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Citation: *J. Chem. Phys.* **128**, 041101 (2008); doi: 10.1063/1.2827457

View online: <http://dx.doi.org/10.1063/1.2827457>

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Fully relativistic calculations on the potential energy surfaces of the lowest 23 states of molecular chlorine

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(Received 13 November 2007; accepted 30 November 2007; published online 24 January 2008)

The electronic structure and spectroscopic properties (R_e , ω_e , $\omega_e x_e$, β_e , and T_e) of the ground state and the 22 lowest excited states of chlorine molecule were studied within a four-component relativistic framework using the MOLDIR program package. The potential energy curves of all possible 23 covalent states were calculated using relativistic complete open shell configuration interaction approach. In addition, four component multireference configuration interaction with single and double excitation calculations were performed in order to infer the effects due to dynamical correlation in vertical excitations. The calculated properties are in good agreement with the available experimental data. © 2008 American Institute of Physics. [DOI: 10.1063/1.2827457]

Chlorine, one of the few homonuclear diatomic molecules, which exists under normal conditions in nature, is a commonly used industrial commodity.¹ It is one of the top ten chemicals produced (by gross weight) and it has wide range of applications, as bleaching agent for paper, chlorinated solvents, for water purification, and other chemical processes including pharmaceuticals. In addition, it is of atmospheric and environmental interest,² it is a plasma processing gas³ used in plasma etching of semiconductors, and it has gas ultraviolet (UV) laser applications.^{4,5}

Despite its economical and technological importance, several features in its spectra remain unclear. It is known that the first absorption band of Cl₂ molecule is located in the UV region with a maximum at 330 nm and corresponds to the Cl₂ excitation to the valence states correlating with the Cl(²P_{3/2}) and Cl(²P_{1/2}) atomic asymptotes, identified in this paper as Cl and Cl*, respectively.

The absorption spectrum is attributed mostly to the transition from the ground state $X^1\Sigma_g^+$ to the lowest repulsive $C^1\Pi(1_u)$ state. In the red wing, $A^3\Pi(1_u) \leftarrow X$ and $B^3\Pi(0_u^+) \leftarrow X$ continuum bands are visible, though they are much weaker than the main $C \leftarrow X$ peak.⁶ In the adiabatic case,⁷ the A and C states correlate to the ground state asymptote, Cl+Cl, while the B state correlates to a higher dissociation limit, Cl+Cl*. So far, much effort has been made on surveying the dissociation behavior^{8–12} of Cl₂. Experimental information on the $B \leftarrow X$ absorption band is quite uncertain, since it is significantly overlapped by the more intense $C \leftarrow X$ band as well as the weaker $A \leftarrow X$ band. The uncertainty about the $B \leftarrow X$ absorption band is so significant that

the vertical excitation energy of the B state differs by thousands of wave numbers in different studies.^{9,13,14} The A state is even more difficult to obtain because the $A \leftarrow X$ transition is very weak. As a consequence, information about the potential energy curves for relevant excited states is far from being complete and ambiguous. Only the lowest five states [$X^1\Sigma_g^+$, $B^3\Pi(0_u^+)$, $A'^3\Pi(2_u)$, $A^3\Pi(1_u)$, and $B'^3\Pi(0_u^-)$] of the 23 possible valence states¹⁵ are well characterized experimentally,^{16–19} in spite of many experimental efforts.^{20–25}

The first *ab initio* potential curves for the Cl₂ molecule were computed by Peyerimhoff and Buenker²⁶ more than 25 years ago under the Λ - Σ approximation and served as the mainly theoretical basis for analysis of experimental data. Although semiempirical relativistic intermediate neglect of differential overlap (INDO) calculations were performed in Cl₂ 15 years ago,²⁷ only recently, *ab initio* calculations including spin-orbit coupling have been performed^{28–33} for some low lying valence states (usually) applying a relativistic core potential approach. Therefore, high accurate theoretical potential curves are of interest to understand Cl₂ spectra, as well as the analysis of nonadiabatic processes³⁴ and experimental data regarding the Cl₂ dissociation.

The goal in the present work is to obtain a detailed theoretical description of the spectroscopic properties for all 23 valence states of Cl₂ dissociating into neutral atoms. For this purpose, correlated four-component relativistic calculations were carried out to determine the potential energy curves of all states that correlate into the $^2P_J + ^2P_J$ ($J=3/2$ or $1/2$) states using the average of configurations Dirac-Hartree-Fock approach.³⁵ This approach allows us to assess the spin-orbit coupling on the spectroscopic properties and makes it possible to assign all 23 covalent states. In order to obtain better relativistic vertical excitation energies, supplementary multireference configuration interaction with single and

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TABLE I. Spectroscopic properties for the excited states of chlorine (improved potential energy curves based on COSCI results).

State		R_e (Å)	D_e (eV)	D_0 (eV)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	B_e (cm ⁻¹)	T_e (eV)
$X:(1)_g^+$	This work	1.987	2.51	2.48	563	2.86	0.244	0.00
	Expt.	1.988 ^a	2.49 ^a		559.75 ^a		0.244 ^b	
	Expt.		2.51 ^c		559.72 ^d	2.72 ^d		
	Expt.				559.71 ^e	2.70 ^e	0.243 ^e	
	Theor. ^f	2.017 ^f	2.33 ^f		549.7 ^f	2.78 ^f		
	Theor. ^g	2.013 ^g	2.40 ^g		549 ^g	2.98 ^g		
$A':(1)2_u$	This work	2.473	0.39	0.38	244	4.21	0.158	2.12
	Expt.	2.431 ^h	0.39 ^h		258 ^h	5.46 ^h	0.163 ^h	2.13 ^{b,h}
$A:(1)1_u$	This work	2.478	0.36	0.34	241	4.35	0.157	2.16
	Expt.	2.433 ⁱ	0.31 ^f		265 ⁱ	5.14 ⁱ		2.16 ^b
	Expt.	2.43 ^j	0.35 ^j		256 ^j	5.1 ^j		2.16 ^j
	Theor. ^f	2.467 ^f	0.29 ^f		237.5 ^f	5.76 ^f		
	Theor. ^g	2.450 ^g	0.29 ^g		265 ^g	5.86 ^g		
$B':(1)0_u^-$	This work	2.480	0.32	0.30	238	4.55	0.157	2.20
	Expt. ^k	2.430 ^k	0.31 ^k		253 ^k	5.76 ^k	0.163 ^k	2.20 ^k
$B:(1)0_u^+$	This work	2.475	0.42	0.41	243	4.14	0.157	2.20
	Expt.	2.435 ^d	0.42 ^d		255.38 ^d	4.59	0.162 ^b	2.21 ^b
	Theor. ^f	2.464 ^f	0.36 ^f		240 ^f	5.26 ^f		
	Theor. ^g	2.450 ^g	0.40 ^g		259 ^g	4.60 ^g		
$B'':(2)1_u$	This work	2.881	0.03	0.03	84	9.06	0.116	2.48
	Theor.							2.45 ^l
$(1)2_g$	This work	3.646	0.02	0.02	31	-0.17	0.073	2.50
$a:(1)1_g$	This work	3.477	0.03	0.03	42	2.23	0.080	2.49
$a':(2)0_g^+$	This work	3.932	0.01	0.01	48	7.20	0.062	2.51
$(1)0_g^-$	This work	3.337	0.03	0.03	47	5.67	0.087	2.60
$(2)1_g^g$	This work	3.345	0.04	0.04	55	4.16	0.064	2.59
$(2)0_u^-$	This work	3.932	0.00	0.00	36	14.12	0.062	2.51
$(3)1_u$	This work	3.874	0.01	0.00	52	10.14	0.064	2.51
	Theor.							2.56 ^l
$(3)0_g^+$	This work	3.332	0.03	0.02	98	5.65	0.087	2.60
$(3)1_g$	This work	3.816	0.02	0.01	49	3.08	0.066	2.61
$(2)2_g$	This work	3.941	0.01	0.01	33	4.44	0.062	2.62
$(4)0_g^+$	This work	3.740	0.02	0.02	44	2.39	0.069	2.72
$(3)0_u^-$	This work	3.808	0.04	0.03	126	4.53	0.066	2.59
$(1)3_u$	This work	5.042	0.01	0.01	37	10.25	0.038	2.61
$b':(2)2_u$	This work	3.891	0.02	0.01	37	2.84	0.064	2.61
$(4)1_u$	This work	4.738	0.00	0.00	16	7.14	0.043	2.63
$C:(5)1_u$	This work	3.746	0.02	0.01	35	4.52	0.069	2.72
$(4)0_u^-$	This work	3.830	0.01	0.01	34	2.34	0.066	2.72

^aReference 43.^bReference 45.^cReference 44.^dReferences 31 and 16.^eReference 23.^fReference 28.^gReference 31.^hReference 17.ⁱReference 18.^jReference 24.^kReference 19.^lReference 46.

double excitation (MRCISD) calculations were also performed.

All calculations presented in this work were performed using the fully relativistic *ab initio* MOLFDIR (Ref. 36) program package in a similar way previously described in a paper from de Jong *et al.*³⁷ The chlorine nucleus was represented by a Gaussian charge distribution³⁸ with an exponential value of $0.384\,827\,492\,2 \times 10^{+09}$, and the basis set used

was the contracted aug-cc-pVTZ basis taken from Visscher and Dyall.³⁹ The speed of light was taken to be 137.035 989 5 a.u.

The potential energy surfaces of all the states were calculated at 46 different bond distances using the average of configurations Dirac-Hartree-Fock followed by the complete open shell configuration interaction (COSCI) approach, where full CI was performed in the open shell space of the

TABLE II. Calculated relativistic vertical excitation energies (eV) at the experimental ground state equilibrium length compared to literature data.

Nonrelativistic Λ - Σ states	Relativistic Ω states	COSCI	MRCISD	MRCISD+ Q	Dominant configurations	Theor.	Expt.
$^1\Sigma_g^+$	$X:(1)0_g^+$	0.00	0.00	0.00	2440		
$^3\Pi_u$	$A':(1)2_u$	3.17	3.11	3.07	2431	3.35 ^a	
	$A:(1)1_u$	3.21	3.15	3.11	2431	3.38 ^a	
						2.88 ^b	
						3.12 ^c	
	$B':(1)0_u^-$	3.25	3.20	3.16	2431	3.41 ^a	
	$B:(1)0_u^+$	3.25	3.20	3.16	2431	3.41 ^a	3.20 ^d
$^1\Pi_u$						2.93 ^b	2.91 ^e
						3.07 ^c	$\sim 3^f$
	$B'':(2)1_u$	4.09	3.94	3.90	2431	3.69 ^a	3.72 ^d
						3.70 ^b	3.75 ^e
$^3\Pi_g$						4.27 ^c	3.76 ^g
	$(1)2_g$	6.09	6.04	5.98	2341		
	$a:(1)1_g$	6.13	6.07	6.02	2341		
	$a':(2)0_g^+$	6.17	6.11	6.05	2341		
$^1\Pi_g$	$(1)0_g^-$	6.17	6.11	6.05	2341		
	$(2)1_g$	6.67	6.67	6.64	2341		
$^3\Sigma_u^+$	$(2)0_u^-$	6.68	6.98	7.02	1441		
	$(3)1_u$	6.68	6.98	7.02	1441		
$^3\Sigma_g^-$	$(3)0_g^+$	7.13	7.05	7.00	2422		
	$(3)1_g$	7.14	7.06	7.01	2422		
$^1\Delta_g$	$(2)2_g$	7.52	7.53	7.53	2422		
$^1\Sigma_g^+$	$(4)0_g^+$	7.84	7.88	7.88	2422		
$^1\Sigma_u^-$	$(3)0_u^-$	8.52	8.77	8.82	2332		
$^3\Delta_u$	$(1)3_u$	8.56	8.82	8.87	2332		
	$b':(2)2_u$	8.64	8.90	8.94	2332		
	$(4)1_u$	8.71	8.97	9.02	2332		
$^3\Sigma_u^+$	$C:(5)1_u$	8.75	8.99	9.03	2332		
	$(4)0_u^-$	8.77	9.02	9.06	2332		

^aReference 27.^bSFR+SO1+SO2 calculation taken fr. Ref. 32.^cSAC-CI-SO1 calculation taken fr. Ref. 32.^dReference 14.^eReference 13.^fReference 9.^gReference 47.

$3p$ spin orbitals. Since performing a multireference CI at all points of the potential energy surface would be computationally very expensive, we pragmatically improved the curves by a simple empirical correction,^{40,37} matching the ground state potential energy curve to the experimentally determined Rydberg-Klein-Rees ground state²⁰ and shifting all the excited states in a similar fashion.

MRCISD calculations were performed to estimate the effects of dynamical correlation and relaxation on the vertical excitation energies and they were calculated at the experimental ground state R_e . Higher order corrections were estimated using the so-called Davidson correction,⁴¹ denoted as MRCISD+ Q . The multireference active space contains the $3s$ spinor in RAS1, the $3p$ spinors in RAS2, and 160 virtual spinors in RAS3, and the COSCI wave functions

were used as the reference wave functions for these calculations. The RAS3 space encompasses all virtuals with energies of less than 4.26 hartrees in COSCI calculation.

The equilibrium bond lengths (R_e), vibrational frequencies (ω_e), anharmonicity constants ($\omega_e x_e$), rotational constant (β_e), and dissociation energies (D_e) were obtained through 15th-order polynomial fit using FIT_1D (Ref. 42) program.

Potential energy curves of the 22 lowest excited states and ground state that dissociate into neutral atoms ($\text{Cl}+\text{Cl}$, $\text{Cl}+\text{Cl}^*$, and Cl^*+Cl^*), resulting from $\sigma_g^k \pi_u^l \pi_g^m \sigma_u^n$ configurations where $k+l+m+n=10$ electrons in 12 spin orbitals, were calculated. The calculated spectroscopic parameters (R_e , ω_e , $\omega_e x_e$, D_e , D_0 , β_e , and T_e) for these states are presented in Table I together with available experimental

data^{43–45} and results from other theoretical work.⁴⁶

Comparing our results with the experimental values available, we found that (a) the calculated bond distances (R_e) for the excited states are all systematically larger by less than 0.05 Å, (b) the values of D_e have discrepancies smaller than 0.01 eV for the majority of states, (c) the vibrational frequencies ω_e are within 15 cm⁻¹, and (d) the differences for β_e are less than 6 cm⁻¹ and T_e values are 0.01 eV lower for the worse cases.

For the 18 higher covalent states, there are only theoretical T_e values for two states: $(2)1_u$ and $(3)1_u$, with values of 2.45 and 2.56 eV, respectively. Our COSCI values for these states are 2.48 and 2.51 eV, respectively. For all other states, the spectroscopic constants are presented for the first time. Generally, the splitting of the calculated states due to spin-orbit interaction agrees reasonably well with the observed splittings and the nondynamical correlation effects are apparently sufficiently described by COSCI calculations in the spinor space spanned by the $3p$ spinors.

In Table II, the calculated vertical excitation energies are presented. The results are compared with those of Peyerimhoff and Buenker,²⁶ Roszak and Lipinski,²⁷ and available experimental data.^{9,13,14,47} The assignment is given to the states based on their main character at the ground state R_e .

Experimental values of vertical excitations are available for two states, $B:(1)0_u^+$ and $(2)1_u$. The experimental values of vertical excitation for $B:(1)0_u^+$ vary from 2.90 to 3.20 eV (Samartzis *et al.*⁹ suggest a value close to 3 eV), whereas the experimental values for $(2)1_u$ state are closer to each other, 3.72 and 3.75 eV. Our theoretical results are in reasonable agreement with available experimental data, being at relativistic MRCISD+ Q level, 3.26 and 3.90 eV for $B:(1)0_u^+$ and $(2)1_u$, respectively. From Table II, it can be seen that the dynamical correlation is important to obtain accurate vertical excitation energies. For the state $(2)1_u$, the excitation energy lowers from the COSCI value of 4.09 to 3.94 eV at MRCISD level and 3.90 eV at MRCISD+ Q level.

There are just few theoretical calculations with spin-orbit coupling and experimental work regarding the vertical excitation energies of Cl₂, and they are concentrated on relativistic states that originated from nonrelativistic $^3\Pi_u[A':(1)2_u, A:(1)1_u, B':0_u^-, \text{ and } B:0_u^+]$ and $^1\Pi_u[(2)1_u]$.

Roszak and Lipinski,²⁷ using a semiempirical INDO with spin-orbit corrections, found very good agreement for vertical excitation energy of $(2)1_u$ state but a worse agreement for $B:0_u^+$. Honda *et al.*,³² using a spin-free (scalar relativistic) Hamiltonian with one- and two-electron spin-orbit interactions (SFR+SO1+SO2) and symmetry adapted cluster CI with one-electron spin-orbit interactions (SAC-CI-SO1), studied three excited states of chlorine molecule $[A:(1)1_u, B:0_u^+, \text{ and } (2)1_u]$. They found for $(2)1_u$ state values of 3.70 eV (SAC-CI-SO1) and 4.27 eV (SFR+SO1+SO2), while as described before, we found a 3.90 eV value at MRCISD+ Q level.

With respect to $B:0_u^+$, Honda *et al.*³² found the values of 2.93 eV (SAC-CI-SO1) and 3.07 eV (SFR+SO1+SO2), which are between the lowest (2.91 eV) and highest (3.20 eV) experimental values available. Our relativistic MRCISD+ Q for $B:0_u^+$ and $B':0_u^-$ are both 3.16 eV. Roszak

and Lipinski found also found an equal value for $B:0_u^+$ and $B':0_u^-$, but it is 3.42 eV.

For the $A:(1)1_u$ state, there are only theoretical values. Our MRCISD+ Q value, 3.11 eV, is very similar to the value found by Honda *et al.*³² with SAC-CI-SO1 approach, 3.12 eV. The SFR+SO1+SO2 result by Honda *et al.*³² is found to be significantly lower (2.88 eV), whereas the value found by Roszak and Lipinski for this state is considerably higher (3.38 eV) compared with our MRCISD+ Q result.

The spectroscopic properties and potential energy curves of the ground state and all possible covalent excited states for Cl₂ molecule were calculated within a four-component relativistic framework with COSCI approach. Tables I and II display the spectroscopic properties derived from their curves and the results are in good agreement with available data. The corrected curves for all states with their assignment can be downloaded as Supplementary Material.⁴⁸

This research was performed in part using the Molecular Science Computing Facility (MSCF) in the William R. Wiley Environmental Molecular Sciences Laboratory (EMSL), a national scientific user facility sponsored by the U.S. Department of Energy's Office of Biological and Environmental Research and located at the Pacific Northwest National Laboratory (PNNL), operated for the Department of Energy by Battelle. L.G.M. de Macedo also would like to acknowledge Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for Junior Scientist Fellowship (Grant Nos. 07/50679-9 and 06/64976-5).

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