

Theoretical Study of the Au–Ethylene Interaction

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ABSTRACT: The basis-set dependence and quasirelativistic and nonrelativistic effects on the Au–C₂H₄ interaction are examined at the ab initio level. The effects on the interaction energies are modulated by *f*-type polarization orbitals, using 19-VE quasirelativistic pseudopotentials. Oscillation in the equilibrium Au–C distance as well as in the interaction energy are sensitive to the electron correlation potential. These effects are evaluated at several levels of theory, ranging from MP2 to CCSD(T). The nature of the Au–C₂H₄ interaction is related to a simple dispersion expression involving the individual properties of each component and its long-distance behavior. © 1999 John Wiley & Sons, Inc. *Int J Quant Chem* 73: 317–324, 1999

Key words: gold–ethylene Interaction; ab initio calculations; quasi-relativistic effects; pseudopotentials

Introduction

The complexes of transition-metal (M) with small ligands (L), in particular, hydrocarbons (acetylene, ethylene, etc.), deserves considerable interest because of their relevance in bond activation and other catalytic processes [1–5]. It has been shown that M–hydrocarbons (M = coinage group) complexes could be generated by condensation in gas matrices at cryogenic temperatures [6, 7]. These complexes may be considered as the smallest models to study the interactions between the metallic surfaces and hydrocarbons [8].

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The experimental and theoretical results in the case of ethylene have shown that the Cu, Ag, and Au atoms formed both mono- and bisligand complexes [9, 10]. These results have permitted the establishment that the interactions between the metals and the ethylene are van der Waals type [11]. This is observed in the complexes M–C₂H₄ (M = Cu, Ag, and Au), in their ²A₁ ground state, which appear to be weakly bound. No bonding is obtained at the RHF (Hartree–Fock) level, and the complexes are essentially stabilized by weak dispersion forces [11]. The magnitudes of the interaction energy and Au–C distance in Au–ethylene were about 0.019123 au and 243 pm, respectively [11]. These results are obtained when electronic correlation at the MP2 (second-order Møller–Ples-

set) level is included, together with a 11-valence electron (VE) pseudopotential for gold [12], without *f*-type polarization orbitals. However, it has been demonstrated that in the treatment of inorganic complexes presenting weak van der Waals interactions, the incorporation of one or two *f* polarization functions is necessary, since the interaction energy is sensitive to the basis set [13, 14].

On the other hand, the van der Waals systems are frequently classified on the basis of the leading stabilization energy term. According to this criterion, they can be denominated as ionic, electrostatic, hydrogen-bonded, or charge-transfer complexes [15]. The intermolecular interactions, in general, can be analyzed in terms of electrostatic, induction, short-range Pauli repulsion, and dispersion [16]. The electrostatic term comprises interactions between the charges or the higher electrostatic multipole moments. The induction terms describe the interaction between these moments and static polarizabilities (α_L). The dispersion terms arise from the frequency-dependent polarizabilities, $\alpha_L(\omega)$, of each component. Here, we are interested in the understanding of the nature of the intermolecular forces that contribute to stabilize the Au–ethylene complex.

In the present work, we undertook a systematic theoretical study of the Au–C₂H₄ π -type complex (Fig. 1). We first examined the influence of the basis set, ab initio methods, and pseudopotentials used and the explicit influence of relativity in the ground state (2A_1). Moreover, we tried to identify the dominant contributions to the attraction forces by considering the long-range limits. The nature of the interaction is related to gold and ethylene individual properties at the interaction orientations.

Computational Details

To perform all the calculations, the Gaussian 94 package [17] was used. The 19-VE quasirelativistic (QR) pseudopotentials (PP) of Andrae et al. [18], Schwedtfeger et al. [19] (QR and nonrelativistic, NR), and Stevens et al. [20] and 11-VE “LANL1DZ” [21] pseudopotentials were employed for gold. The carbon atom was treated by 4-VE [22] (see Table I). We employed zero, one, or two *f*-type polarization functions for Au. The *f* orbitals are necessary for the weak intermolecular interactions, as was demonstrated previously for the gold atom [23,

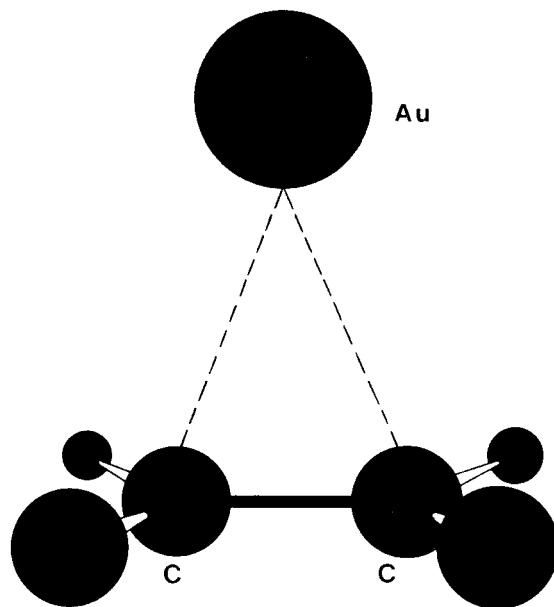


FIGURE 1. Assumed structure of the Au–ethylene complex with C_{2v} symmetry.

24]. We used a fixed geometry of ethylene for studying the Au–C₂H₄ intermolecular interaction (C_{2v} symmetry, see Fig. 1). We fully optimized the geometry at the MP2 level for the C₂H₄ unit (D_{2h} symmetry). The optimized structure has the following geometrical parameters: $R_{C-C} = 133.5$ pm, $R_{C-H} = 109.2$ pm, and $\angle HCC = 121.47^\circ$. The ethylene moiety is expected to be weakly perturbed when complexing with gold in the ground state. The relaxation of ethylene was found to be negligible in complexes with Cu and Ni [8, 11].

The interaction energy $V(R)$ of the complex was obtained according to Eq. (1); a counterpoise correction for the basis-set superposition error (BSSE) [25] on ΔE was thereby performed. The calculations were carried out at the MP2 level for different basis sets of gold. Furthermore, we studied the effect of the electronic correlation at higher MP3, MP4(SDQ), CCSD, and CCSD(T) levels, using Andrae et al.’s PP with two *f*-type orbitals:

$$\Delta E = E_{AB}^{(AB)} - E_A^{(AB)} - E_B^{(AB)} = V(R). \quad (1)$$

The optimized interaction energies, $V(R_e)$, and Au–C distances, R_e , for the complexes are shown in Tables II and III. We fit the calculated points using the four-parameter Eq. (2), which has previ-

TABLE I
Basis sets and PP used in the present work.

Case	Atom	PP	Basis	Remarks
	H	—	(4s1p) / [2s1p]	$\alpha_p = 0.80$
	C	Bergner et al.	(4s4p1d) / [6s5p3d]	$\alpha_p = 0.1561, \alpha_d = 0.80$
1	Au	Andrae et al.	(8s6p5d) / [6s4p3d]	
2	Au	Andrae et al.	(8s6p5d1f) / [6s5p3d1f]	$\alpha_f = 0.20$
3	Au	Andrae et al.	(8s6p5d2f) / [6s5p3d2f]	$\alpha_f = 0.20, 1.19$
4	Au	Schwertfeger et al. (QR)	(8s6p5d2f) / [6s5p3d2f]	$\alpha_f = 0.20, 1.19$
5	Au	Schwertfeger et al. (NR)	(8s6p5d2f) / [6s5p3d2f]	$\alpha_f = 0.20, 1.19$
6	Au	Stevens et al.	(8s6p5d2f) / [6s5p3d2f]	$\alpha_f = 0.20, 1.19$
7	Au	11-EV LANL1DZ	LANL1DZ basis for Au	$\alpha_f = 0.20, 1.19$

ously been used in other systems [26]:

$$V(R) = Ae^{-BR} - CR^n. \quad (2)$$

Differentiating Eq. (2) twice with respect to R , yields the force constant F [Eq. (3)]. This expression provides an estimate of the force constants $F(\text{AuC})$:

$$F(\text{AuC}) = V''(R) \\ = AB^2e^{-BR} - Cn(n+1)R^{-(n+2)}. \quad (3)$$

Results and Discussion

SHORT-DISTANCE BEHAVIOR AND ELECTRONIC CORRELATION EFFECTS

HF/MP2 Results

We used the 19-VE QR pseudopotential of Andrae et al. for case 1 (see Table I) at the HF and

MP2 levels. At the HF level, the Au-ethylene interaction is found to be repulsive for the complex and no real chemical bond is established (see Fig. 2). However, when we calculated the interaction energy at the MP2 level, a one-minimum potential, at a 303.38 pm Au—C distance, was obtained.

Effects of Pseudopotential on Au

The basis set was now kept constant for the PPs of Andrae et al. [18], Schwertfeger et al. [19], and Stevens et al. [20], while for the case of 11-VE LANL1DZPP, we used the basis of Hay and Wadt [21]. Two f orbitals with $\alpha_f = 0.20$ and 1.19 were used in all four cases. The interaction energies at the MP2 level for the Au—C₂H₄ complex are shown in Figure 3. The Au—C distances present an average value of 249.5 pm for the 19-VE PPs. The HF curves are invariably repulsive (not shown here). The 11-VE LANL1DZ PP underestimates the Au—C attraction. The 19-VE PPs (Andrae et al., Schwertfeger et al., and Stevens et al.), are also very close in energy.

TABLE II
Optimized Au—C distances, R_e , for the Au—C₂H₄ complex at the MP2 level and PPs.

Case	R_e	$V(R_e)$	F
1	303.88	-0.001533	0.000665
2	255.13	-0.007104	0.009239
3	248.30	-0.009267	0.012234
4	249.30	-0.008833	0.011546
5	256.50	-0.007066	0.008356
6	250.90	-0.008511	0.010826
7	273.30	-0.005839	0.007061

Distance R_e in pm; interaction energy $V(R_e)$ in au; force constant $F(\text{Au—C})$ in 10^2 Nm^{-1} .

TABLE III
Optimized Au—C distance, R_e , for the Au—C₂H₄ complex (case 3) at different levels.

Method	R_e	$V(R_e)$	F
MP2	248.30	-0.009267	0.012234
MP3	295.80	-0.001673	0.001279
MP4SQT	273.40	-0.003018	0.003078
CCSD	278.20	-0.003058	0.002749
CCSD(T)	268.80	-0.004981	0.004241

Distance R_e in pm; $V(R_e)$ in au; force constant $F(\text{Au—C})$ in 10^2 Nm^{-1} .

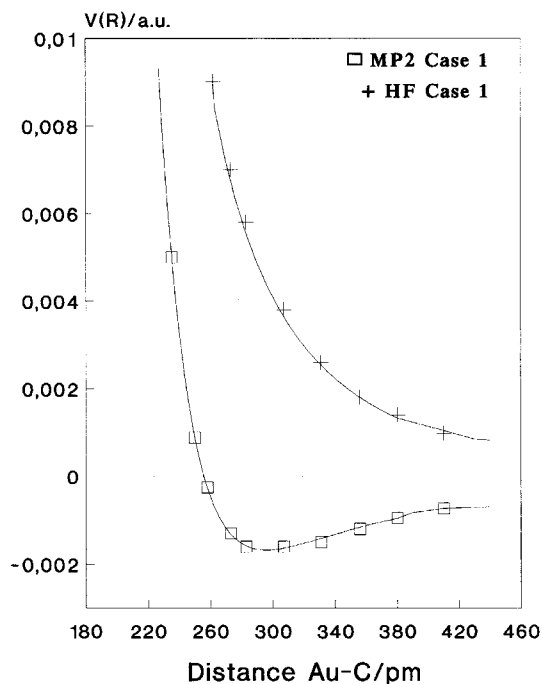


FIGURE 2. HF and MP2 potential energy curves for case 1. Calculated point fitted to Eq. (2).

Effects of the Basis Set

We can estimate the effect of the basis-set on the pseudopotential of Andrae et al. in Figure 4. It can be seen that adding $\alpha_f = 1.19$ to the previously used $\alpha_f = 0.20$ improves the interaction energy. The interaction energy is stabilized in about 23% from $1f$ to $2f$. On the other hand, when two f orbitals are included in case 1, the interaction energy is stabilized by about 78%. Moreover, the Au—C equilibrium distance is reduced by about 18% (from 303.88 to 248.30 pm). Thus, the incorporation of f -type polarization orbitals is necessary for a correct description of this complex.

Relativistic Effect

We show that the relativistic effect in the interaction of the complex via the QR and NR PPs of Schwerdfeger et al. [19] at the MP2 level. The results displayed in Figure 5 show that the interaction energy in Au—C₂H₄ is stabilized by 20.4% (from -0.007066 to -0.008833 au) on going from nonrelativistic to quasirelativistic pseudopotentials. Thus, the relativistic effect is present and contributes to increase the interaction between gold and ethylene.

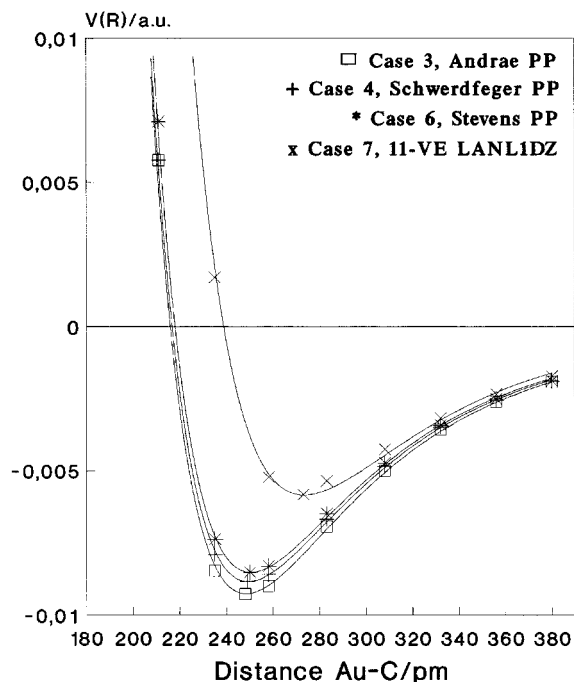


FIGURE 3. Calculated Au—C₂H₄ interaction energies $V(R)$ from different pseudopotential models.

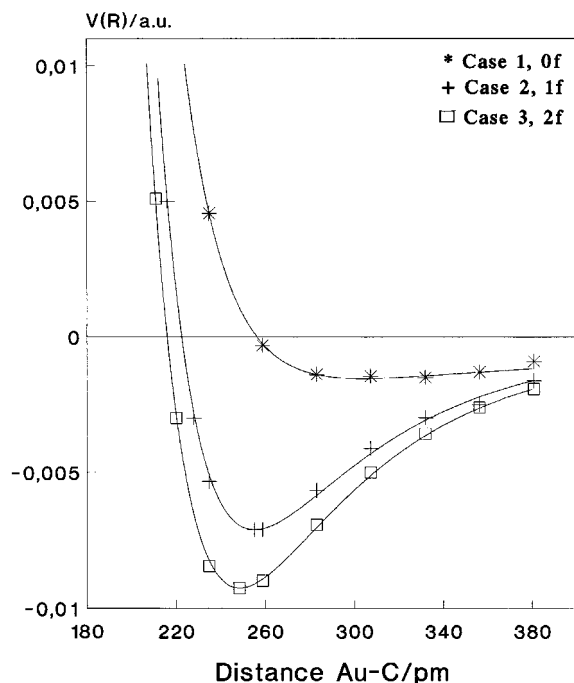


FIGURE 4. Effects of changing the Au basis set from (\square) $2f$, ($+$) $1f$, and ($*$) $0f$ orbitals.

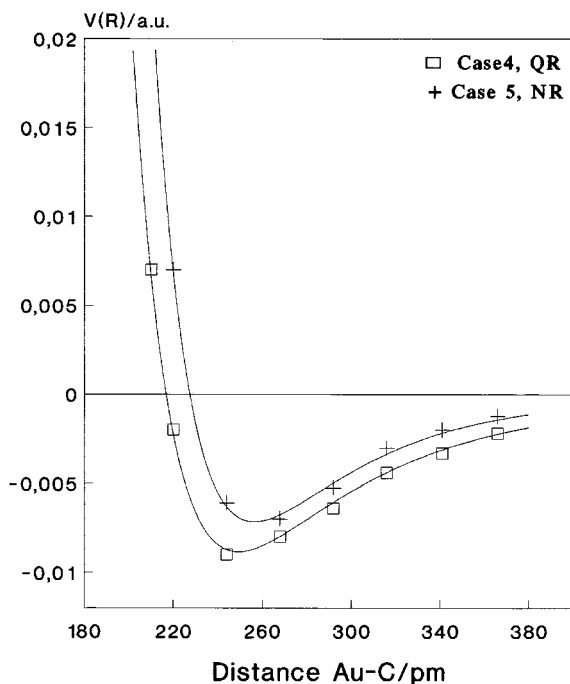


FIGURE 5. Relativistic effect on the attraction in the Au—C₂H₄ complex. (□) QR and (+) NR PPs of Schwerdtfeger et al.

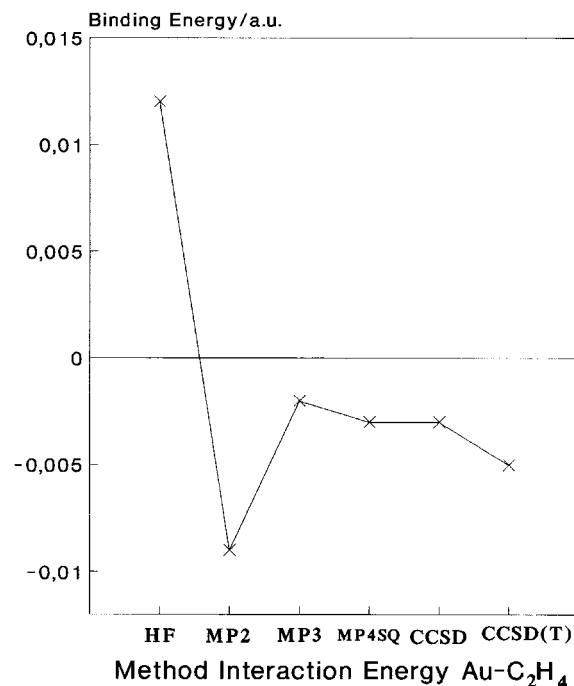


FIGURE 7. Effect of the method used on the minimal interaction energy $V(R_e)$.

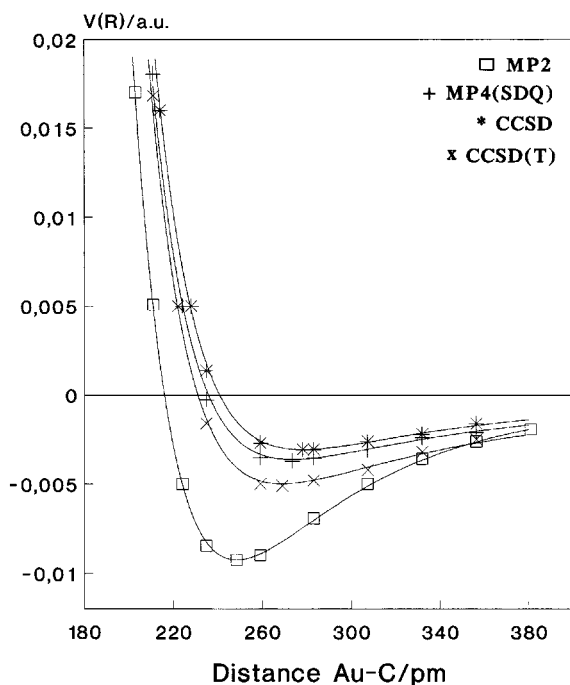


FIGURE 6. Potential energy curves $V(R)$ from different electron-correlation model potentials.

Correlation Effects

We now consider the effect of the electronic correlation in the complex at the MP3, MP4(SDQ), CCSD, and CCSD(T) levels, respectively. We optimized the Au—C distances (R_e) for the complex using the methods described above, with Andrae et al.'s PP [18] and including two f orbitals. We used the geometry obtained at the MP2 level. The results are given in Table III and Figure 6.

We can observe a strong oscillation in the equilibrium distance Au—C(R_e) as well as in the interaction energy upon changing the electronic correlation potential. Figure 7 shows the minimal interaction energies in each methodology. For the HF calculations, we took the Au—C distance obtained at the MP2 level as a reference.

The main conclusion here is that the interaction energy obtained at the MP2 level, $\Delta E(\text{MP2})$, nearly vanishes at the MP3 level. But at the MP4(SDQ) and CCSD levels, it is recovered. The triplet excitations in CCSD(T) strongly contribute with approximately one-half the MP2 result.

In general, the energetic and Au—C interaction analyses show that for many systems the convergence of the perturbation theory is oscillatory, indicating that higher-order terms may be important

[27, 28]. Moreover, slow convergence is seen in many molecules or systems where spin-contamination effects in the starting UHF wave function are significant [27]. This oscillation occurs in transition-metal systems, particularly if $(n - 1)d$ to ns excitations are involved [28]. This is especially stressed for the case of gold.

LONG-DISTANCE BEHAVIOR

In this section, we study the long-distance effect in the Au—C₂H₄ complex using the interaction energy at the MP2 level. We can split the interaction energy $\Delta E(\text{MP2})$ as shown in Eq. (4):

$$\Delta E(\text{MP2}) = \Delta E(\text{HF}) + \Delta E^{(2)}, \quad (4)$$

where $\Delta E(\text{HF})$ is the interaction energy evaluated from a self-consistent field (SCF) supermolecule calculation at the Hartree–Fock (HF) level. $\Delta E^{(2)}$ is a useful approximation to the dispersion energy at second order of the many-body perturbation treatment (MBPT) [15, 29]. In the long-range intermolecular forces theory [16, 30], the total potential has a dispersion contribution (V_{disp}) [31–33], which is attractive and it may be associated with the $\Delta E^{(2)}$ term. The remaining contributions correspond to components of the electronic (V_{elec}), inductive (V_{ind}), and short-range Pauli repulsion (V_{short}) forces. They are represented in the $\Delta E(\text{HF})$ term [32]. Hence, our aim was to relate the intermolecular potential dispersion given by Eq. (5) with the $\Delta E^{(2)}$ term from MBPT. We used the approximate London formula [32].

$$V_{\text{disp.}} = -3/2 \frac{I_A I_B}{I_A + I_B} \frac{\alpha_A \alpha_B}{R^6}, \quad (5)$$

where α_A and α_B are the electric dipole polarizabilities of the separate fragments A and B , and I_A and I_B are their first ionization potentials [34]. These properties are given in Table IV for each fragment studied.

TABLE IV
Electronic properties at MP2.

Properties	Au	C ₂ H ₄
α	27.4687	20.2191
IP	0.2919	0.3709

Dipole polarizabilities (α , au) and ionization potential (IP, au). We used case 3 for gold.

The intermolecular interaction energy at the MP2 level for the Au—C₂H₄ complex (case 3) in the long-distance R regime is shown in Figure 8. An energy minimum occurs at $R_e = 248.3$ pm. At this distance, the attractive and repulsive terms cancel each other. The main repulsive term, the Pauli repulsion, already occurs at the HF level (Fig. 2). The total MP2 curve lies below the $\Delta E^{(2)}$ curve near R_e , but above it for large R . The long-range behavior can be compared with R^{-6} attractive terms of the dispersion contribution estimated from Eq. (5). The agreement is reasonable. The extrapolation from large R to R_e gives additional proof that the dispersion term is an important contribution to the Au–ethylene attraction.

POPULATION ANALYSIS

Finally, the Mulliken and NBO population analyses were computed for case 3: AuC₂H₄, C₂H₄, and Au (Table V). These analysis were both based on the correlated densities. The Mulliken population shows a charge transfer from ethylene toward the metal (0.4321 e). This would suggest a strong interaction in the complex with a dative interaction similar to that found in the classical

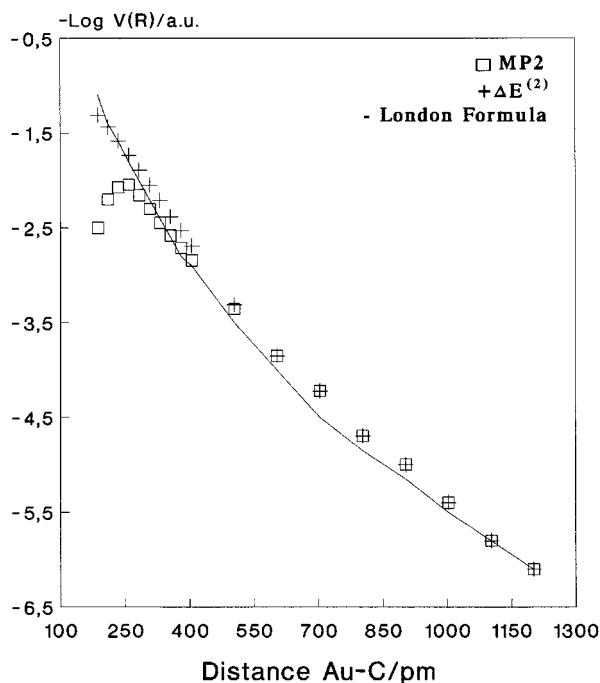


FIGURE 8. Interaction energy, $V(R)$ (\square), at MP2 level ($+$) its $\Delta E^{(2)}$ components at MBPT, and ($-$) the London formula at long-distance behavior.

TABLE V
Gross atomic population for AuC₂H₄, C₂H₄, and Au;
Mulliken analysis.

	Atom	Atomic charge	Total
AuC ₂ H ₄	Au	-0.4321	19.4320
	C	0.0229	3.9770
	H	0.0966	0.9030
C ₂ H ₄	C	-0.0897	4.0897
	H	0.0449	0.9551
Au	Au	0.0000	19.0000

Dewar-Chat-Duncanson model [35, 36]. However, this is not observed either in the magnitude of the interaction energy or in the attractive potential at the HF level. This result shows that the Mulliken population analysis is not appropriate for the Au-C₂H₄ van der Waals complex.

A different situation is observed when we perform a natural bond order (NBO) [37] analysis (see Table VI). The data show a small charge transfer from ethylene toward the metal (of the order of 0.018 *e*). The gross population per atom shell shows that the *s* and *p* orbitals for Au, the latter at a lesser extent, tends to take benefit of this transfer by increasing their occupation. One may also notice that the *d* shell for Au is slightly depopulated. In this complex, hybridization between Au and C₂H₄ orbitals does not exist. Thus, the binding in AuC₂H₄ is due essentially to dispersion forces.

Conclusions

The present study provides further information about to the nature of the interactions in the

Au-ethylene complex. We found that the interactions are due to a correlation electronic effect, strengthened by relativistic contributions. The following points summarize these ideas:

1. The incorporation the *f* basis increases the interaction.
2. All three 19-VE pseudopotentials give similar results, whereas 11-VE LANL1DZ underestimates the attraction.
3. The interaction energy presents a strong oscillation upon changing the higher levels in electronic correlation, on going from MP2 to MP3, MP4(SDQ), CCSD, and CCSD(T) models.
4. If quasirelativistic effects are omitted, the attraction $V(R_e)$ decreases to 20% at the 19-VE PP level.
5. The model system presents an R^{-6} behavior at large distances. This result provides proof about the relevance of the dispersive character of the interaction.
6. The NBO analysis in the complex shows a small charge transfer from ethylene toward gold, but we cannot think about a dative interaction similar to that proposed in the Dewar-Chat-Duncanson model.

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TABLE VI
NBO analysis for AuC₂H₄, C₂H₄, and Au.

	Atom	NBO charge	NBO electron configuration
AuC ₂ H ₄	Au	-0.0180	6s ^{1.08} 5d ^{9.90} 6p ^{0.03} 6d ^{0.01}
	C	-0.4236	2s ^{1.07} 2p ^{3.32} 3s ^{0.01} 3p ^{0.02} 3d ^{0.01}
	H	0.2163	1s ^{0.78}
C ₂ H ₄	C	-0.3734	2s ^{1.06} 2p ^{3.30} 3s ^{0.01} 3p ^{0.01} 3d ^{0.01}
	H	0.1867	1s ^{0.81}
Au	Au	0.0000	6s ^{1.0} 5d ^{10.0}

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