ORIGINAL PAPER

Fully relativistic rovibrational energies and spectroscopic constants of the lowest $X{:}(1)0_g^+$, $A'{:}(1)2_u$, $A{:}(1)1_u$, $B'{:}(1)0_u^-$ and $B{:}(1)0_u^+$ states of molecular chlorine

**Daniel F. S. Machado · Valter H. C. Silva ·
Cristiano S. Esteves · Ricardo Gargano ·
Luiz G. M. Macedo · Kleber C. Mundim ·
Heibbe C. B. de Oliveira**

Abstract The main goal of this paper is to present the rovibrational energies and spectroscopic constants of the Cl_2 molecular system in the relativistic states $X{:}(1)0_g^+$, $A'{:}(1)2_u$, $A{:}(1)1_u$, $B'{:}(1)0_u^-$ and $B{:}(1)0_u^+$. More precisely, we have evaluated the Cl_2 ω_e, $\omega_e x_e$, $\omega_e y_e$, α_e, γ_e and B_e rovibrational spectroscopic constants using two different procedures. The first was obtained by combining the rovibrational energies, calculated through solving Schrödinger's nuclear equation and the diatomic rovibrational energy equation. The second was obtained by using the Dunham method. The calculated properties are in good agreement with available experimental data.

Introduction

The study of Cl_2 is of great interest to theoretical chemists and physicists. This molecule has a wide range of other applications, it has atmospheric and environmental importance [1], it acts as a plasma processing gas for the use in plasma etching of semiconductors [2] and has ultraviolet gas laser applications [3, 4]; it is a bleaching agent for paper [5] and is used in chlorinated solvents [6], for water purification [7], and in other chemical processes including pharmaceuticals [8, 9]. High accurate theoretical potential energy curves (PECs) are of interest to understand Cl_2 spectra and to analyze nonadiabatic processes [10]. In addition, the accurate bond dissociation energy for ground and excited electronic states of Cl_2 is an important measure for its thermochemistry properties.

In a previous paper, Macedo and de Jong [11] determined a set of electronic energies at different internuclear distances for the ground state and 22 lowest excited states of the chlorine molecular system calculated within a four-component relativistic framework. The *ab initio* PECs of all possible covalent states were calculated using the relativistic complete open shell configuration interaction approach. More details of the computational procedure to determine the Cl_2 relativistic PEC can be obtained in reference [11]. The authors also calculated some spectroscopic constants (B_e, ω_e and $\omega_e x_e$) using 15th-order polynomial fit, but they did not determine the rovibrational energies of the related system.

The goal in the present work is to obtain the accurate rovibrational energies and spectroscopic constants of the Cl_2

D. F. S. Machado · V. H. C. Silva · K. C. Mundim ·
H. C. B. de Oliveira (✉)
Instituto de Química, Universidade de Brasília,
70919-970 Brasília, DF, Brazil
e-mail: heibbe@unb.br

V. H. C. Silva
Ciências Exatas e Tecnológicas, Universidade Estadual de Goiás,
CP459, 75001970 Anápolis, GO, Brazil

C. S. Esteves
Faculdade de Ciências Integradas do Pontal,
Universidade Federal de Uberlândia,
38302-000 Ituiutaba, MG, Brazil

R. Gargano
Instituto de Física, Universidade de Brasília,
CP04455, CEP 70919-970 Brasília, DF, Brazil

L. G. M. Macedo
Laboratório de Planejamento e Desenvolvimento de Fármacos,
Universidade Federal do Pará,
CP 11101, 66075-110 Belém, PA, Brazil

Table 1 Parameters obtained for Cl_2 qBO PEC of X:(1) 0_g^+, A':(1)2_u, A:(1)1_u, B':(1)0_u^- and B:(1) 0_u^+ relativistic states

$[\alpha]$(hartree)	X:(1) 0_g^+	A':(1)2_u	A:(1)1_u	B':(1)0_u^-	B:(1)0_u^+
α_1	0.00552	0.01473	0.02484	0.01938	0.02754
α_2	−0.33159	−0.11016	−0.11325	−0.10496	−0.13303
α_3	0.26640	0.25978	0.19732	0.20517	0.24099
α_4	−0.01584	−0.08206	−0.03015	−0.03154	−0.03415
α_5	−0.00948	−0.43750	−0.36394	−0.38544	−0.44695
α_6	−0.01311	0.34131	0.28472	0.29745	0.34156
α_7	−0.00207	0.15918	0.12939	0.13695	0.15590
α_8	0.00634	−0.24486	−0.22581	−0.23890	−0.26725
α_9	0.00448	0.11278	0.10990	0.11706	0.13205
α_{10}	−0.00288	−0.02753	−0.02441	−0.02573	−0.03026
β(bohr^{-1})	0.65289	0.31148	0.35815	0.35096	0.31109
r_e(bohr)	3.73800	4.63821	4.64919	4.66978	4.65965
q	0.80933	2.07271	1.36456	1.40784	1.58657

system in the X:(1)0_g^+, A':(1)2_u, A:(1)1_u, B':(1)0_u^- and B:(1)0_u^+ relativistic states. More precisely, we have evaluated the Cl_2 rovibrational energies, ω_e, $\omega_e x_e$, $\omega_e y_e$, α_e, γ_e and B_e using the PEC of five covalent states published in ref[11]. To assure the accuracy of fit, the relativistic PECs was fitted using the analytical function based on polynomial q-bond order coordinates of the tenth degree (qBO) [12]. From these analytical forms, we evaluated the Cl_2 rovibrational spectroscopic constants for each state using two different procedures. The first was obtained by combining the rovibrational energies, obtained through solving Schrödinger's nuclear equation and the diatomic rovibrational energy equation. The second was determined by using the Dunham method [13].

The present work is organized as follows. "Methodologies" provides a short commentary on the methodologies adopted to determine the Cl_2 rovibrational energies and spectroscopic constants. "Results and discussion" refers to the results and the consequent discussion. Conclusions are summarized in Section 4.

Methodologies

As stated above, in the present work the Cl_2 electronic energies for ground state and for the excited states A':(1) 2_u, A:(1)1_u, B':(1)0_u^- and B:(1)0_u^+ were fitted using the qBO PEC that is given by

$$V^{qBO}([\alpha], q, \rho, \beta) = \sum_{j=1}^{N=10} \alpha_j \left(\exp_q(-\beta\rho)\right)^j, \quad (1)$$

where $\exp_q(-\beta\rho) = [1 - (1 - q)\beta\rho]^{\frac{1}{1-q}}$ is named the q-Exponential function [14], being a generalization of the conventional function based on the Tsallis statistic [15], $\rho = r - r_e$ and r_e is the equilibrium bond length of the diatomic

system. The q-exponential function has been applied successfully to a variety of problems in electronic structure [12, 16–20]. $[\alpha]$, q and β are adjustable parameters. All coefficients were optimized using a hybrid procedure based on the
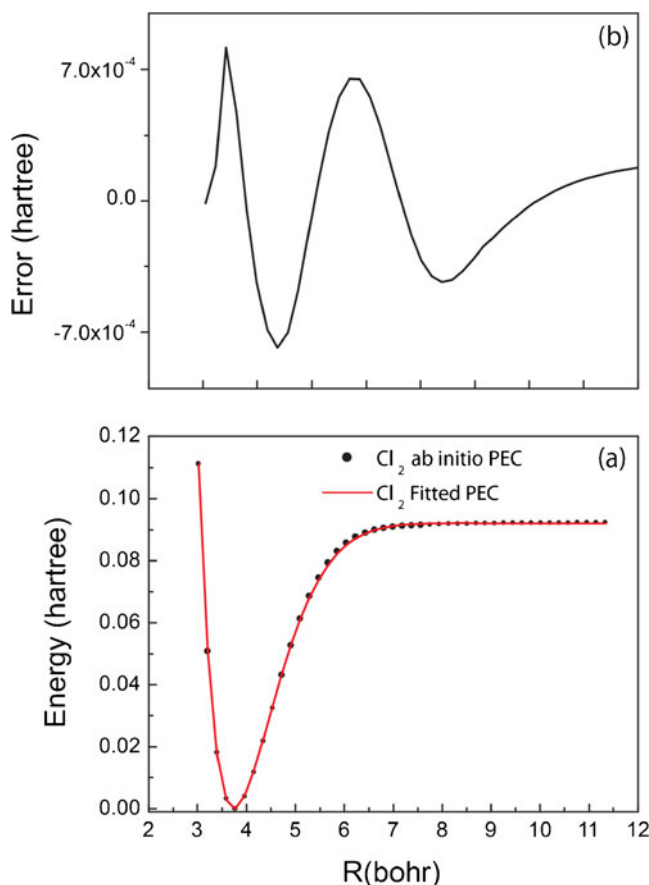
Fig. 1 (a) Comparison between the qBO (solid line) and *ab initio* (circle) PEC and (b) error between qBO and *ab initio* PEC of the X : (1) 0_g^+ relativistic state of Cl_2 system

Table 2 Calculation of Cl_2 rovibrational spectroscopic constants (in cm^{-1}) of the X: (1) 0_g^+, A′:(1)2$_u$, A:(1)1$_u$, B′:(1)0_u^- and B:(1) 0_u^+ relativistic states, determined via Dunham method. The values in brackets were obtained using the reduced mass of ref [35]

State		ω_e(cm^{-1})	$\omega_e x_e$(cm^{-1})	B_e(cm^{-1})	$\alpha_e \times 10^{-3}$(cm^{-1})
X:(1) 0_g^+	This work	559.71 [563.55]	2.70 [2.74]	0.243 [0.246]	1.613 [1.646]
	Expt. [35]	564.9	2.72	0.244	1.7
	Expt. [36]	559.72	2.72		
	Expt. [37]	559.71	2.70	0.243	
	Expt. [38]			0.244	
	Theor. [11]	563	2.86	0.244	
	Theor. [39]	549.7	2.78		
	Theor. [36]	549	2.98		
A′:(1)2$_u$	This work	258.00 [259.77]	5.46 [5.53]	0.158 [0.160]	2.647 [2.702]
	Expt. [40]	258	5.46	0.163	
	Theor. [11]	244	4.21	0.158	
A:(1)1$_u$	This work	264.00 [266.81]	5.14 [5.21]	0.157 [0.159]	2.314 [2.362]
	Expt. [41]	265	5.14		
	Expt. [42]	256	5.1		
	Theor. [11]	241	4.35	0.157	
	Theor. [39]	237.5	5.76		
	Theor. [36]	265	5.86		
B′:(1)0_u^-	This work	251.28 [253.00]	5.68 [5.76]	0.156 [0.158]	2.602 [2.656]
	Expt. [43]	253	5.76	0.163	
	Theor. [11]	238	4.55	0.157	
B:(1) 0_u^+	This work	253.64 [255.38]	4.53 [4.59]	0.156 [0.158]	2.317 [2.365]
	Expt. [36]	255.38	4.59		
	Expt. [38]			0.162	
	Theor. [11]	243	4.14	0.157	
	Theor. [39]	240	5.26		
	Theor. [36]	259	4.60		

global optimization method known as Generalized Simulated Annealing (GSA) [21–25], the simplex gradient [26] and Levenberg-Marquardt [27, 28] methods.

Considering the vibrational movement of the nuclei around the equilibrium position as approximately harmonic, the vibrational energies can be expanded near the point $v + \frac{1}{2}$. Analogous to the vibrational case, the rotational energies can be expanded near the point $j(j+1)$. So the diatomic rovibrational energy equation [29] is the following:

$$\varepsilon_{i,j} = \omega_e \left(v + \tfrac{1}{2}\right) - \omega_e x_e \left(v + \tfrac{1}{2}\right)^2 + \omega_e y_e \left(v + \tfrac{1}{2}\right)^3 + \cdots \\ + \left[B_e - \alpha_e \left(v + \tfrac{1}{2}\right) + \gamma_e \left(v + \tfrac{1}{2}\right)^2 + \cdots\right] j(j+1) \cdots \quad (2)$$

where v and j are the vibrational and rotational quantum numbers, respectively. The coefficients of this expansion are called rovibrational spectroscopic constants. $B_e = \frac{h}{8\pi^2 c I_e}$, where I_e denotes the moment of inertia, c is the speed of light and h is Planck's constant.

In the first approach, the rovibrational spectroscopic constants are evaluated in the present work by combining the rovibrational energies $\varepsilon_{i,j}$ obtained from Schrödinger's nuclear equation and Eq. 2. Here, Schrödinger's nuclear equation is solved using the discrete variable representation (DVR) method [30–32]. From this combination one can obtain the equations for rovibrational spectroscopic constants as follows:

$$\begin{cases} \omega_e = \dfrac{1}{24}\left[14(\varepsilon_{1,0} - \varepsilon_{0,0}) - 93(\varepsilon_{2,0} - \varepsilon_{0,0}) + 23(\varepsilon_{3,0} - \varepsilon_{1,0})\right] \\[4pt] \omega_e x_e = \dfrac{1}{4}\left[13(\varepsilon_{1,0} - \varepsilon_{0,0}) - 11(\varepsilon_{2,0} - \varepsilon_{0,0}) + 3(\varepsilon_{3,0} - \varepsilon_{1,0})\right] \\[4pt] \omega_e y_e = \dfrac{1}{6}\left[3(\varepsilon_{1,0} - \varepsilon_{0,0}) - 3(\varepsilon_{2,0} - \varepsilon_{0,0}) + 3(\varepsilon_{3,0} - \varepsilon_{1,0})\right] \\[4pt] \alpha_e = \dfrac{1}{8}\left[-12(\varepsilon_{1,1} - \varepsilon_{0,1}) + 4(\varepsilon_{2,1} - \varepsilon_{0,1}) + 4\omega_e - 923 y_e\right] \\[4pt] \gamma_e = \dfrac{1}{4}\left[-2(\varepsilon_{1,1} - \varepsilon_{0,1}) + (\varepsilon_{2,1} - \varepsilon_{0,1}) + 2\omega_e x_e - 9\omega_e y_e\right] \end{cases} \quad (3)$$

Another methodology used to evaluate the spectroscopic constants was that of Dunham [13], which is obtained by

Table 3 Calculation of Cl_2 rovibrational spectroscopic constants (in cm^{-1}) of the X:(1) 0_g^+, A':(1)2_u, A:(1)1_u, B':(1)0_u^- and B:(1) 0_u^+ relativistic states, determined via Eq. 3. The values in brackets were obtained using the reduced mass of ref [35]

State		$\omega_e(cm^{-1})$	$\omega_e x_e(cm^{-1})$	$\omega_e y_e \times 10^{-2}(cm^{-1})$	$\alpha_e \times 10^{-3}(cm^{-1})$	$-\gamma_e \times 10^{-6}(cm^{-1})$
X:(1) 0_g^+	This work	560.19 [564.03]	2.70 [2.73]	−1.20 [−1.10]	1.61 [1.64]	1.91 [2.02]
	Expt. [35]	564.9	2.72		1.7	
	Expt. [36]	559.72	2.72			
	Expt. [37]	559.71	2.70			
	Expt. [38]	563	2.86			
	Theor. [11]	549.7	2.78			
	Theor. [39]	549	2.98			
A':(1)2_u	This work	254.99 [256.74]	5.53 [5.61]	1.21 [1.24]	2.69 [2.74]	3.77 [3.87]
	Expt. [40]	258	5.46			
	Theor. [11]	244	4.21			
A':(1)1_u	This work	255.97 [257.73]	5.39 [5.47]	−1.65 [−1.68]	2.44 [2.49]	54.62 56.19
	Expt. [41]	265	5.14			
	Expt. [42]	256	5.1			
	Theor. [11]	241	4.35			
	Theor. [39]	237.5	5.76			
	Theor. [36]	265	5.86			
B':(1)0_u^-	This work	251.10 [252.82]	5.68 [5.75]	−2.53 [−2.58]	2.59 [2.64]	65.55 [67.39]
	Expt. [43]	253	5.76			
	Theor. [11]	238	4.55			
B:(1) 0_u^+	This work	249.97 [251.69]	4.72 [4.78]	−0.24 [−0.25]	2.39 [2.45]	36.31 37.35
	Expt. [36]	255.38	4.59			
	Theor. [11]	243	4.14			
	Theor. [39]	240	5.26			
	Theor. [36]	259	4.60			

comparing Eq. 2 and the PEC written with a Taylor expansion around the equilibrium distances. Furthermore, the alternative technique developed by Dijon group [33] could be used to calculate the rovibrational energies.

Table 4 Cl_2 rovibrational energies (in cm^{-1}) of the X:(1) 0_g^+, A':(1)2_u, A:(1)1_u, B':(1)0_u^- and B:(1) 0_u^+ relativistic states. The values in brackets were obtained using the reduced mass of ref [35]

v	j	X:(1) 0_g^+	A':(1)2_u	A:(1)1_u,	B':(1)0_u^-	B:(1) 0_u^+
0	0	279.50[281.41]	125.77[126.62]	124.29[125.12]	123.88[124.72]	122.85[123.68]
1		834.26[839.94]	369.73[372.18]	369.42[371.88]	363.54[365.94]	363.37[365.79]
2		1383.53[1392.89]	602.72[606.62]	603.62[607.53]	591.62[595.43]	594.44[598.31]
3		1927.23[1940.21]	824.83[830.02]	826.78[831.99]	807.97[813.02]	816.03[821.23]
4		2465.31[2481.81]	1036.12[1042.47]	1038.79[1045.15]	1012.42[1018.54]	1028.13[1034.52]
5		2997.68[3017.64]	1236.67[1244.02]	1239.56[1246.90]	1204.80[1211.80]	1230.72[1238.17]
6		3524.29[3547.62]	1426.55[1434.76]	1428.96[1437.13]	1384.89[1392.62]	1423.80[1432.17]
0	1	279.99[281.91]	126.08[126.94]	124.60[125.46]	124.19[125.03]	123.15[124.00]
1		834.74[840.43]	370.03[372.49]	369.73[372.19]	363.85[366.25]	363.68[366.10]
2		1384.01[1393.38]	603.02[606.92]	603.92[607.84]	591.92[595.73]	594.74[598.62]
3		1927.71[1940.69]	825.13[830.32]	827.07[832.29]	808.27[813.31]	816.32[821.52]
4		2465.78[2482.29]	1036.41[1042.76]	1039.08[1045.44]	1012.71[1018.83]	1028.42[1034.81]
5		2998.15[3018.12]	1236.96[1244.31]	1239.841247.19]	1205.07[1212.09]	1231.01[1238.46]
6		3524.76[3548.09]	1426.83[1435.04]	1429.24[1437.41]	1385.16[1392.89]	1424.07[1432.46]

Results and discussion

In this section we present results of dynamics properties of the Cl_2 system in the $X:(1)0_g^+$, $A':(1)2_u$, $A:(1)1_u$, $B':(1)0_u^-$ and $B:(1)0_u^+$ relativistic states. Table 1 shows the fitted parameters of the qBO PEC that generate the best Cl_2 rovibrational and spectroscopic constants, for all relativistic states studied in this work.

Fig. 1a shows both the Cl_2 *ab initio* and fitted PEC of the $X:(1)0_g^+$ state. Figure 1b presents the error between *ab initio* and fitted energies. To avoid a proliferation of figures, only the PEC of the $X:(1)0_g^+$ state was included in Fig. 1. The results of the maximum (minimum) deviation and the χ^2 error found between values for the *ab initio* and fitted energies were: $1.21\times10^{-3}(1.30\times10^{-5})$ and 1.19×10^{-5}, $8.28\times10^{-4}(2.52\times10^{-5})$ and 1.12×10^{-5}, $5.47\times10^{-4}(7.88\times10^{-5})$ and 3.31×10^{-6}, $2.48\times10^{-4}(1.31\times10^{-6})$ and 2.44×10^{-7} and $1.46\times10^{-4}(4.16\times10^{-7})$ and 6.86×10^{-8} hartree for the $X:(1)0_g^+$, $A':(1)2_u$, $A:(1)1_u$, $B':(1)0_u^-$ and $B:(1)0_u^+$ relativistic states, respectively. From these results we can see close agreement between the *ab initio* and fitted energies. Although this is not the focus of this work, it is important to point out that the success of the fitting procedure is, in part, due to the q-exponential function's flexibility. This function is more delocalized than the conventional exponential function, so that for q>1, decay of the q-exponential function is slower than for a conventional exponential one. If q<1, the decay is faster, reaching zero at $\frac{1}{1-q}$. At the limit $q\rightarrow1$, the generalized qBO PEC (Eq. 1) is equivalent to the usual bond order one. Note that for the different values of q parameters the q-exponential function becomes more (less) diffuse for higher (lower) values than one. In all cases, the deviations of the q parameter are relevant to fit, being approximately: 0.20, 1.07, 0.36, 0.40 and 0.58 for fit of $X:(1)0_g^+$, $A':(1)2_u$, $A:(1)1_u$, $B':(1)0_u^-$ and $B:(1)0_u^+$ PECs, respectively.

The Cl_2 $X:(1)0_g^+$, $A':(1)2_u$, $A:(1)1_u$, $X:(1)0_g^+$ and $B':(1)0_u^-$ rovibrational spectroscopic constants obtained through the Dunham method and nuclear Schrödinger solutions (via Eq. 3) are shown in Tables 2 and 3, respectively. We used two different experimental values for Cl_2 reduced mass equal to 17.73 u (^{35}Cl) and 17.48942 u (^{37}Cl) obtained from ref [34] and ref [35], respectively.

All values of ω_e, $\omega_e x_e$ and B_e are in excellent agreement with experimental data [35–43]. This is particularly notable for the $X:(1)0_g^+$ relativistic state, the deviation between $\omega_e(\omega_e x_e)$ calculated in this work and that in ref [34] is 0.00(0.00) cm^{-1}, when we used the Dunham method, and under 0.48(0.00) cm^{-1} when we calculated via Eq. 3, both using the reduced mass obtained from ref [34]. In contrast, for the same state and using the reduced mass obtained from ref [35], the deviation between $\omega_e(\omega_e x_e)[\alpha_e]$ calculated in this

work and that in ref [35] is under 1.35(0.02)[0.054] cm^{-1}, when we used the Dunham method, and 0.87(0.01)[0.06] cm^{-1} when we calculated via Eq. 3. This is a very satisfactory result. The values of ω_e, $\omega_e x_e$ and α_e obtained according to the Dunham method are very close to those determined via Eq. 3. Indeed, the Dunham method presented results closer to the experimental one, when compared to those obtained using Eq. 3. It is also important to emphasize that although we used the same *ab initio* energies as Macedo and de Jong [11] our results present the best agreement with experimental results available in literature. Although the deviations are small, it is worth stressing that even when a qBO PEC of the tenth degree is used we can still have a slight (χ^2) problem of accuracy in the electronic energy fit procedure.

Table 4 lists a set of rovibrational energies obtained by solving the Schrödinger nuclear equation with v varying between 0 and 6, and j between 0 and 1. In this case, we again used the same two values for Cl_2 reduced mass, as cited above. The difference of values for rovibrational energies using the reduced mass obtained from ref [34] and ref [35], respectively, are relatively large. For example, for the $\varepsilon_{0,0}$ this difference is about 1.91 cm^{-1}, while for the $\varepsilon_{6,0}$ it is about 23.33 cm^{-1}.

Conclusions

In this paper we have calculated dynamics properties of $X:(1)0_g^+$, $A':(1)2_u$, $A:(1)1_u$, $B':(1)0_u^-$ and $B:(1)0_u^+$ relativistic states of Cl_2 system. To this end, we used the PEC obtained using correlated four-component relativistic calculations. The calculated values of equilibrium vibrational frequency (ω_e), anharmonic constant ($\omega_e x_e$) and rotational constant (B_e) are in excellent agreement with experimental data available in the literature. This fact suggests that the results of other spectroscopic constants and rovibrational energies presented in this work have the same accuracy. This accurate Cl_2 PEC study, for different relativistic states, is of fundamental importance to many issues, including atom-atom collisions, prediction of cluster structures, and chemical reactivity.

References

1. Maric D, Burrows JP, Meller R, Moortgat GK (1993) A study of the UV-visible absorption-spectrum of molecular chlorine. J Photochem Photobiol A 70(3):205–214
2. Malyshev MV, Donnelly VM, Samukawa S (1998) Ultrahigh frequency versus inductively coupled chlorine plasmas: comparisons of Cl and Cl-2 concentrations and electron temperatures measured by

trace rare gases optical emission spectroscopy. J Appl Phys 84 (3):1222–1230

3. Bates DR (1985) Ion Ion Recombination in an Ambient Gas. Adv Atom Mol Phys 20:1–40

4. Morgan WL (1992) A critical-evaluation of low-energy electron-impact cross-sections for plasma processing modeling.I:, Cl2, F2, and HCl. Plasma Chem Plasma P 12(4):449–476

5. Edelstein SM (1948) The role of chemistry in the development of dyeing and bleaching. J Chem Edu 25(3):144. doi:10.1021/ed025p144

6. Lu C, Bjerg PL, Zhang FJ, Broholm MM (2011) Sorption of chlorinated solvents and degradation products on natural clayey tills. Chemosphere 83(11):1467–1474. doi:10.1016/j.chemosphere.2011.03.007

7. Aoki T (1989) Continuous-flow method for simultaneous determination of monochloramine, dichloramine, and free chlorine - application to a water-purification plant. Environ Sci Technol 23(1):46–50

8. SanchezPedreno C, Ortuno JA, Hernandez J (1996) Determination of chlorine and dissolved oxygen in waters and of ascorbic acid in pharmaceuticals by iodimetric potentiometric titration using a plasticized poly(vinyl chloride) membrane electrode. Anal Chim Acta 333(1–2):107–113

9. Pinkston KE, Sedlak DL (2004) Transformation of aromatic ether- and amine-containing pharmaceuticals during chlorine disinfection. Environ Sci Technol 38(14):4019–4025. doi:10.1021/Es0353681

10. Clark AP, Brouard M, Quadrini F, Vallance C (2006) Atomic polarization in the photodissociation of diatomic molecules. Phys Chem Chem Phys 8(48):5591–5610. doi:10.1039/B612590e

11. de Macedo LGM, de Jong WA (2008) Fully relativistic calculations on the potential energy surfaces of the lowest 23 states of molecular chlorine. J Chem Phys 128(4). doi:10.1063/1.2827457

12. Esteves CS, de Oliveira HCB, Ribeiro L, Gargano R, Mundim KC (2006) Modeling diatomic potential energy curves through the generalized exponential function. Chem Phys Lett 427(1–3):10–13. doi:10.1016/j.cplett.2006.06.020

13. Dunham JL (1932) The Energy Levels of a Rotating Vibrator. Phys Rev 41(6):721–731

14. Borges EP (1998) On a q-generalization of circular and hyperbolic functions. J Phys a-Math Gen 31(23):5281–5288

15. Tsallis C (1988) Possible generalization of Boltzmann-Gibbs statistics. J Stat Phys 52(1–2):479–487

16. Salviano LR, Esteves CS, de Oliveira HCB, Mundim KC, Ribeiro L, Gargano R (2010) Use of generalized exponential function to build three-dimensional reactive surfaces. Physica A 389(17):3604–3612. doi:10.1016/j.physa.2010.04.031

17. Mundim KC (2005) An analytical procedure to evaluate electronic integrals for molecular quantum mechanical calculations. Physica A 350(2–4):338–348. doi:10.1016/j.physa.2004.11.062

18. de Oliveira HCB, Esteves CS, Gargano R, do Nascimento MAC, Malbouisson LAC, Mundim KC (2008) Molecular properties calculations using the q-Integral method. Int J Quantum Chem 108 (13):2540–2549. doi:10.1002/Qua.21706

19. de Oliveira HCB, Rangel FC, Esteves CS, Vieira FMC, Mundim KC (2009) Calculation of MP(2) and coupled-cluster molecular properties using the q-integral method. J Phys Chem A 113 (52):14691–14698. doi:10.1021/Jp904807b

20. Rangel FC, de Oliveira HCB, Montel ALB, Mundim KC (2010) Calculation of DFT molecular properties using the q-Integral method. Physica A 389(22):5208–5215. doi:10.1016/j.physa.2010.06.030

21. Mundim KC, Tsallis C (1996) Geometry optimization and conformational analysis through generalized simulated annealing. Int J Quantum Chem 58(4):373–381

22. Moret MA, Pascutti PG, Mundim KC, Bisch PM, Nogueira E (2001) Multifractality, Levinthal paradox, and energy hypersurface. Phys Rev E 63(2)

23. Lopez LEE, Gargano R, Mundim KC, Neto JJS (2002) The Na+ HF reactive probabilities calculations using two different potential energy surfaces. Chem Phys Lett 361(3–4):271–276

24. de Andrade MD, Mundim KC, Malbouisson LAC (2005) GSA algorithm applied to electronic structure: Hartree-Fock-GSA method. Int J Quantum Chem 103(5):493–499. doi:10.1002/Qua.20580

25. De Andrade MD, Nascimento M, Mundim K, Malbouisson L (2006) GSA algorithm applied to electronic structure II: UHF-GSA method. Int J Quantum Chem 106(13):2700–2705. doi:10.1002/Qua.21080

26. Nelder JA, Mead R (1965) A Simplex-Method for Function Minimization. Comput J 7(4):308–313

27. Marquardt DW (1963) An algorithm for least-squares estimation of nonlinear parameters. J Soc Indust Applied Math 11(2):431–441

28. Levenberg K (1944) A method for the solution of certain problems in least squares. Quart Applied Math 2:164–168. doi:citeulike-article-id:2946351

29. Murrell JN, Carter S, Farantos SC, Huxley P, Varandas AJC (1984) Molecular potential energy functions. Wiley, New York

30. Neto JJS, Costa LS (1998) Numerical generation of optimized discrete variable representations. Braz J Phys 28(1):1–11

31. Light JC, Carrington T (2000) Discrete-variable representations and their utilization. Adv Chem Phys 114:263–310

32. Light JC, Hamilton IP, Lill JV (1985) Generalized discrete variable approximation in quantum mechanics. J Chem Phys 82(3):1400–1409. doi:citeulike-article-id:8249090

33. Boudon V, Champion JP, Gabard T, Loëte M, Michelot F, Pierre G, Rotger M, Wenger C, Rey M (2004) Symmetry-adapted tensorial formalism to model rovibrational and rovibronic spectra of molecules pertaining to various point groups. J Mol Spectrosc 228(2):620–634. doi:10.1016/j.jms.2004.02.022

34. Radzig AA, Smirnov BM (1985) Reference Data on Atoms, Molecules and Ions. Springer-Verlag, Berlin ; New York

35. Herzberg G (1989) Molecular spectra and molecular structure, vol 1. Spectra of diatomic molecules, 2nd edn. Krieger, Malaber

36. Kokh DB, Alekseyev AB, Buenker RJ (2004) Theoretical study of the UV photodissociation of Cl-2: Potentials, transition moments, extinction coefficients, and Cl*/Cl branching ratio. J Chem Phys 120(24):11549–11556. doi:10.1063/1.1753554

37. Bermejo D, Jimenez JJ, Martinez RZ (2002) High-resolution stimulated Raman spectroscopy of Cl-35(2), Cl-37(2), and (ClCl)-Cl-35-Cl-37. J Mol Spectrosc 212(2):186–193. doi:10.1006/jmsp.2002.8535

38. NIST Chemistry WebBook ,NIST Standard Reference Database Number 69 (2010) National Institute of Standards and Technology. http://webbook.nist.gov. Accessed 22 July 2011

39. Asano Y, Yabushita S (2001) Theoretical study on the nonadiabatic transitions in the photodissociation processes of Cl(2). J Phys Chem A 105(43):9873–9882. doi:10.1021/Jp0120561

40. Tellinghuisen PC, Guo BC, Chakraborty DK, Tellinghuisen J (1988) The D'-]a' Transition in Cl2. J Mol Spectrosc 128(1):268–277

41. Ishiwata T, Ishiguro A, Obi K (1991) Optical optical double-resonance spectroscopy of Cl2 - analysis of the Alpha-3-Pi(1u)-Chi-1-Sigma-G+system. J Mol Spectrosc 147(2):300–320

42. Tellinghuisen J, Chakraborty DK (1987) Identification and analysis of the D'-]a' transition in the emission-spectrum of Cl-2. Chem Phys Lett 134(6):565–570

43. Ishiwata T, Kasai Y, Obi K (1991) Optical optical double-resonance spectroscopy of Cl2–1st observation and analysis of the Og-(3p1) ion-pair state and the lower-lying B′ 3-Pi(0u-) valence state. J Chem Phys 95(1):60–65