



On the numerical determination of Dunham's coefficients: An application to $X^1\Sigma^+HCl$ isotopomers

N. Inostroza^{a,1}, J.R. Letelier^{b,*}, M.L. Senent^{a,*}

^aDepartamento de Astrofísica Molecular e Infrarroja, Instituto de Estructura de la Materia, CSIC, Serrano 121, 28006 Madrid, Spain

^bDepartamento de Ciencia de los Materiales, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Ave. Tupper 2069, Casilla, 2777 Santiago, Chile

ARTICLE INFO

Article history:

Received 19 December 2009

Received in revised form 25 January 2010

Accepted 25 January 2010

Available online 1 February 2010

Keywords:

HCl

Ab initio

IR

Spectra

ABSTRACT

Rovibrational transition energies of the centrifugally distorted oscillator for the manifold of the HCl isotopomers are computed by means of an efficient variational–numerical method. The starting points are the potential energy surface determined using highly correlated *ab initio* calculations (RCCSD(T), MRCI+Q) and the aug-cc-pV6Z and the aug-cc-pCV5Z basis sets. From these data, it is shown how to calculate the mechanical and spectroscopic parameters corresponding to the ground electronic state of the diatomic molecule as well as the coefficients for the Dunham expansion. The relevance of the electronic correlation for an accurate description of the system and the effect of the core correlation are also discussed.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

In the previous work [1–3] we had shown how, by means of a variational–numerical solution of the Schrödinger equation [1], the set of rovibrational transitions of a centrifugally distorted diatomic oscillator, can be obtained efficiently. We applied the methodology to CH^+ [2] and CF^+ [3]. The starting point was the theoretical potential energy surface (PES) of the non-rotating oscillator calculated by an appropriate accurate *ab initio* method. Since the numerical solution of the corresponding Schrödinger equation is exact, it was pointed out then that the quality of the results strongly depend on the quality of the PES, which is expected to reproduce the real potential curve over a wide range of internuclear distances. In this work, the mechanical and spectroscopic parameters of various isotopomers of HCl obtained using different *ab initio* procedures are compared. HCl represents a species suitable for testing methodology [4–7], because it is a well-characterized molecule for which previous experimental and theoretical works are available [8–26]. Furthermore, the growing interest on the role of molecules containing halogen elements in the interstellar chemistry is motivating new spectroscopic studies [8].

* Corresponding authors.

E-mail addresses: n.inostroza@iem.cfmac.csic.es (N. Inostroza), jletelie@ing.uchile.cl (J.R. Letelier), senent@damir.iem.csic.es, senent@iem.cfmac.csic.es (M.L. Senent).

¹ Address: Departamento de Ciencias Químicas, Facultad de Ecología y Recursos Naturales, Universidad Andrés Bello, Santiago, Chile.

The potential energy surface of HCl is computed using highly correlated mono- and multi-configurational *ab initio* methods to evaluate the effect of static and dynamic correlations, because static correlation can play an important job in the long range regions. Thus, we used RCCSD(T) (partially spin-restricted open shell couple cluster theory with triple corrections) [27–29] and MRCI+Q (multi-configuration reference internally contracted configuration interaction + Davidson correction) [30,31] methods implemented in MOLPRO [32]. The RCCSD(T) calculations have been performed defining two sets of core orbitals, one containing five orbitals (1s2s2p of Cl) and one containing the 1s orbital. The employed basis sets have been the correlation consistent aug-cc-pV6Z basis for molecular *valence correlation* effects and the correlation consistent aug-cc-pCV5Z basis for molecular *core-valence correlation* effects [33], respectively. For MRCI, the active space has been defined with all the valence orbitals; five orbitals of Cl were optimized in spite of the fact that they have been double occupied in all the configurations. For this selection, we have taken into consideration the previous experience in the treatment of third row atoms [34], and the previous experience in the studies of the basis set enlargement effect on vibrational problems [35,36].

In all these cases, the equilibrium distances and dissociation energies were taken as an initial test of the quality of the calculations, nevertheless, these two parameters are not very significant since to obtain the correct vibrational energy level manifold one has to have the correct curvature of the PES along the complete rank of internuclear distances and the position of the minimum is irrelevant.

The employed numerical procedure for diatomics allows us to avoid the analytical fit of surface that may be arduous for many polyatomic molecules.

2. Theoretical method

Briefly, we solve, by numerical integration, Eq. (1) for arbitrary values E^* of the energy

$$-\frac{1}{2} \frac{d^2 \Psi(r, E^*)}{dr^2} + \left[V(r) + \frac{\hbar^2 J(J+1)}{\mu r^2} \right] \Psi(r, E^*) = E^* \Psi(r, E^*) \quad (1)$$

where $V(r)$ is the *ab initio* PES for the non-rotating oscillator. As it was shown [1,2], eigenvalues are found taking into consideration that the zeros of the function

$$W[\Psi(x, E^*)] = \frac{\frac{1}{2} \int \{\Psi'(x, E^*)\}^2 dx + \int V(x) \{\Psi(x, E^*)\}^2 dx}{\int \{\Psi(x, E^*)\}^2 dx} - E^* \quad (2)$$

are the exact solutions of the Schrödinger equation.

The vibrational $\{E_{v,J}\}$ energies, which are the eigenvalues of Eq. (1), are obtained for $J = 0, 1, 2, 3, \dots$. Next, the rovibrational transitions that fulfill the required selection rules, namely, $\Delta v = \pm 1$ and $\Delta J = 0, \pm 1$, are then computed subtracting the appropriate rovibronic energy values. The band center will correspond to $v = 0 \rightarrow v = 1$ and $\Delta J = 0$ transition.

Following Dunham's semiclassical treatment for the conventional perturbational approach to the determination of diatomic molecule rotation–vibration energies, the levels are expanded in the power series [37] and represented as

$$E_{v,J} = \sum_{(l,m) \neq (0,0)} Y_{l,m} \left(v + \frac{1}{2} \right)^l [J(J+1)]^m \quad (3)$$

where the Dunham's expansion coefficients $Y_{l,m}$ are constant and $Y_{0,0}$ represents the electronic energy. Following Refs. [2,3] energy levels for the various isotopomers are written as:

$$E_{v,J}^\alpha = \sum_{(i,l) \neq (0,0)} Y_{i,l}^{(\alpha)} \left(\frac{\mu^{(0)}}{\mu^\alpha} \right)^{L+\frac{l}{2}} \left(v + \frac{1}{2} \right)^i [J(J+1)]^l \quad (4)$$

where the superscript α refers to one isotopomer different than the most abundant H^{35}Cl , whose reduced mass is taken as $\mu^{(0)}$. In the same reference, an additional expression to account for Born–Oppenheimer breakdown correction is also included.

In this work, the Dunham's coefficients for all the isotopomers are calculated independently by introducing the appropriate reduced mass μ^α of each α -isotopomer in Eq. (1). Also, if non-adiabatic calculations are needed, they should be included as part of the *ab initio* determination of the PES and the consequences should be reflected in the shape and curvature of this function.

By the procedure described above, we have computed vibrational energy levels $E_{v,J}$ for different values of the vibrational quantum number ($v = 0, 1, 2, \dots, 8$) by solving Eq. (1) for values of the rotational quantum number up to $J = 9$. This has been done using the PES computed with various theoretical *ab initio* methods.

There are two different ways to compute the Dunham's coefficients; in both, the starting point is a least square fitting, in one of the quantum numbers, of the manifold of energy levels keeping constant the other one. If we choose to keep $v = \text{constant}$ and use J as fitting variable and fit to the function $\sum_l C_{vl} [J(J+1)]^l$, then Eq. (5) follows

$$E_{v,J} = \sum_L C_{vL} [J(J+1)]^L = \sum_L \left(\sum_i Y_{iL} \left(v + \frac{1}{2} \right)^i \right) [J(J+1)]^L \quad (5)$$

We then obtain sets of fitting coefficients $\{C_{vL}\}_v$ with $v = 0, 1, 2, \dots$ and $J = 0, 1, 2, \dots$. These coefficients are readily identified with the familiar expansion [38] for rotational energies

$$E(v, J) = E_v^{(0)} + B_v J(J+1) + D_v J^2(J+1)^2 + H_v J^3(J+1)^3 + L_v J^4(J+1)^4 + \dots$$

However, if we choose to keep $J = \text{constant}$ and use v as fitting variable

$$E_{v,J} = \sum_L C_{ij} \left[\left(v + \frac{1}{2} \right) \right]^i = \sum_i \left(\sum_L Y_{iL} [J(J+1)]^L \right) \left(v + \frac{1}{2} \right)^i \quad (6)$$

we obtain the expansion for vibrational anharmonicity

$$E_{v,J} = E_{0J} + (\omega_e)_J \left(v + \frac{1}{2} \right) + (\omega_e x_e)_J \left(v + \frac{1}{2} \right)^2 + (\omega_e y_e)_J \left(v + \frac{1}{2} \right)^3 + (X)_J \left(v + \frac{1}{2} \right)^4 + \dots$$

In view of Eq. (5), we may solve the systems of equations to compute the Dunham's coefficients Y_{iL} ,

$$\left(\sum_i Y_{iL} \left(v + \frac{1}{2} \right)^i \right) = C_{vL} \quad (7)$$

obtaining together all the coefficients corresponding to the values of v and L supplied as input. For example, for $L = 2$, we obtain the system of equations

$$\begin{aligned} Y_{02} \left(0 + \frac{1}{2} \right)^0 + Y_{12} \left(0 + \frac{1}{2} \right)^1 + Y_{22} \left(0 + \frac{1}{2} \right)^2 + \dots &= C_{02} \\ Y_{02} \left(1 + \frac{1}{2} \right)^0 + Y_{12} \left(1 + \frac{1}{2} \right)^1 + Y_{22} \left(1 + \frac{1}{2} \right)^2 + \dots &= C_{12} \\ Y_{02} \left(2 + \frac{1}{2} \right)^0 + Y_{12} \left(2 + \frac{1}{2} \right)^1 + Y_{22} \left(2 + \frac{1}{2} \right)^2 + \dots &= C_{22} \end{aligned} \quad (8)$$

whose solution yields the set $\{Y_{i2}\}$, $i = 1, 2, \dots$ of Dunham's coefficients.

Nevertheless, the simplest way is to make a second least square fitting, with v as fitting variable, and fit the C_{vL} coefficients to the function $(\sum_i Y_{iL} (v + \frac{1}{2})^i)$. The fitting coefficients thus obtained are directly identified with those of the Dunham's expansion.

3. Results and discussion

In Table 1, the equilibrium bond distances and the fundamental anharmonic frequencies calculated with MRCI+Q/aug-cc-pV6Z, RCCSD(T)/core{5}/aug-cc-pV6Z {core,5} and RCCSD(T)/aug-cc-pCV5Z {core,1} are shown. The corresponding equilibrium bond lengths have been evaluated to be 1.2727, 1.2758 and 1.2737 Å

Table 1

Equilibrium bond distance R_e , total electronic energies E and anharmonic fundamentals ν_e of HCl calculated with various *ab initio* methods.

	R_e (Å)	E (au)	ν_e (cm ⁻¹)
MRCI+Q/aug-cc-pV6Z	1.2727	-460.437687	2906.01
RCCSD(T)/aug-cc-pV6Z	1.2758	-460.374383	2888.62
RCCSD(T)/aug-cc-pCV5Z	1.2737	-460.722362	2893.92
<i>Previous works</i>			
NIST (a)	1.274545		
Fitting previous data (b)	1.2746		
Fitting previous data (c)	1.274572		
CEPA/GTO (d)	1.278		
MRD-Cl+Q/DZP (e)	1.277		

(a) Ref. [7] – NIST base data; (b) Ref. [16]; (c) Ref. [17]; (d) Ref. [18]; (e) Ref. [21].

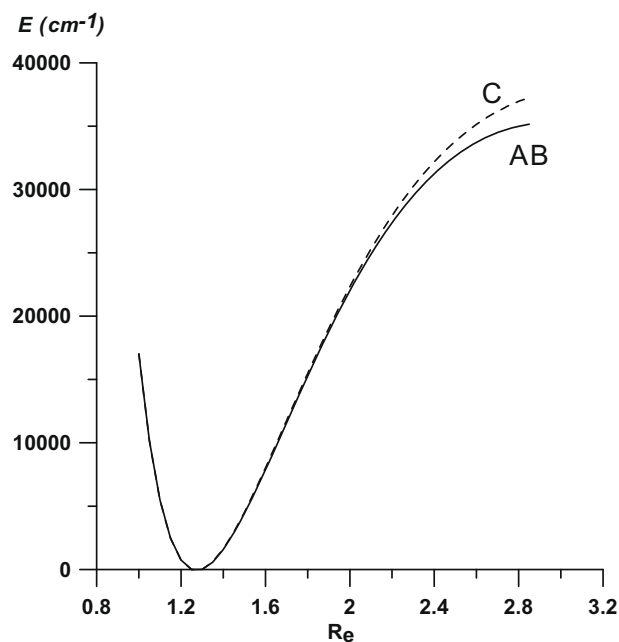


Fig. 1. Potential energy surfaces [cm^{-1}] calculated with RCCSD(T)/aug-cc-pV6Z (A), RCCSD(T)/aug-cc-pCV5Z (B) and MRCI/cc-pV6Z (C).

comparable with the experimental one of 1.274545 Å collected by the NIST base data [7]. Previous theoretical works provide 1.2746 Å [16] and 1.274571 Å [17], values obtained by taking into consideration the breakdown of the Born–Oppenheimer approximation and the isotopic effects.

The potential energy surfaces for the $X^1\Sigma^+$ ground electronic state of HCl have been generated as a function of the internuclear distance r from the electronic energies of a grid of internuclear distances ranging from $r=0.75$ [Å] to $r=5$ [Å] with a spacing of $\Delta r=0.05$ [Å]. In Fig 1, the three potential energy surfaces, the monoreferential RCCSD(T)/aug-cc-pV6Z {core,5} (A curve), the RCCSD(T)/aug-cc-pCV5Z {core,1} (B curve) and the multireferential MRCI+Q/aug-cc-pV6Z (C curve), are compared. As was expected, the three surfaces are coincident in the depth region but diverge for large bond distances because the different electronic configuration weights in the wave function vary with the enlargement of the

Table 2

Rovibrational energy levels [cm^{-1}] calculated from the RCCSD(T)/aug-cc-pV6Z potential energy surface.

v	J	H ³⁵ Cl	D ³⁵ Cl	T ³⁵ Cl	H ³⁷ Cl	D ³⁷ Cl	T ³⁷ Cl
1	0	2888.62	2092.70	1740.73	2886.51	2089.69	1737.08
2	0	5675.51	4132.69	3445.15	5671.44	4126.83	3438.00
3	0	8361.40	6120.62	5113.74	8355.52	6112.05	5103.24
4	0	10945.45	8056.61	6746.69	10937.92	8045.49	6733.00
5	0	13426.30	9940.39	8344.02	13417.28	9926.88	8327.28
0	1	21.63	11.17	7.677	21.59	11.14	7.64
1	1	2909.59	2103.63	1748.27	2907.44	2100.59	1744.59
2	1	5695.82	4143.38	3452.56	5691.71	4137.48	3445.38
3	1	8381.00	6131.06	5121.00	8375.09	6122.46	5110.47
4	1	10964.30	8066.80	6753.82	10956.75	8055.65	6740.09
0	2	64.86	33.51	23.03	64.76	33.41	22.93
1	2	2951.52	2125.49	1763.35	2949.31	2122.38	1756.96
2	2	5736.41	4164.75	3467.36	5732.25	4158.80	3460.12
3	2	8420.20	6151.94	5135.53	8414.23	6143.28	5124.94
0	3	129.68	67.01	46.05	129.48	66.82	45.86
1	3	3014.37	2158.26	1785.96	3012.07	2155.07	1782.12
2	3	5797.26	4196.81	3489.56	5793.01	4190.76	3482.23
3	3	8478.95	6183.25	5157.32	8472.90	6174.50	5146.64
0	4	216.04	111.66	76.74	215.71	111.33	76.42
1	4	3098.11	2201.95	1816.10	3095.69	2198.63	1812.13
ZPVE		1415.93	998.22	815.81	1414.81	996.66	813.75

bond length. The dissociation energy calculated with MRCI/cc-pV6Z, expected to be more accurate for the asymptotes, is 4.69 eV, which compares well to the previous value of 4.6 eV [21]. The MRCI dipole moment is 1.1393 D whereas it has been evaluated to be 1.1085 D through the electric resonance spectra [14].

As can be expected, fundamental frequencies calculated with the three potential energy surfaces differ in less than a 0.4%. All the employed *ab initio* methods are highly correlated ones and describe well the depth region in which static correlation does not play an important roll. The size-consistent RCCSD(T) method and the largest basis set provide the most accurate results for the Dunham's coefficients. The effect of the core correlation appears to be less important. To summarize the results, the lowest rovibrational energies calculated with the most accurate surface (RCCSD(T)/aug-cc-pV6Z) are shown in Table 2.

In Table 3, the Dunham's coefficients of six isotopomers calculated from the RCCSD(T)/aug-cc-pV6Z {core,5} surface are shown. Calculated rovibrational levels up to $v=20$ and $J=9$ were included in the least square fitting ($R^2=1.0$ and $\sigma=0.1$). Table 4 displays the

Table 3

Dunham's Y_{il} [cm^{-1}] coefficients calculated from the RCCSD(T)/aug-cc-pV6Z potential energy surface.

i	L	H ³⁵ Cl	D ³⁵ Cl	T ³⁵ Cl	H ³⁷ Cl	D ³⁷ Cl	T ³⁷ Cl
1	0	2992.878	2146.239	1771.556	2990.606	2143.348	1773.896
2	0	-53.278	-27.331	-18.730	-53.193	-27.246	-18.641
3	0	0.88691	0.29913	0.16418	0.88220	0.29531	0.15789
4	0	-0.13145	-0.02760	-0.01146	-0.13020	-0.02669	-0.00971
5	0	0.01134	0.00104	0.00017	0.01116	0.00091	-0.00012
0	1	10.97691	5.64607	3.87303	10.96213	5.62789	3.85472
1	1	-0.32931	-0.12004	-0.06954	-0.33124	-0.11395	-0.06233
2	1	5.59e-3	5.34e-4	1.82e-3	3.86e-3	-6.20e-3	-7.05e-3
3	1	-3.46e-3	-6.66e-4	-1.25e-3	5.9e-4	3.14e-3	4.14e-3
4	1	7.43e-4	2.6e-4	4.37e-4	-4.15e-4	-8.7e-4	-1.28e-3
0	2	5.0e-6	1.57e-4	1.4e-5	-1.29e-3	4.38e-4	1.22e-4
1	2	1.31e-3	-7.78e-4	-1.68e-4	1.67e-3	-1.81e-3	-1.03e-3
2	2	5.8e-3	4.84e-4	-1.1e-5	-9.22e-4	1.73e-3	1.22e-3
3	2	6.4e-5	-6.9e-5	1.08e-4	1.26e-4	-7.78e-4	-6.75e-4
0	3	-1.04e-4	-4.6e-5	-1.6e-4	1.10e-4	-6.2e-5	-1.8e-4
1	3	2.54e-4	1.19e-4	3.9e-4	-2.66e-4	1.77e-4	6.5e-5
2	3	-1.57e-4	-8.1e-5	-2.2e-4	1.59e-4	-1.56e-4	-7.5e-5
3	3	3.2e-5	2.0e-5	1.0e-6	-3.0e-5	6.4e-5	3.9e-5
0	4	7.0e-6	3.0e-6	1.0e-6	-8.0e-6	3.0e-6	1.0e-6
1	4	-1.8e-5	-7.0e-6	-3.0e-6	1.8e-5	-8.0e-6	-2.0e-6

more significant spectroscopic parameters for six different isotopomers $H^{35}Cl$, $D^{35}Cl$, $T^{35}Cl$, $H^{37}Cl$, $D^{37}Cl$ and $T^{37}Cl$, the harmonic frequencies ω_e , the $\omega_e x_e$ anharmonic contributions, the equilibrium rotational constants B_e , the centrifugal distortion constants D_e and the α rovibrational constants, calculated from the three *ab initio* methods cited above. We compare our calculated parameters with the previous experimental data. As HCl is a well-characterized molecule, experimental parameters for the more abundant isotopomers are tabulated from many years ago [4–7]. As previous studies are numerous, we have restricted the experimental data collected in Table 4 to the NIST base data [7] and the more recent papers.

The energies of Eq. (3) thus the Dunham's coefficients were carried out only up to $J=4$ and $v=5$, this was done so because although the first parameters Y_{10} , Y_{02} , Y_{01} and Y_{11} (see Table 4) are in a very good agreement with the experimental data, the accu-

racy decreases with the energy. These results clearly show that even though the PES in the neighborhood of the minimum is reasonably well represented, these methods fail to represent correctly the potential curve in the whole range of the internuclear distances. In this work we intended to point out this behavior. We used the energy values for the integration procedure as they came out of the *ab initio* calculation and the method of computing eigenvalues is very sensitive to it.

The calculation for all the isotopomers compares well with the experimental data than that for $H^{35}Cl$.

4. Conclusions

In this paper, the HCl isotopomers Dunham's coefficients are calculated with a numerical variational procedure from three po-

Table 4

Significant molecular constants [cm^{-1}] determined by various *ab initio* methods. Calculated parameters are compared with the previous work data.

	$\omega_e (Y_{10})$	$\omega_e x_e (-Y_{20})$	$B_e (Y_{01})$	$D_e (-Y_{02})$	$\alpha (-Y_{11})$
<i>H³⁵Cl</i>					
MRCI+Q/aug-cc-pV6Z	3009.574	52.998	10.197	1.72e−4	0.29760
RCCSD(T)/aug-cc-pV6Z	2992.877	53.278	10.977	5.00e−6	0.32931
RCCSD(T)/aug-cc-pCV5Z	2999.158	53.832	10.18134	4.87e−4	0.29729
<i>Previous works [Ref.] (method)</i>					
NIST (a)	2990.946	52.8186	10.59341	5.3194e−4	0.30718
FTIR (b)	2990.925	52.8000	10.59330	5.3164e−4	0.30700
Fit. prev. data (c)	2960.320	51.7020	10.37639	5.0994e−4	0.29754
CEPA/GTO (d)	3034.0	50.1	10.62		0.297
CEPA/GTO (d)	2977.2	53.2	10.74		0.309
Rota. emiss. spec. (e)	2991.000		10.593		
<i>D³⁵Cl</i>					
MRCI+Q/aug-cc-pV6Z	2158.510	27.209	5.24590	2.56e−4	0.11024
RCCSD(T)/aug-cc-pV6Z	2146.518	27.331	5.64607	1.57e−4	0.12014
RCCSD(T)/aug-cc-pCV5Z	2151.952	27.610	5.23668	5.19e−4	0.10888
<i>Previous works [Ref.] (method)</i>					
Fourier spectra (f)	2145.152	27.1736	5.44881	1.4049e−4	0.11330
FTIR (b)	2145.133	27.1593	5.44878	1.4063e−4	0.11322
<i>T³⁵Cl</i>					
MRCI+Q/aug-cc-pV6Z	1787.653	18.660	3.59958	1.26e−4	0.06902
RCCSD(T)/aug-cc-pV6Z	1777.713	18.730	3.87303	1.40e−5	0.06954
RCCSD(T)/aug-cc-pCV5Z	1781.428	18.921	3.59197	2.97e−4	0.06192
<i>Previous works [Ref.] (method)</i>					
Fourier spectra (f)	1776.588	18.6407	3.73721	6.6163e−5	0.06434
<i>H³⁷Cl</i>					
MRCI+Q/aug-cc-pV6Z	3007.296	52.924	10.18166	2.42e−4	0.29873
RCCSD(T)/aug-cc-pV6Z	2990.605	53.193	10.96213	1.29e−3	0.33124
RCCSD(T)/aug-cc-pCV5Z	2996.889	53.760	10.16500	2.62e−4	0.29597
<i>Previous works [Ref.] (method)</i>					
Fourier spectra (f)	2988.7033	52.7569	10.57734	5.2975e−4	0.30651
IR emission (g)	2988.6707	52.7199	10.57724	5.2995e−4	0.30622
FTIR (b)	2988.6603	52.7200	10.57726	5.3006e−4	0.30630
<i>D³⁷Cl</i>					
MRCI+Q/aug-cc-pV6Z	2155.324	27.127	5.22840	4.98e−4	0.10451
RCCSD(T)/aug-cc-pV6Z	2143.348	27.246	5.62789	4.38e−4	0.11395
RCCSD(T)/aug-cc-pCV5Z	2147.838	27.531	5.22552	1.19e−3	0.11945
<i>Previous works [Ref.] (method)</i>					
Fourier spectra (f)	2142.032	27.1143	5.43280	1.3966e−4	0.11280
FTIR (b)	2141.9744	27.0793	5.43275	1.3980e−4	0.11274
<i>T³⁷Cl</i>					
MRCI+Q/aug-cc-pV6Z	1783.816	18.574	3.58206	5.10e−4	0.06200
RCCSD(T)/aug-cc-pV6Z	1773.896	18.641	3.85472	2.11e−4	0.06233
RCCSD(T)/aug-cc-pCV5Z	1777.603	18.831	3.57537	3.92e−4	0.05688
<i>Previous works [Ref.] (method)</i>					
Fourier spectra (f)	1772.7743	18.5607	3.72118	6.5596e−5	0.06392

(a) Ref. [7] – NIST base data; (b) Ref. [22]; (c) Ref. [24]; (d) Ref. [18]; (e) Ref. [26]; (f) Ref. [19]; (g) Ref. [20].

tential energy surfaces determined using highly correlated *ab initio* methods. The results for a well-characterized molecule, that is, HCl, are accurate enough to be confident with the employed methodology for further use in more sophisticated systems. The numerical procedure allows us to avoid the analytical fit of surface that may be arduous for many molecules. RCCSD(T) and MRCI calculations describe well the depth regions of the potential although the size-consistent RCCSD(T) method provides the best spectroscopic parameters. Both surfaces diverge in the large range region.

Acknowledgments

M.L. Senent and N. Inostroza acknowledge the MICINN (Spain) for the Grant No. AYA2008-00446. N. Inostroza acknowledges the fellowships MAEC-AECI. The authors acknowledge the “Centro de Supercomputación de Galicia, CESGA” for computing facilities.

References

- [1] C.A. Utreras-Díaz, J.R. Letelier, *Comput. Chem.* 19 (1995) 39.
- [2] J.R. Letelier, M.L. Senent, *Spectrochim. Acta Part A* 65 (2006) 1030.
- [3] N. Inostroza, J.R. Letelier, P. Fuentealba, M.L. Senent, *Spectrochim. Acta Part A* 71 (2008) 798.
- [4] C. Haeusler, P. Berchowitz, *Comptes Rendus* 246 (1958) 3040.
- [5] JANAF Chemical Tables, D.R. Stull Project Director, Midland, MI, 1965.
- [6] G. Herzberg, *Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules*, second ed., Krieger, Malabar, FL, 1989.
- [7] F.J. Lovas, E. Tiemann, J.S. Coursey, S.A. Kotochigova, J. Chang, K. Olsen, R.A. Dragoset, *Diatom Spectral Database (version 2.0)*, National Institute of Standards and Technology, Gaithersburg, MD, 2003. Available from: <<http://physics.nist.gov/Diatom>> (accessed 27.11.09).
- [8] D.A. Neufeld, M.G. Wolfire, *Astrophys. J.* 706 (2009) 1594.
- [9] B.H. Van Horne, C.D. Hause, *J. Chem. Phys.* 25 (1956) 56.
- [10] L.H. Jones, E.S. Robinson, *J. Chem. Phys.* 24 (1956) 1246.
- [11] D.H. Rank, D.P. Eastman, B.S. Rao, T.A. Wiggins, *J. Opt. Soc. Am.* 52 (1962) 1.
- [12] D.H. Rank, B.S. Rao, T.A. Wiggins, *J. Mol. Spectrosc.* 17 (1965) 122.
- [13] D.U. Webb, K.N. Rao, *J. Mol. Spectrosc.* 28 (1968) 121.
- [14] E.W. Kaiser, *J. Chem. Phys.* 33 (1970) 1686.
- [15] F.C. DeLucia, P. Helminger, W. Gordy, *Phys. Rev. A* 3 (1971) 1849.
- [16] P.R. Bunker, *J. Mol. Spectrosc.* 5 (1972) 478.
- [17] J.K. Watson, *J. Mol. Spectrosc.* 45 (1973) 99.
- [18] W. Meyer, P. Rosmus, *J. Chem. Phys.* 63 (1975) 2356.
- [19] G. Guelachvili, P. Niay, P. Bernage, *J. Mol. Spectrosc.* 85 (1981) 271.
- [20] C.M. Clayton, D.W. Merdesa, J. Pliva, T.K. McCubbin Jr., R.H. Tipping, *J. Mol. Spectrosc.* 98 (1983) 168.
- [21] J.S. Wright, R.J. Bruenker, *J. Chem. Phys.* 83 (1985) 4059.
- [22] T. Parekunnel, T. Hirao, R.J. Le Roy, P.F. Bernath, *J. Mol. Spectrosc.* 195 (1999) 185.
- [23] R.S. Ram, P.F. Bernath, *J. Mol. Spectrosc.* 207 (2001) 285.
- [24] T.I. Velichko, S.N. Mikhailenko, *Opt. Spectrosc.* 92 (2002) 871.
- [25] G. Cazzoli, C. Puzzarini, *J. Mol. Spectrosc.* 226 (2004) 161.
- [26] H. Uehara, K. Horiai, S. Umeda, *Chem. Phys. Lett.* 404 (2005) 116.
- [27] P.J. Knowles, C. Hampel, H.-J. Werner, *J. Chem. Phys.* 99 (1993) 5219.
- [28] P.J. Knowles, C. Hampel, H.-J. Werner, *J. Chem. Phys.* 112 (2000) 3106.
- [29] J.D. Watts, J. Gauss, R.J. Bartlett, *J. Chem. Phys.* 98 (1993) 8718.
- [30] H.-J. Werner, P.J. Knowles, *J. Chem. Phys.* 89 (1988) 5803.
- [31] P.J. Knowles, H.-J. Werner, *Chem. Phys. Lett.* 145 (1988) 514.
- [32] R.D. Amos, A. Bernhardsson, A. Berning, P. Celani, D.L. Cooper, M.J.O. Deegan, A.J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, P.J. Knowles, T. Korona, R. Lindh, A.W. Loyd, S.J. McNicholas, F.R. Manby, W. Meyer, M.E. Mura, A. Nicklass, P. Palmieri, R. Pitzer, G. Rauhut, M. Schutz, U. Schumann, H. Stoll, A.J. Stone, R. Tarroni, T. Thorsteinsson, H.-J. Werner, *MOLPRO, A Package of Ab initio Programs Designed by H.J. Werner and P.J. Knowles*, version 2006.1.
- [33] K.A. Peterson, T.H. Dunning Jr., *J. Chem. Phys.* 117 (2002) 10548.
- [34] G. Chambaud, P. Rosmus, M.L. Senent, P. Palmieri, *Mol. Phys.* 92 (1997) 399.
- [35] M.L. Senent, *J. Phys. Chem. A* 108 (2004) 6286.
- [36] M.L. Senent, S. Wilson, *Int. J. Quant. Chem.* 82 (2001) 282.
- [37] J.L. Dunham, *Phys. Rev.* 41 (1932) 713. *ibid* 41 (1932) 731.
- [38] J.M. Hutson, B.J. Howard, *Mol. Phys.* 41 (1980) 1123.