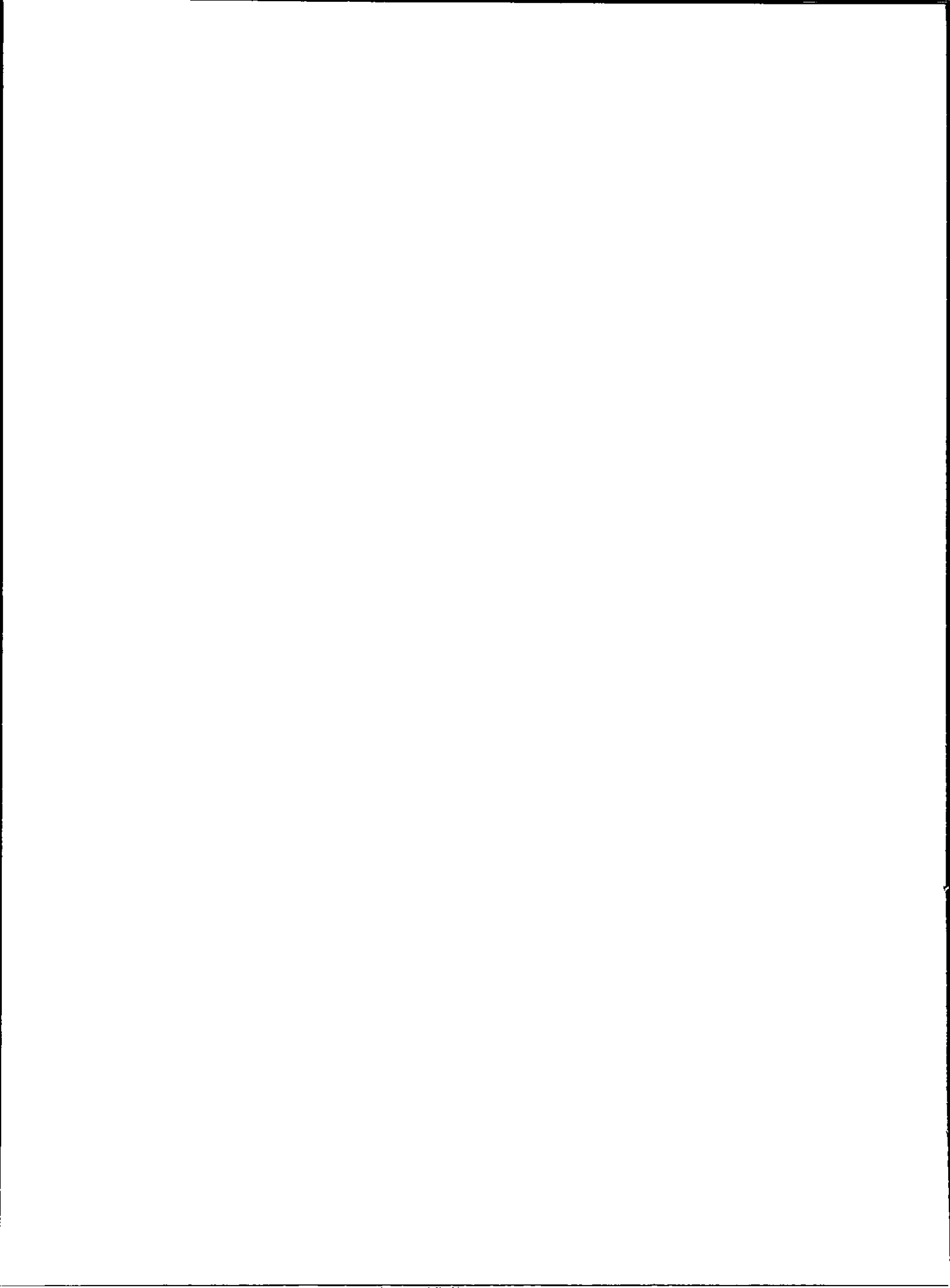
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Volume II

A Celebration of the
Contributions of Robert G. Parr



CHARACTERIZATION OF CHEMICAL REACTIONS THROUGH CLASSICAL CONCEPTS AND DFT DESCRIPTORS.

SOLEDAD GUTIÉRREZ-OLIVA, PABLO JAQUE
AND ALEJANDRO TORO-LABBÉ

*Laboratorio de Química Teórica Computacional (QTC),
Facultad de Química, Pontificia Universidad Católica de Chile.
Casilla 306, Correo 22, Santiago, Chile.*

In this paper we point out that classical concepts of reactivity in connection with DFT descriptors are adequate and powerful tools for characterizing chemical reactions. The conceptual classical model, in which a reaction proceeds from one energy minimum to another via an intermediate maximum, together with the principles of maximum hardness and minimum polarizability provide the necessary elements to discuss the activation and relaxation processes in terms of the activation chemical potential and hardness. Illustrative examples of representative systems undergoing internal rotations, intramolecular rearrangements and double proton transfer confirm the validity of this approach.

1 Introduction

1.1 *Classical Concepts of Chemical Reactivity.*

Chemical processes can be characterized through reaction profiles that illustrate the way in which the properties of the reacting systems changes as a function of the reaction coordinate (RC). These properties may be either global (energy, chemical potential, hardness, polarizability, etc.) or local (electronic populations, Fukui functions, etc.). Within the Born-Oppenheimer approximation the RC represents the nuclear reorganization that takes place as the reaction move forward, i.e. the bond lengths and bond angles that change during the chemical reaction, the RC is therefore a multidimensional coordinate¹⁻³. In many cases the reaction coordinate may be a conformational variable connecting two conformations that can be viewed as the reactants and products of a chemical reaction, unfortunately in most chemical processes the RC is quite difficult to visualize. In this work we are concerned with elementary reactions within the framework of transition state theory in which reactants (**R**) change into products (**P**) passing by a transition state (**TS**), with all three states connected by a given RC⁴.

Understanding chemical reactivity allows one to predict the reaction mechanism and to determine how the activation energy depends on specific proper-

ties of the reactants and products. In this context the identification of these properties and the characterization of the transition state becomes especially important. For the first purpose Density Functional Theory (DFT)⁵⁻⁸ is well suited to describe the electronic reorganization that takes place during a chemical reaction through the definition of global and local reactivity properties. On the other hand, to characterize transition states there is a set of interesting conceptual tools that give complementary insights on their structure and properties⁵. These conceptual tools are: (a) the well known Hammond postulate (HP)⁹ that interrelates the position of the transition structure to the exothermicity of the reaction, the HP states that if the TS is near in energy to a given adjacent stable complex, then it should be also similar in structure to the same complex; (b) the Leffler's postulate¹⁰ suggests a mechanistic interpretation of the so-called Brønsted coefficient (β)¹¹: it is a measure of the location of the TS along the RC, this defines β as a similarity index that can be interpreted as the degree of resemblance of the TS with respect to the product; (c) the Marcus equation (ME)¹² that provides a simple expression for the activation energy in terms of the reaction energy and the structural properties of reactants and products; and (d) the Principle of Maximum Hardness (PMH)¹³⁻¹⁵ that asserts that molecular systems at equilibrium tend to states of high hardness, therefore TS's are expected to present a minimum value of hardness¹⁶⁻¹⁸. Although these principles are not widely applicable they provide a conceptual framework to rationalize transition states and to help characterize the reaction mechanisms. The connection between DFT and classical reactivity concepts is the subject of this chapter.

1.2 DFT Descriptors of Chemical Reactivity.

Within the conceptual frame of DFT, the ground-state energy of a chemical system is a functional of the electron density $\rho(\vec{r})$. This means that all properties of the system are determined by $\rho(\vec{r})$. Since the theorems of Hohenberg-Kohn^{19,20} establishes a correspondence between the electron density and the external potential $v(\vec{r})$, a complete characterization of an N -particle wavefunction needs only N and $v(\vec{r})$ and the energy of the system may be expressed as a function of the electron number N and a functional of the external potential $v(\vec{r})$, so $E[\rho(\vec{r})] \equiv E[N, v(\vec{r})]$. The total differential of the energy is given by^{5,7}:

$$dE = \mu dN + \int \rho(\vec{r}) dv(\vec{r}) d\vec{r}, \quad (1)$$

where

$$\mu = \left(\frac{\partial E}{\partial N} \right)_v \quad \text{and} \quad \rho(\vec{r}) = \left[\frac{\delta E}{\delta v(\vec{r})} \right]_N, \quad (2)$$

are the chemical potential and the ground-state electron density, respectively. The chemical potential is a global property that characterizes the escaping tendency of electrons from the equilibrium system²¹, μ is a function of N and a functional of $v(\vec{r})$, ($\mu \equiv \mu[N, v(\vec{r})]$) and has the following total differential:

$$d\mu = \eta dN + \int f(\vec{r}) dv(\vec{r}) d\vec{r}, \quad (3)$$

where

$$\eta = \frac{1}{2} \left(\frac{\partial \mu}{\partial N} \right)_v \quad \text{and} \quad f(\vec{r}) = \left[\frac{\delta \mu}{\delta v(\vec{r})} \right]_N = \left(\frac{\partial \rho(\vec{r})}{\partial N} \right)_v, \quad (4)$$

are the hardness^{22,23} and the Fukui function^{24,25} of the system, respectively. η can be seen as a resistance to charge transfer, it is a global property of the system and depends on both N and $v(\vec{r})$. $f(\vec{r})$ is a local property of the system and it measures the reactivity of the different sites within the molecule. The total differential of $\eta[N, v(\vec{r})]$ is:

$$d\eta = \gamma dN + \int h(\vec{r}) dv(\vec{r}) d\vec{r}, \quad (5)$$

where

$$\gamma = \frac{1}{3} \left(\frac{\partial \eta}{\partial N} \right)_v \quad \text{and} \quad h(\vec{r}) = \left[\frac{\delta \eta}{\delta v(\vec{r})} \right]_N = \left(\frac{\partial f(\vec{r})}{\partial N} \right)_v. \quad (6)$$

γ is a global property measuring the change in the hardness due to the variation of the electron number²⁶, $h(\vec{r})$ is a local property that measures the fluctuation of the chemical hardness due to a change in the external potential, or through the Maxwell relation, it can be seen as the response of the Fukui function to a change in the total number of electrons.

When a reaction move forward along the RC, a redistribution of the ground-state electron density is occurring, the resulting change of the energy can be rationalized in terms of the response of the system when changing N and $v(\vec{r})$ and can be characterized through the above defined global and local indexes, these are used as chemical reactivity descriptors²⁷. The response of the

system when N is varied for a fixed $v(\vec{r})$ is measured by μ and η while local properties, such as the Fukui function, measure the response of the system for changing the external potential at constant N . Since the Fukui functions are the specific subject of other contributions to this book, here we are going to focus our attention to the analysis of the evolution of global molecular properties during a chemical reaction. However, along the reaction coordinate the external potential certainly changes and to understand the behavior of the system for changing $v(\vec{r})$ at constant N , we will use the polarizability (α), a global property of the system. Chattaraj *et al* have proposed the principle of minimum polarizability (PMP)^{28,29} which states that the natural direction of evolution of any system is toward a state of minimum polarizability. In general the conditions of minimum polarizability and maximum hardness complement the minimum energy criterion for molecular stability, and are criteria that we will use to characterize our systems.

Chemical potential, hardness and its inverse, the softness ($S = 1/2\eta$) are among the most important global properties aimed at describing chemical reactivity. In numerical applications, μ and η are calculated through the following approximate equations based upon the finite difference approximation and the Koopmans' theorem³⁰:

$$\mu \approx -\frac{1}{2}(I + A) \simeq \frac{1}{2}(\varepsilon_L + \varepsilon_H) \quad (7)$$

and

$$\eta \approx \frac{1}{2}(I - A) \simeq \frac{1}{2}(\varepsilon_L - \varepsilon_H), \quad (8)$$

I is the ionization potential, A is the electron affinity, ε_H and ε_L are the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively.

1.3 Reaction Coordinates.

Within the transition state theory it is assumed that a reaction proceeds from one energy minimum to another via a reaction coordinate (RC) passing by an intermediate maximum, this classical picture is displayed in Figure 1(a) represented by an energy profile where the stationary points are connected through the RC. At the transition state the eigenvector for the imaginary frequency characterizes the RC and the whole reaction path may be determined from standard calculations that defines the intrinsic reaction

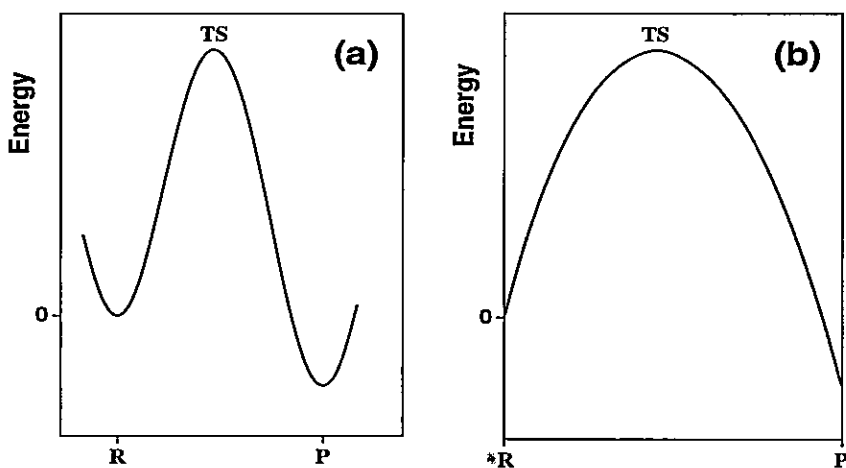


Figure 1. Generic energy profiles along the reaction coordinate (a) and the reduced reaction coordinate (b).

coordinate (IRC) ³¹⁻³³. On the other hand, it is always possible to express the RC in terms of a reduced reaction coordinate (RRC) running from 0 to 1 thus measuring the reaction progress when going from reactants to products. In Figure 1(b) we show a schematic view of the same energy profile but now along a new reduced variable called ω ^{34,35}. It is important to point out that the ω -representation provides a correct and straightforward characterization of the position and the energy of the transition state, this allows to handle chemical process in a quite simple and schematic way, and without losing relevant information.

This chapter is organized as follows, in section 2 we give the theoretical background for rationalizing internal rotation reactions and in section 3 we describe the theoretical tools aimed at rationalizing bond breaking and transfer reactions. Section 4 contains a subject that is a little different although it lies within the study of formation reactions, the characterization of additivity schemes aimed at determining aggregate's properties from the combination of constituent fragments' properties. In the light of the combination of classical reactivity and DFT concepts, in section 5 we briefly analyze few illustrative ex-

amples of rotational isomerization, intramolecular reordering and intermolecular proton transfer reactions. In section 6 we present the conclusions of the present work and suggest few directions for future research.

2 Rotational Isomerization Processes.

In this section we are concerned with the study of the internal rotation process from the perspective of the simultaneous evolution of the potential energy (V), the electronic chemical potential (μ) and the molecular hardness (η). Let us consider a *trans* \rightleftharpoons *cis* conformational transformation occurring through the internal rotation with respect to a given bond in the molecule, in such a case the RC is the torsional angle α that is measured from the *trans* ($\alpha = 0$) to the *cis* ($\alpha = \pi$) conformations. The model potential that we use to describe internal rotations is ³⁶:

$$V(\alpha) = \frac{1}{4}K_V(1 - \cos^2 \alpha) + \frac{1}{2}\Delta V^\circ(1 - \cos \alpha), \quad (9)$$

where the *trans* conformation is taken as the origin of the energy; K_V is the sum of the torsional force constants of the *trans* and *cis* conformations ($K_V = k_t + k_c$) and $\Delta V^\circ = (V(\pi) - V(0))$ is the energy difference between the reference isomers ³⁴⁻³⁶.

In conformational reactions the reduced reaction coordinate ω is called *conformational function* and it measures the reaction progress when going from reactants to products. The conformational function for the internal rotation is defined as:

$$\omega(\alpha) = \frac{1}{2}(1 - \cos \alpha), \quad (10)$$

and in the ω -representation the potential energy is given by:

$$V[\omega] = K_V f[\omega] + \omega \Delta V^\circ, \quad (11)$$

with $f[\omega] = \omega(1 - \omega)$. Since the only requirement on $f(\omega)$ is that it must be symmetric with respect to $\omega = 0.50$, there are many functions qualifying with this condition that can be used to express the potential energy of Eqn.(11).

Since μ and η are global properties of the system, their evolution along ω can be expressed through the same analytic form used for $V[\omega]$ ^{37,38}:

$$\mu[\omega] = K_{\mu}f[\omega] + \omega\Delta\mu^{\circ}, \quad (12)$$

and

$$\eta[\omega] = K_{\eta}f[\omega] + \omega\Delta\eta^{\circ}. \quad (13)$$

The parameters $(\Delta\mu^{\circ}, K_{\mu})$ and $(\Delta\eta^{\circ}, K_{\eta})$ have the same meaning that $(\Delta V^{\circ}, K_V)$ have for $V[\omega]$. To determine the numerical values of the parameters of Eqns.(11)–(13) we use a prescription we gave in previous works^{36–38}. It is important to point out that since V , μ and η depend on the same function $f(\omega)$ it is possible to establish analytic relations between them although the extend of the application of this relations is still matter of research³⁹.

The position of the TS can be determined by differentiating Eqn.(9) and through Eqn.(10) we obtain:

$$\left(\frac{dV}{d\alpha}\right)_{\alpha=\alpha_0} = 0 \Rightarrow \cos \alpha_0 = -\frac{\Delta V^{\circ}}{K_V} \Rightarrow \omega(\alpha_0) \equiv \beta = \frac{1}{2} + \frac{\Delta V^{\circ}}{2K_V}. \quad (14)$$

β is the Brønsted coefficient and following the Leffler interpretation it measures the degree of resemblance of the TS with respect to the products. Putting β in Eqn.(11) yields to the following expression for the energy barrier hindering the internal rotation:

$$V[\beta] \equiv \Delta V^{\ddagger} = \frac{1}{4}K_V + \frac{1}{2}\Delta V^{\circ} + \frac{(\Delta V^{\circ})^2}{4K_V}. \quad (15)$$

This is the Marcus equation¹², it was originally proposed to characterize electron transfer processes but later on have been shown to be useful in the interpretation of the activation energy of many chemical reactions. Note that the Marcus equation is consistent with the Leffler definition of the Brønsted coefficient as the derivative of the activation energy with respect to the reaction energy ΔV° . Indeed the Marcus equation provides the necessary framework for a quantitative analytic representation of the Hammond postulate through the Leffler interpretation of the Brønsted coefficient.

3 Bond Breaking and Transfer Reactions.

3.1 Introduction.

The above analytic results can be used to characterize the transition states of more complex chemical processes since within the transition state theory any chemical reaction can be rationalized in terms of elementary steps that links reactants, transition states and products: $\mathbf{R} \rightarrow (\mathbf{TS})^\ddagger \rightarrow \mathbf{P}$ ⁴. The stationary states are connected by the intrinsic internal reaction coordinate (IRC) that comes out from standard calculations, along the IRC it is possible to define the profiles of energy, chemical potential, hardness and polarizability that allows one to characterize the reaction and the properties of the transition state. To characterize the TS we use again the Marcus equation and the Brønsted coefficient. The energy barrier ΔE^\ddagger is then given by:

$$\Delta E^\ddagger = \frac{1}{4}K + \frac{1}{2}\Delta E^\circ + \frac{(\Delta E^\circ)^2}{4K}. \quad (16)$$

From the knowledge of ΔE° and ΔE^\ddagger we can obtain the parameter K that in turn we use to determine the position of the TS along the IRC, assuming the validity of the Brønsted coefficient already defined:

$$\beta = \frac{1}{2} + \frac{\Delta E^\circ}{2K} \quad (17)$$

It is very important to note that to characterize the position of the TS there is no need of an explicit definition of the reaction coordinate, the Marcus equation provides the necessary framework to get insight on the TS.

3.2 Activation Properties: Chemical Potential, Hardness and the ME.

For isoenergetic reactions the ME reduces to:

$$\Delta E_0^\ddagger \equiv \frac{1}{4}K \quad (18)$$

and the TS is located halfway between reactants and products ($\beta = 1/2$). The quantity ΔE_0^\ddagger is our equivalence with the so called Marcus' intrinsic activation energy. This is the barrier height for the case in which there is no energetic driving force, this quantity should be related to purely electronic properties such as chemical potential and hardness. The ME can now be rewritten as:

$$\Delta E^\ddagger = \Delta E_0^\ddagger + \frac{1}{2}\Delta E^\circ + \frac{(\Delta E^\circ)^2}{16\Delta E_0^\ddagger}. \quad (19)$$

Inspection of Eqn.(19) indicates that when the reaction is exergonic ($\Delta E^\circ < 0$) ΔE^\ddagger is smaller than the intrinsic barrier whereas for endergonic reactions ($\Delta E^\circ > 0$) ΔE^\ddagger becomes larger than the intrinsic barrier. As already mentioned, the intrinsic barrier should be interpreted in terms of electronic and structural properties, in this context in a recent paper we have suggested that the Marcus' intrinsic barrier can be rationalized in terms of the electronic properties μ and η . The following expression relating ΔE_0^\ddagger as been proposed⁴⁰:

$$\Delta E_0^\ddagger = \frac{1}{2}Q_\eta\Delta\mu^\ddagger + \frac{1}{2}Q_\mu\Delta\eta^\ddagger, \quad (20)$$

where $\Delta\mu^\ddagger \equiv [\mu(TS) - \mu(R)]$ and $\Delta\eta^\ddagger \equiv [\eta(TS) - \eta(R)]$ are the activation chemical potential and hardness, respectively. The parameters Q_η, Q_μ have been related to the amount of electronic charge transferred during the chemical reaction, they can be determined numerically through:

$$Q_\eta = \frac{(\Delta E^\ddagger - \Delta E^\circ)}{(\Delta\mu^\ddagger - \Delta\mu^\circ)}, \quad (21)$$

and

$$Q_\mu = \frac{(\Delta E^\ddagger - \Delta E^\circ)}{(\Delta\eta^\ddagger - \Delta\eta^\circ)}; \quad (22)$$

Note that the validity of the PMH leads to opposite curvature for the energy and hardness, this entails a negative value for the parameter Q_μ .

3.3 Reaction Mechanisms.

The concept of reaction mechanism is related to the notion of molecular structure in that any reactive process can be represented by nuclear displacements of the molecular system in going from the reactants to the products. These displacements are related with the forces acting on the system to bring reactants into products. Let assume the force acting on the system depends only on the position along the reaction coordinate, it is then defined as:

$$F(\omega) = -\frac{dE}{d\omega}, \quad (23)$$

assuming that $E(\omega)$ can be expressed as ⁴⁰:

$$E(\omega) = K\omega(1 - \omega) + \omega\Delta E^\circ, \quad (24)$$

then,

$$F(\omega) = -(K + \Delta E^\circ) + (2K)\omega. \quad (25)$$

To have an adequate description of the whole chemical reaction it is useful to distinguish the different processes taking place along the reaction coordinate. In the reactants region an activation process is taking place with the following associated activation work:

$$W_{act} = \int_0^\beta F(\omega)d\omega = \Delta E^\ddagger, \quad (26)$$

in the product region we have a relaxation process, the work associated is:

$$W_{rel} = \int_\beta^1 F(\omega)d\omega = \Delta E^\circ - \Delta E^\ddagger. \quad (27)$$

Isoenergetic reactions present the transition state at $\beta = 1/2$, in absolute values the activation work is equal to the relaxation work. In contrast to this, exoenergetic reactions are characterized by an early transition state ($\beta < 1/2$) and by an activation work smaller than the relaxation work. Finally, an endoenergetic reaction is characterized through a $\beta > 1/2$ and an activation work larger than the relaxation work.

It is important to point out that the use of Eqns. (19) and (20) together with Eqns. (26) and (27), provides the necessary elements to discuss the activation and relaxation works in terms of the activation chemical potential and hardness. This opens new ways to link classical reactivity concepts with the DFT reactivity descriptors.

Now we can identify the activation and relaxation processes as being driven by chemical potential and hardness, respectively. To do so we assume Eqn.(20) valid for all ω and define the energy profile as:

$$E(\omega) = \frac{1}{2}Q_{\eta}\mu(\omega) + \frac{1}{2}Q_{\mu}\eta(\omega). \quad (28)$$

Consequently, the force appears to be splitted into two contributions that are associated to chemical potential and hardness driving processes:

$$F(\omega) = -\frac{1}{2}Q_{\eta} \frac{d\mu}{d\omega} - \frac{1}{2}Q_{\mu} \frac{d\eta}{d\omega}. \quad (29)$$

Using straightforward definitions and considering that $Q_{\mu} < 0$ to comply with the PMH, $F(\omega)$ can be splitted as:

$$F(\omega) = -F_{\mu}(\omega) + F_{\eta}(\omega). \quad (30)$$

This equation permits a qualitative analysis of $F(\omega)$ in terms of the sign that it takes when moving along ω :

$$(0 \leq \omega < \beta) : \quad F(\omega) < 0 \quad \Rightarrow \quad F_{\mu}(\omega) > F_{\eta}(\omega) \quad (31)$$

and when going from the reactants to the transition state (the activation process), it is the chemical potential term that drives the reaction. At the transition state we have that:

$$(\omega = \beta) : \quad F(\beta) = 0 \quad \Rightarrow \quad F_{\mu}(\beta) = F_{\eta}(\beta) \quad (32)$$

and both driving forces are equilibrated and cancels to each other. When stepping down from the transition state to the products (the relaxation process), we have:

$$(\beta < \omega \leq 1) : \quad F(\omega) > 0 \quad \Rightarrow \quad F_{\eta}(\omega) > F_{\mu}(\omega) \quad (33)$$

and this part of the reaction is controlled by the hardness term as the system rearrange himself to reach a maximum hardness configuration. In summary, this simple model suggest that activation processes are basically driven by μ whereas relaxation processes are driven by η .

4 Formation Reactions: Fragment Chemistry.

If it is possible to estimate safely the molecular electronic descriptors from constituent fragments, then it would be also possible to estimate the corresponding properties of transition states from combination of known reactants structures and properties through the application of adequate additivity schemes. Within this context it is worth to explore how properties of fragment combine themselves to approach quantitatively the values measured or calculated for a given resulting molecule or aggregate. In such a situation the suitability of the combined models reviewed in this work may increase considerably.

The establishment of rigorous foundations for the concept of electronegativity and hardness allows for the introduction of combination schemes relating the properties of the constituent fragments to the properties of the resulting molecules or aggregates. Although the bonding potential and redistribution of the electron density among the fragments are not considered in these procedures, the use of combination rules is quite appealing mainly because of their predictive quality. To relate the molecular electronegativity to those of the constituent atoms or fragments Sanderson proposed a geometric mean equalization principle that defines the molecular electronegativity as the geometric mean of the electronegativities of the n_f constituent atoms or fragments ⁴¹:

$$\mu_{n_f}^s = - \left(\prod_x^{n_f} |\mu_x| \right)^{1/n_f}, \quad (34)$$

where μ_x is the chemical potential of fragment x . From the Sanderson's formula for μ , we estimate molecular or aggregate hardnesses as ^{42,43}:

$$\eta_{n_f}^s = \frac{\mu_{n_f}^s}{n_f} \sum_x^{n_f} \frac{\eta_x}{\mu_x}, \quad (35)$$

η_x is the hardness of fragment x .

There are other methods for calculating μ and η , for example Ghosh *et al* ⁴⁴ expresses the aggregate hardness as the reciprocal of the aggregate softness computed as the average of the softness of the constituent fragments, accordingly it is calculated as:

$$\frac{1}{\eta_{n_f}^g} = \frac{1}{n_f} \sum_x \frac{1}{\eta_x}, \quad (36)$$

Another aggregation scheme has been introduced by Chattaraj *et al*⁴⁵ which expresses the hardness of the aggregate molecule as the geometric mean of the respective hardness of the constituent fragments as follows:

$$\eta_{n_f}^d = \left(\prod_x \eta_x \right)^{1/n_f} \quad (37)$$

More recently we have proposed expressions for determining μ and η of a composite system, these are^{46,47}:

$$\frac{1}{\mu_{n_f}^o} = \sum_x \left(\frac{f_x}{\mu_x} \right), \quad (38)$$

and

$$\eta_{n_f}^o = (\mu_{n_f}^o)^2 \sum_x \frac{1}{(\mu_x)^2} [f_x \eta_x - h_x \mu_x], \quad (39)$$

where h_x is a measure of the fluctuation of the chemical hardness due to a change in the external potential, or through the Maxwell relation, it can be seen as the response of the Fukui function to a change in the total number of electrons:

$$h_x = \left(\frac{\delta \eta_x}{\delta v} \right)_N = \left(\frac{\partial f_x}{\partial N} \right)_v. \quad (40)$$

Determination of the chemical potential and hardness of a composite system from the property of the isolated fragments by means of the above equations produce results that are in very good agreement with the ones determined with other schemes, as can be verified in the next section.

5 Applications.

5.1 Computational Details.

Full geometry optimization for all the species along the reaction coordinates for all the reactions considered in this paper have been performed using the Gaussian 94/98 packages^{48,49}. In addition to this, frequency calculations were performed on the reference species and transition states for a complete characterization of these states.

The results for the internal rotation of HXNX (X=O,S) were obtained through DFT(B3LYP) calculations with standard 6-311G** basis sets. For the inversion of diimine, the reaction coordinate is the angle NNH along which we have performed DFT(B3LYP)/6-311G** calculations to determine the profiles of the global properties we are interested in. In this case, we had to perform extra calculations since the standard basis set was not able to give reasonable results for polarizability, to obtain reasonable values for this property, we have used the Sadlej's basis set⁵⁰ that is designed to reproduce molecular electric properties, especially polarizabilities. For double proton transfer reactions we present results at the RHF level of theory with the standard 6-311G** basis set.

5.2 Rotational Isomerization of HXNX.

In this section we will discuss results for the *trans* \rightleftharpoons *cis* isomerization reaction of HXNX (X=O,S), Figure 2. Among a number of systems we have studied during the last years, we have chosen nitrous acid HO-NO and its sulfur analogue HS-NS because they are quite simple systems that can undergo rotational isomerization. Besides, compounds containing an S(O)-N bond may serve as a prototype for the S(O)-N linkage in some oximes and inorganic compounds^{34,35,51} that we are interested in.

In Figure 3 we display the profiles of energy, chemical potential, hardness and polarizability along the torsional angle defined as the dihedral angle HXNX. Note that the corresponding scales are not explicit to stress the qualitative information that is interesting within the context of this article.

Figure 3 provides an illustration of the validity of the principles of maximum hardness and minimum polarizability in these rotational systems. The energy minimum is associated with a maximum of hardness and a minimum of polarizability whereas the TS is associated with a hardness minimum and a

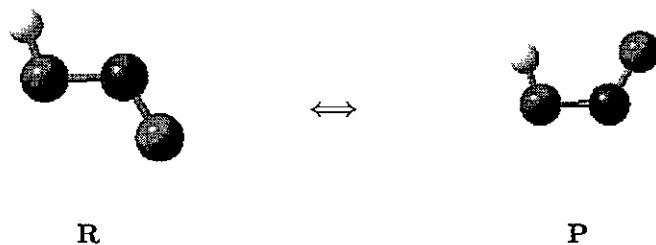


Figure 2. Representation of the conformational equilibrium in the rotational isomerization reaction of HXNX (X=O,S) molecules.

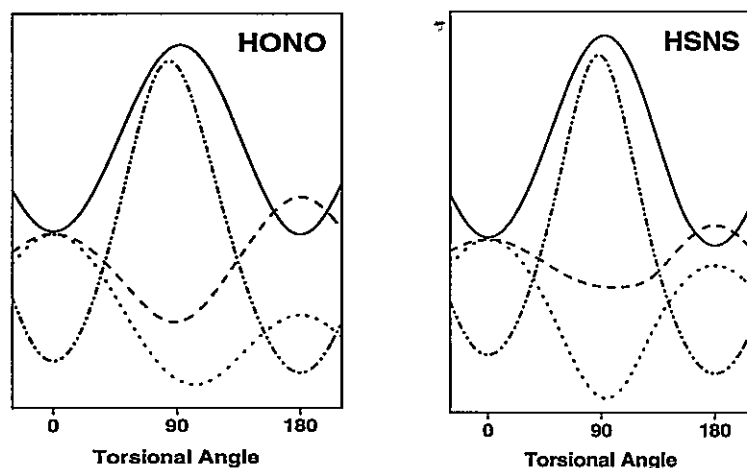


Figure 3. Profiles of energy (—), chemical potential (···), hardness (---) and polarizability (-·-) along the torsional angle for the internal rotation isomerization reaction of HXNX molecules.

maximum of polarizability. In these cases the maximum hardness and minimum polarizability condition nicely complement the minimum energy criterion for molecular stability. In Table 1 (columns two and three) we quoted the characteristic values of the properties under study.

Table 1. Relevant activation and reaction properties for the processes under study (E , μ , and η in kcal/mol; α is in atomic units.)

| Properties | HONO | HSNS | HNNH | (HCOOH) ₂ | (HCSSH) ₂ |
|--------------------------|----------|----------|----------|----------------------|----------------------|
| ΔE° | -0.2396 | -1.1207 | 3.3534 | 0.0 | 0.0 |
| ΔE^\ddagger | 13.0050 | 15.3879 | 49.5864 | 17.9311 | 37.3895 |
| $\Delta \mu^\circ$ | -5.5221 | -1.9453 | -1.1860 | 0.0 | 0.0 |
| $\Delta \mu^\ddagger$ | -10.2284 | -12.1109 | 22.6876 | -1.7633 | -1.9327 |
| $\Delta \eta^\circ$ | 2.5100 | 1.1295 | 0.4706 | 0.0 | 0.0 |
| $\Delta \eta^\ddagger$ | -6.2123 | -3.5768 | -19.7258 | -6.1245 | -7.7497 |
| $\Delta \alpha^\circ$ | -0.1030 | -0.4130 | 0.4670 | 0.0 | 0.0 |
| $\Delta \alpha^\ddagger$ | 2.7100 | 6.8190 | 0.2760 | 1.0890 | 17.6313 |

5.3 Intramolecular Rearrangement Reactions.

We refer the reader to the different types of intramolecular rearrangement reactions that we have studied recently, keto-enol and imine-enamine tautomerisation processes have studied in the light of the ideas depicted in this chapter with very encouraging results^{52,53}. A number of systems undergoing intramolecular rearrangement have also been studied emphasizing their Hammond or anti-Hammond character in relation with the PMH⁵⁴. Among these rearrangement reactions we want to include in this review the inversion mechanism for the *trans* \rightleftharpoons *cis* isomerization reaction of diimide (HN=NH) that has been for long time a challenging system for theoretical methods. Diimine or diazene is a short lived species that has been identified as one of the decomposition products of the hydrazoic acid and hydrazine reaction. Although diimine cannot be isolated under ordinary conditions, its infrared spectrum suggest that isomerization may occurs through the inversion mechanism⁵⁵.

In Figure 4 are displayed the profiles of energy, chemical potential, hardness and polarizability along the inversion coordinate.

The profiles displayed in Figure 4 exhibit the trends that are expected from the PMH and PMP, the TS has been found to be softer and more polarizable than the reference stable conformations. The correctness of the trends shown by the different properties indicate that inversion may be the right mechanism

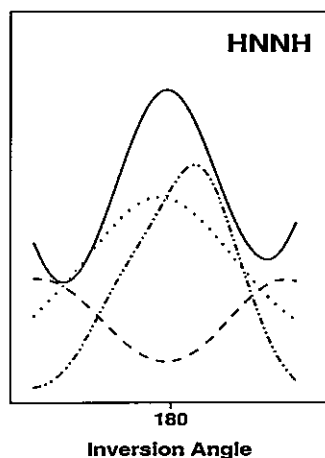


Figure 4. Profiles of energy (—), chemical potential (···), hardness (- - -) and polarizability (- · -) along the inversion coordinate for the inversion isomerization reaction of diimine.

for isomerization of diimine, the other mechanisms that has been suggested is a rotation around the double bond but it presents a higher energy barrier 39,55.

5.4 Double Proton Transfer in $(HCXXH)_2$.

Proton transfer (PT) is one of the simplest and fundamental reactions in chemistry, it is important in oxidation-reduction reactions occurring in many chemical and biological process. Double proton transfer (2PT) in simple systems has been used to model key properties of many chemically and biologically important multiproton transfer systems.

Recently we have performed an extensive study of 2PT reactions in bimolecular complexes formed by combinations of molecules of the type $CHX-YH$ ($X, Y=O, S$) We have observed an interesting feature: the energetic properties of all bimolecular complexes lie within an interval whose extrema are defined by the corresponding energetic values of $(HCOOH)_2$ and $(HCSSH)_2$. Therefore in this review we decided to focus our attention on the synchronous 2PT processes occurring in $(HCOOH)_2$ and $(HCSSH)_2$, as indicated schematically

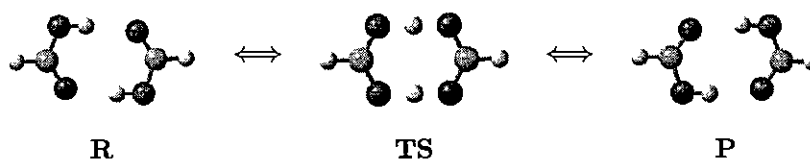


Figure 5. Schematic reaction diagram for double-proton transfer.

in Figure 5.

Characterization of various properties of the transition states of 2PT reactions allows one to identify the specific interactions stabilizing the complexes and helps determine the physical nature of the energy barrier for the simultaneous transfer of two protons. The profiles of E , μ , η and α for double proton transfer of formic acid and dithioformic acid dimers, were obtained through single points calculations of the fully optimized structures indicated by the IRC procedure, they are displayed in Figure 6. We first note that in both reactions μ presents intermediate values between E and η . As can be seen, the profiles of μ decreases to reach a quite flat region around the TS, where three critical points can be perceived. The profiles of η and α indicate the simultaneous validity of the principles of maximum hardness and minimum polarizability. Transition state structures are therefore characterized through a maximum value of energy and polarizability and a minimum value of hardness, as required by the PMH and PMP⁴³.

In Figure 7 we display the force profiles determined by numeric differentiation of the energy profiles given in Figure 6. Note that $F(\omega)$ is negative in the reactants region and it is positive in the products region, this allows to distinguish the different processes taking place along the reaction coordinate as shown in section 3. It is interesting to note that the force profiles present critical points around the TS, this may be defining regions where the specific interactions and electronic reordering may be of different nature than those encountered at the vicinity of reactants and products. These results suggest that determination of local properties such as electronic population and Fukui functions at the vicinity of the TS may be useful as complementary information for characterizing more specific aspects of the reaction mechanism.

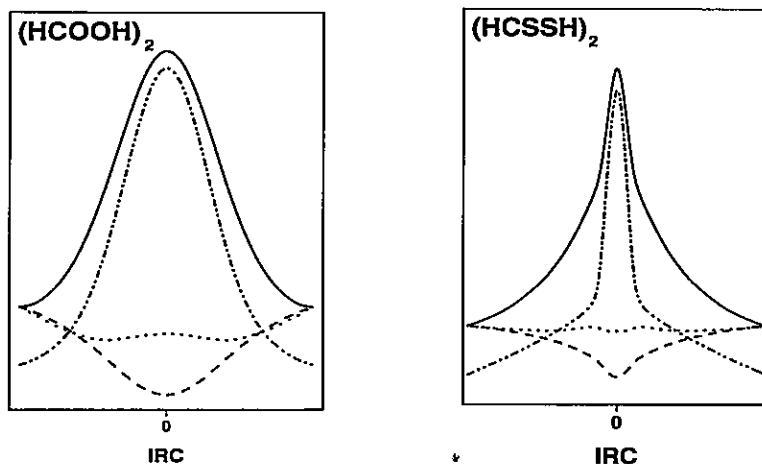


Figure 6. Profiles of E (—), μ (···), η (---) and α (-·-·) in 2PT reactions.

5.5 Formation Reactions.

To illustrate the validity of additivity schemes to determine μ and η we are going to review results that we have obtained for the formation of cyclic bimolecular structures which are established by two hydrogen bonds. Combinations of monomeric units of formic (HCO-OH), thione-formic (HCS-OH), thiol-formic (HCO-SH) and dithioformic (HCS-SH) acids, leads to ten cyclic bimolecular complexes, C1 to C10. For the ten resulting bimolecular complexes we have determined μ and η using the different additivity schemes discussed in section 4 with $n_f = 2$, the results are quoted in Tables 2 and 3. Second column contains the *ab initio* reference values. In Table 3 appear two values for the hardness determined from Eqn.(39), since it is no possible to obtain an explicit evaluation of h_x , we first calculated η using $h_x = 0$ (fourth column); a rough estimation of h_x from four symmetric reference dimers was enough to get a new set of hardness values from Eqn.(39), these are quoted in the fifth column of Table 3.

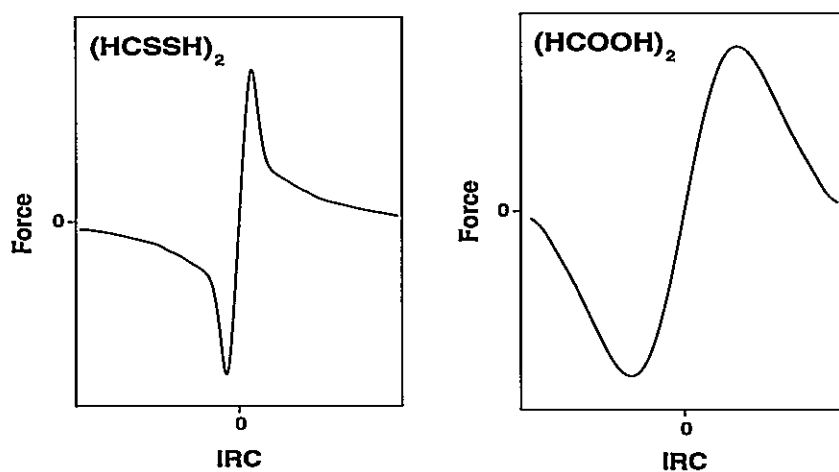


Figure 7. Profiles of the force along the IRC in 2PT reactions.

Table 2. Comparison of aggregate's chemical potential determined from different addition schemes. (All values are in atomic units.)

| System | μ | Eq.(34) | Eq.(38) |
|--------------|---------|---------|---------|
| HCOOH··HCOOH | -0.1503 | -0.1554 | -0.1554 |
| HCOOH··HCSOH | -0.1411 | -0.1476 | -0.1463 |
| HCSOH··HCSOH | -0.1462 | -0.1402 | -0.1402 |
| HCOOH··HCOSH | -0.1402 | -0.1470 | -0.1456 |
| HCOOH··HCSSH | -0.1601 | -0.1543 | -0.1540 |
| HCOSH··HCSOH | -0.1320 | -0.1397 | -0.1396 |
| HCSSH··HCSOH | -0.1604 | -0.1466 | -0.1471 |
| HCOSH··HCOSH | -0.1331 | -0.1391 | -0.1391 |
| HCSSH··HCOSH | -0.1511 | -0.1460 | -0.1466 |
| HCSSH··HCSSH | -0.1576 | -0.1532 | -0.1532 |

It can be noticed that in most cases, Eqns. (38) and (39) gives a better approach to the reference *ab initio* value than do the other approaches. We conclude that our additivity scheme for μ and η , which incorporates the fragment condensed Fukui function (which is approximated by the electronic population of the fragment), yields consistently better results compared to those obtained

Table 3. Comparison of aggregate's hardness determined from different addition schemes. (All values are in atomic units.)

| System | η | Eq.(35) | Eq.(39) | Eq.(39) | Eq.(36) | Eq.(37) |
|---------------|--------|---------|---------|---------|---------|---------|
| HCOOH...HCOOH | 0.3204 | 0.3138 | 0.3138 | 0.3204 | 0.3138 | 0.3138 |
| HCOOH...HCSOH | 0.2251 | 0.2652 | 0.2565 | 0.2575 | 0.2591 | 0.2631 |
| HCSOH...HCSOH | 0.2169 | 0.2206 | 0.2206 | 0.2169 | 0.2206 | 0.2206 |
| HCOOH...HCOSH | 0.2609 | 0.2863 | 0.2813 | 0.2842 | 0.2849 | 0.2861 |
| HCOOH...HCSSH | 0.2021 | 0.2563 | 0.2416 | 0.2433 | 0.2440 | 0.2503 |
| HCOSH...HCSOH | 0.2215 | 0.2408 | 0.2407 | 0.2388 | 0.2390 | 0.2399 |
| HCSSH...HCSOH | 0.1966 | 0.2108 | 0.2102 | 0.2067 | 0.2096 | 0.2098 |
| HCOSH...HCOSH | 0.2607 | 0.2608 | 0.2608 | 0.2607 | 0.2608 | 0.2608 |
| HCSSH...HCOSH | 0.2000 | 0.2319 | 0.2303 | 0.2288 | 0.2261 | 0.2282 |
| HCSSH...HCSSH | 0.1965 | 0.1996 | 0.1996 | 0.1965 | 0.1996 | 0.1996 |

following the other schemes. In fact this brings out the vital importance of the *weight* of the constituent fragments within the composite system. The consequent encouraging results open up the possibility that better approximations of the Fukui function can enhance the quality of prediction of global aggregate properties from the constituent fragment properties. Characterization of TS properties using these addition schemes under the constraint imposed by the reactivity models seems to be an interesting subject to explore in the future.

6 Concluding Remarks.

In this paper we wanted to point out that classical concepts of reactivity in connection with DFT descriptors are adequate and powerful tools for characterizing chemical reactions. Within the framework of the Hammond postulate and Marcus equation we have introduced the principle of maximum hardness to check the expected consistency between energetic and electronic properties. A number of useful formulae aimed at rationalizing chemical reactions in terms of the change of relevant electronic properties along the reaction coordinate have been derived and used for understanding the qualitative behavior of processes having different values for the reaction energy. Many of the relationships that have been discussed in this review have been applied with success in the quantitative rationalization of different kind of chemical reactions.

The conceptual classical model used to represent chemical reactions provides

the necessary elements to discuss the activation and relaxation processes in terms of the activation chemical potential and hardness. An important qualitative result of our study is that in a chemical reaction the activation process is controlled by the change in the chemical potential while the relaxation process is controlled by the change in the chemical hardness. We believe that this qualitative observation, although certainly not general, may open new ways to link classical reactivity concepts with the DFT reactivity descriptors.

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Characterization of copper clusters through the use of density functional theory reactivity descriptors

Pablo Jaque and Alejandro Toro-Labbé^{a)}

Laboratorio de Química Teórica Computacional (QTC), Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Correo 22, Santiago, Chile

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In this paper we study nine neutral copper clusters through the theoretical characterization of their molecular structures, binding energy, electronic properties, and reactivity descriptors. Geometry optimization and vibrational analysis were performed using density functional theory calculations with a hybrid functional combined with effective core potentials. It is shown that reactivity descriptors combined with reactivity principles like the minimum polarizability and maximum hardness are operative for characterizing and rationalizing the electronic properties of copper clusters. © 2002 American Institute of Physics. [DOI: 10.1063/1.1493178]

I. INTRODUCTION

The interest in the study of small metal clusters has grown considerably in the last years because new experimental and theoretical techniques have been developed allowing detailed characterizations of this type of systems.¹ Much information is now available concerning clusters' spectroscopy, structure, and their chemical reactivity toward small molecules. Transition metal clusters are particularly interesting for their potential use in many processes like heterogeneous catalysis, in organometallic chemistry or new electronic materials.¹⁻³

Cluster properties are very sensitive to the number of atoms, and they can sometimes change dramatically with the addition or removal of one atom from the cluster. The research in cluster chemistry has been guided to study the dependence of different properties upon the size of the cluster, and hopefully how these properties tend to the bulk values. Properties such as ionization potentials, electron affinities, chemical reactivity, investigations of ion abundances, and dissociation energies of alkali-metal and transition-metal clusters have been reported.⁴⁻⁹ In particular, copper clusters have been extensively studied both experimentally and theoretically.¹⁰⁻²⁹

In this paper we provide a new viewpoint to understand and if possible to predict properties of atomic aggregates. In this context, the aim of this paper is to characterize neutral copper clusters in terms reactivity descriptors that have already been used with success in rationalizing different kinds of molecular structures and chemical reactions.^{30,31} Density functional theory (DFT) (Ref. 32) has provided the basis for rigorous mathematical definitions of reactivity descriptors like chemical potential (μ), electronegativity (χ), chemical hardness (η), softness ($S=1/\eta$), etc. All of these are well established global quantities in chemical reactivity studies and are going to be used in this paper to characterize copper clusters. Although local and nonlocal quantities such as the condensed Fukui function,^{32,33} local softness,³² and

electrophilicity³⁴ have also been introduced in the theory to characterize specific sites within a molecule, in the present study we are going to focus our attention on the study of global reactivity indexes.

The understanding of any molecular system and its reactivity requires the knowledge of the energy hypersurface, however, the computational cost involved in determining such a surface is very high especially in metal cluster systems. In this context, great attention is paid to the computation of DFT-descriptors as indicators of reactivity and stability. This procedure may avoid the detailed study of the energy hypersurface.

The chemical potential (μ) characterizes the escaping tendency of electrons from equilibrium, and it is the Lagrange multiplier associated with the normalization constraint in DFT that has been identified as the negative of the electronegativity ($\mu=-\chi$).³⁵ On the other hand the hardness (η) can be seen as a resistance to charge transfer and softness ($S=1/\eta$) that has been qualitatively related to the polarizability (α) of the system.^{30,36-38}

Although the use of DFT-based reactivity concepts in the field of solid state systems is quite meager, there are a few interesting applications. The hardness concept has been used by Del Pino *et al.*³⁹ to study segregation of As and Ga in germanium crystallites, and by Mendizabal *et al.*⁴⁰ to study the charge capacity of TiS₂ intercalated with Li.

A major focus of attention and discussion in the application of DFT to chemical reactivity is the principle of maximum hardness (PMH) proposed by Pearson.³⁸ The PMH asserts that molecular systems at equilibrium present the highest value of hardness. Parr and Chattaraj⁴¹ provided a rigorous proof for this principle based on a combination of statistical mechanics and the fluctuation-dissipation theorem, they concluded that the PMH holds under the constraints that the chemical potential and the external potential ($v(r)$) must remain constant upon distortion of molecular structures. However many studies show that the PMH may hold even though μ and $v(r)$ vary during the chemical processes.^{42,43}

More recently, on the basis of an inverse relationship

^{a)}Electronic mail: atola@puc.cl

between hardness and polarizability, Chattaraj *et al.* have proposed a minimum polarizability principle (MPP) (Ref. 44, 45) which states that the natural direction of evolution of any system is toward a state of minimum polarizability. There are many studies confirming the validity of the MPP on different kind of reactions and systems. We have verified the MPP in internal rotations reactions, vibrational dynamics,⁴⁵ and proton transfer reactions.⁴³ More recently, Hohm⁴⁶ studied complete fragmentation reactions for a large number of molecules containing atoms of the first and second periods as well as Fe and Os, he found that the most stable isomer has the lowest polarizability in agreements with the MPP.

In the context of the characterization of chemical reactions and reactivity descriptors, the PMH and MPP are widely accepted electronic structures principles, that complement the minimum energy criterion for molecular stability. With the aim of assessing the use of the aforementioned DFT-concepts and principles in the characterization of solid state systems, we perform in this paper a detailed study of the energetic and electronic properties of Cu_n ($n=1-9$), with special attention on the performance of the different descriptors to get information on the behavior of copper clusters.

In the next section we present a summary of the theoretical elements we use here; Sec. III contains the computational details; Sec. IV is devoted to the results and discussion; and in Sec. V we draw our conclusions.

II. THEORETICAL BACKGROUND

In DFT, the chemical potential and molecular hardness for the N -electron system with total energy E and external potential $v(r)$ are defined as the following first and second derivatives of the energy with respect to N :^{32,35,36}

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{v(r)} = -\chi \quad (1)$$

and

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(r)} = \frac{1}{2} \left(\frac{\partial \mu}{\partial N} \right)_{v(r)}. \quad (2)$$

In numerical applications, μ and η are calculated through the following approximate versions of Eqs. (1) and (2), based upon the finite difference approximation and the Koopmans theorem,³²

$$\mu \approx -\frac{1}{2}(\text{IP} + \text{EA}) \approx \frac{1}{2}(\varepsilon_L + \varepsilon_H) \quad (3)$$

and

$$\eta \approx \frac{1}{2}(\text{IP} - \text{EA}) \approx \frac{1}{2}(\varepsilon_L - \varepsilon_H). \quad (4)$$

IP is the ionization potential, EA is the electron affinity, ε_H and ε_L are the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively. The electrophilicity index is in turn defined as³⁴

$$\omega = \frac{\mu^2}{2\eta}. \quad (5)$$

This quantity is a measure of the propensity of a system that acquires electronic charge from the surroundings. Considering clusters or metallic surfaces as binding environments, ω can be useful in analyzing the interaction with small molecules. It is possible to define a local version of ω , by using the additivity property of softness, i.e., $\omega = (\mu^2/2)S = (\mu^2/2)\sum_x s_x$, where s_x corresponds to the local softness of the specific site x within the cluster, then $\omega_x = (\mu^2/2)s_x$.

The response of the system is measured by μ and η when N is varied for a fixed $v(r)$. In contrast to this, the polarizability of the system may be used to understand the behavior of the system for changing $v(r)$ at constant N . The mean polarizability is calculated from the polarizability tensor components as

$$\langle \alpha \rangle = \frac{1}{3}(\alpha_{XX} + \alpha_{YY} + \alpha_{ZZ}). \quad (6)$$

The static polarizability represents one of the most important observables for the understanding of the electronic properties of clusters, it is proportional to the number of electrons of the systems, and it is very sensitive to the delocalization of valence electrons as well as to the structure and shape of the system.

III. COMPUTATIONAL METHODS

Electronic structure calculations for metals require the treatment of electron correlation, in this context, density functional methods provide a good alternative to post-Hartree-Fock methods. The functionals that we use are the Becke-3 for exchange and Perdew-Wang 91 for correlation (B3PW91),^{47,48} and the basis set used for copper atoms is LANL2DZ for effective core potentials.⁴⁹ The geometry optimization of copper clusters were performed in redundant internal coordinates as described by Schlegel and co-workers.⁵⁰ Vibrational analysis were performed in order to be sure that the structures obtained corresponds to stable clusters. All calculations have been carried out using the GAUSSIAN 98 package.⁵¹

Chemical potential and hardness were obtained through Eqs. (3) and (4), respectively, using ionization potentials and electron affinities, and the results were compared to $\mu^{(H,L)}$ and $\eta^{(H,L)}$ obtained through the use of the HOMO and LUMO orbital energies. Indeed, we have calculated the energy of cations and anions at the geometry of the neutral systems to determine the vertical $\text{IP} = [E(N-1) - E(N)]$ and $\text{EA} = [E(N) - E(N+1)]$ values from the standard ΔSCF procedure. These values are then used in Eqs. (3) and (4) to obtain what we called $\mu^{(\text{IP,EA})}$ and $\eta^{(\text{IP,EA})}$. Note that in all cases the ground state of neutral and ionic systems correspond to their lowest multiplicity.

The polarizability tensor components were determined analytically as the second derivative of the energy with respect to the cartesian components of the electric field ($\alpha_{ij} = -(\partial^2 E / \partial F_i \partial F_j)_{F=0}$). For the calculation of the dipole polarizability, the use of pseudopotentials is well justified because this is primarily a property of the outer shells electrons of the atoms and the core electrons contributions are expected to be negligible.

TABLE I. Experimental and theoretical estimations of structural and electronic properties for Cu_2 . r_0 =equilibrium distance; ν =vibrational frequency; BE=binding energy; IP=vertical ionization potential; EA=vertical electron affinity. In brackets is reported the % error (expt.-calc.).

| Property | B3PW91 (this work) | GGA (this work) | LSDA ^a | LSDA ^b | Experiment |
|----------------------|-----------------------|--------------------|-------------------|-------------------|----------------------------|
| $r_0/\text{Å}$ | 2.25(-1.35) | 2.27(-2.25) | 2.18(1.80) | 2.21(0.45) | 2.22 ^c |
| ν/cm^{-1} | 260(1.89) | 236(10.94) | 292(-10.19) | 269(-1.51) | 265 ^c |
| BE/eV | 1.93(7.21) | 2.21(-6.25) | 2.72(-30.77) | 2.22(-6.73) | 2.08 ^d |
| IP/eV | 7.8016(1.30) | 8.36(-5.77) | 8.61(-8.93) | 8.73(-10.45) | 7.9042±0.0008 ^e |
| EA/eV | 0.5880(29.67) | 0.93(-11.24) | 0.97(-16.03) | 1.15(-37.56) | 0.836±0.006 ^f |
| | | | | 0.96(-14.83) | |

^aReference 25.^bReference 26.^cReference 27.^dReference 28.^eReference 29.^fReference 18.

IV. RESULTS AND DISCUSSION

A good estimation of ionization potentials and electron affinities is crucial for a reliable estimation of chemical potential and hardness. These properties are quite sensitive to the exchange and correlation functional used in the DFT calculations. In this context, De Proft *et al.*⁵² have investigated the performance of many DFT methods in the computation of IP and EA for atomics and simple molecular systems with the results that hybrid functionals gave good estimations for these properties. In light of these data, Perdew–Wang 91 for correlation and Becke-3 for exchange seems to be a reasonable choice for the functionals used in this paper.

First we have tested the validity of the scheme of calculation used here by comparing our results of Cu_2 with previously and recently published theoretical data based on local spin density approximation (LSDA) (Refs. 25, 26) and with the available experimental data.^{18,27–29} We have also performed all electron calculations on Cu_2 using the generalized gradients approximation (GGA) with the exchange-correlation functional Perdew–Burke–Ernzerhof⁵³ and a DZVP2 basis set implemented in the ALLCHEM program.⁵⁴ All these results are quoted in Table I.

We first note in Table I that our results of structure, frequency, ionization potential, and binding energy are in good agreement with the experimental and others theoretical data. Only vertical electron affinity is unsatisfactorily estimated. It is well known that electron affinities are considerably more difficult to calculate accurately than ionization energies, basically due to the fact that ionization is an endothermic process while electron attachment can either be endothermic or exothermic. Electron affinities are much smaller in magnitude than ionization energies, and the additional electron tends to make the charge distribution in the anion more diffuse than in neutral and cationic systems. To account for the spatial extent of the outer orbitals, it would be necessary to include more diffuse basis functions in the atomic basis set used in the calculations.^{55,56}

In a recent paper Balbuena *et al.*²⁰ have calculated the adiabatic EA at the same level of theory used by us lowering the error from 30% to 26%. Calaminici *et al.*^{22,26} have reported all electron DFT calculations of EA's of copper clusters improving the agreement with experimental data. In Table I, fifth column, are quoted two of their values for EA, the second value was obtained through a scaling procedure

that lowered the error to 15%. On the other hand, the all electrons GGA calculations that we have performed on the Cu_2 led to a considerably better value of EA although our original estimation of the other properties were not improved. Taking into account that most properties reported in Table I are in quite good agreement with the experimental data and having reached a fair compromise between the quality of the result and the computational cost, we conclude that the level of calculation chosen is good enough to account for the structural, energetic, and electronic properties of Cu_n ($n = 1-9$).

A. Structure and stability of copper clusters

1. The structure of Cu_n ($n=2,9$)

In Fig. 1 are displayed the optimized structures of the ground state of neutral copper clusters from dimer to nonamer. Note that Cu_2 is a 1D structure, Cu_3 to Cu_6 are 2D systems, while Cu_7 to Cu_9 are 3D systems; all these structures are energy minima. In Table II are quoted the values of the average Cu–Cu bond length ($\langle r_{\text{Cu-Cu}} \rangle$) and the mean coordination number (CN) with the size of the cluster, CN was calculated as the arithmetic mean of the bond lengths of the first neighbors at each site. The variation of $\langle r_{\text{Cu-Cu}} \rangle$ with n shows that structural transitions are occurring when going from 1D to 2D and from 2D to 3D clusters, as illustrated in Fig. 2. As expected, the three-dimensional clusters are those that better approach the experimental distance in the bulk metal (2.556 Å).⁵⁷ On the other hand, we note that CN increases linearly with n , and this behavior is indicative of an increase of the electronic delocalization degree and of the binding force.

2. Binding energy

In Table III are displayed the values of total energy for the neutral copper clusters together with the binding energies (BE), or total atomization energies, that have been calculated as

$$\text{BE} = nE_{\text{Cu}} - E_{\text{Cu}_n} \quad (7)$$

Also included in Table III are the experimental BE's (Refs. 12, 13) that were determined from a thermodynamical cycle using the results of collision induced dissociation (CID) ex-

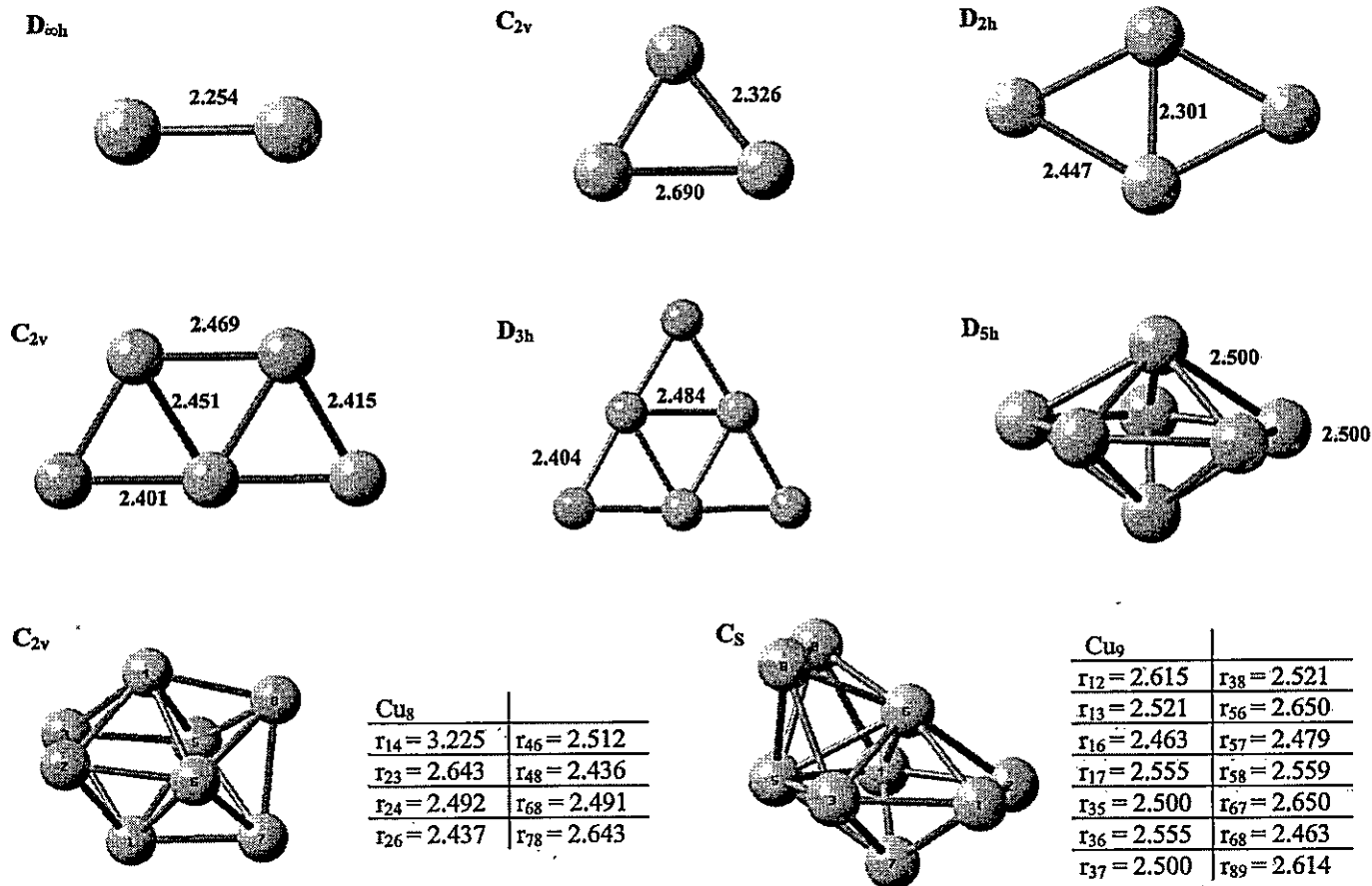


FIG. 1. Ground-state structures of neutral copper clusters, Cu_n (n=2-9).

periments of anionic and cationic copper clusters together with electron affinities or detachment energies and ionization potentials of neutral clusters reported in the literature.^{10,11,18,29} It is interesting to stress the fact that our BE values lie within the range imposed by the CID experimental values being closer to the CID of anionic clusters. In Fig. 3 we display theoretical and experimental binding energies as a function of the cluster size. We observe that our results follow correctly the quantitative and qualitative trends of the experimental data.

Another property included in Table III is the binding energy per atom (BE/n), that is expected to reach the metal

TABLE II. Average bond length $\langle r_{\text{Cu-Cu}} \rangle$ in Å and mean coordination number (CN) of Cu_n clusters.

| Cluster | $\langle r_{\text{Cu-Cu}} \rangle$ | CN |
|-------------------|------------------------------------|-----|
| Cu | | |
| Cu ₂ | 2.254 | 1.0 |
| Cu ₃ | 2.447 | 2.0 |
| Cu ₄ | 2.418 | 2.5 |
| Cu ₅ | 2.429 | 2.8 |
| Cu ₆ | 2.431 | 3.0 |
| Cu ₇ | 2.500 | 4.3 |
| Cu ₈ | 2.501 | 4.5 |
| Cu ₉ | 2.534 | 5.1 |
| Expt ^a | 2.556 | 12 |

^aReference 57.

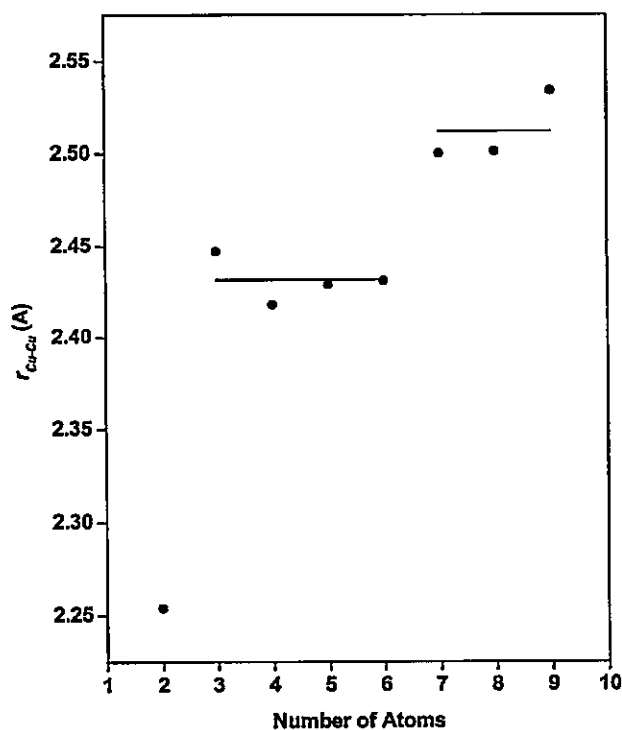


FIG. 2. Dependence of the average Cu-Cu bond length ($\langle r_{\text{Cu-Cu}} \rangle$) with the size of the cluster.

TABLE III. B3PW91/LANL2DZ energy (a.u.) of the fully optimized structures of copper clusters Cu_n ($n = 1-9$) and binding energies BE and BE/ n (in eV).

| Cu_n | $-E$ | BE | BE/ n | BE(expt) ^a | BE(expt) ^b |
|-----------------|------------|---------|---------|-----------------------|-----------------------|
| Cu | 196.15426 | | | | |
| Cu ₂ | 392.37926 | 1.9250 | 0.9625 | 2.04±0.17 | 1.81±0.14 |
| Cu ₃ | 588.57325 | 3.0061 | 1.0020 | 3.19±0.26 | 2.57±0.27 |
| Cu ₄ | 784.80931 | 5.2320 | 1.3080 | 5.91±0.33 | 4.60±0.81 |
| Cu ₅ | 981.03363 | 7.1384 | 1.4277 | 7.76±0.37 | 6.19±1.13 |
| Cu ₆ | 1177.27957 | 9.6332 | 1.6055 | 10.32±0.49 | 7.99±1.37 |
| Cu ₇ | 1373.51538 | 11.8523 | 1.6932 | 12.98±0.66 | 9.04±1.58 |
| Cu ₈ | 1569.76050 | 14.3247 | 1.7906 | 15.96±0.75 | 11.20±1.77 |
| Cu ₉ | 1765.97437 | 15.9468 | 1.7719 | | 12.22±1.84 |

^aCID experiments on the anionic clusters (Ref. 12).^bCID experiments on the cationic clusters (Ref. 13).

cohesive energy in the limit of an infinitely large cluster [the experimental cohesive energy of copper is 3.50 eV (Ref. 57)]. It is clear that the clusters studied here are still too small to produce a reasonable estimation of the cohesive energy of copper, however, it can be easily shown that our BE/ n values lie within the region defined by the CID experimental data. The agreement observed with the experimental data^{12,13} and other theoretical results^{22,25,26} is certainly validating the methodology used in this paper.

On the other hand, note that BE and BE/ n increase with the size of the cluster, and we observe a maximum value of BE/ n in Cu₈. It is well known that the magnitude of BE/ n gives information about the strength of chemical bonds in clusters, thus it might help to determine the stability and reactivity of the system. In metallic clusters the increase of this property is due to a high electronic delocalization which

is originated by the high coordination of the atoms. From the CN and BE/ n values quoted in Tables II and III, we obtain a good linear relation between BE/ n and CN: BE/ n (CN) = 0.7413 + 0.2234 · CN ($r=0.94$). Now, introducing the experimental cohesive energy of copper (BE/ $n=3.50$ eV) into the above linear equation we estimate the average value of CN to be quite close to CN=12, which corresponds to the experimental coordination number in the bulk. This indicates that the analytic form produced from our results is reliable enough to help rationalize experimental data. We conclude that the level of calculation used throughout this paper is adequate for characterizing binding energies and may provide correct estimations of the DFT-descriptors we are interested in.

3. Relative stability

The stability of metal clusters is studied through the energy difference,

$$\Delta_2 E(n) = E(n+1) + E(n-1) - 2E(n), \quad (8)$$

where n is the number of atoms in the cluster. This quantity is known as the relative binding energy of a cluster with n atoms respect to those with $(n+1)$ and $(n-1)$ atoms. High values of $\Delta_2 E(n)$ indicate that the cluster Cu _{n} is more stable than its neighbors Cu _{$n-1$} and Cu _{$n+1$} . In Fig. 4 we show $\Delta_2 E$

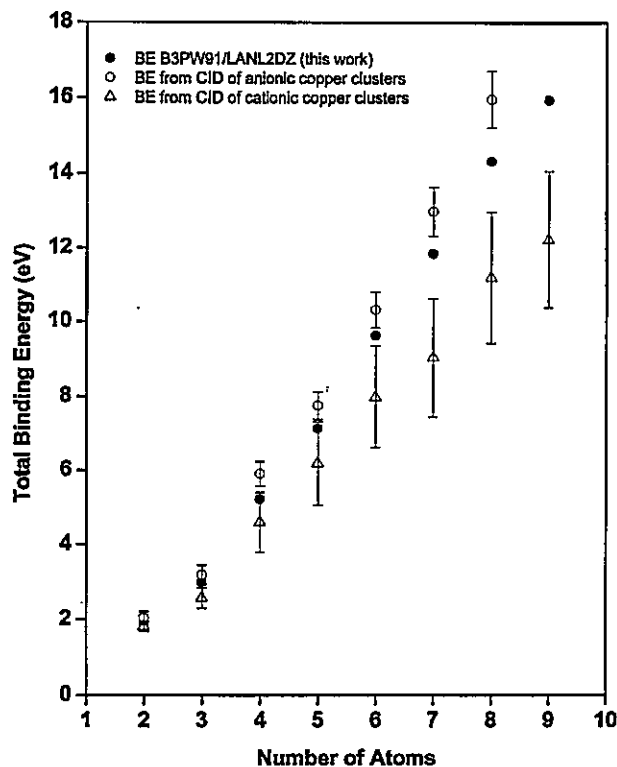


FIG. 3. Experimental CID and theoretical binding energies (BE) as functions of the size of the cluster.

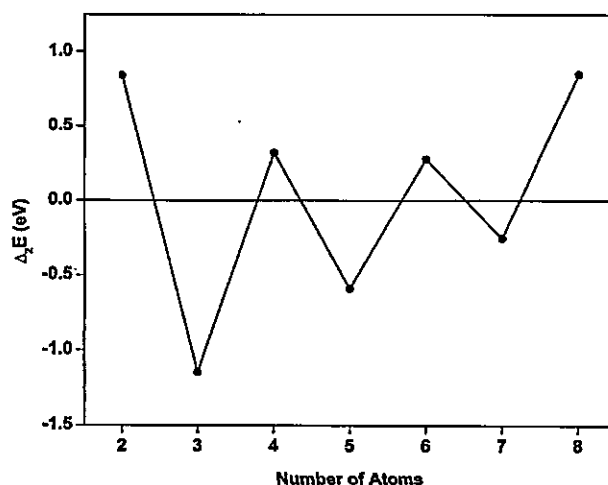
FIG. 4. Second energy difference ($\Delta_2 E$) as function of size of the cluster.

TABLE IV. B3PW91/LANL2DZ energies (a.u.) and frontier orbital energies (eV) for the neutral and ionic clusters Cu_n ($n=1-9$).

| Cu_n | $-E$ | $-E_{\text{cation}}$ | $-E_{\text{anion}}$ | $-\varepsilon_H$ | $-\varepsilon_L$ |
|---------------|------------|----------------------|---------------------|------------------|------------------|
| Cu | 196.15426 | 195.87159 | 196.17788 | 5.1824 | 2.7522 |
| Cu_2 | 392.37926 | 392.09256 | 392.40087 | 5.4962 | 2.1122 |
| Cu_3 | 588.57325 | 588.36121 | 588.60133 | 3.9756 | 2.5905 |
| Cu_4 | 784.80931 | 784.57161 | 784.85392 | 4.6823 | 2.6711 |
| Cu_5 | 981.03363 | 980.80719 | 981.09078 | 4.5384 | 2.9655 |
| Cu_6 | 1177.27957 | 1177.02022 | 1177.31292 | 5.4246 | 2.0967 |
| Cu_7 | 1373.51538 | 1373.29607 | 1373.57336 | 4.4175 | 2.9802 |
| Cu_8 | 1569.76050 | 1569.51666 | 1569.80145 | 5.0978 | 2.3753 |
| Cu_9 | 1765.97437 | 1765.77822 | 1766.00064 | 3.9304 | 2.6901 |

as a function of n , we observe an oscillating behavior and identify clusters with even n as being more stable [$\Delta_2 E(n)$ present local maxima] than the clusters with odd n . This is so because clusters with an even n present closed-shell states.

In Table IV are displayed the values of energy for the N , $(N-1)$, and $(N+1)$ electron systems together with the highest occupied (ε_H) and lowest unoccupied molecular orbital (ε_L) energies. We note that the frontier MO energies present a similar oscillating behavior as observed for $\Delta_2 E$. Clusters with an even n have a large HOMO-LUMO energy gap and therefore are expected to be less reactive than clusters with an odd number of atoms. As already mentioned, the stability exhibited by even clusters is due to their closed-shell configurations that always comes along with an extra stability. It is important to mention that this result is in agreement with the electronic shell jellium model,^{58,59} where filled-shells cluster with 2, 8, 18, 20, 40, 58, 92, ... valence electrons have increased stability, the mass spectra of cluster distribution shows pronounced intensity in clusters with these number of atoms, the so-called magic numbers.^{58,59}

B. Electronic properties

1. Ionization potential

Table V displays our theoretical results together with the available experimental values^{10,11,18,29} of vertical ionization potentials and electron affinities of the nine copper clusters studied in this work.

We first note the oscillating behavior of the IP which is due to the change of spin multiplicity of the ground state of this series, and clusters with n even are closed-shell systems, whereas odd-numbered copper clusters are open-shell systems. Therefore even clusters present the higher values of the IP with respect to their neighboring odd systems, because it is more difficult to remove an electron from the doubly occupied HOMO of a closed-shell system than from a single occupied HOMO of an open-shell system. This result is consistent with the variation of HOMO energy along the series (see Table IV).

Our computed ionization potentials show an overall very good quantitative agreement with the experimental results, as can be seen in Fig. 5(a), where a nice linear correlation of experimental and theoretical results is obtained. At this point it is interesting to check the validity of the Koopman's theorem for estimating ionization potentials from the energy of the HOMO. Figure 5(b) shows a fairly good linear relation between the experimental IPs and the HOMO energies. However, the IP's determined using the Koopman's theorem applied to the Kohn-Sham HOMO orbital are systematically underestimating the experimental value (see Tables IV and V), in agreement with recent studies aimed at comparing Hartree-Fock and Kohn-Sham orbitals.⁶⁰ It is well known that in a Kohn-Sham calculation the approach of IP by the HOMO energy is a measure of the quality of the functional employed, and that only at the limit of the exact functional, $\text{IP} = -\varepsilon_H$. In this context the satisfactory agreement shown

TABLE V. Vertical ionization potentials and electron affinities for Cu_n . All values are in eV.

| Cu_n | IP | IP(expt) | EA | EA(expt) ^a |
|---------------|--------|----------------------------|--------|-----------------------|
| Cu | 7.6919 | 7.724 ^b | 0.6427 | 1.235±0.005 |
| Cu_2 | 7.8016 | 7.9042±0.0008 ^b | 0.5880 | 0.836±0.006 |
| Cu_3 | 5.7700 | 5.80±0.04 ^c | 0.7641 | 2.37±0.01 |
| Cu_4 | 6.4682 | 7.15±0.75 ^d | 1.2139 | 1.45±0.05 |
| Cu_5 | 6.1618 | 6.3±0.1 ^c | 1.5551 | 1.94±0.05 |
| Cu_6 | 7.0573 | 7.15±0.75 ^d | 0.9075 | 1.96±0.05 |
| Cu_7 | 5.9678 | 6.1±0.05 ^c | 1.5777 | 2.16±0.1 |
| Cu_8 | 6.6353 | 7.15±0.75 ^d | 1.1143 | 1.57±0.05 |
| Cu_9 | 5.3376 | 5.35±0.05 ^c | 0.7149 | 2.40±0.05 |

^aReference 18.

^bReference 29.

^cReference 10.

^dReference 11.

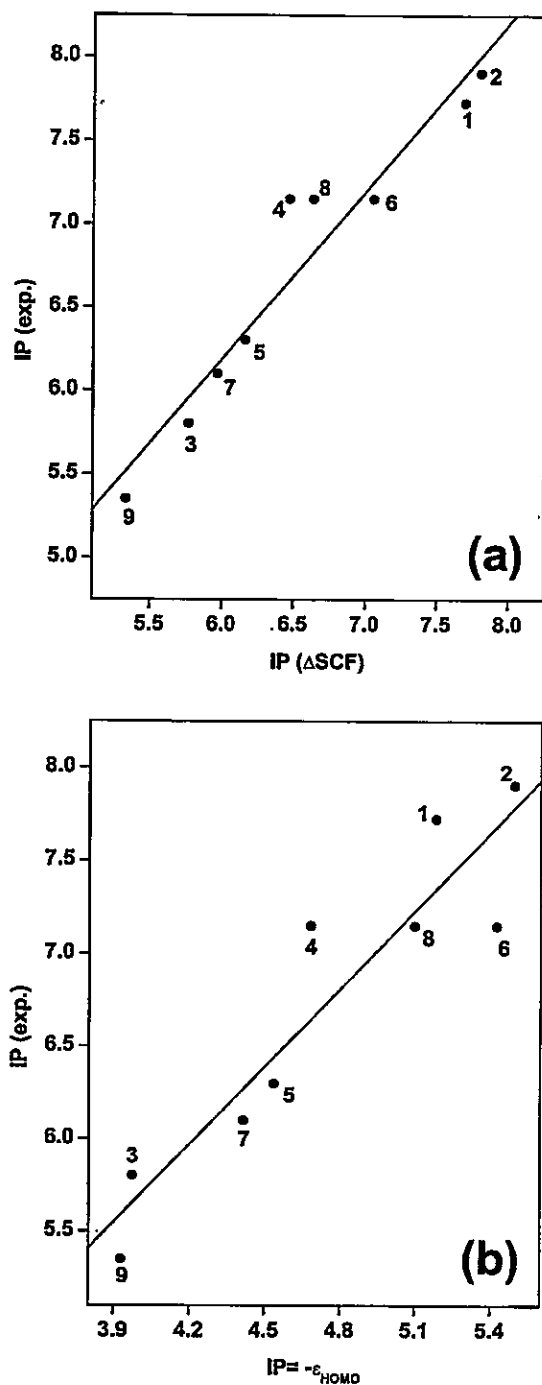


FIG. 5. Comparison of experimental and theoretical ionization potentials along the series Cu_n ($n=1-9$): (a) theoretical IPs from ASCF ($r=0.96$); (b) theoretical IPs from HOMO energies ($r=0.93$). All values are in eV.

TABLE VI. Chemical potential, chemical hardness, and electrophilicity index of Cu_n ($n=1-9$). All values are in eV.

| Cu_n | $\mu^{(\text{IPEA})}$ | $\mu^{(\text{H,L})}$ | $\mu^{(\text{exp})}$ | $\eta^{(\text{IPEA})}$ | $\eta^{(\text{H,L})}$ | $\eta^{(\text{exp})}$ | $\omega^{(\text{IPEA})}$ | $\omega^{(\text{H,L})}$ | $\omega^{(\text{exp})}$ |
|---------------|-----------------------|----------------------|----------------------|------------------------|-----------------------|-----------------------|--------------------------|-------------------------|-------------------------|
| Cu | -4.1673 | -3.9673 | -4.4795 ± 0.0050 | 3.5246 | 1.2151 | 3.2445 ± 0.0050 | 2.4636 | 6.4765 | 3.0923 ± 0.0068 |
| Cu_2 | -4.1948 | -3.8042 | -4.3701 ± 0.0061 | 3.6068 | 1.6920 | 3.5341 ± 0.0061 | 2.4393 | 4.2765 | 2.7019 ± 0.0071 |
| Cu_3 | -3.2671 | -3.2831 | -4.0850 ± 0.0412 | 2.5030 | 0.6925 | 1.7150 ± 0.0412 | 2.1322 | 7.7820 | 4.8651 ± 0.1359 |
| Cu_4 | -3.8411 | -3.6767 | -4.3000 ± 0.7517 | 2.6272 | 1.0056 | 2.8500 ± 0.7517 | 2.8079 | 6.7214 | 3.2439 ± 1.1727 |
| Cu_5 | -3.8585 | -3.7519 | -4.1200 ± 0.1118 | 2.3034 | 0.7864 | 2.1800 ± 0.1118 | 3.2318 | 8.9501 | 3.8932 ± 0.2494 |
| Cu_6 | -3.9824 | -3.7606 | -4.5550 ± 0.7517 | 3.0749 | 1.6640 | 2.5950 ± 0.7517 | 2.5789 | 4.2496 | 3.9977 ± 1.4871 |
| Cu_7 | -3.7728 | -3.6989 | -4.1300 ± 0.1118 | 2.1951 | 0.7187 | 1.9700 ± 0.1118 | 3.2422 | 9.5189 | 4.3292 ± 0.2964 |
| Cu_8 | -3.8748 | -3.7353 | -4.3600 ± 0.7517 | 2.7605 | 1.3625 | 2.7900 ± 0.7517 | 2.7195 | 5.1203 | 3.4067 ± 1.2379 |
| Cu_9 | -3.0263 | -3.3103 | -3.8750 ± 0.0707 | 2.3114 | 0.6202 | 1.4750 ± 0.0707 | 1.9812 | 8.8349 | 5.0900 ± 0.2771 |

in Figs. 5 confirm the reliability of our results and the overall adequateness of the employed methodology.

2. Chemical potential, molecular hardness, and electrophilicity

After discussing the structure, the relative stability of the different clusters and the determination of ionization potentials and electron affinities, we can focus our attention on the characterization and rationalization of copper clusters through the use of DFT-descriptors and electronic structure principles of chemical reactivity. We are interested in whether one can safely introduce these concepts to rationalize the behavior of the clusters.

In Table VI we display experimental and computed values of μ , η , and ω obtained from Eqs. (3), (4), and (5) with experimental and computed values of IP and EA, and using the frontier orbital energies (ε_H and ε_L). We have performed the error analysis for the resulting properties obtained from the experimental data (IP and EA) given in Table V.

Figure 6 shows the behavior of property $P(=\mu, \eta, \omega)$ with n . Calculations using ionization potentials and electron affinities given in Table V give rise to $P^{(\text{IPEA})}$; the use of frontier orbitals energies given in Table IV led to $P^{(\text{H,L})}$; as already mentioned, the experimental values [$P^{(\text{exp})}$] were obtained from the experimental IP and EA values given in Table V. Table VI shows that Cu_4 , Cu_6 , and Cu_8 present the larger error bars in the experimental data, this is due to the 10% error coming out from their experimental ionization potentials.

The chemical potential is related to charge transfer from a system of high μ to another system with a lower value of the chemical potential. Therefore we expect the clusters with odd n to present maximum values of μ because they are open shell systems and after the transfer of one electron these systems will close their electronic shell, and the resulting systems will be more stable than the original open-shell clusters (see Table IV). In Fig. 6(a) we note that the experimental values of μ follow the expected trend, an oscillating behavior with local maxima in clusters with odd n . In particular Cu_3 and Cu_9 present the highest values of $\mu^{(\text{exp})}$, and these systems are able to transfer an electron to close their electronic shell leading to systems with 2 and 8 valence electrons, respectively. This again is in agreement with the magic number prediction for stability in the jellium model.

Chemical hardness has been established as an electronic quantity that in many cases may be used to characterize the

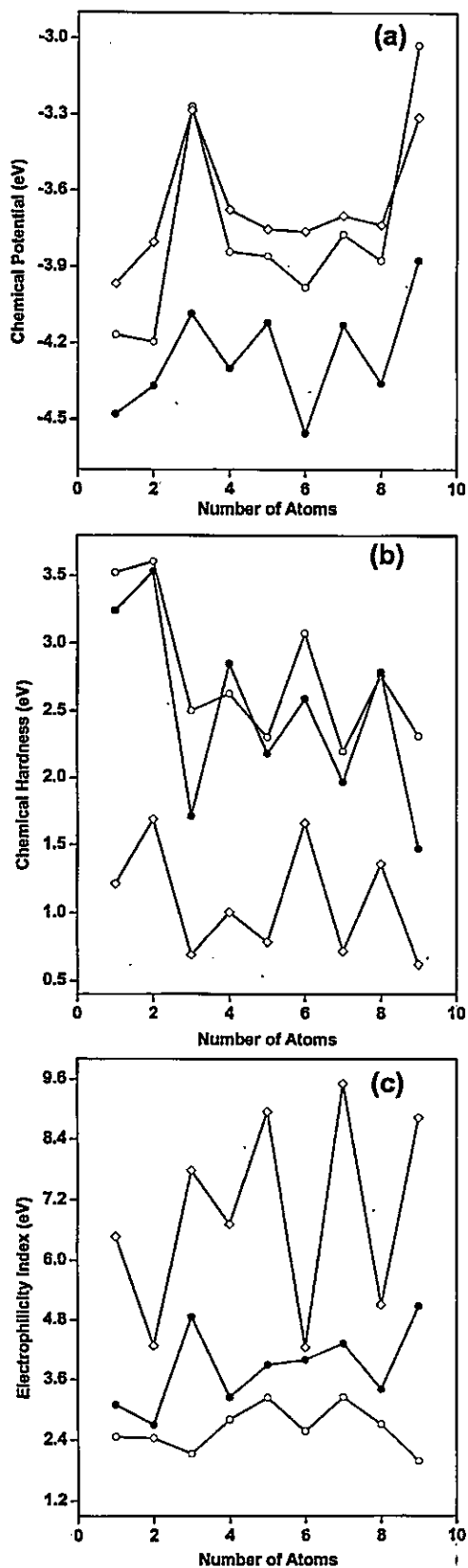


FIG. 6. (a) Chemical potential, (b) chemical hardness, and (c) electrophilicity index as function of size of the cluster. [$P^{(IEEA)}$ = \circ —; $P^{(exp)}$ = \bullet —; $P^{(H,L)}$ = \diamond —, $P = \mu, \eta, \omega$].

relative stability of molecules and aggregates through the PMH.^{41–43} Assuming that the PMH holds in these systems, we expect the hardness to present an oscillating behavior

with local maxima at the clusters with even n , as found for the relative energy in Fig. 4. Figure 6(b) shows that closed-shell even clusters present higher values of hardness than their odd open-shell neighboring clusters. We observe the even–odd oscillating feature similar to that already stressed in Fig. 4. Stable clusters (n even) are harder than their neighbors systems (n odd). These results confirm the statement that the stability of even clusters is determined by the closed electronic shell structure as a manifestation of the PMH.^{61,62} Our results are also in agreement with those recently reported by Mineva *et al.*,⁶³ where the same even–odd alternation rule for hardness was found in sodium clusters.

Finally, it is important to mention that hardness shows quite a stable behavior and qualitative trends of $\eta^{(IEEA)}$ are quite the same as $\eta^{(H,L)}$, thus validating the use of the two forms Eq. (4). On the other hand we note that in most cases $\eta^{(IEEA)}$ and $\eta^{(H,L)}$ define the limits where the experimental data lies, and this suggests specific computation strategies to predict upper and lower boundaries for experimental hardness.

The EA's values determined in our calculation undermine the corresponding electrophilicity value, so in the general discussion of this property we discard the $\omega^{(IEEA)}$ data. The computed electrophilicity indexes $\omega^{(H,L)}$ present a general behavior that is quite close to the one featured by the experimental data as is shown in Fig. 6(c). Along the series we observe an even–odd oscillatory trend, and the maximum electrophilic power is found at the odd clusters because of their already mentioned capacity to close the electronic shell by receiving an electron. Copper clusters with odd n are more willing to accept electronic charge from the environment than do even clusters.

3. Polarizability

We have mentioned that the polarizability can be used to understand the behavior of the system when the external potential is changed at constant N . This property is considered one of the most important observables for understanding the electronic properties of clusters. In this context, Moullet *et al.*⁶⁴ have reported LDA calculations of the electric dipole polarizability tensor for several isomers of sodium clusters. They have shown how the comparison of the calculated polarizability with the experimental data can be used to identify the specific isomer actually observed in the experiments.

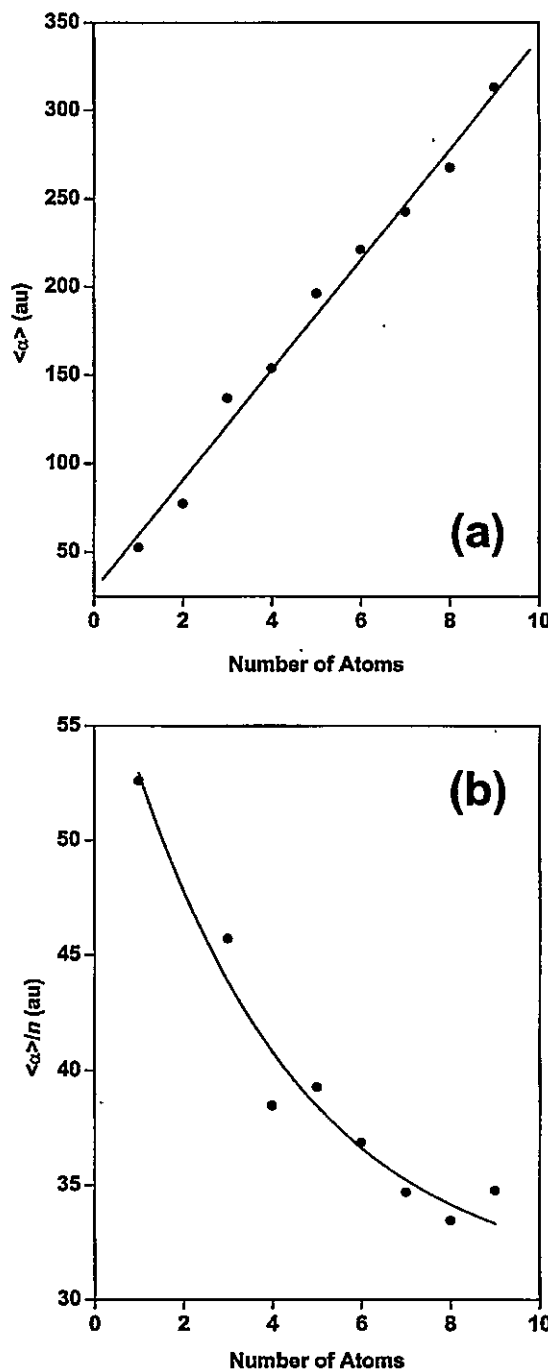
In Table VII we show the average B3PW91/LANL2DZ polarizability calculated using Eq. (6) and the mean polarizability per atom ($\langle\alpha\rangle/n$). Unfortunately, there is no measurement of static electric polarizabilities for these systems to compare with our results. However, polarizability calculations on copper clusters have been carried out by many authors.^{23,65,66} Polarizability is very sensitive to the quality of the basis set⁶⁷ and it is sometimes recommended to use diffuse functions to describe the distortions of the electron density due to the external electric field. However, sometimes the errors inherent to the theoretical method are in an opposite direction with respect to the errors produced by the basis set. Hence a careful calibration of the basis set can achieve a compensation of errors producing a final result hopefully better than expected.

TABLE VII. Static mean polarizability $\langle\alpha\rangle$ and mean polarizability per atom ($\langle\alpha\rangle/n$) of copper clusters. All values are in a.u.

| Cu_n | $\langle\alpha\rangle$ | $\langle\alpha\rangle/n$ |
|-----------------|------------------------|--------------------------|
| Cu | 52.610 | 52.610 |
| Cu ₂ | 77.574 | 38.787 |
| Cu ₃ | 137.148 | 45.716 |
| Cu ₄ | 153.948 | 38.487 |
| Cu ₅ | 196.506 | 39.301 |
| Cu ₆ | 221.212 | 36.869 |
| Cu ₇ | 242.873 | 34.696 |
| Cu ₈ | 267.640 | 33.455 |
| Cu ₉ | 312.970 | 34.774 |

First of all let us briefly review the previous calculations. Pou-Amérgo *et al.*⁶⁵ have investigated the polarizability of the copper atom using the modified coupled pair functional (MCPF) method and a finite field approach with an external field of 0.01 a.u. They used five different contracted basis sets ($5s4p3d2f1g, 6s5p4d3f2g, 7s6p5d4f3g, 8s7p6d5f4g, 21s15p10d6f4g$) which yield to the following polarizabilities of atomic copper: 30.48 a.u., 40.72 a.u., 50.0 a.u., 52.96 a.u., and 53.44 a.u., respectively. It is clear that our calculated value at the B3PW91/LANL2DZ level of theory (52.61 a.u.) is fairly close to the best values of Pou-Amérgo *et al.* Also Sadlej *et al.*⁶⁶ have calculated the polarizability of few metals using high-level-correlated-relativistic calculations. The reported value for the copper atom was 46.50 a.u., again in very good agreement with our present result. More recently Calaminici *et al.*²³ have presented a GGA all electrons study of static polarizabilities and polarizability anisotropy calculations of copper clusters with a triple zeta plus valence polarization basis set (TZVP) augmented with seven field-induced polarization (FIP) functions. They obtained $\langle\alpha\rangle=47.02$ a.u. for Cu quite close to Sadlej, Pou-Amérgo, and our own calculations. This satisfactory agreement of our results with all electrons results indicates that the core contributions to $\langle\alpha\rangle$ are quite negligible and reliable polarizability values at a reasonable computational cost can be obtained using DFT combined with pseudopotentials and a double zeta basis set. On the other hand we have checked the stability of the polarizability values with respect to the grid quality by performing calculations on Cu and Cu₂ using three different grids (coarse, fine, and ultrafine in GAUSSIAN 98 program). The results show that the polarizability values are independent of the choice of the grid.

In Fig. 7 we display $\langle\alpha\rangle$ and $\langle\alpha\rangle/n$ with the cluster size. In Fig. 7(a) we note that when going from Cu to Cu₉ the polarizability of the copper clusters increases monotonically showing the expected proportionality with n (or the total electrons number). We note in Table VII that $\langle\alpha\rangle/n$ oscillates when going from Cu to Cu₅, and afterwards it looks like it starts to converge to a value of about 34 a.u. We have fitted these results to an exponential decay of first order, i.e., $\langle\alpha\rangle/n=A+Be^{-Cn}$, and the results are displayed in Fig. 7(b). From this fitting we can predict a value of 31.14 a.u. for $\langle\alpha\rangle/n$ in the copper's bulk.

FIG. 7. (a) Calculated polarizability ($r=0.99$) and (b) polarizability per atom ($r=0.96$) as function of the size of the cluster.

C. Chemical reactivity: The PMH and MPP

We have already mentioned that Cu₈ presents the highest value of cohesive energy and the lowest value of polarizability per atom in agreement with the minimum polarizability principle.

To show that consistency between energetic and electronic descriptors has been reached, in Fig. 8 we show a good linear relation between BE/n and $\langle\alpha\rangle/n$ indicating that systems with strong bonds (or high electronic delocalization degree) present minimum values of polarizability per atom, in agreement with the MPP. On the other hand, Cu₈ also

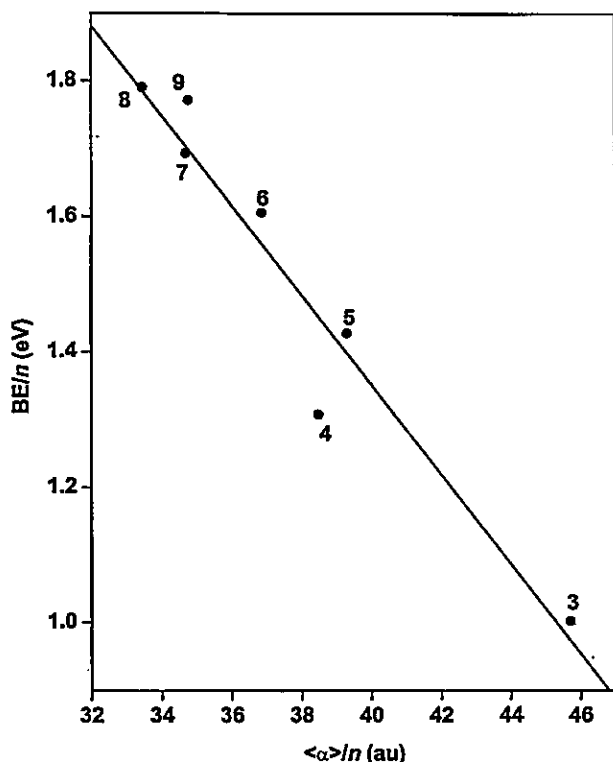


FIG. 8. Correlation between the binding energy per atom and the polarizability per atom along the series ($n=1-9$; $r=-0.97$).

presents a maximum value of η with respect to its neighbors, in agreement with the PMH.

V. CONCLUSIONS

We have studied small neutral copper clusters at the B3PW91 level of theory combined with pseudopotentials. Our results of geometry, binding energy, and ionization potential showed good agreement with experimental and others theoretical data. The general trend that we have found is that clusters with an even number of copper atoms are more stable (or less reactive) than clusters with an odd number of atoms.

The reactivity descriptors presented in this paper are useful tools in the rationalization of theoretical and experimental data, and this allows us to get new insights on more complex systems involved in heterogeneous catalysis and in cluster's fragmentation reactions. We have found that the more stable is the cluster the less polarizable and the harder it is, in agreement with MPP and PMH, respectively. This shows that the minimum polarizability and maximum hardness principles are operative in the characterization of these kinds of systems.

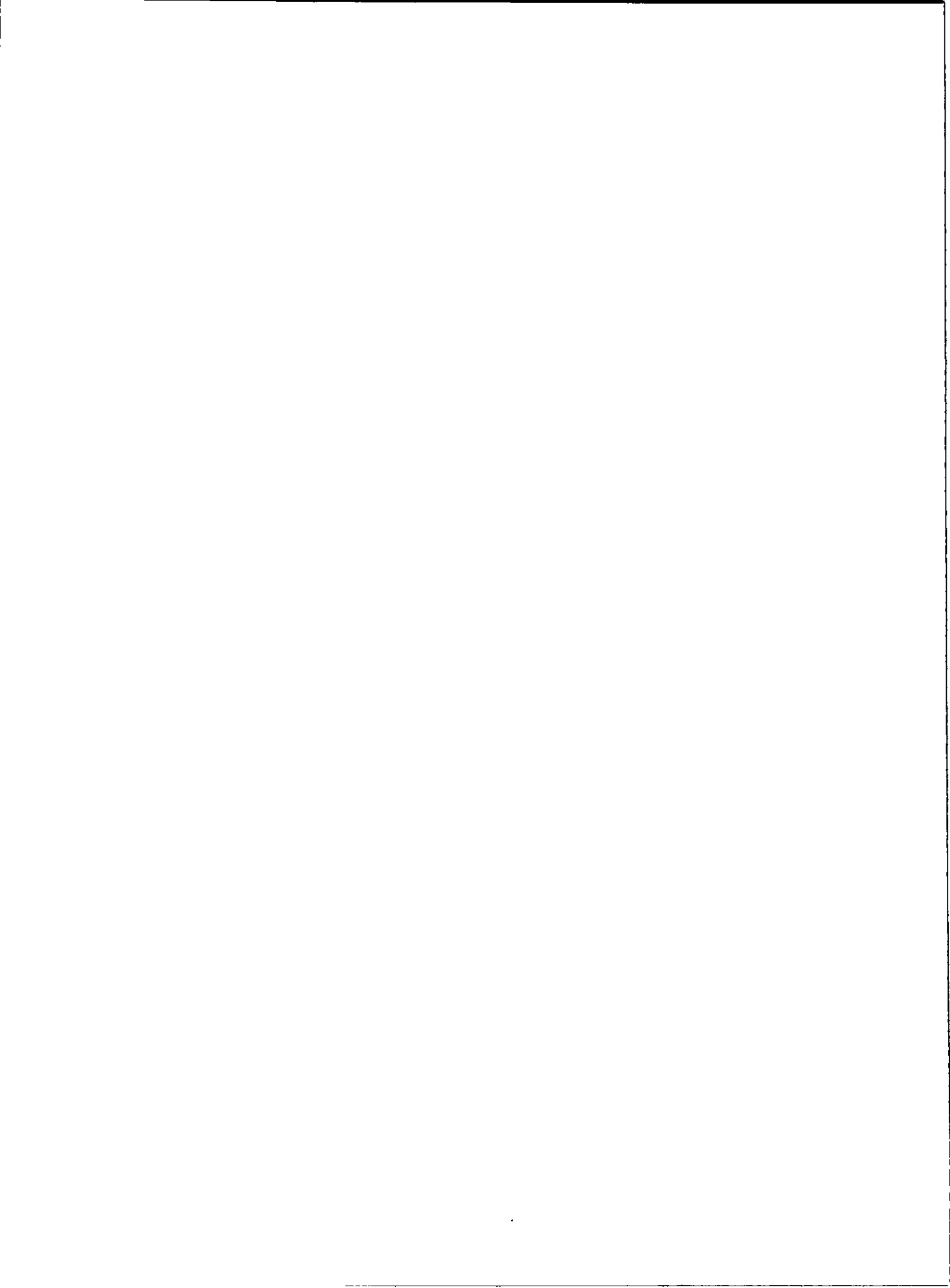
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Towards understanding the molecular internal rotations and vibrations and chemical reactions through the profiles of reactivity and selectivity indices: an *ab initio* SCF and DFT study

PRATIM K. CHATTARAJ^{1*}, SOLEDAD GUTIÉRREZ-OLIVA²,
PABLO JAQUE² and ALEJANDRO TORO-LABBÉ^{2*}

¹Department of Chemistry, Indian Institute of Technology,
Kharagpur, 721 302, India

²Laboratorio de Química Teórica Computacional (QTC),
Departamento de Química Física, Facultad de Química,
Pontificia Universidad Católica de Chile,
Casilla 306, Correo 22, Santiago, Chile

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Ab initio SCF and DFT(B3LYP) calculations are performed with 6-311G** basis sets for obtaining insights into molecular internal rotations in HXNX (X = O, S), different vibrational modes in water and double proton transfer reaction in (HONO)₂. While chemical reactivity is analyzed in terms of the profile of the global reactivity parameters, such as energy, chemical potential, hardness, polarizability, molecular valency and electrophilicity indices, the site selectivity is understood through the variations in local descriptors, such as the Fukui function and atomic valency. Principles of maximum hardness and molecular valency and the minimum polarizability principle are found to be valid in almost all cases. Rotational isomerization reactions can be better characterized by making use of the maximum hardness principle along with Hammond's postulate. Extremum points in electrophilicity during internal rotations, vibrations and chemical reaction can be located from those of chemical potential and hardness. The Fukui function and atomic valency show inverse behaviour in most cases.

1. Introduction

Density functional theory (DFT) [1, 2] has been quite successful in providing a theoretical basis for popular qualitative chemical concepts, such as electronegativity (χ) [3, 4] and hardness (η) [5, 6]. Pauling [3] introduced the concept of electronegativity as 'the power of an atom in a molecule to attract electrons to itself'. 'All the constituent atoms in a molecule have the same electronegativity value which is roughly equal to the geometric mean of the electronegativities of the corresponding isolated atoms', according to Sanderson's electronegativity equalization principle [7]. The idea of hardness was put forward by Pearson [5, 8] in his famous hard-soft acids and bases (HSAB) [5, 7] principle which states that 'among potential partners of equal electronegativity hard likes hard and soft likes soft'. Another hardness-related principle is the maximum hardness principle (PMH) [10, 11] whose statement is 'there seems to be a rule of nature that molecules arrange themselves so as to be as

hard as possible'. Polarizability (α) was one of the most important properties on which the concepts of hardness and softness were originally developed [5, 6]: a hard species is less polarizable and a soft species is more polarizable. Based on this inverse relationship [12] between α and η , a minimum polarizability principle (MPP) [13, 14] has been proposed which states that [13] 'the natural direction of evolution of any system is toward a state of minimum polarizability'. It has also been shown [15] that 'a system is harder and less polarizable in its ground state than in any of its excited states'. Molecular valency [16, 17] (V) also often becomes maximum for the most stable configuration/conformation.

As a complement to the above-mentioned global reactivity indices, local reactivity descriptors usually condensed to an atom, such as the Fukui function (f_k^\pm), local softness (s_k), electrophilicity index (ω_k) and atomic valency (V_k), are necessary for explaining site selectivity in a molecule and identify specific interactions which characterize the reaction mechanisms [2, 8, 18].

*Authors for correspondence. e-mail: pkc@chem.iitkgp.ernet.in; atola@puc.cl

In the present work the internal rotations and resulting rotational isomerization in HXNX (X=O,S), different symmetric and asymmetric vibrational modes of water and the intermolecular double proton transfer reaction in (HONO)₂ are studied at the *ab initio* SCF level as well as using DFT. Profiles of reactivity indices, such as μ , η , α and V , and the relevant selectivity indices, such as f_k^\pm and V_k for the above-mentioned processes, are characterized and discussed in the light of reactivity-selectivity principles.

In section 2, we present the theoretical background necessary to follow the forthcoming analysis, details of computations are presented in section 3 while section 4 deals with the results and discussion. Finally section 5 contains our concluding remarks.

2. Theoretical background

2.1. Chemical reactivity

Electronegativity (χ) and hardness (η) have been defined respectively as the following first-order and second-order derivatives for an N -electron system with total energy E ,

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(\mathbf{r})} \quad (1)$$

and

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\mathbf{r})}, \quad (2)$$

where $v(\mathbf{r})$ is the external potential which is produced by external charges to the system of electrons; μ is the chemical potential, that is a Lagrange multiplier associated with the normalization constraint of DFT [1,2]. Recently Parr *et al.* [19] have provided the following definition for the electrophilicity index (ω)

$$\omega = \frac{\mu^2}{2\eta}, \quad (3)$$

which measures the energy stabilization upon electronic saturation of the system, when electrons flow from the surroundings with a higher chemical potential than that of the system. These global reactivity parameters and the associated electronic structure principles have been very helpful in understanding chemical reactivity and form the backbone of any reactivity theory [20].

2.2. Site selectivity

Local reactivity descriptors like the Fukui function ($f(\mathbf{r})$) and local softness ($s(\mathbf{r})$) are necessary for explaining site selectivity in a molecule. The Fukui function is

defined as [18]

$$f(\mathbf{r}) = \left(\frac{\delta\mu}{\delta v(\mathbf{r})}\right)_N = \left(\frac{\partial\rho(\mathbf{r})}{\partial N}\right)_{v(\mathbf{r})}; \quad (4)$$

in the absence of orbital relaxation it becomes just the density of the frontier molecular orbital and makes a bridge between Fukui's frontier orbital theory [21] and DFT [1,2]. Owing to the discontinuity [22] of the derivative $(\partial\rho(\mathbf{r})/\partial N)_{v(\mathbf{r})}$ at an integral value of N , three different types of $f(\mathbf{r})$ can be defined as follows:

$$\begin{aligned} f^+(\mathbf{r}) &= \left(\frac{\partial\rho(\mathbf{r})}{\partial N}\right)_{v(\mathbf{r})}^+ \approx [\rho_{N+1}(\mathbf{r}) - \rho_N(\mathbf{r})] \approx \rho_L(\mathbf{r}), \\ f^-(\mathbf{r}) &= \left(\frac{\partial\rho(\mathbf{r})}{\partial N}\right)_{v(\mathbf{r})}^- \approx [\rho_N(\mathbf{r}) - \rho_{N-1}(\mathbf{r})] \approx \rho_H(\mathbf{r}), \\ f^o(\mathbf{r}) &= \frac{1}{2}[f^+(\mathbf{r}) + f^-(\mathbf{r})]; \end{aligned} \quad (5)$$

at point \mathbf{r} , $f^+(\mathbf{r})$ measures reactivity toward a nucleophilic attack, $f^-(\mathbf{r})$ measures reactivity toward an electrophilic attack and $f^o(\mathbf{r})$ measures reactivity toward a radical attack. Connection with the frontier orbital theory is achieved through $\rho_H(\mathbf{r})$ and $\rho_L(\mathbf{r})$, the frontier orbitals (HOMO and LUMO) densities. With all other factors remaining the same, the maximum value of the Fukui function at a given site would be preferred by a reagent because that will cause the largest change in the chemical potential as indicated in equation (4) [2, 18]. The above quantities can also be condensed to an atom k in a molecule in terms of the population on that atom [23], namely,

$$\begin{aligned} f_k^+ &= \int_k [\rho_{N+1}(\mathbf{r}) - \rho_N(\mathbf{r})] d\mathbf{r} = [q_k(N+1) - q_k(N)], \\ f_k^- &= \int_k [\rho_N(\mathbf{r}) - \rho_{N-1}(\mathbf{r})] d\mathbf{r} = [q_k(N) - q_k(N-1)], \\ f_k^o &= \frac{1}{2}[f_k^+ + f_k^-] = \frac{1}{2}[q_k(N+1) - q_k(N-1)]. \end{aligned} \quad (6)$$

Within the frozen core approximation, these quantities can also be condensed by considering only the contributions of the frontier orbitals on a given atom, thus leading to [24]:

$$\begin{aligned} f_k^+ &= \int_k \rho_L(\mathbf{r}) d\mathbf{r} = \rho_k^L, \\ f_k^- &= \int_k \rho_H(\mathbf{r}) d\mathbf{r} = \rho_k^H, \\ f_k^o &= \frac{1}{2}[f_k^+ + f_k^-] = \frac{1}{2}[\rho_k^L + \rho_k^H], \end{aligned} \quad (7)$$

where ρ_k^L and ρ_k^H are the electronic population on atom k associated with the frontier orbitals LUMO and

HOMO, respectively. Local softness can be defined as [25]

$$s(\mathbf{r}) = f(\mathbf{r}) \cdot S, \quad (8)$$

where the global softness (S) is given by [26]

$$S = \frac{1}{2\eta}. \quad (9)$$

Different variants of local softness and their condensed-to-atom variants can be obtained by substituting $f(\mathbf{r})$ or f_k from equations (5) and (6), respectively. A local version of the HSAB principle is also known [27, 28]. Klopman [29] has shown that the hard-hard interactions are predominantly ionic in nature and hence 'charge-controlled', whereas the soft-soft interactions are mainly covalent in nature and hence 'frontier-controlled'. These local quantities and the related structure principles are important in analyzing the preferred site of attack as well as the type of attack by a reagent [20].

On the other hand, ω , equation (3), can also be written in terms of local contributions through the softness, equation (9), which can be written as a sum of local condensed contributions centred on the different atoms in the molecule ($S = \sum s_k$):

$$\omega = \frac{\mu^2}{2\eta} = \mu^2 \cdot S = \mu^2 \cdot \sum_k s_k = \sum_k \omega_k, \quad (10)$$

with $\omega_k = \mu^2 \cdot s_k$ being the local electrophilicity power associated with centre k .

Chemical processes produce changes in the electronic distribution on different regions of the molecular topology; Fukui functions, as well as local softness and electrophilicity, are good measures for the electronic distribution at a given atomic centre within the molecule. Complementary to these site reactivity indices, the atomic valency (V_k) provides a measure of the localization of electron density at the bond regions associated with an atom; it is calculated by adding the off-diagonal elements of the first-order density matrix as [16]:

$$V_k = \sum_{t \neq k} \left[\sum_{a \in k} \sum_{b \in t} D_{ab} D_{ba} \right], \quad (11)$$

thus giving a measure of the covalent bonds borne by atom k within the molecule. The V_k values of an atom are always very close to their classical valency although they may fluctuate from molecule to molecule. Deviations from the classical valency integer value are mainly due to the ionic character of the bond formed by atoms of different electronegativities [16, 17]. Following Klopman's observation about specific local interactions

[29], a reactive centre in local soft-soft interactions is expected to be associated with a minimum value of V_k (a maximum deviation from the classical valency) whereas for hard-hard interactions a maximum value of V_k (a minimum deviation from the classical valency) should be in order.

The molecular valency (V) is obtained as

$$V = \frac{1}{2} \sum_k V_k \quad (12)$$

and is a measure of the covalent bonds within the molecule; a molecule described by covalent or slightly polar covalent bonds in its minimum energy conformation is expected to present a maximum value of V [17].

It is important to know how these reactivity and selectivity parameters vary during the progress of a physico-chemical process like molecular internal rotations, molecular vibrations or chemical reactions.

2.3. Characterization of transition states

To characterize the energy of transition states (TS) in internal rotations and proton transfer processes we use the Marcus equation (ME) [30]:

$$\Delta E^\ddagger = \Delta E_0^\ddagger + \frac{1}{2} \Delta E^\circ + \frac{(\Delta E^\circ)^2}{16 \Delta E_0^\ddagger}, \quad (13)$$

where ΔE_0^\ddagger is the intrinsic energy barrier which can be determined by solving the second-degree equation resulting from rearrangement of equation (13) and using the calculated values of ΔE^\ddagger and ΔE° , which is the reaction energy. Note that for symmetric reactions $\Delta E^\circ = 0$ and the energy barrier reduces to ΔE_0^\ddagger [31]. The ME has been used successfully in the rationalization of activation energies in different kinds of chemical reactions [31]. In particular, within the framework of the Hammond postulate [32], the Marcus equation can be used to determine the position of the transition state along the reaction coordinate. This can be achieved by using the Brønsted coefficient which, following the Leffler postulate [33], is defined as the derivative of the activation energy with respect to the reaction energy [31]:

$$\beta = \left(\frac{d\Delta E^\ddagger}{d\Delta E^\circ} \right) = \frac{1}{2} + \frac{\Delta E^\circ}{8 \Delta E_0^\ddagger}. \quad (14)$$

In symmetric reactions ($\Delta E^\circ = 0$), the TS is located exactly midway between reactants and products ($\beta = 0.50$) whereas for exothermic reactions ($\Delta E^\circ < 0$) $\beta < 0.50$ indicating that the TS is closer to reactants and $\beta > 0.50$ for endothermic reactions ($\Delta E^\circ > 0$) indicating that the TS is closer to the products, in agreement with the Hammond postulate [20, 31, 32].

3. Details of computation

A three-point finite difference approximation to the derivatives in equations (1) and (2) gives [2, 8]

$$\mu = -\frac{1}{2}(I + A) \quad (15)$$

and

$$\eta = \frac{1}{2}(I - A), \quad (16)$$

where I and A are the ionization potential and electron affinity, respectively. Further use of Koopman's theorem provides [34]:

$$\mu = \frac{1}{2}(\varepsilon_L + \varepsilon_H) \quad (17)$$

and

$$\eta = \frac{1}{2}(\varepsilon_L - \varepsilon_H), \quad (18)$$

where ε_L and ε_H are the lowest unoccupied and highest occupied molecular orbital energies, respectively. The μ and η values are calculated using equations (17) and (18) and in certain cases equations (15) and (16) were used for comparison purposes. The electrophilicity index and the molecular valency are obtained from equations (3) and (12), respectively.

Condensed-to-atom Fukui functions are obtained using the corresponding electronic population in equations (6) and (7); atomic valencies (V_k) were calculated by adding the off-diagonal matrix elements of the bond order matrix, equation (11).

In the present work we study internal rotations in HONO and HSNS, molecular vibrations in H₂O and the double proton transfer reaction in (HONO)₂; these processes are illustrated in figure 1. All the calculations have been carried out at the *ab initio* SCF level with the standard 6-311G** basis set occasionally supplemented by additional diffuse functions 6-311++G**. The DFT calculations are performed with B3LYP exchange-correlation functionals [35, 36] and 6-311G** basis set. Geometry optimization and frequency calculation (mainly to check the number of imaginary frequencies) are accomplished with the Gaussian 98 program [37]. Polarizability is calculated using both Pople's and Sadlej's [38] basis set. The profiles for the chemical reactions of different global reactivity indices E , μ , η , α , V and ω are obtained through single point calculations of the fully optimized structures previously determined during the intrinsic reaction coordinate (IRC) procedure [39, 40].

4. Results and discussion

4.1. Rotational isomerization of HXNX (X=O,S)

4.1.1. Chemical reactivity

Figure 1 (a) illustrates the *trans* \leftrightarrow *cis* isomerization of HXNX, X=O,S. Table 1 presents various global reactivity parameters, namely, E , μ (calculated using equations (15) and (17)), η (calculated using equations (16) and (18)), V , $\langle\alpha\rangle$, its out-of-plane component α_{zz} and the dipole moment (DM) for the reactant, transition state and products associated with the rotational isomerization of HONO and HSNS at HF/6-311G** and B3LYP/6-311G** levels. Polarizability values calculated using both Pople's and Sadlej's basis sets are reported. In all cases the reactant and product have no imaginary frequencies whereas the transition state has one imaginary frequency, as expected. At the HF and DFT levels considered here, the *trans* \leftrightarrow *cis* rotational isomerization of HONO and HSNS are thermodynamically favourable, in both cases the *cis* conformer being slightly more stable than the *trans* isomer.

In both cases the transition state corresponds to maximum energy, minimum hardness and minimum molecular valency values vindicating the validity of the principle of maximum hardness (PMH) and the maximum molecular valency principle (MMVP). The μ and η values calculated using either the finite difference approximation (equations (15) and (16)) or the frontier orbitals energies (equations (17) and (18)) show similar trends.

For HONO $\langle\alpha\rangle$ is maximum at the TS but it is minimum at the transition state of HSNS, a case already pointed out [41] in the context of internal rotation of formamide and thioformamide. Based on the prescription of Ghanty and Ghosh [41] we also present the zz component of α calculated using Pople's as well as Sadlej's basis sets. The α_{zz} values for transition states of all the internal rotations calculated at all levels of theory are larger than the corresponding reactant and product values which can be considered to be a signature of the minimum polarizability principle (MMP). Note that the α_{zz} component refers to the out-of-plane (perpendicular) component for the reactant, the transition state and the product. In all cases (α_{zz}) using the Pople and Sadlej's basis sets provide identical trends, *trans*-HONO is more polar than *cis*-HONO but *cis*-HSNS is more polar than *trans*-HSNS.

Torsional potential energy and electronic properties were evaluated in 10° increments along the torsional angle θ within the interval $0^\circ \leq \theta \leq 180^\circ$. Figure 2 depicts the resulting qualitative profiles at the Hartree-Fock level of E , μ (equation (17)), η (equation (18)), V , $(\alpha_{zz})_{\text{Sadlej}}$ and ω for the internal rotations in HONO (figure 2 (a)) and HSNS (figure 2 (b)). The B3LYP/

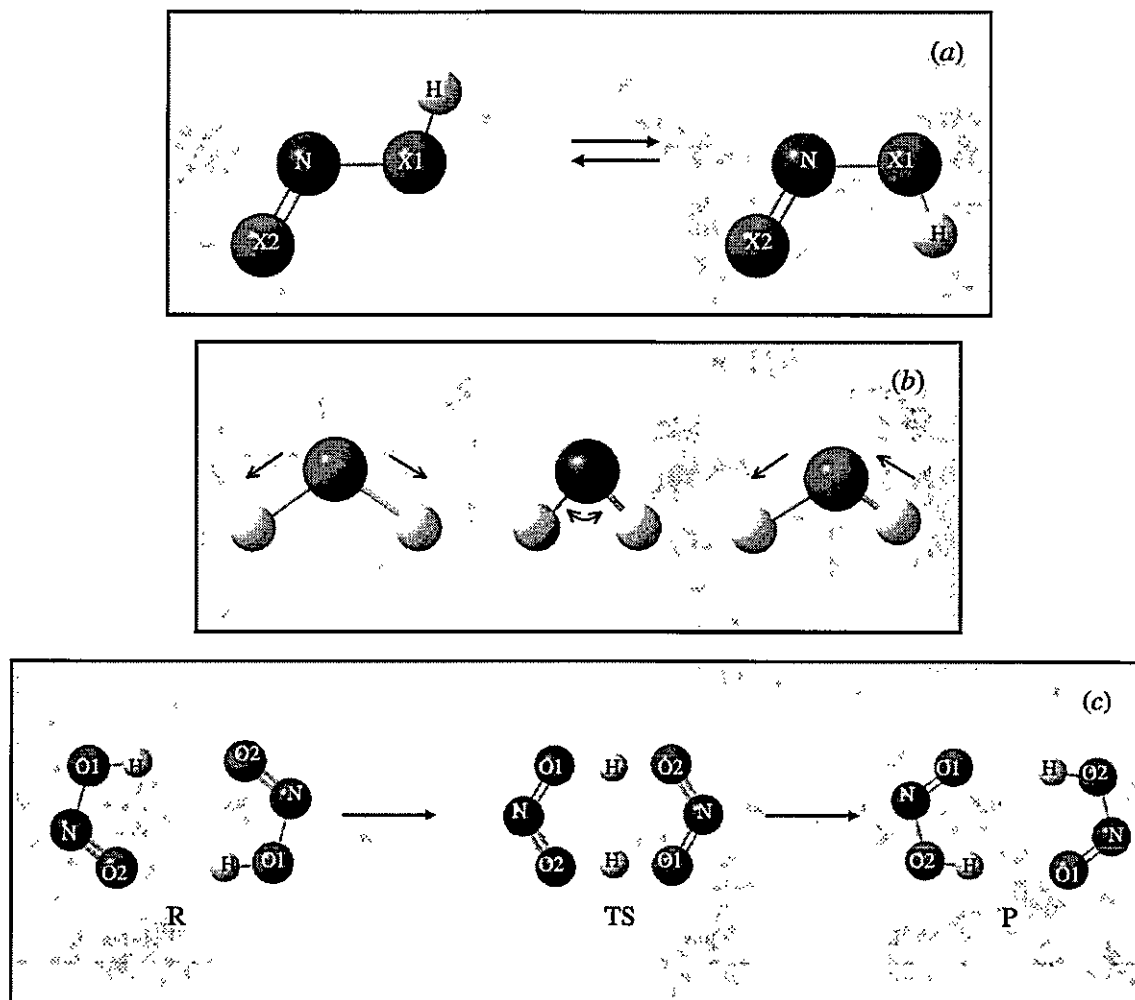


Figure 1. Illustration of the processes studied: (a) the *trans* \leftrightarrow *cis* rotational isomerization of HXNX, X=O,S; (b) molecular vibration of the water molecule and (c) the double proton transfer reaction in $(\text{HONO})_2$.

Table 1. Global properties at the stationary points for the isomerization reaction of HONO and HSNS. First entry corresponds to the HF results whereas the second entry displays the DFT results. (E , $\langle \alpha \rangle$ and α_{zz} are in au; μ and η in eV; DM is in Debye.)

| | E | μ (equation 15) | μ (equation 17) | η (equation 16) | η (equation 18) | $\langle \alpha \rangle$ | α_{zz} | V | DM |
|-------------------------------|-------------|------------------------|------------------------|-------------------------|-------------------------|--------------------------|---------------|--------|--------|
| HONO | | | | | | | | | |
| <i>trans</i> | -204.700158 | -4.3542 | -4.4627 | 6.1825 | 7.7635 | 13.448 | 7.488 | 3.7597 | 2.5469 |
| ($\theta = 0$) | -205.761769 | -7.1580 | -5.1239 | 8.1045 | 2.6803 | 15.352 | 7.806 | 3.9783 | 2.0645 |
| <i>TS</i> ($\theta = 92.6$) | -204.682531 | -6.0247 | -4.8028 | 4.8137 | 7.5213 | 13.535 | 9.477 | 3.6886 | 1.8656 |
| <i>TS</i> ($\theta = 92.5$) | -205.741044 | -5.9158 | -5.5675 | 5.6491 | 2.4109 | 15.334 | 10.516 | 3.8779 | 1.6155 |
| <i>cis</i> | -204.701446 | -4.6280 | -4.7811 | 6.2477 | 7.9104 | 13.268 | 7.402 | 3.7497 | 1.5730 |
| ($\theta = 180$) | -205.762150 | -5.4478 | -5.3634 | 6.2392 | 2.7892 | 15.110 | 7.703 | 3.9815 | 1.5151 |
| HSNS | | | | | | | | | |
| <i>trans</i> | -850.021798 | -5.0664 | -4.4736 | 4.2301 | 4.8546 | 40.576 | 19.690 | 3.7540 | 1.9299 |
| ($\theta = 0$) | -851.727234 | -5.1876 | -4.8872 | 3.9436 | 1.3062 | 43.653 | 20.249 | 3.9734 | 2.1297 |
| <i>TS</i> ($\theta = 93.8$) | -850.001284 | -4.7842 | -4.7539 | 3.5933 | 4.7403 | 37.645 | 25.386 | 3.6253 | 1.7356 |
| <i>TS</i> ($\theta = 92.7$) | -851.702711 | -6.0386 | -5.4124 | 4.1972 | 1.1511 | 42.099 | 27.068 | 3.8109 | 1.6378 |
| <i>cis</i> | -850.022786 | -5.1513 | -4.5764 | 4.2442 | 4.8850 | 40.189 | 19.316 | 3.7627 | 2.2822 |
| ($\theta = 180$) | -851.729019 | -6.5095 | -4.9716 | 5.2023 | 1.3551 | 43.380 | 19.836 | 3.9993 | 2.3820 |

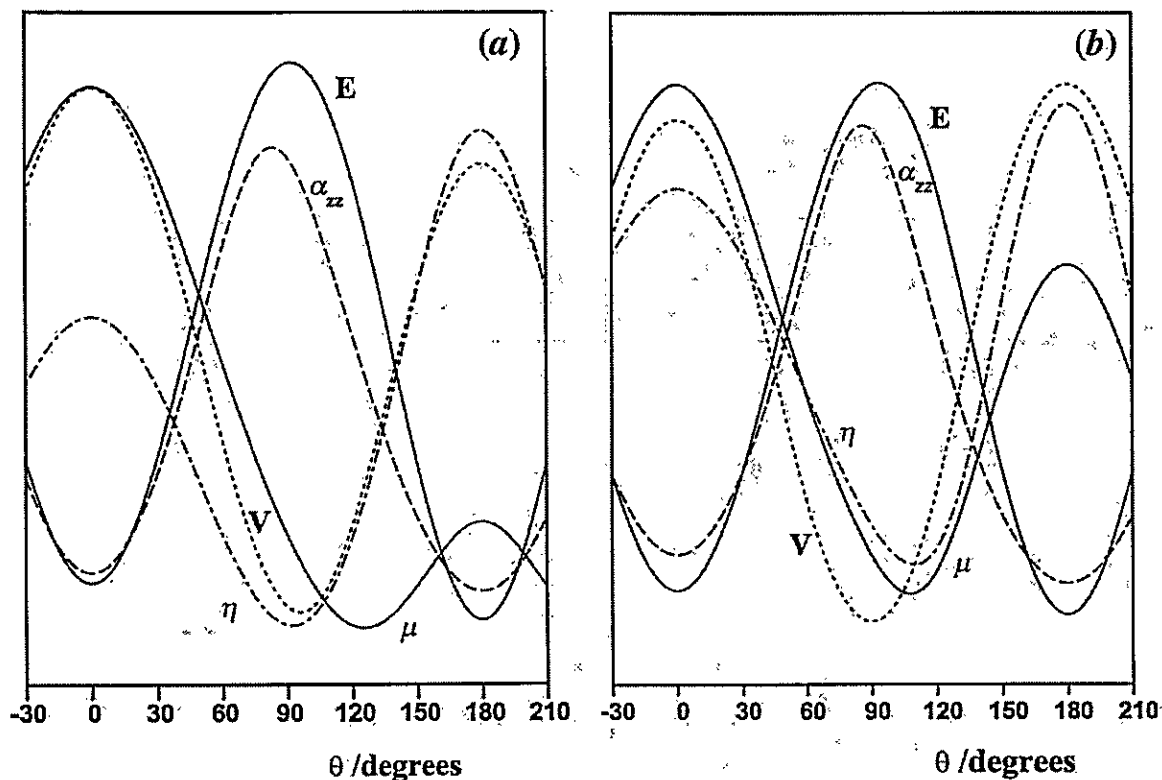


Figure 2. HF/6-311G** qualitative profiles along the torsional coordinate of global reactivity properties of (a) HONO and (b) HSNS. Representative numerical values for these properties are given in tables 1 and 2.

Table 2. Activation properties of the isomerization reaction of HONO and HSNS. All values are in kcal mol⁻¹.

| | ΔE^o | ΔE^\ddagger | $\Delta\mu^o$ | $\Delta\mu^\ddagger$ | $\Delta\eta^o$ | $\Delta\eta^\ddagger$ | β |
|-------------|--------------|---------------------|---------------|----------------------|----------------|-----------------------|---------|
| HONO | | | | | | | |
| HF | -0.8082 | 11.0611 | -7.3424 | -7.8428 | 3.3876 | -5.5852 | 0.4912 |
| DFT | -0.2391 | 13.0051 | -5.5230 | -10.2296 | 2.5113 | -6.2125 | 0.4977 |
| HSNS | | | | | | | |
| HF | -0.6200 | 12.8728 | -2.3706 | -6.4638 | 0.7010 | -2.6358 | 0.4941 |
| DFT | -1.1201 | 15.3884 | -1.9463 | -12.1113 | 1.1277 | -3.5767 | 0.4912 |

6-311G** profiles show the same trends for most properties and therefore are not included in the figure. As already mentioned, in or around the TS, E , α_{zz} and ω are maxima and μ , η and V are minima for all cases, validating PMH, MPP and MMVP. Within this frame, extremization of ω can be analyzed in terms of the same for μ and η : extremals (maximum or minimum) for μ and η correspond to an extremal in ω . Specifically the point at which both μ and η are maxima (minima), ω would be a minimum (maximum). The exact location of the extrema in ω would also be governed by the corresponding extremal locations in μ and η .

Table 2 provides relative values at HF/6-311G** and B3LYP/6-311G** levels of the energy (ΔE^o and ΔE^\ddagger) chemical potential ($\Delta\mu^o$ and $\Delta\mu^\ddagger$) and hardness ($\Delta\eta^o$

and $\Delta\eta^\ddagger$), these latter quantities being calculated using equations (17) and (18). Also included in the table is the Brønsted coefficient β (equation (14)) which indicates whether the TS is closer to the reactant or the product. As pointed out earlier by Toro-Labbé and co-workers [31], for any reaction the product is the hardest species for the Hammond-type reaction while the reactant is the harder for an anti-Hammond-type reaction. The rotational isomerizations in HONO and HSNS are of Hammond type, both reactions are exoenergetic ($\Delta E^o < 0$) and $\beta < 0.5$, in agreement with the simultaneous validity of the PMH and the Hammond postulate.

It is interesting to note that at both HF and DFT levels, the torsional barriers of HONO and HSNS are quite close to each other, in both calculations HSNS

presenting a slightly higher value of ΔE^\ddagger than HONO. This is indicating that the nature of the torsional barrier is quite the same for both isomerization reactions. On the other hand, it should be mentioned that zero point energy (ZPE) corrections have no noticeable effect on the barriers given in table 2.

4.1.2. Site selectivity

The profiles of site selectivity indices are displayed in figure 3. Condensed Fukui functions (f_k) were determined using equations (7) which in most cases also assume their extremum values in or around the TS; the same trends are observed when using the finite difference approximation of equations (6). Atomic valencies remain quite constant along the reaction coordinate with the exception of V_{O1} in HONO and V_{S1} in HSNS which present minima at the TS. This confirms the above observation about the common nature of the torsional potential barrier of HONO and HSNS. As for the atomic valencies, Fukui functions are not strongly dependent on the torsional angle; the most remarkable changes of the Fukui function along θ are observed in the electrophilic functions of the oxygen atoms and they are nicely opposite as expected. Besides, most reactivity pattern for electrophilic or nucleophilic attacks remains quite constant along θ .

It is interesting to note that the V_{X1} profiles are inverse to those of f_{X1}^- . This fact may be explained as follows: since all V_k s are positive and the maximum value of V implies stability, a larger V_k site is supposed to be less reactive, which is the reverse of the situation if the site has larger f_k since that implies more reactivity [2, 18].

4.2. Molecular vibrations

4.2.1. Chemical reactivity

The vibrational modes of water which are studied here are illustrated in figure 1(b). HF/6-311G** qualitative profiles of different global reactivity indices associated with the symmetric (A_1) stretching and bending and asymmetric (B_2) stretching vibrational modes of water are presented in figure 4; the B3LYP/6-311G** profiles show exactly the same trends and therefore are not included in the figure. As already pointed out by Pearson and Palke [42], for the symmetric stretching and bending modes none of these properties except E (and η for the bending mode) attains a clear-cut extremum. For the symmetric stretching mode it can be observed that η , V , α and ω tend to unphysical extremum values when the hydrogen atoms collapse toward the oxygen atom. This behaviour is due to the strong variation of the external potential during the symmetric vibrations. More interesting results are obtained from the asymmetric stretching mode of

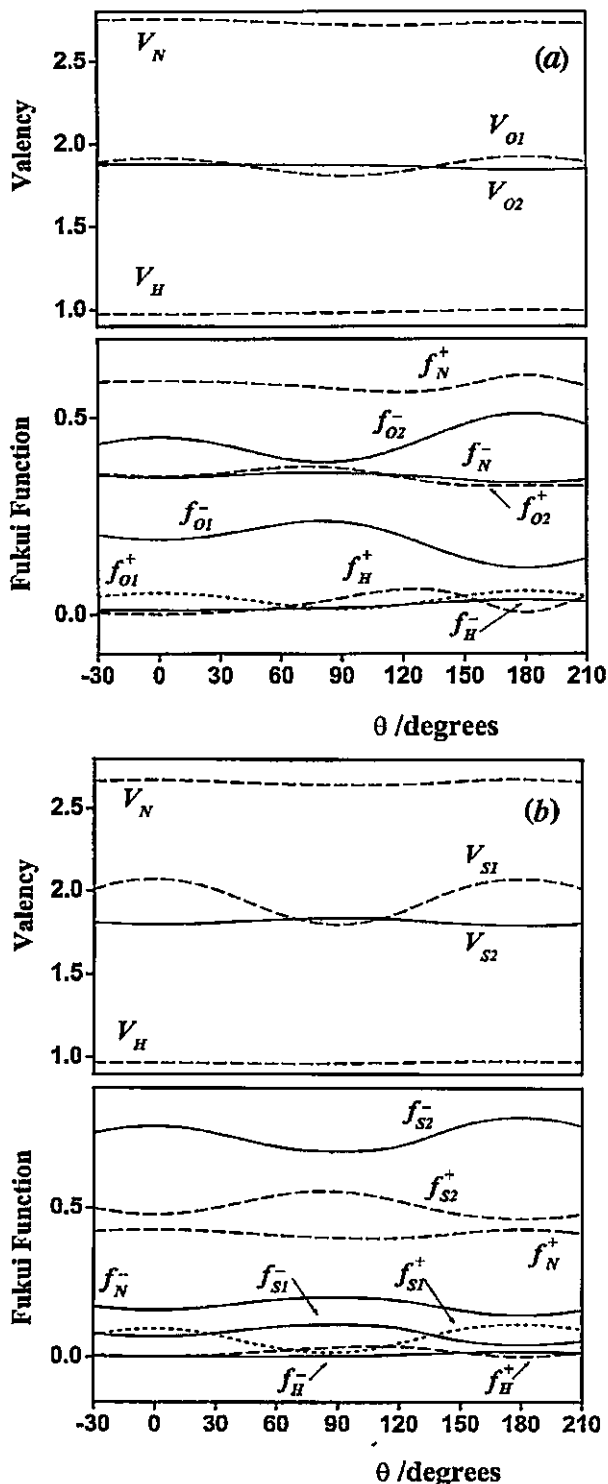


Figure 3. HF/6-311G** profiles along the torsional coordinate of local selectivity properties of (a) HONO and (b) HSNS.

vibration where the external potential remains constant during the nuclear motion (figure 4(c)). At the equilibrium geometry, E , α and ω are minima and μ , V and η are maxima confirming the validity of PMH,

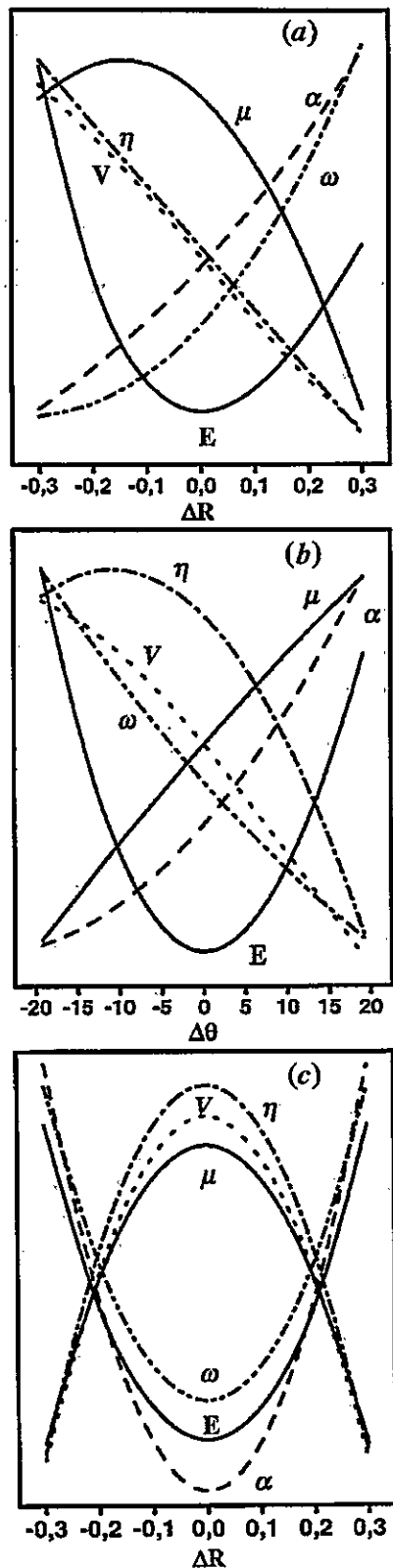


Figure 4. HF/6-311G** qualitative profiles of global reactivity properties along the vibrational modes of water: (a) symmetric stretching; (b) asymmetric bending and (c) asymmetric stretching.

MPP and MMVP. Since both μ and η are maxima for $\Delta R=0$, ω attains its minimum value at the equilibrium configuration.

Figure 5 displays plots of α_{Sadlej} versus α_{Pople} and μ and η calculated with equations (15) and (16) versus those quantities calculated using equations (17) and (18) for the asymmetric stretching of H_2O at the HF/6-311G** level. The linear behaviour in all cases confirms that the use of either two possibilities to obtain the property to characterize the asymmetric molecular vibration is adequate and leads to the right description of the property during the vibrational motion.

4.2.2. Site selectivity

Figure 6 displays the profiles of site selectivity descriptors during the molecular vibrations at the HF level; similar trends have been found for the DFT calculations. Fukui functions have been determined using the molecular orbital approximation, equations (7), although similar trends are obtained using the finite difference approximation of equations (6). It can be observed in figures 6(a) and (b) that most local properties remain constant as the vibrational coordinate changes. In the asymmetric stretching (figure 6(c)) again most local properties remain constant during the vibrational motion and we observe that f_{O}^+ and V_{O} show opposite behaviour as the bond length varies, as expected from the chemical intuition. Note that the $\{f_{\text{H1}}^+, f_{\text{H2}}^+\}$ and $\{V_{\text{H1}}, V_{\text{H2}}\}$ pairs intersect at the equilibrium geometry. It tells us that when electrophilicity at any centre goes down during oscillation it increases at some other centre and they become equal at the equilibrium position. The opposite behaviour of f_{H1}^+ and f_{H2}^+ confirms that this asymmetric stretching is the reactive mode for the dissociation of water. In all these plots HF/6-311G** and B3LYP/6-311G** calculations show identical behaviour in almost all cases. The same trends are also observed for the orbital Fukui functions.

4.3. Double proton transfer in $(\text{HONO})_2$

4.3.1. Chemical reactivity

Figure 1(c) displays an illustration of the synchronic double proton transfer reaction in $(\text{HONO})_2$; this is a symmetric reaction in which reactants are equal to products and the transition state is found exactly midway between these species. Table 3 presents numerical values of various global reactivity parameters for the reactant (product) and transition state for the double proton transfer in $(\text{HONO})_2$ at HF/6-311G** and B3LYP/6-311G** levels. Since the protons are transferred synchronically, the profiles are symmetric and the dipole moment is zero along the reaction coordinate. Polarizability values calculated using Pople's basis

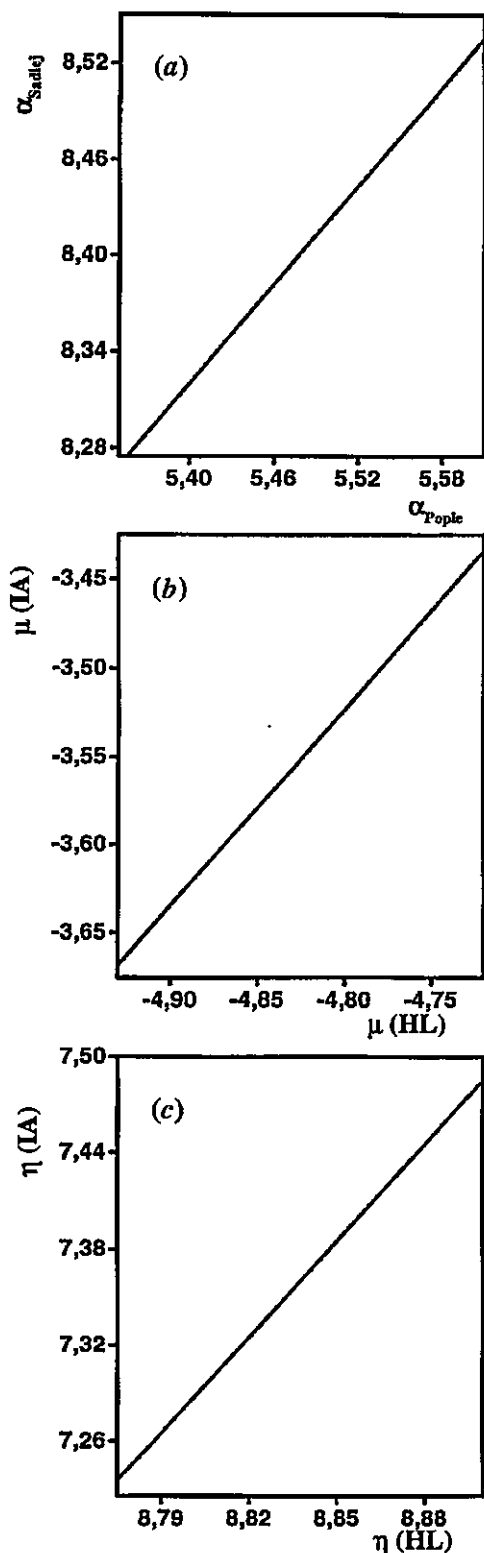


Figure 5. Characterization of the asymmetric stretching mode of water: correlation between (a) polarizabilities determined using different basis sets (Sadlej and Pople); (b) chemical potential determined using equations (15) and (17); (c) molecular hardness determined using equations (16) and (18).

set are also reported. In both calculations the reactant (product) has no imaginary frequencies whereas the transition state has one imaginary frequency, as expected.

Figure 7 presents the HF/6-311G** qualitative profiles of ΔE , $\Delta\mu$, $\Delta\eta$, $\langle\alpha\rangle_{\text{Pople}}$, $\langle\alpha_{zz}\rangle_{\text{Pople}}$, V and ω along the intrinsic reaction coordinate (IRC) of the double proton transfer reaction in (HONO)₂. All the profiles are symmetric owing to the symmetry of reactant and product, which happens to be the same dimer. At the TS ($IRC = 0$), all properties attain extremum values and it can be confirmed that the PMH, MPP and MMVP are valid for this reaction. It is interesting to note that μ is quite constant along the IRC and its profile attains a local maximum with two minima symmetrically positioned around the $IRC = 0$. Note that the position of these critical points coincides with the position of critical or inflection points of η , ω , α , α_{zz} and V . The critical points in μ , although hardly perceptible, may help characterize the mechanism of the reaction; the proton transfer is initiated by the displacement of the whole monomeric structures to favour the subsequent proton transfer that starts to occur within the TS region which is indicated in figure 7. This region can be defined unambiguously as the region delimited by the critical points of the force profile [14, 20, 31]. Similarly a local minimum at the TS bracketed by two local maxima is observed for the V profile. The maximum value of V at the reactants (products) together with the minimum at the TS confirms the MMVP. The profile of ω is governed by those of μ (mainly) and η ; ω presents a local maximum at the TS with $\omega_{\text{TS}} \gg \omega_{\text{Reactant(Product)}}$. All the above-discussed trends were also obtained at the B3LYP/6-311G** level.

Table 4 provides relative values at HF/6-311G** and B3LYP/6-311G** levels of the activation properties such as energy (ΔE^\ddagger) chemical potential ($\Delta\mu^\ddagger$) and hardness ($\Delta\eta^\ddagger$); the latter are calculated using equations (17) and (18). It is interesting to note that the B3LYP barrier is about half that of the HF barrier, with the same relation obtained for the activation hardness. The ZPE correction does not considerably change the barrier heights reported in table 4.

4.3.2. Site selectivity

The profiles along the intrinsic reaction coordinate of local selectivity properties are displayed in figure 8. For the double proton transfer reaction the condensed Fukui functions at the oxygen sites show reciprocal trends along the IRC when compared with those of the corresponding atomic valencies, a fact which is also observed in the cases of molecular internal rotations and vibrations. Any site with larger f_k signals high reactivity

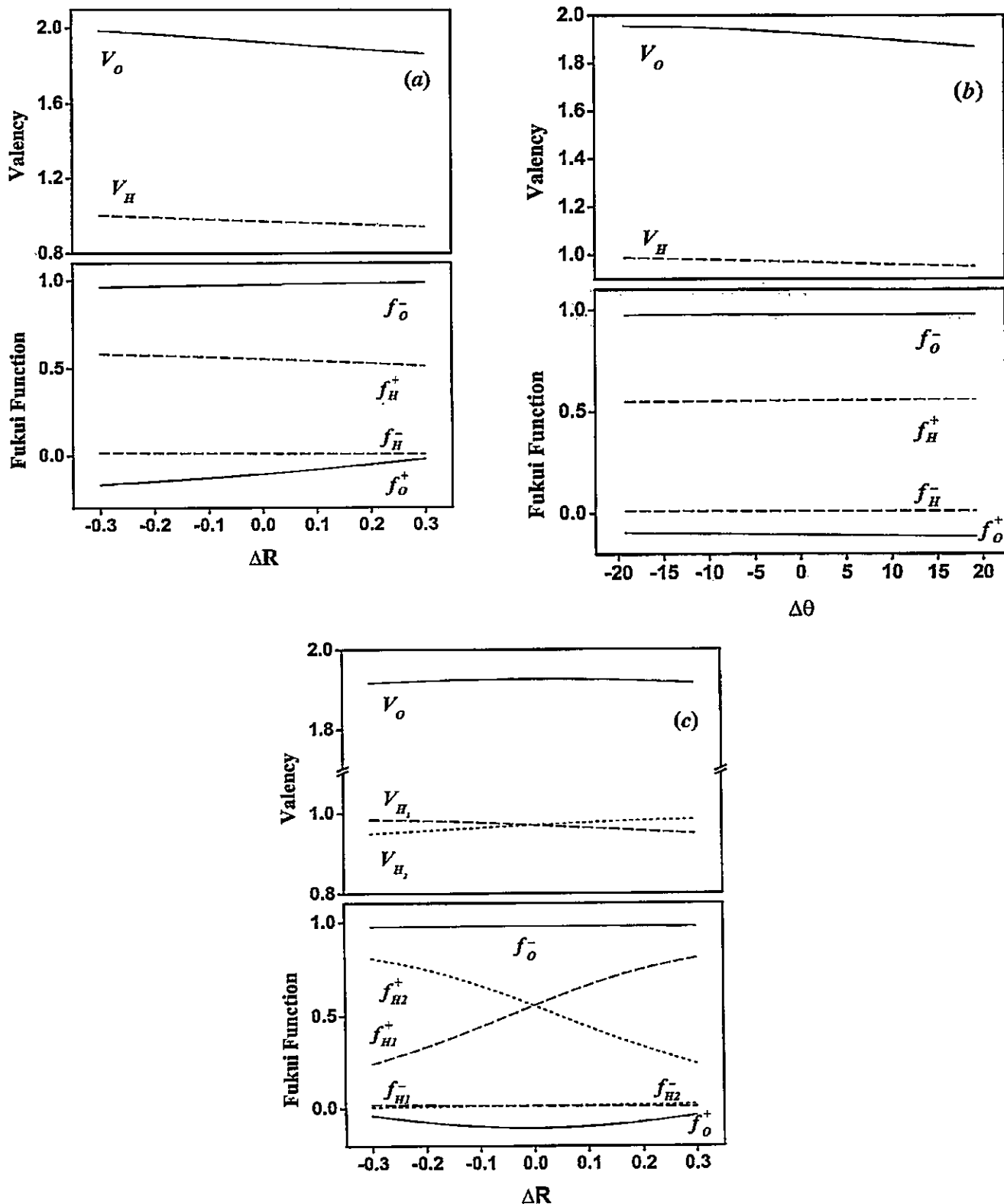


Figure 6. HF/6-311G** profiles of local selectivity properties along the vibrational modes of water: (a) symmetric stretching; (b) asymmetric bending and (c) asymmetric stretching.

Table 3. Reference values of global properties of reactant (product) and transition state (TS) associated with the double proton transfer in $(\text{HONO})_2$. E , $\langle \alpha \rangle$ and α_{zz} are given in au whereas μ , η are in eV. The first entry corresponds to HF results and the second entry to B3LYP results.

| | E | μ (equation 15) | μ (equation 17) | η (equation 16) | η (equation 18) | $\langle \alpha \rangle$ | α_{zz} | V |
|------|-------------|------------------------|------------------------|-------------------------|-------------------------|--------------------------|---------------|--------|
| R(P) | -409.411104 | -4.9907 | -5.0754 | 6.9757 | 7.7024 | 26.643 | 14.715 | 7.4699 |
| | -411.534460 | -7.8537 | -5.6513 | 7.3094 | 2.5919 | 30.601 | 15.364 | 7.9659 |
| TS | -409.363061 | -5.1093 | -5.1159 | 6.4796 | 7.0991 | 27.681 | 14.895 | 7.3706 |
| | -411.509790 | -5.7351 | -5.6641 | 4.9591 | 2.2801 | 30.928 | 15.503 | 7.9545 |

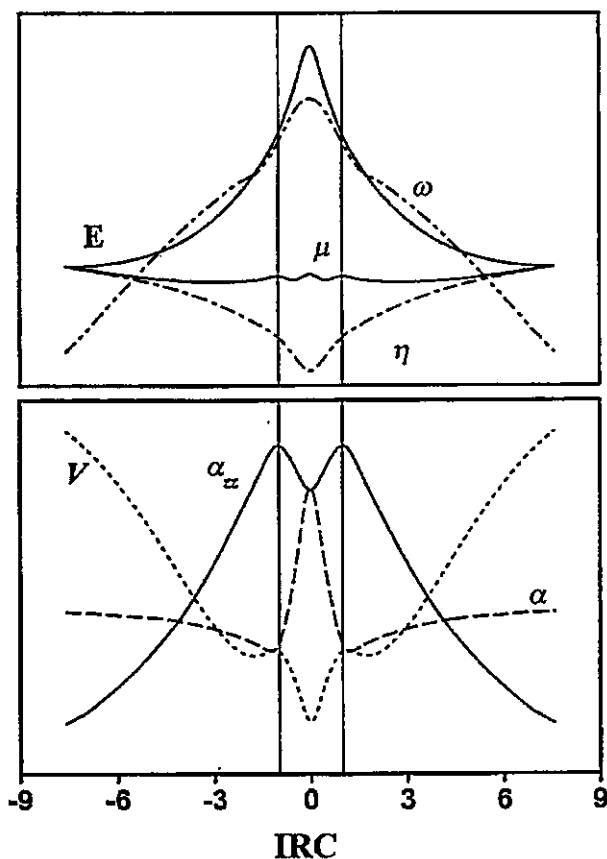


Figure 7. HF/6-311G** qualitative profiles of global reactivity properties along the internal reaction coordinate (IRC) of the synchronic double proton transfer reaction in $(\text{HONO})_2$. The region where the transfer occurs is defined by the vertical lines around the TS.

while that with high V_k implies more stability. The most pronounced changes are noticed in the profiles of f_k^\pm for the single-bonded and double-bonded oxygen atoms. Both the single-bonded and double-bonded O centres (O1 and O2, respectively) are always more reactive towards electrophiles than nucleophiles ($f_{\text{O}2}^- > f_{\text{O}2}^+$ and $f_{\text{O}1}^- > f_{\text{O}1}^+$) although they (f^+ and f^-) exhibit similar profiles along the IRC for both O1 and O2.

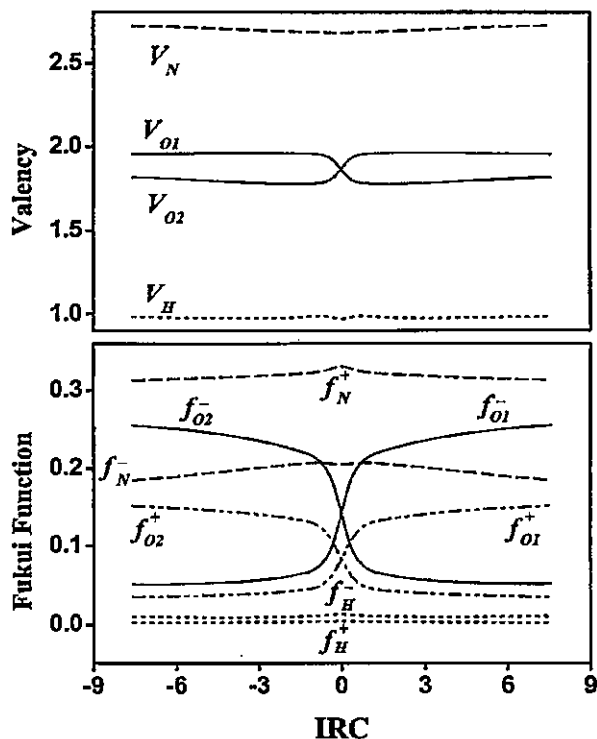


Figure 8. HF/6-311G** profiles of local selectivity properties along the internal reaction coordinate (IRC) of the double proton transfer reaction in $(\text{HONO})_2$.

Similar profiles are exhibited by $f_{\text{O}1}^\pm$; they start from a smaller value, increase suddenly near the TS and then level off. The profiles of $f_{\text{O}1}^-$ and $f_{\text{O}2}^-$ intersect at the TS as is the case with $f_{\text{O}1}^+$ and $f_{\text{O}2}^+$ which would help in locating the TS. The hydrogen profiles of Fukui functions and the valency remain more or less constant, suddenly decrease around the TS and then again remain more or less constant. The sudden change of these properties occurs exactly within the region defined in the above paragraphs and confirms the reaction mechanism in that the actual proton transfer starts at the vicinity of the transition state. On the other hand, while V_N exhibits a broad minimum along the IRC, the nucleophilic Fukui function f_N^- shows a local maximum around the TS

Table 4. Activation properties associated with the double proton transfer in (HONO)₂. All values are in kcal mol⁻¹ but the polarizability is given in au.

| Method | ΔE^\ddagger | $\Delta\mu^\ddagger$ (equation 17) | $\Delta\eta^\ddagger$ (equation 18) | $\Delta\omega^\ddagger$ | $\Delta\alpha^\ddagger$ | $\Delta\alpha_{zz}^\ddagger$ |
|--------|---------------------|---------------------------------------|--|-------------------------|-------------------------|------------------------------|
| RHF | 30.1474 | -0.9339 | -13.9123 | 3.9479 | 1.038 | 0.180 |
| B3LYP | 15.4807 | -0.2952 | -7.1902 | 20.1594 | 0.327 | 0.139 |

indicating an increasing propensity towards an electrophilic attack.

5. Concluding remarks

Molecular internal rotations in HONO, HSNS, various symmetric and asymmetric stretching and bending vibrations in H₂O and the double proton transfer reaction in (HONO)₂ have been studied at the Hartree-Fock and DFT levels. Profiles of global and local reactivity and selectivity parameters have been determined.

For the internal rotations it has been found that the transition states are associated with maximum values in E , α_{zz} and ω and minimum values in μ , η and V confirming the validity of the principles of maximum hardness and molecular valency and the minimum polarizability principle. The extremal point in ω can be located by knowing the same for μ and η . Maxima (minima) in both μ and η correspond to the minimum (maximum) in ω . The Fukui function and the atomic valency at a given atomic site show an inverse relationship.

For the symmetric vibrational modes, except E , no other property attains its extremum during vibration. For the asymmetric stretching mode the equilibrium configuration is characterized by minimum E and α values and maximum μ , η and V values as would have been expected from PMH, MPP and MMVP. Since both μ and η are maxima at the equilibrium point, ω becomes a minimum. The electrophilic and nucleophilic Fukui functions in general show inverse behaviour during the vibrational coordinate variation as is the case with f_k and V_k . It implies that if a centre becomes more favourable toward an electrophilic attack for a given vibrational mode it would simultaneously become less favourable towards a nucleophilic attack.

The E , $\langle\alpha\rangle$ and α_{zz} profiles pass through maxima and the η profile passes through a minimum in the transition state of the double proton transfer reaction in (HONO)₂ acting as signatures of MPP and PMH. The V value for the transition state is much smaller than those of the reactant and the product which may be considered to be a consequence of MMVP. The μ value in the transition state is a local maximum in between two minima, a

feature which is also reflected in the profile of other global and local properties. The V_k and f_k profiles exhibit opposite trends for this reaction and oxygen centres always prefer electrophilic attack to nucleophilic attack. The intersection points of the electrophilic (nucleophilic as well) Fukui functions for the single- and double-bonded oxygen centres may be used to locate the transition state. The N-centre becomes more prone towards electrophilic attack at the transition state.

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The Formation of Neutral Copper Clusters From Experimental Binding Energies and Reactivity Descriptors.

Pablo Jaque and Alejandro Toro-Labbé¹

Laboratorio de Química Teórica Computacional (QTC),
Facultad de Química, Pontificia Universidad Católica de Chile.
Casilla 306, Correo 22, Santiago, Chile.

Abstract

In this paper we study and rationalize the formation of neutral copper clusters from dimer to nonamer using the available experimental data of binding energies and electronic properties. A complete and consistent picture of the formation of copper clusters in term of the changes in chemical potential and hardness emerges indicating that the one-atom growth reactions are mainly driven by changes in hardness. An analytic expression for the binding energy as a function of the cluster size is proposed and used to predict the growth pattern of copper clusters.

¹e-mail: atola@puc.cl

1. Introduction.

The interest in the study of small metal clusters has grown considerably in the last years because new experimental and theoretical techniques have been developed allowing detailed characterizations of this type of systems [1, 2]. Much information is now available concerning clusters' spectroscopy, structure and their chemical reactivity toward small molecules. Transition metals clusters are particularly interesting for their potential use in many processes like heterogeneous catalysis, in organometallic chemistry or new electronic materials [1, 3].

An interesting topic in clusters science is the study of the evolution of clusters' properties when increasing the number of constituent atoms. Neutral copper clusters even-numbered are closed-shell systems whereas odd-numbered copper clusters are open-shell systems [4–10]. In investigations on ion abundances [11–13], ionization potentials [14–18], electron affinities [19] and binding energies of neutral and charged copper clusters (Cu_n) [20, 21], a typical behavior known as even-odd alternation has been found. In this paper our main goal is to provide a new viewpoint to understand the formation reaction $Cu_{n-1} + Cu \longrightarrow Cu_n$ ($n = 2 - 9$), in doing so the observed even-odd alternation of binding energies will be analyzed in detail. Our approach consists in the rationalization of the available experimental data of binding energies through the use of reactivity descriptors calculated from experimental data of ionization potentials and electron affinities [14–21]. As a result of this approach, correlations between energetic and electronic properties can emerge, such correlations are expected to be useful in understanding the formation reaction of copper clusters and may provides new elements to

rationalize growth reactions of metal clusters.

In a recent paper [10] we have characterized neutral copper clusters ($Cu_n=1-9$) in terms of calculated chemical reactivity descriptors defined within the frame of Density Functional Theory (DFT) and usually used to study the reactivity pattern of molecules and molecular aggregates [10,22,23]. The set of reactivity descriptors, electronic chemical potential (μ), chemical hardness (η) and electrophilicity index (ω), together with chemical reactivity principles such as the principle of maximum hardness, define quite powerful tools to analyze and rationalize different processes experienced by complex systems [10,23–26].

A formation reaction can be seen as resulting from the combination and redistribution of atom's and fragment's electron densities, giving rise to a new electronic distribution from which the electronic descriptors of the new aggregate are derived. DFT [27] is quite well suited to describe such electronic reorganization processes as it provides the basis for rigorous mathematical definitions of reactivity descriptors such as chemical potential, electronegativity [28], chemical hardness [29], softness ($S = 1/\eta$), etc., all these are well established global quantities in chemical reactivity studies and are going to be used in this paper to study the formation process of copper clusters Cu_n ($n=2-9$) in one atom growth reactions.

The chemical potential characterizes the escaping tendency of electrons from equilibrium, it is the Lagrange multiplier associated with the normalization constraint in DFT, on the other hand, it is the negative of the electronegativity ($\chi = -\mu$) [28]. Hardness represents the resistance to charge transfer

while softness is a measure of the propensity of the system to change its electronic distribution, it has been qualitatively related to the polarizability α [27, 29–31]. On the other hand, the electrophilicity index measures the stabilization of a system when it acquires electronic charge from the surroundings [32].

A major focus of attention and discussion in the application of DFT to chemical reactivity is the principle of maximum hardness (PMH) proposed by Pearson [30], the PMH asserts that molecular systems at equilibrium present the highest value of hardness, the PMH is a widely accepted electronic structure principle, that in most cases complement the minimum energy criterion for molecular stability. The PMH provides an independent criterion to rationalize the behavior of chemical reactions.

In the next Section we present a summary of the theoretical element we use here, Section 3 contains the results and discussion and in Section 4 we draw our conclusions.

2. Theoretical Background.

In DFT, the chemical potential and molecular hardness for an N -electron system with total energy E and external potential $v(\vec{r})$ are defined as the following first and second derivatives of the energy with respect to N [27–29]:

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{v(\vec{r})} = -\chi \quad (1)$$

and

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(\vec{r})} = \frac{1}{2} \left(\frac{\partial \mu}{\partial N} \right)_{v(\vec{r})}. \quad (2)$$

In numerical applications, μ and η are calculated through the following approximate versions of Eqns. (1) and (2), based upon the finite difference approximation, where these derivatives are calculated numerically as energy differences between systems with $(N-1)$, N and $(N+1)$ electrons [27]:

$$\mu \approx -\frac{1}{2} (IP + EA) = \frac{1}{2} [E(N+1) - E(N-1)] \quad (3)$$

and

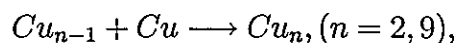
$$\eta \approx \frac{1}{2} (IP - EA) = \frac{1}{2} [E(N+1) + E(N-1) - 2E(N)], \quad (4)$$

$IP = [E(N-1) - E(N)]$ is the ionization potential and $EA = [E(N) - E(N+1)]$ is the electron affinity. The electrophilicity index is in turn defined as [32]:

$$\omega = \frac{\mu^2}{2\eta}. \quad (5)$$

Considering clusters or metallic surfaces as a binding environments, ω can be especially suited to analyze the interaction with small molecules in heterogeneous catalysis processes.

Let us consider the following process, referred to as one-atom growth reaction:



the overall energy change that corresponds to the binding energy is given by $\Delta E = E(P) - [E(R1) + E(R2)]$, with $P=Cu_n$ is the product of the reaction and $R1=Cu_{n-1}$ and $R2=Cu$ are the reactants. When dealing with an electronic property, say Ω , we define: $\Delta\Omega = \Omega(P) - \mathcal{S}\{\Omega(R)\}$, ($\Omega = \mu, \eta$) and $\mathcal{S}\{\Omega(R)\} \equiv \Omega_S(R)$ is the Sanderson's average of the property associated to the reactants R1 and R2. The Sanderson's average of the chemical potential of reactants is given by the geometric mean of the chemical potentials of R1 and R [23, 25, 33–35]:

$$\mathcal{S}\{\mu\} = -[\mu_{R1} \cdot \mu_{R2}]^{1/2} \equiv \mu_S. \quad (6)$$

The Sanderson's average for the hardness of reactants is obtained by differentiating $\mathcal{S}\{\mu\}$ with respect to N thus obtaining [23, 25, 35, 36]

$$\mathcal{S}\{\eta\} = \left(\frac{\partial\mu_S}{\partial N}\right)_{v(\vec{r})} = \frac{\mu_S}{2} \left[\left(\frac{\eta}{\mu}\right)_{R1} + \left(\frac{\eta}{\mu}\right)_{R2} \right] \equiv \eta_S. \quad (7)$$

The difference between the averaged values ($\mathcal{S}\{\mu\}$ and $\mathcal{S}\{\eta\}$) with respect to the actual values obtained using Eqns. (3) and (4) might be attributed to relaxation of the electron density after bonding, the quantification of this difference may help understand the reordering of the electron density as the reaction takes place.

3. Results and Discussion.

A. Binding Energy, Ionization Potential and Electron Affinity.

Table I shows the experimental values of binding energies of the neutral co-

pper clusters (Cu_n) recently reported by Spasov *et al.* [20] and Ingólfsson *et al.* [21]. These authors have performed collision-induced dissociation (CID) experiments to study stability and fragmentation pathways for anionic and cationic copper clusters, respectively. Experimental data of bond energy for $Cu-Cu_{n-1}$ systems are therefore obtained from a thermodynamic cycle using dissociation energy of one atom loss from charged copper clusters and electron affinities [19], in the case of anionic clusters [20], or ionization potentials [14–18], for cationic clusters [21]. In our analysis we have considered the average values (ΔE) which are also given in Table I.

ΔE present an oscillatory behavior, even-numbered clusters present highest values of binding energy than odd-numbered clusters *i.e.* chemical bonds in clusters with even n are stronger than in clusters with odd n . Therefore in one-atom fragmentation reactions, clusters with even number of atoms are more stable than clusters with odd number of atoms. This is because clusters with even n present closed-shell electronic configurations that comes along with an extra stability whereas clusters with odd number of atoms present open-shell configurations [4–6,9,10] that makes them more reactive, this is in agreement to recent studies where it has been observed that odd-numbered clusters exhibit a high reactivity in front of NO [37] and O₂ [38]. On the other hand, in the limit of very large clusters the binding energy can be approached to the negative of the vaporization energy of the bulk solid, the experimental value for this property is 3.50 eV [39] and it will be used as a reference value in the forthcoming discussion.

The experimental values of ionization potentials [14–18] and electron affinities [19] reported in the literature for the copper clusters considered in this

work are quoted in Table II. It should be noticed that both properties follow an even–odd oscillatory pattern which is again attributed to the change of spin multiplicity of the ground state of neutral copper clusters, even-numbered clusters present higher and lower values of IP and EA , respectively, with respect to their neighboring odd-numbered systems. Therefore in the ionization process it is more difficult to remove an electron from the doubly occupied highest occupied molecular orbital (HOMO) than from a single occupied molecular orbital (SOMO) of an open-shell configuration cluster. In contrast to this, the electron attachment process will be more favorable in clusters with odd n because the electron will occupy a half-filled orbital (SOMO), as is expected from the high values of EA of these systems.

Size Dependence of IP and EA . Metal clusters are aggregates that have different properties than a single atom or the bulk metal, in fact these are the extreme that can be seen as infinitely small and infinitely large clusters. We have analyzed the evolution of IP and EA with the size of the clusters, both properties are expected to converge to the work function (Φ) in the limit as $n \rightarrow \infty$, *i.e.* to the value of the polycrystalline copper: $\Phi = 4.65 \text{ eV}$ [40]. In this context, it has been shown that the evolution of a property P , such as IP and EA , as a function of the number of atoms n can be described through the following analytic form [41]:

$$P(n) = P(\infty) + A \cdot n^{-1/3}, \quad (8)$$

where $P(\infty)$ corresponds to the property value in the limit of the bulk metal and A is a fitting parameter. Figure 1 displays the IP and EA values of the clusters, the straight lines are two-points references lines defined from the

following boundary conditions:

$$n^{-1/3} = \begin{cases} 0 \implies n \rightarrow \infty, \text{ bulk limit} \implies EA = IP = \Phi = 4.65 \text{ eV} \\ 1 \implies n = 1, \text{ atomic limit} \implies EA = 1.24 \text{ eV}; IP = 7.72 \text{ eV} \end{cases}$$

from the above conditions, the two-points reference lines of IP and EA are given by:

$$IP(n) = IP(\infty) + A_{IP} \cdot n^{-1/3} \quad (9)$$

and

$$EA(n) = EA(\infty) + A_{EA} \cdot n^{-1/3} \quad (10)$$

where $IP(\infty) = EA(\infty) = \Phi$; the values of the slopes are: $A_{IP} = 3.07$ and $A_{EA} = -3.41$. These results will be used in turn to define reference lines for μ and η .

It should be noticed that all clusters, excepting Cu_3 present lower values of EA than what is expected from the reference EA line. On the other hand, the IP values of even and odd-numbered clusters present different behavior with respect to the reference IP line, even clusters present higher values than what is expected from the reference line whereas odd clusters present lower values with respect to the reference IP s. This observation prompts us to conclude that the characteristic odd-even oscillatory behavior of electronic properties that depend on IP and EA should be mainly determined by the

ionization potential rather than the electron affinity.

B. Electronic Global Properties.

Using the values of IP and EA given in Table II in Eqns. (3) and (4), numerical values of chemical potential and molecular hardness are obtained, with these data the electrophilicity index for clusters from Cu to Cu_9 are estimated through Eqn. (5), the resulting numerical values are quoted in Table III. Also included in this Table are the Sanderson's average of the electronic properties of reactants (μ_S and η_S) obtained using Eqns. (6) and (7) from the corresponding values of Cu_{n-1} and Cu . The use of Sanderson's average properties in Eqn. (5) produces ω_S . It can be noticed that all DFT-descriptors present the characteristic even-odd pattern already observed in other properties this is also true for μ when excepting the reference Cu atom. This results is again attributed to the change in the spin multiplicity of ground state along the series.

Chemical Potential and Charge Transfer. When two systems are brought together, charge transfer occurs from a system with high μ to the system with a lower value of μ . From Table III it can be noticed that clusters with odd n (open-shell clusters) present high value of μ this indicates that open-shell systems have a more marked tendency to charge transfer than closed-shell configurations (even n). The tendency to close their electronic shell by losing one electron, as indicated in Figure 1, explain the relatively high reactivity presented by odd-numbered clusters, this is in agreement with some recent experimental studies [37,38].

In the context of formation reaction of molecules and aggregates, when two

components (in this case Cu and Cu_{n-1}) come into interaction, their μ 's tend to equalize and thus determining the direction of charge transfer, in all cases the transfer direction is from Cu_{n-1} to Cu , the only exception to this rule occurs in the formation of Cu_7 . An estimation of the charge transfer (ΔN) involved in the formation process of a two-fragment reaction can be obtained through the following expression [27, 28, 30]:

$$\Delta N = \frac{(\mu_1 - \mu_2)}{2(\eta_1 + \eta_2)} \quad (11)$$

The values of ΔN as well as its two contributions are quoted in Table IV. It is interesting to note that in general ΔN is quite small although in the formation of even clusters it becomes large mainly due to the small value of the hardness term, indeed the difference of chemical potentials ($|\mu_1 - \mu_2|$) is almost constant along the series, the average value being 0.37 eV for even clusters (Cu_2 is not included in this analysis) and 0.12 eV for odd clusters, thus showing a dispersion of few tenth of eV. The factor $2(\eta_1 + \eta_2)$ present a clear difference in the formation of clusters with odd and even n , the average values of $2(\eta_1 + \eta_2)$ is 11.04 eV for even clusters and 12.37 eV for odd clusters. This indicates that the formation of strong bonds in even-numbered clusters is characterized by a high electronic charge transfer between the reactants (Cu and Cu_{n-1}) until that their μ 's are equalized.

Figure 2(a) displays the values of μ and η together with their references lines obtained from $IP(n)$ and $EA(n)$, Eqns. (9) and (10), respectively. The two-points reference line for μ is given by:

$$\mu(n) = -\frac{1}{2}[IP(n) + EA(n)] = -\Phi + 0.17 \cdot n^{-1/3} \approx -\Phi, \quad (12)$$

that shows a very weak dependence of μ upon n , result that is confirmed by the experimental data points that appear scattered around the reference line. Constancy of μ along $n^{-1/3}$ indicates that η must be the property that drives the formation reactions of copper clusters.

The fact that the average of the experimental μ values is very close to the negative of the work function Φ indicates that chemical bonds in Cu clusters are expected to be similar to those in the bulk metal, this observation is in agreement with recent works on the topology of the electron density for face-centered cubic (*fcc*) copper [42] and copper clusters. These results add evidence to validate the use of metallic clusters in heterogenous catalysis as adequate models. It is interesting to note in Figure 2(a) that Cu_3 and Cu_9 present the highest values of μ along the series, this can be explained in term of ability of these two clusters to lose an electron to close their electronic shell thus leading to systems with 2 and 8 valence electrons, respectively, in agreement with the magic numbers into the jellium model, such a capacity to lose an electron is reflected in low values of the ionization potentials of Cu_3 and Cu_9 (see Table II). On the other hand, these clusters present the highest values for electron affinity thus showing their capacity to gain one electron, however this process do not lead to products that complains with the requirement for extra stability associated to closed shell systems in jellium model.

Chemical Hardness. The chemical hardness has been established as an electronic quantity that in many cases may be used to characterize the relative stability of molecules and aggregates through the PMH [30]. From Table III it should be noted that clusters with even n are harder than their neigh-

bors systems following an opposite trend to the binding energy (ΔE), this results is in agreement with the PMH.

Figure 2(a) also shows the experimental hardness data-points together with the two-points reference line determined from Eqns. (9) and (10):

$$\eta(n) = \frac{1}{2}[IP(n) - EA(n)] = \eta_{Cu} \cdot n^{-1/3}. \quad (13)$$

It should be noticed that η presents a quite strong dependence upon the size of the cluster with a slope that can be approached to the hardness of atomic copper. A close view of Figure 2(a) indicates that the η reference line fits correctly the values for odd clusters whereas those of even clusters are systematically above the line. This indicates that the extra stability of even clusters due to the closing shell effect, is accompanied by an increase of the hardness value. In this context, since the average η value of even clusters is above that of odd clusters by more than 0.8 eV, it is apparent that a simple model, such as that of Eqn. (13), is not able to reproduce the hardness variation upon $n^{-1/3}$, of both even and odd clusters, in a unified way.

When the η values of odd and even clusters are fitted separately against $n^{-1/3}$ under the condition that $\eta(\infty) = 0$, the reference straight lines displayed in Figure 2(b) are obtained, correlation coefficients are $r = 0.97$ and 0.98 , respectively. The slope of even clusters (4.70 eV) is larger than that of odd clusters (3.17 eV), which in turn is quite close to $\eta_{Cu} = 3.25 \text{ eV}$ of the η reference line that can describe correctly the growth pattern of odd clusters only. In summary, even clusters appear to be harder than odd clusters, this is evidence that the PMH holds for these systems.

Electrophilicity. Once discussed the behavior of μ and η , a comment on the trend observed in the electrophilicity index is in order (see Table III). In Cu_n the behavior presented by ω is mainly due to the term 2η since, as already pointed out, μ remains quite constant along the series, clusters with odd n are considerably softer than those with even n , this leads to high values of ω . The quantification of the maximum electronic charge that can be acquired by the systems until it reaches a stabilization energy, $\Delta E = -\omega$, is given by $\Delta N_{max} = -(\mu/\eta)$ [32], these values are quoted in Table IV. Note that clusters with odd n will acquire more charge until saturation than clusters with even n which are more stable because they are already saturated. Therefore the maximum electrophilic power presented by odd clusters is due basically to low values of η , this results is in agreement with the expected capacity of odd clusters to reach a closed-shell electronic configuration by accepting electronic charge from their surroundings.

Relaxation Effects. The difference between the electronic property calculated using the Sanderson's average (Eqns. (6) and (7)) with respect to the actual value determined from the *IPs* and *EAs* (Eqns. (3) and (4)) allows one to quantify the effect of relaxation and redistribution of the electronic density due to the new bonding interactions between Cu_{n-1} and Cu . In the context of one-atom growth reactions, note that μ_S values are quite close to the actual values obtained using Eqn. (4), this is due to the fact that $\mu(Cu_n)$ results from combination of $\mu(Cu_{n-1})$ and $\mu(Cu)$ that are quite close to each other. In contrast to this, comparison of η_S and η indicate that the formation of odd clusters is accompanied by stronger reordering than in even-numbered clusters which can be attributed to structural and spin density polarization effects. These results confirm the statement that the stability of even cluster

is determined by closed shell electronic structure as a manifestation of the PMH [43,44].

Table III shows that the chemical potential and hardness values using the Sanderson's formulae leads to the opposite trend with respect to the experimental one, this does not mean that the Sanderson's method is not right to estimate electronic properties of copper clusters from isolated fragments, but it suggests that the expected trend might be obtained through combination of other fragments. There are many possible reactions that lead to Cu_n from combination of different size clusters, in this paper we chose $Cu + Cu_{n-1} \rightarrow Cu_n$ and from the numerical viewpoint, these fragments lead to quite correct results for formation of even numbered clusters whereas that for odd clusters μ_S and η_S do not match the reference values. On the other hand, using the values of μ and η given in Table III it can be checked out that when different fragments are used to produce Cu_n thus leading to different formation reactions, for example $Cu_2 + Cu_{n-2} \rightarrow Cu_n$, then the correct trend of the even-odd oscillation is obtained. Although not shown here, the experimental trend of μ and η is reproduced when the combinations $Cu + Cu_{n-1}$ and $Cu_2 + Cu_{n-2}$ are used. Different formation and fragmentation pathways in neutral copper clusters can be discussed in the light of the above considerations, this will be treated in a forthcoming study.

C. Rationalization of Growing Reactions. The $\{\mu, \eta, E\}$ Representation. The connections between energy and electronic descriptors is of considerable theoretical interest since the change in electronic properties is related to the reaction mechanism, therefore the relation between energy and electronic properties allows one to connect the energetic and mechanistic as-

pects of a formation process, there are few interesting and useful attempts to relate electronic descriptors to reaction energies [24, 36, 45]. In this context, Gázquez *et al.* [45] have established a relationship between energy and hardness differences whereas that in more recent papers [24, 36], we have shown that different aspects of a chemical event are well described in a representation where the chemical potential and molecular hardness are taken as independent variables. In this context we write: $E \equiv E[\mu, \eta]$, with total differential:

$$dE = Q_\eta d\mu + Q_\mu d\eta \quad (14)$$

where

$$Q_\eta = \left(\frac{\partial E}{\partial \mu} \right)_\eta ; \quad Q_\mu = \left(\frac{\partial E}{\partial \eta} \right)_\mu . \quad (15)$$

The parameters Q_η and Q_μ are related to the charge redistributed among the atoms in the molecule during the chemical reaction. Therefore within this model and in the context of one-atom growth reactions it is possible to write the binding energy (ΔE) in term of two contribution, namely: ΔE_η and ΔE_μ , where the index is indicating that either the hardness or the chemical potential has been held constant during the stepwise process:

$$\Delta E = \Delta E_\eta + \Delta E_\mu, \quad (16)$$

each contribution can be written as:

$$\Delta E_\eta = \Delta E_\eta^\circ + Q_\eta \Delta \mu \quad (17)$$

and

$$\Delta E_{\mu} = \Delta E_{\mu}^{\circ} + Q_{\mu} \Delta \eta. \quad (18)$$

Where ΔE_{η}° , ΔE_{μ}° , Q_{η} and Q_{μ} are parameters that are determined through linear regressions; $\Delta\mu$ and $\Delta\eta$ are defined using the Sanderson's average as $\Delta\Omega = \Omega(P) - \mathcal{S}\{\Omega(R)\}$ ($\Omega = \mu, \eta$, see section 2). It is interesting to note that within this framework one can write the energy change through Eqns. (17) or (18) that depend only on two parameters each, when the chemical process is mainly driven by μ or η , respectively. Combination of Eqns. (17) and (18) is adequate when both electronic properties are driven the reaction [24]. On the other hand, note that a necessary condition for the principle of maximum hardness to be satisfied is that Q_{μ} must be negative. A decreasing ΔE_{μ} (higher stability) should be accompanied by increasing values of $\Delta\eta$.

It has been already pointed out that since μ remains quite constant when going from one clusters to another, hardness drives the formation processes and Eqn. (18) should help rationalize them. In Figure 3 we display ΔE vs $\Delta\eta$, it can be noticed that there is an inverse relation between these properties, in agreement with the PMH. Values of $Q_{\mu} = -0.514$ and $\Delta E_{\mu}^{\circ} = -1.881$ eV were determined through linear regression. Note that the linear regression procedure has been performed considering the experimental error of the binding energies.

In order to test the consistency of our model, we have recalculated the binding energies of Cu_n from Cu_{n-1} and Cu putting $\Delta\eta$, calculated from data given in Table III, into the Eqn. (18) and using the fitting parameters of

Figure 3, this gives the values displayed in Figure 4 that are compared with the experimental data of binding energies. It is interesting to note that the binding energies obtained through our approach reproduce the right tendency showing a fairly good agreement with the experimental values. Therefore, it is possible to estimate reasonably good binding energies of clusters only from their IP and EA values through the use of the two-parameter model, Eqn. (18). We conclude that hardness is the key property that drives the reactions.

D. A Model for the Binding Energy. The above results open the way to characterize the binding energy as a function of the size of the cluster by introducing the size dependence through the already established equations relating η with n . Figure 2(b) indicate that $\eta_{even} = 4.70 \cdot n^{-1/3}$ and $\eta_{odd} = 3.20 \cdot n^{-1/3}$, therefore $\Delta\eta = \pm \frac{3}{2} \cdot n^{-1/3}$ where the plus sign applies when an even numbered cluster is being formed and the minus sign is appropriate for formation of odd numbered clusters. Now putting $\Delta\eta = \pm \frac{3}{2} \cdot n^{-1/3}$ in Eqn. (18) and using the fact that the value of $\Delta E_{\mu}^{\circ} \sim -1.88 \text{ eV}$ (see Figure 3) is approximately equal to the half of the negative of the experimental vaporization energy of bulk copper ($\Delta E_{bulk}^{\circ} = 3.50 \text{ eV}$) that is to say $\Delta E_{\mu}^{\circ} = -\frac{1}{2}\Delta E_{bulk}^{\circ}$, then:

$$\Delta E(n) \cong \frac{\Delta E_{bulk}^{\circ}}{2} \pm \frac{3}{2} Q_{\mu} n^{-1/3}, \quad (19)$$

In Figure 5 is displayed the evolution of binding energy with n as obtained through Eqn. (19), note the expected oscillatory behavior that allows one to extrapolate to large systems. It is remarkable that a simple two-parameters equation determined from data in the small clusters region be able to produce the right trends and be semiquantitative in the region of large clusters and

bulk limit. When $n \rightarrow \infty$ $\Delta E(n) \rightarrow \frac{\Delta E_{\text{bulk}}^{\circ}}{2}$ (-1.88 eV) which should be compared with experimental vaporization energy of bulk copper (-3.50 eV), the observed difference can be attributed to the simplicity of the model used here and to structural relaxation effects that are not considered in our approach. However, the values of binding energies produced for the reference clusters (Cu_n , $n=2-9$) are quite close to the experimental values given in Table I thus validating the qualitative extrapolation displayed in Figure 5. It is worth to point out that rationalization of the experimental binding energies achieved here through Eqns. (18) and (19) open a new way to estimate the energy involved in the formation processes when only the electronic properties are available.

4. Concluding Remarks.

In this work reactivity descriptors have been used to characterize and rationalize the growth of neutral copper clusters. Available experimental data of binding energies, ionization potentials and electron affinities have been used to rationalize the formation reactions, it has been shown that the characteristic even-odd oscillatory behavior of electronic properties that depend on IP and EA is mainly due to fluctuations of the ionization potential.

The one-atom growing reaction of copper clusters is mainly driven by changes in hardness, whereas that chemical potential is found to be quite independent of the clusters size thus indicating that chemical bonds do not change their nature when going from discrete systems to the bulk material. This adds evidence to validate the use of metallic clusters in heterogeneous catalysis as

adequate prototype models.

Analytic relationships between energy and electronic properties were shown to be useful to get insight on the reaction mechanism, it makes possible to estimate binding energies of clusters only from their monoelectronic properties like IP and EA . The relations established in this work allows to estimate trends of binding energy in terms of electronic properties and/or cluster size. Although the model is not quantitative to predict the binding energy of bulk copper, it works very well in the regime of small or medium sizes where binding energy varies strongly. On the other hand, the theoretical tools presented here can be very useful to predict growing and trends for electronic properties in the study of complex systems such as those found in heterogeneous catalysis and cluster's fragmentation reactions.

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Table I. Experimental values of binding energies for Cu_n ($n=2-9$). All values are in eV.

| Cu_n | $-\Delta E^a$ | $-\Delta E^b$ | $-\Delta E$ |
|--------|-----------------|-----------------|-----------------|
| Cu_2 | 2.04 ± 0.17 | 1.81 ± 0.14 | 1.93 ± 0.11 |
| Cu_3 | 1.15 ± 0.20 | 0.76 ± 0.23 | 0.96 ± 0.15 |
| Cu_4 | 2.72 ± 0.20 | 2.03 ± 0.76 | 2.38 ± 0.39 |
| Cu_5 | 1.85 ± 0.17 | 1.59 ± 0.78 | 1.72 ± 0.40 |
| Cu_6 | 2.56 ± 0.32 | 1.80 ± 0.77 | 2.18 ± 0.42 |
| Cu_7 | 2.66 ± 0.44 | 1.05 ± 0.79 | 1.86 ± 0.45 |
| Cu_8 | 2.98 ± 0.35 | 2.16 ± 0.79 | 2.57 ± 0.43 |
| Cu_9 | | 1.02 ± 0.50 | 1.02 ± 0.50 |

^a from CID experiments on the anionic clusters [20].

^b from CID experiments on the cationic clusters [21].

Table II. Experimental values of ionization potentials and electron affinities for Cu_n ($n=1-9$). All values are in eV.

| Cu_n | IP | EA^a |
|--------|-----------------------|-------------------|
| Cu | 7.724^b | 1.235 ± 0.005 |
| Cu_2 | 7.9042 ± 0.0008^c | 0.836 ± 0.006 |
| Cu_3 | 5.80 ± 0.04^d | 2.37 ± 0.01 |
| Cu_4 | 7.15 ± 0.75^e | 1.45 ± 0.05 |
| Cu_5 | 6.3 ± 0.1^d | 1.94 ± 0.05 |
| Cu_6 | 7.15 ± 0.75^e | 1.96 ± 0.05 |
| Cu_7 | 6.1 ± 0.05^d | 2.16 ± 0.1 |
| Cu_8 | 7.15 ± 0.75^e | 1.57 ± 0.05 |
| Cu_9 | 5.35 ± 0.05^d | 2.40 ± 0.05 |

^a Reference [19]

^b Reference [14]

^c Reference [15]

^d Reference [16]

^e Reference [18]

Table III. Chemical potential, chemical hardness and electrophilicity index of Cu_n ($n=1-9$). All values are in eV.

| Cu_n | $-\mu$ | $-\mu_S$ | η | η_S | ω | ω_S |
|--------|---------------------|----------|---------------------|----------|---------------------|------------|
| Cu | 4.4795 ± 0.0050 | | 3.2445 ± 0.0050 | | 3.0923 ± 0.0068 | |
| Cu_2 | 4.3701 ± 0.0061 | 4.4795 | 3.5341 ± 0.0061 | 3.2445 | 2.7019 ± 0.0071 | 3.0923 |
| Cu_3 | 4.0850 ± 0.0412 | 4.4245 | 1.7150 ± 0.0412 | 3.3914 | 4.8651 ± 0.1359 | 2.8862 |
| Cu_4 | 4.3000 ± 0.7517 | 4.2777 | 2.8500 ± 0.7517 | 2.4471 | 3.2439 ± 1.1727 | 3.7389 |
| Cu_5 | 4.1200 ± 0.1118 | 4.3888 | 2.1800 ± 0.1118 | 3.0438 | 3.8932 ± 0.2494 | 3.1641 |
| Cu_6 | 4.5550 ± 0.7517 | 4.2960 | 2.5950 ± 0.7517 | 2.6924 | 3.9977 ± 1.4871 | 3.4274 |
| Cu_7 | 4.1300 ± 0.1118 | 4.5171 | 1.9700 ± 0.1118 | 2.9226 | 4.3292 ± 0.2964 | 3.4908 |
| Cu_8 | 4.3600 ± 0.7517 | 4.3012 | 2.7900 ± 0.7517 | 2.5835 | 3.4067 ± 1.2379 | 3.5805 |
| Cu_9 | 3.8750 ± 0.0707 | 4.4193 | 1.4750 ± 0.0707 | 3.0145 | 5.0900 ± 0.2771 | 3.2394 |

Table IV. Estimation of charge transfer (ΔN) associated to the formation of neutral copper cluster and their contribution in terms of $(\mu_1 - \mu_2)$ and $2(\eta_1 + \eta_2)$. Maximum electronic charge (ΔN_{max}) that can be acquired by copper clusters.

| Cu_n | $(\mu_1 - \mu_2)$ | $2(\eta_1 + \eta_2)$ | ΔN | $\Delta N_{max} = -(\mu/\eta)$ |
|--------|-------------------|----------------------|------------|--------------------------------|
| Cu | | | | 1.3806 |
| Cu_2 | 0.0000 | 12.9780 | 0.0000 | 1.2366 |
| Cu_3 | 0.1094 | 13.5572 | 0.0081 | 2.3819 |
| Cu_4 | 0.3945 | 9.9190 | 0.0398 | 1.5088 |
| Cu_5 | 0.1795 | 12.1890 | 0.0147 | 1.8899 |
| Cu_6 | 0.3595 | 10.8490 | 0.0331 | 1.7553 |
| Cu_7 | -0.0755 | 11.6790 | -0.0065 | 2.0965 |
| Cu_8 | 0.3495 | 10.4290 | 0.0335 | 1.5627 |
| Cu_9 | 0.1195 | 12.0690 | 0.0099 | 2.6271 |

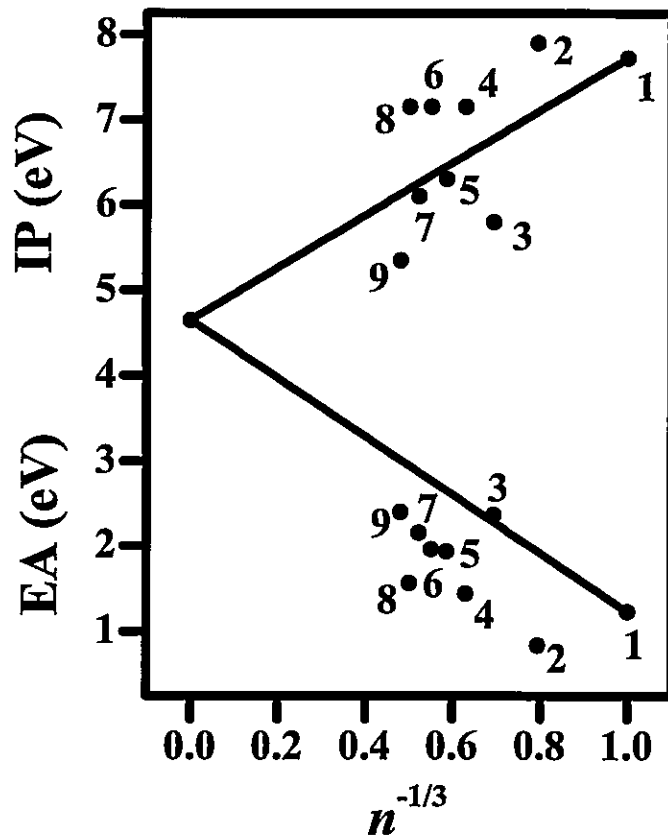


Figure 1: Jaque and Toro-Labbé.

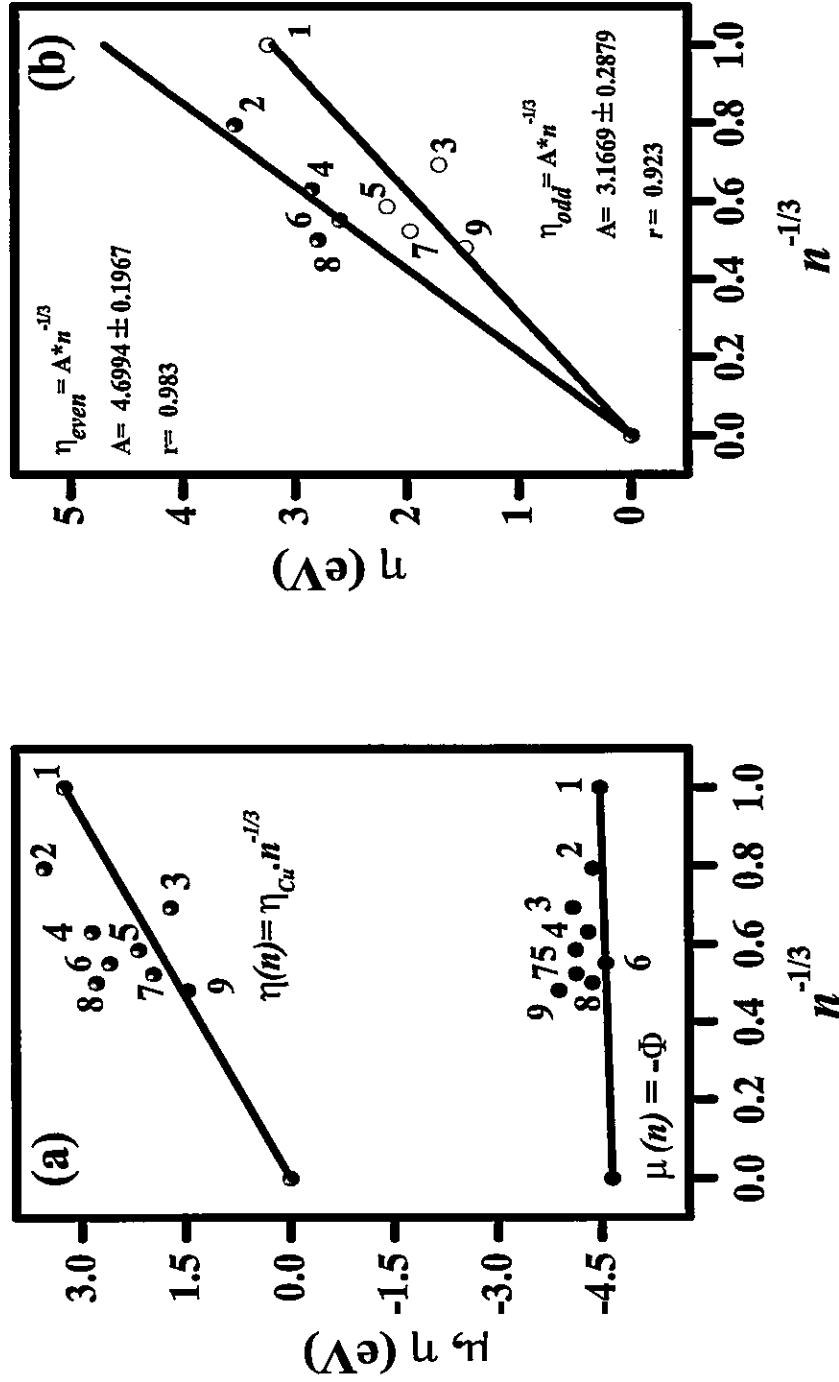


Figure 2: Jaque and Toro-Labbé.

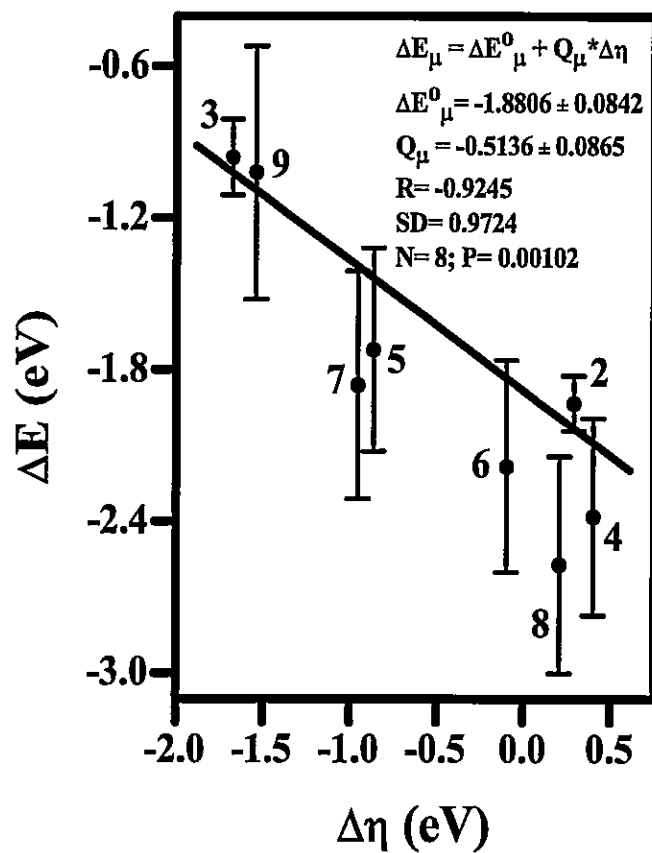


Figure 3: Jaque and Toro-Labbé.

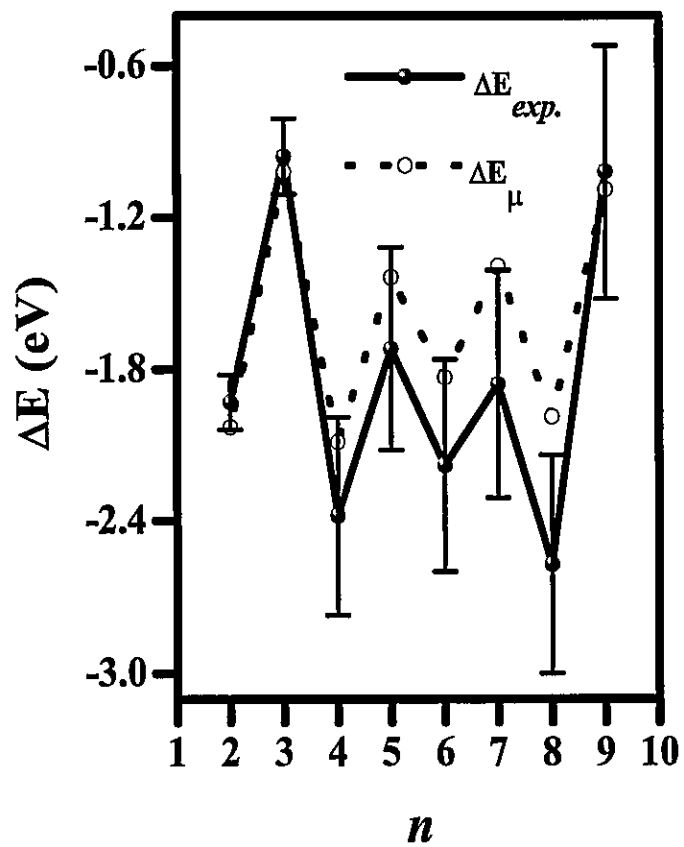


Figure 4: Jaque and Toro-Labbé.

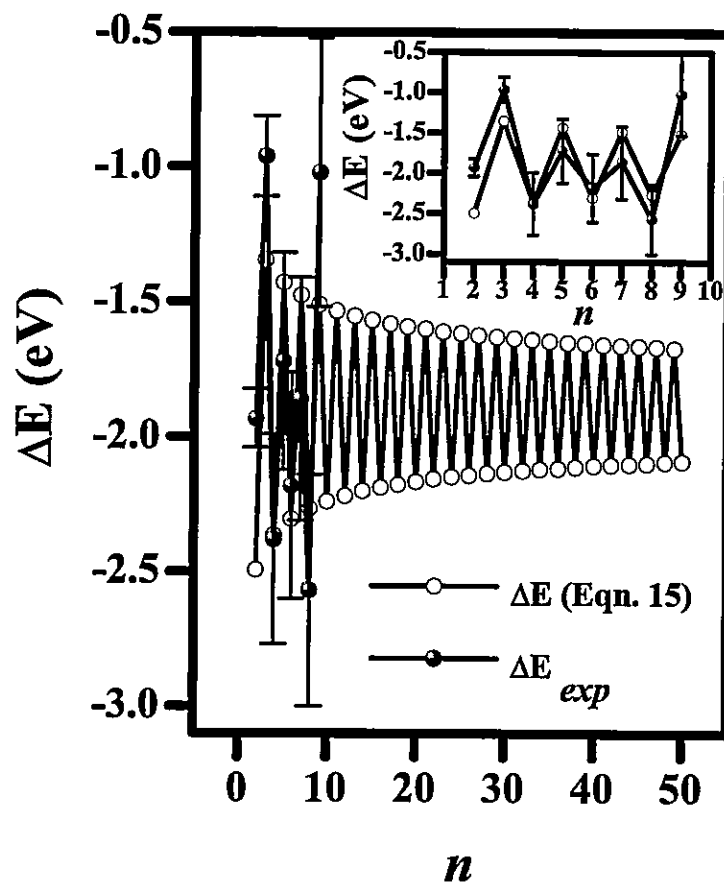


Figure 5: Jaque and Toro-Labbé.

Caption of the Figures.

Figure 1. Experimental values of IP and EA for copper clusters as a function of cluster size.

Figure 2. (a) Experimental values of μ and η and (b) dependence of η as a function of cluster size.

Figure 3. Relation between binding energies and chemical hardness in the growth reaction of Cu_n .

Figure 4. Comparison of the binding energies (ΔE_μ) obtained through Eqn. (14) with the experimental data (ΔE).

Figure 5. Binding energy as a function of cluster size predicted by Eqn. (15). The insert compares the predicted data with the available experimental data of Table I.