Theoretical investigations of spectroscopic parameters and molecular constants for electronic ground state of Cl_2 and its isotopes*

Shi De-Heng(施德恒)[a)b)†], Zhang Xiao-Niu(张小妞)[b)], Liu Hui(刘 慧)[a)], Zhu Zun-Lue(朱遵略)[b)], and Sun Jin-Feng(孙金锋)[b)]

[a)] *College of Physics & Electronic Engineering, Xinyang Normal University, Xinyang* 464000, *China*

[b)] *College of Physics & Information Engineering, Henan Normal University, Xinxiang* 453007, *China*

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The potential energy curve of the $Cl_2(X^1\Sigma_g{}^+)$ is investigated by the highly accurate valence internally contracted multireference configuration interaction (MRCI) approach in combination with the largest correlation-consistent basis set, aug-cc-pV6Z, in the valence range. The theoretical spectroscopic parameters and the molecular constants of three isotopes, $^{35}Cl_2$, $^{35}Cl^{37}Cl$ and $^{37}Cl_2$, are studied. For the $^{35}Cl_2(X^1\Sigma_g{}^+)$, the values of D_0, D_e, R_e, ω_e, $\omega_e\chi_e$, α_e and B_e are obtained to be 2.3921 eV, 2.4264 eV, 0.19939 nm, 555.13 cm^{-1}, 2.6772 cm^{-1}, 0.001481 cm^{-1} and 0.24225 cm^{-1}, respectively. For the $^{35}Cl^{37}Cl(X^1\Sigma_g{}^+)$, the values of D_0, D_e, R_e, ω_e, $\omega_e\chi_e$, α_e and B_e are calculated to be 2.3918 eV, 2.4257 eV, 0.19939 nm, 547.68 cm^{-1}, 2.6234 cm^{-1}, 0.00140 cm^1 and 0.23572 cm^{-1}, respectively. And for the $^{37}Cl_2(X^1\Sigma_g{}^+)$, the values of D_0, D_e, R_e, ω_e, $\omega_e\chi_e$, α_e and B_e are obtained to be 2.3923 eV, 2.4257 eV, 0.19939 nm, 540.06 cm^{-1}, 2.5556 cm^{-1}, 0.00139 cm^{-1} and 0.22919 cm^{-1}, respectively. These spectroscopic results are in good agreement with the available experimental data. With the potential of Cl_2 molecule determined at the MRCI/aug-cc-pV6Z level of theory, the total of 59 vibrational states is predicted for each isotope when the rotational quantum number J equals zero ($J = 0$). The theoretical vibrational levels, classical turning points, inertial rotation and centrifugal distortion constants are determined when $J = 0$, which are in excellent accordance with the available experimental findings.

Keywords: isotope effect, spectroscopic parameter, molecular constant, vibrational level

PACC: 3440, 3120C, 3520G

1. Introduction

Natural chlorine consists of 75.5% ^{35}Cl and 24.5% ^{37}Cl. The abundances[1] of three corresponding diatomic species are $^{35}Cl_2$ 57.0%, $^{35}Cl^{37}Cl$ 37.0% and $^{37}Cl_2$ 6.0%, respectively. In experiment,[1−15] the spectroscopic parameters and the molecular constants of these isotopes were investigated extensively, and a number of detailed results were reported in the past several decades. However, in theory, surprisingly, no investigations can be found up to this day about the spectroscopic parameters and the molecular constants of these isotope molecules, though fruitful data[16−29] exist everywhere about the spectroscopic parameters and the molecular constants of the Cl_2.

For this reason, in the present paper, we will in detail investigate the spectroscopic parameters and the molecular constants of these isotope species, $^{35}Cl_2(X^1\Sigma_g{}^+)$, $^{35}Cl^{37}Cl(X^1\Sigma_g{}^+)$ and $^{37}Cl_2(X^1\Sigma_g{}^+)$. The remainder of the present paper is organized as follows. First, the potential energy curve (PEC) of the $Cl_2(X^1\Sigma_g{}^+)$ is calculated by the highly accurate valence internally contracted multireference configuration interaction (MRCI) approach[30,31] in combination with the largest correlation-consistent basis set,[32,33] aug-cc-pV6Z, in the valence range. Then, with the PEC of $Cl_2(X^1\Sigma_g{}^+)$ molecule, obtained at the MRCI/aug-cc-pV6Z level of theory, the spectroscopic parameters and the molecular constants of these isotopes are determined, and a total of 59 vibrational states for each species is predicted when the rotational quantum number J is equal to zero. The present work is the first theoretical investigation on the spectroscopic parameters and the molecular con-

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†Corresponding author. E-mail: scattering@sina.com.cn

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stants of these isotopes so far.

2. Theoretical details

We calculate the PEC of $Cl_2(X^1\Sigma_g{}^+)$ molecule by the full valence complete active space self-consistent field (CASSCF) approach, which the MRCI calculations are based on. Therefore, the full valence CASSCF is employed as the reference wavefunction for the MRCI calculations in the present work. The present calculations are carried out in the MOLPRO 2008.1 program package[34] with the largest correlation-consistent basis set,[32,33] aug-cc-pV6Z, in the valence range.

In the MOLPRO, only the Abelian point group symmetry is used. For molecules with degenerate symmetry, an Abelian subgroup must be employed. That is to say, for the diatomic molecule such as Cl_2 with $D_{\infty h}$ symmetry, it will be substituted by D_{2h} symmetry in such an order of the irreducible representations as $A_g/B_{1g}/B_{2g}/B_{3g}/A_u/B_{1u}/B_{2u}/B_{3u}$. In the CASSCF and subsequent MRCI calculations, these eight kinds of states are evaluated. Specifically, for the $Cl_2(X^1\Sigma_g{}^+)$ molecule, eight molecular orbitals (MOs) are placed into the active space, including two A_g's, one B_{1g}, one B_{2g}, two A_u's, one B_{1u} and one B_{2u} symmetry MOs, which correspond to the 3s3p shells of the Cl atom. The rest of the electrons in the molecule are positioned into the closed-shell orbitals, including three A_g's, one B_{1g}, one B_{2g}, three A_u's, one B_{1u} and one B_{2u} symmetry MOs. However, when we use these MOs (five A_g's, two B_{1g}'s, two B_{2g}'s, five A_u's, two B_{1u}'s and two B_{2u}'s) to calculate the PEC of the $Cl_2(X^1\Sigma_g{}^+)$, we find that the obtained PEC is not smooth. It is very obvious that a break suddenly occurs when the internuclear separation is about 0.42 nm. Analysis shows that this situation is caused by crossings of the PECs between the ground state and the excited one. To improve the smoothness of the PEC, we place more MOs into the active space, including one additional A_g MO. With these MOs (six A_g's, two B_{1g}'s, two B_{2g}'s, five A_u's, two B_{1u}'s and two B_{2u}'s) used, the $Cl_2(X^1\Sigma_g{}^+)$ PEC obtained here are both smooth and convergent over the present internuclear distance range.

The PEC calculations are performed in steps of 0.02 nm over an internuclear distance range from about 0.09 to 2.08 nm. Only near the equilibrium position, will the step be changed into 0.005 nm. The smaller step is adopted around the $Cl_2(X^1\Sigma_g{}^+)$ equilibrium position so that the properties of the PEC are displayed more clearly.[35–37] We use the module VIBROT in MOLCAS 7.4 program package,[38] so that we can identify the $^{35}Cl_2(X^1\Sigma_g{}^+)$, $^{35}Cl^{37}Cl(X^1\Sigma_g{}^+)$ and $^{37}Cl_2(X^1\Sigma_g{}^+)$ isotopes and calculate spectroscopic parameters and molecular constants. In these calculations, the PEC used here is the potential of the $Cl_2(X^1\Sigma_g{}^+)$, which is determined at the MRCI/aug-cc-pV6Z level of theory. The present spectroscopic parameters are listed in Table 1 for these three isotope species, $^{35}Cl_2(X^1\Sigma_g{}^+)$, $^{35}Cl^{37}Cl(X^1\Sigma_g{}^+)$ and $^{37}Cl_2(X^1\Sigma_g{}^+)$.

Table 1. Comparisons of spectroscopic parameter between the present work and the available measurements and other theories for the $^{35}Cl_2(X^1\Sigma_g{}^+)$, $^{35}Cl^{37}Cl(X^1\Sigma_g{}^+)$ and $^{37}Cl_2(X^1\Sigma_g{}^+)$ isotopes at the MRCI/aug-cc- pV6Z level of theory.

source	D_e/eV	R_e/nm	ω_e/cm^{-1}	$\omega_e\chi_e$/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}	D_0/eV
$^{35}Cl_2(X^1\Sigma_g{}^+)$							
this work	2.4264	0.19939	555.13	2.6772	0.24225	0.001481	2.3921
Exp.[5]	–	0.1985	573.5	2.49	–	–	–
Exp.[6]	–	–	559.71	2.7013	–	0.001477	–
Exp.[7]	2.5139	–	559.75	2.6943	0.24415	0.001516	2.4793
Exp.[8]	–	–	–	–	–	–	2.4793
Exp.[9]	–	–	560(1)	2.65(2)	–	–	–
Exp.[10]	–	–	–	–	–	–	2.479367(19)
Exp.[11]	2.5151	–	–	–	–	–	–
Exp.[12]	2.5139	0.19878	559.71	2.70	0.24407	0.00153	2.4794
Exp.[13]	–	–	560.50	2.9043	0.2438	0.00168	2.4873(12)
Exp.[14]	–	–	562.3	2.70(5)	–	–	–
Exp.[15]	2.5140	0.1987	559.7	2.67	0.2439	0.0014	2.47936
$^{35}Cl^{37}Cl(X^1\Sigma_g{}^+)$							
this work	2.4257	0.19939	547.68	2.6234	0.23572	0.00140	2.3918
Exp.[6]	–	–	552.100	2.62845	–	0.0014191	–

Table 1. (continued)

source	D_e/eV	R_e/nm	ω_e/cm^{-1}	$\omega_e\chi_e$/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}	D_0/eV
Exp.[7]	2.5139	–	552.14	2.6207	0.23759	0.001459	2.4793
Exp.[9]	–	–	553(1)	2.75(2)	–	–	–
Exp.[14]	–	–	554.6	2.66(5)	–	–	–
$^{37}Cl_2(X^1\Sigma_g^+)$							
this work	2.4257	0.19939	540.06	2.5556	0.22919	0.00139	2.3923
Exp.[7]	2.5139	–	544.42	2.5480	0.23099	0.001400	2.4793
Exp.[14]	–	–	546.8	2.62(5)	–	–	–
$Cl_2(X^1\Sigma_g^+)$							
theory[16]	0.71	0.234	372	5.3	0.18	0.009	–
theory[17]	2.36	0.2016	510	3.4	0.23	0.002	2.3284
theory[18]	–	0.2019	588	–	0.233	–	–
theory[19]	2.49	0.2020	552	–	–	–	2.455
theory[20]	–	0.2000	–	–	–	–	2.03
theory[21]	1.43	0.2066	493	–	–	–	–
theory[22]	2.4	0.1999	–	–	–	–	–
theory[23]	2.4080	0.1997	554.6	2.81	0.242	0.0015	2.3737
theory[24]	2.1856	0.2019	544	–	–	–	–
theory[25]	2.44	0.1982	561	–	–	–	–
theory[26]	–	0.1996	560.6	2.01	–	–	–
theory[27]	2.37	0.1984	576	–	–	–	–
theory[28]	–	0.19906	–	–	–	–	–
theory[29]	2.2636	0.2016	544.5	–	–	–	–

To evaluate the effects on the spectroscopic parameters of these isotopes by the relativistic corrections, we perform the investigations by adding the second-order Douglas–Kroll Hamiltonian approximation (DKH2)[39,40] into the $Cl_2(X^1\Sigma_g^+)$ PEC calculations at the present MRCI/aug-cc-pV6Z level of theory. For the $^{35}Cl_2(X^1\Sigma_g^+)$ species the D_e, R_e, ω_e and $\omega_e\chi_e$ are 2.4414 eV, 0.19941 nm, 555.68 cm^{-1} and 2.7018 cm^{-1}, respectively. For the $^{37}Cl^{35}Cl(X^1\Sigma_g^+)$ species, the D_e R_e ω_e and $\omega_e\chi_e$ are 2.4414 eV, 0.19941 nm, 548.14 cm^{-1} and 2.6325 cm^{-1}, respectively. And for the $^{37}Cl_2(X^1\Sigma_g^+)$ species, the D_e, R_e ω_e and $\omega_e\chi_e$ are 2.4414 eV, 0.19941 nm, 540.50 cm^{-1} and 2.5627 cm^{-1}, respectively. By careful comparison, as a whole, we find that the spectroscopic parameters determined at the relativistic corrections are improved very little when compared with those obtained at the non-relativistic corrections. Because the complete relativistic correction calculations consume more CPU time, the present investigations are still limited to the non-relativistic corrections.

Then, we take into considerations the effects on the spectroscopic parameters by the core-valence correlation corrections. As we know, in the valence range, the largest basis set is the aug-cc-pV6Z. No corresponding aug-cc-pcV6Z basis set exists. Therefore, we cannot directly show the effects on the spectroscopic parameters by the core-valence correlation corrections under the same condition. In the core-valence correlation range, the largest basis set is the aug-cc-pcV5Z. We have computed the spectroscopic parameters for these isotopes by the PEC obtained at the MRCI/aug-cc-pcV5Z level of theory with the aid of module VIBROT in MOLCAS 7.4 program package.[38] For the $^{35}Cl_2$ ($X^1\Sigma_g^+$), the D_e, R_e, ω_e and $\omega_e\chi_e$ are 2.4253 eV, 0.19948 nm, 553.78 cm^{-1} and 2.6619 cm^{-1}, respectively. For the $^{37}Cl^{35}Cl(X^1\Sigma_g^+)$, the D_e, R_e, ω_e and $\omega_e\chi_e$ are 2.4253 eV, 0.19948 nm, 546.29 cm^{-1} and 2.5956 cm^{-1}, respectively. And for the $^{37}Cl_2(X^1\Sigma_g^+)$, the D_e, R_e ω_e and $\omega_e\chi_e$ are 2.4253 eV, 0.19948 nm, 538.69 cm^{-1} and 2.5239 cm^{-1}, respectively. By comparison with the available measurements,[6,7,13–15] we find that the D_e and ω_e values obtained at the aug-cc-pcV5Z basis set become slightly worse than those determined at the aug-cc-pV6Z. Only R_e becomes ratherish better.

According to the above analyses, here we select the aug-cc-pV6Z basis set for the investigation of spectroscopic parameters and molecular constants without taking into considerations the effects induced by the relativistic or core-valence correlation corrections.

3. Results and discussion

3.1. Spectroscopic parameters

For a convenient comparison with the experimental findings and other theoretical results, we collect the spectroscopic parameters available from these experiments[5−15] and theories,[16−29] and list them in Table 1.

No theoretical results can be found about these isotopes, whereas a number of theoretical investigations[16−29] exist for the $Cl_2(X^1\Sigma_g{}^+)$ molecule. Of these investigations, the earliest one was made by Heil *et al.*,[16] in which the complete configuration interaction was calculated in terms of Hartree–Fock (HF) atomic orbitals. From Table 1, it is easy to find that their D_e and ω_e values are too small when compared with the present ones. Ten years later, Das[17] obtained the spectroscopic parameters using the pseudopotential technique. Similar to the results in Ref. [16], their D_e and ω_e values[17] are also small when compared with the present ones. Sakai *et al.*[18] carried out the calculations by the restricted Roothaan–Hartree–Fock self-consistent field (SCF) method with several basis sets, and obtained their favourite spectroscopic parameters at the MINI-4* set. Peyerimhoff and Buenker[19] made the calculations by the multi-reference single- and double-excitation configuration interaction (MRD-CI) approach with the standard atomic orbital basis set, which consists of a total of 74 Cartesian Gaussian orbitals. As can be seen in Table 1, only several limited spectroscopic parameters have been evaluated in their calculations.

Lately, McLean *et al.*[20] calculated the values of R_e and D_0 by the configuration interaction method including single and double excitations from the valence orbitals of the single HF configuration with the Slater basis set. Stevens *et al.*[21] computed the values of D_e, R_e and ω_e by the compact effective potential and efficient shared-exponent basis set. Becherer and Ahlrichs[22] evaluated the values of D_e and R_e using three kinds of methods with several groups of CGTO basis sets, and their favourite results were derived at the CPF/A3d2f1g level of theory. However, in a similar way to that in Refs. [18] and [19], only limited spectroscopic parameters were determined in their calculations.

Recently, Woon and Dunning[23] made the benchmark calculations of spectroscopic parameters using the CCSD(T) approach with a series of correlation-consistent basis sets.[32,33] By comparison, one can easily find that their best favorite results were determined at the cc-pV5Z basis set. As shown in Table 1, as a whole, the accuracy of their results is only equivalent to ours when compared with the measurements of the $^{35}Cl_2(X^1\Sigma_g{}^+)$ species. However, their investigations were not concerned with any isotope molecules. Visscher and Dyall[24] evaluated the effects on the D_e, R_e and ω_e by the relativistic and core-valence correlation corrections. From Table 1, we can find that their values of D_e and R_e are poor when compared with the present ones. Dolg[25] studied the spectroscopic properties such as harmonic frequency, bond length and dissociation energy by the quasirelativistic pseudo-potential model. Fossgaard *et al.*[26] evaluated the spectroscopic parameters, R_e, ω_e and $\omega_e\chi_e$, by the four-component relativistic density functional theory (DFT) with the series of correlation-consistent basis sets. And their results closest to the experiments were obtained at the cc-pVTZ set. Although some of their spectroscopic parameters[23,25] are superior to the present ones, as listed in Table 1, only several limited spectroscopic parameters were evaluated in their investigations.[23−26]

Very recently, Lee *et al.*[27] took into considerations the spin–orbit effects on the spectroscopic parameters (bond length, dissociation energy and harmonic frequency) using the shape-consistent relativistic effective core potential (RECP) with the basis set of cc-pVTZ quality. In their calculations, several approaches such as HF, MP2, CCSD and CCSD(T) were employed. By comparison with the available experiments,[5−15] it is not difficult to find that their best favourite results were determined at the MP2 level of theory. Coriani *et al.*[28] performed the molecular geometry calculations by the HF, MP2, CCSD and CCSD(T) theories in combination with the correlation-consistent basis sets.[32,33] Comparing with the available experiments, we can determine that their best favourite R_e was obtained at CCSD(T)/cc-pwcVQZ level of theory. Of course, this R_e value is superior to ours. Haiduke *et al.*[29] calculated the values of D_e, R_e and ω_e by the DKH2–CCSD(T) theory with the prolapse-free relativistic adapted Gaussian basis set (RAGBS). As given in Table 1, their results are inferior to the present ones when compared with the available experiments.

According to the above discussion and Table 1, for the $^{35}Cl_2(X^1\Sigma_g{}^+)$ isotope, for example, one can

easily calculate the deviations of spectroscopic parameters, R_e, ω_e, B_e and α_e from the experiments[15] to be only 0.30%, 0.82%, 0.71% and 0.18%, respectively. The difference between the present $\omega_e\chi_e$ result and the experimental one[15] is somewhat large, but compared with the latest experiments,[5] the difference between them is only 2.7%. As to the $^{37}Cl_2(X^1\Sigma_g^+)$ isotope, two groups of experiments[7,14] can be found to our knowledge. The differences between the present results and these experiments are small. For example, the deviations of the ω_e, $\omega_e\chi_e$, B_e and α_e from the experiments[7] are only 0.80%, 0.30%, 0.78% and 0.71%, respectively. Similar to the $^{35}Cl_2(X^1\Sigma_g^+)$ and $^{37}Cl_2(X^1\Sigma_g^+)$ isotopes, one can also easily judge that the spectroscopic parameters for the $^{37}Cl^{35}Cl(X^1\Sigma_g^+)$ molecule are in excellent agreement with the experimental data.[6,7,9,14] Because no theoretical spectroscopic investigations exist about these isotopes, we say that the present investigations are not only the first results but also the accurate results.

3.2. Vibrational manifolds

Based on the PEC of $Cl_2(X^1\Sigma_g^+)$ molecule, we determine the vibrational levels, classical turning points, inertial rotation and centrifugal constants of these three isotopes with the aid of module VIBROT in MOLCAS 7.4 program package.[38] For the length limitation of the paper, we only list these results for the first 30 vibrational levels in Tables 2–5.

There have been several groups of experiments[2,4,6,13] reporting the vibrational levels and inertial rotation constants of the $^{35}Cl_2(X^1\Sigma_g^+)$ isotope. For a convenient comparison with our results, we also list them in Table 2, in which the present vibrational levels are given until $\upsilon = 29$. From Table 2, the good agreement can be found between these experiments[2,4,6,13] and the present ones. For example, for the vibrational level, the present results are lower than those experiments[4] only by 0.36%, 0.84%, 1.01% and 1.19% when $\upsilon = 0$, 3, 10 and 15, respectively. And for the inertial rotation constant B_υ, the deviations of the present values from the experiments[2] are only 0.68%, 0.69%, 0.75% and 0.93% when $\upsilon = 0$, 5, 10 and 16, respectively; and the differences between the present results and the measurements[4] are also only 0.62%, 0.69%, 0.75% and 0.90% when $\upsilon = 0$, 5, 10 and 15, respectively. These show that the present results presented in Table 2 are reliable.

Table 2. Comparison of vibrational level and classical turning point between the present work and the available experiments for the $^{35}Cl_2(X^1\Sigma_g^+)$ molecule when $J = 0$ at the MRCI/aug-cc-pV6Z level of theory.

υ	$G(\upsilon)/cm^{-1}$			B_υ/cm^{-1}				
	this work	Exp.[13]	Exp.[4]	this work	Exp.[4]	Exp.[2]	Exp.[6]	Exp.[13]
0	276.89	279.5	279.178	0.241742	0.243251	0.243394	0.24321	–
1	826.62	834.3	833.476	0.240232	0.241771	0.241870	0.24172	0.2412
2	1370.88	1383.4	1382.360	0.238714	0.240276	0.240339	0.24023	0.2395
3	1909.58	–	1925.814	0.237183	0.238769	0.238800		
4	2442.64	2464.9	2463.807	0.235639	0.237248	0.237255		
5	2969.99	–	2996.301	0.234084	0.235714	0.235702		
6	3491.54	3524.2	3523.243	0.232515	0.234141	0.234141		
7	4007.20	–	4044.577	0.230933	0.232573	0.232573		
8	4516.91	4561.3	4560.243	0.229337	0.230996	0.230996		
9	5020.58	–	5070.178	0.227725	0.229411	0.229411		
10	5518.13	–	5574.318	0.226097	0.227815	0.227815		
11	6009.48	6074.5	6072.604	0.224451	0.226209	0.226209		
12	6494.54	–	6564.981	0.222787	0.224591	0.224591		
13	6973.25	–	7051.400	0.221105	0.222959	0.222959		
14	7445.51	7535.4	7531.823	0.219405	0.221314	0.221314		
15	7911.24	–	8006.227	0.217684	0.219653	0.219653		
16	8370.37	–		0.215940		0.217974		
17	8822.82	8941.6		0.214172				
18	9268.50	–		0.212380				
19	9707.33	–		0.210562				

Table 2. (continued)

υ	$G(\upsilon)/\mathrm{cm}^{-1}$			$B_\upsilon/\mathrm{cm}^{-1}$				
	this work	Exp.[13]	Exp.[4]	this work	Exp.[4]	Exp.[2]	Exp.[6]	Exp.[13]
24	11795.99	11996.3		0.201027				
25	12192.05			0.199016				
26	12580.70			0.196966				
27	12961.86			0.194872				
28	13335.45			0.192728				
29	13701.38			0.190533				

Similar to the case of vibrational levels, there are also several groups of experiments[3,4,13] concerning with the classical turning points of $^{35}Cl_2(X^1\Sigma_g{}^+)$ isotope. For a convenient comparison with the present results, we also present them in Table 3. In a way similar to that in Table 2, here we still give the present classical turning points until $\upsilon = 29$. By simple comparison, it is not difficult to find that excellent agreement exists between the present results and all those experimental data.[3,4,13] For example, for the $R_{\min}$, the present results are larger than those experiments[3] only by 0.33%, 0.40%, 0.52% and 0.59% when $\upsilon = 0$, 10, 20 and 29, respectively; And the present results are larger than those experiments[4] also only by 0.32%, 0.35%, 0.36% and 0.37% when $\upsilon = 0$, 5, 10 and 15, respectively. For the $R_{\max}$, the present results are larger than those experiments[3] only by 0.31%, 0.36%, 0.38% and 0.03% when $\upsilon = 0$, 10, 20 and 29, respectively. These facts further prove that the present results are both reliable and accurate.

Table 3. Comparison of classical turning point between the present work and the available experiments for the $^{35}Cl_2(X^1\Sigma_g{}^+)$ molecule when $J = 0$ at the MRCI/aug-cc-pV6Z level of theory.

υ	$R_{\min}/\mathrm{nm}$				$R_{\max}/\mathrm{nm}$			
	this work	Exp.[3]	Exp.[4]	Exp.[13]	this work	Exp.[3]	Exp.[4]	Exp.[13]
0	0.19381	0.19317	0.19320	0.1958	0.20556	0.20493	0.20496	0.2047
1	0.19005	0.18941	0.18943	0.1935	0.21050	0.20987	0.20988	0.2085
2	0.18762	0.18697	0.18698	0.1918	0.21413	0.21349	0.21350	0.2117
3	0.18572	0.18507	0.18509	–	0.21724	0.21658	0.21659	–
4	0.18414	0.18349	0.18350	0.1891	0.22004	0.21937	0.21938	0.2174
5	0.18278	0.18213	0.18214	–	0.22265	0.22196	0.22197	–
6	0.18157	0.18090	0.18093	0.1871	0.22512	0.22439	0.22442	0.2224
7	0.18048	0.17980	0.17984	–	0.22748	0.22672	0.22677	–
8	0.17949	0.17880	0.17886	0.1853	0.22976	0.22898	0.22904	0.2273
9	0.17858	0.17789	0.17794	–	0.23198	0.23118	0.23124	–
10	0.17774	0.17703	0.17710	–	0.23415	0.23332	0.23340	–
11	0.17695	0.17624	0.17632	0.1835	0.23628	0.23543	0.23551	0.2344
12	0.17621	0.17547	0.17558	–	0.23838	0.23743	0.23760	–
13	0.17552	0.17476	0.17489	–	0.24045	0.23952	0.23966	–
14	0.17487	0.17408	0.17423	0.1818	0.24249	0.24154	0.24170	0.2416
15	0.17425	0.17345	0.17361	–	0.24453	0.24356	0.24373	–
16	0.17367	0.17285		–	0.24654	0.24556		–
17	0.17311	0.17229		0.1804	0.24855	0.24758		0.2491
18	0.17259	0.17175		–	0.25056	0.24959		–
19	0.17208	0.17122		–	0.25255	0.25158		–
20	0.17160	0.17071		0.1794	0.25455	0.25358		0.2674
21	0.17114	0.17024		–	0.25655	0.25561		–
22	0.17070	0.16979		–	0.25855	0.25765		–
23	0.17028	0.16936		–	0.26055	0.25972		–
24	0.16988	0.16895		0.1783	0.26256	0.26181		–
25	0.16949	0.16853		–	0.26458	0.26391		–
26	0.16911	0.16815		–	0.26660	0.26603		–

Table 3. (continued)

υ	$R_{\min}$/nm				$R_{\max}$/nm			
	this work	Exp.[3]	Exp.[4]	Exp.[13]	this work	Exp.[3]	Exp.[4]	Exp.[13]
27	0.16876	0.16778		–	0.26864	0.26821		–
28	0.16841	0.16744		0.1776	0.27068	0.27043		0.2791
29	0.16809	0.16710		–	0.27274	0.27267		–

Table 4 shows the present vibrational levels and inertial rotation constants for the $^{37}Cl_2(X^1\Sigma_g{}^+)$ and $^{35}Cl^{37}Cl(X^1\Sigma_g{}^+)$ isotopes and their comparisons with the available experimental findings[2,6] when the vibrational level is lower than 30. Obviously, the present inertial rotation constants for these two isotopes are in excellent agreement with the corresponding experimental ones.[2,6] For example, for the B_υ, the deviations from the experiments[2] for the $^{35}Cl^{37}Cl(X^1\Sigma_g{}^+)$ are only 0.68%, 0.69%, 0.75% and 0.91% when $\upsilon = 0$, 5, 10 and 16, respectively; and their deviations from the experiments[2] for the $^{37}Cl_2(X^1\Sigma_g{}^+)$ are also only 0.68%, 0.69%, 0.74% and 0.90% when $\upsilon = 0$, 5, 10 and 16, respectively. In combination with the excellent agreement with the available experiments for the $^{35}Cl_2(X^1\Sigma_g{}^+)$ species, we therefore conclude that the B_υ when $\upsilon \geq 17$ and all the $G(\upsilon)$ given in Table 4 are both reliable and accurate.

Table 4. Comparisons of vibrational level and inertial rotation constant between the present work and experiments for the $^{35}Cl^{37}Cl(X^1\Sigma_g{}^+)$ and $^{37}Cl_2(X^1\Sigma_g{}^+)$ isotope species when $J = 0$ at the MRCI/aug-cc-pV6Z level of theory.

υ	$^{35}Cl^{37}Cl(X^1\Sigma_g{}^+)$				$^{37}Cl_2(X^1\Sigma_g{}^+)$			
	$G(\upsilon)$/cm^{-1}	B_υ/cm^{-1}			$G(\upsilon)$/cm^{-1}	B_υ/cm^{-1}		
	this work	this work	Exp.[2]	Exp.[6]	this work	this work	Exp.[2]	Exp.[6]
0	273.18	0.235222	0.236830	0.23665	269.39	0.228702	0.230264	0.23012
1	815.58	0.233773	0.235367	0.23522	804.30	0.227312	0.228862	0.22875
2	1352.61	0.232316	0.233897	0.23379	1333.98	0.225917	0.227454	
3	1884.20	0.230847	0.232420		1858.37	0.224509	0.226038	
4	2410.27	0.229367	0.230938		2377.39	0.223090	0.224617	
5	2930.75	0.227875	0.229448		2890.97	0.221661	0.223190	
6	3445.56	0.226371	0.227950		3399.03	0.220220	0.221753	
7	3954.61	0.224855	0.226445		3901.50	0.218768	0.220312	
8	4457.84	0.223326	0.224933		4398.31	0.217304	0.218864	
9	4955.17	0.221782	0.223412		4889.37	0.215825	0.217406	
10	5446.51	0.220223	0.221882		5374.63	0.214333	0.215940	
11	5931.80	0.218647	0.220342		5854.00	0.212825	0.214465	
12	6410.95	0.217055	0.218791		6327.41	0.211302	0.212980	
13	6883.88	0.215446	0.217226		6794.78	0.209763	0.211482	
14	7350.53	0.213821	0.215650		7256.05	0.208209	0.209973	
15	7810.81	0.212177	0.214059		7711.14	0.206638	0.208451	
16	8264.64	0.210512	0.212451		8159.97	0.205047	0.206913	
17	8711.95	0.208825			8602.48	0.203435		
18	9152.66	0.207116			9038.58	0.201803		
19	9586.69	0.205383			9468.21	0.200149		
20	10013.96	0.203626			9891.29	0.198472		
21	10434.41	0.201844			10307.70	0.196772		
22	10847.94	0.200034			10717.50	0.195046		
23	11254.49	0.198192			11120.48	0.193292		
24	11653.98	0.196318			11516.62	0.191507		
25	12046.32	0.194410			11905.85	0.189691		
26	12431.44	0.192468			12288.08	0.187844		
27	12809.27	0.190487			12663.24	0.185961		
28	13179.73	0.188461			13031.26	0.184039		
29	13542.73	0.186389			13392.08	0.182072		

As concerns D_v, to the best of our knowledge, only reference [2] reported the experimental results for the first 17 vibrational levels. These D_v values are presented in Table 5 for a convenient comparison. It is shown that the present results accord well with these experiments.[2] Averagely, the deviations of the B_v from the experiments are lower than 3%. Because the D_v is a very small quantity as a whole, such deviations are indeed not large.

Table 5. Comparisons of centrifugal constant $[D_v(\times 10^{-7})/\mathrm{cm}^{-1}]$ between the present work and the available experiments for the $^{35}Cl_2(X^1\Sigma_g{}^+)$, $^{35}Cl^{37}Cl(X^1\Sigma_g{}^+)$ and $^{37}Cl_2(X^1\Sigma_g{}^+)$ isotope species when $J = 0$ at the MRCI/aug-cc-pV6Z level of theory.

v	$^{35}Cl_2(X^1\Sigma_g{}^+)$		$^{35}Cl^{37}Cl(X^1\Sigma_g{}^+)$		$^{37}Cl_2(X^1\Sigma_g{}^+)$	
	this work	Exp.[2]	this work	Exp.[2]	this work	Exp.[2]
0	1.85349	1.920	1.75463	1.817	1.65846	1.718
1	1.86396	1.920	1.76459	1.817	1.66764	1.718
2	1.87446	1.920	1.77409	1.817	1.67666	1.718
3	1.88718	1.921	1.78596	1.818	1.68772	1.719
4	1.90011	1.922	1.79809	1.819	1.69904	1.720
5	1.91403	1.925	1.81101	1.822	1.71092	1.723
6	1.92870	1.928	1.82458	1.825	1.72341	1.726
7	1.94484	1.933	1.83959	1.829	1.73737	1.729
8	1.96124	1.939	1.85478	1.835	1.75139	1.734
9	1.97922	1.947	1.87141	1.842	1.76673	1.741
10	1.99941	1.956	1.88997	1.851	1.78376	1.750
11	2.02103	1.968	1.91008	1.861	1.80242	1.758
12	2.04269	1.981	1.93024	1.873	1.82110	1.769
13	2.06530	1.997	1.95114	1.888	1.84039	1.783
14	2.08975	2.016	1.97345	1.905	1.86091	1.798
15	2.11752	2.039	1.99876	1.925	1.88400	1.815
16	2.14727	2.062	2.02633	1.948	1.90910	1.837
17	2.17880		2.05537		1.93578	
18	2.21235		2.08630		1.96420	
19	2.24743		2.11872		1.99393	
20	2.28496		2.15287		2.02535	
21	2.32563		2.18983		2.05901	
22	2.37090		2.23056		2.09575	
23	2.42038		2.27566		2.13678	
24	2.47173		2.32309		2.18016	
25	2.52616		2.37266		2.22527	
26	2.58709		2.42679		2.27393	
27	2.65611		2.48852		2.32881	
28	2.73080		2.55649		2.39012	
29	2.80761		2.62747		2.45516	

According to the approach used in this paper, we have investigated the spectroscopic parameters and molecular constants of the $Cl_2^+(X^2\Pi_g)$, and compared them with the results obtained in Ref. [41]. They are in good agreement with each other. Their detailed results will be reported in the near future.

4. Conclusions

The PEC of the $Cl_2(X^1\Sigma_g{}^+)$ has been investigated by the MRCI theory in combination with the largest correlation-consistent basis set, aug-cc-pV6Z, in the valence range. The molecular constants and spectroscopic parameters of these isotopes, $^{35}Cl_2(X^1\Sigma_g{}^+)$, $^{35}Cl^{37}Cl(X^1\Sigma_g{}^+)$ and $^{37}Cl_2(X^1\Sigma_g{}^+)$, have been studied for the first time. For the $^{35}Cl_2(X^1\Sigma_g{}^+)$, the present D_0, D_e, R_e, ω_e, $\omega_e\chi_e$, α_e and B_e are 2.3921 eV, 2.4264 eV,

0.19939 nm, 555.13 cm^{-1}, 2.6772 cm^{-1}, 0.001481 cm^{-1} and 0.24225 cm^{-1}, respectively. For the $^{37}Cl_2(X^1\Sigma_g{}^+)$, the present D_0, D_e, R_e, ω_e, $\omega_e\chi_e$, α_e and B_e are 2.3923 eV, 2.4257 eV, 0.19939 nm, 540.06 cm^{-1}, 2.5556 cm^{-1}, 0.00139 cm^{-1} and 0.22919 cm^{-1}, respectively. And for the $^{35}Cl^{37}Cl(X^1\Sigma_g{}^+)$, the present D_0, D_e, R_e, ω_e, $\omega_e\chi_e$, α_e and B_e are 2.3918 eV, 2.4257 eV, 0.19939 nm, 548.68 cm^{-1}, 2.6234 cm^{-1}, 0.00140 cm^{-1} and 0.23572 cm^{-1}, respectively. These spectroscopic results accord well with the available measurements. With the PEC of $Cl_2(X^1\Sigma_g{}^+)$ determined at the MRCI/ aug-cc-pV6Z level of theory, the total of 59 vibrational states is predicted for each isotope when the rotational quantum number J equals zero. Theoretical vibrational levels, classical turning points, inertial rotation and centrifugal distortion constants are determined when $J = 0$ for the first time. Compared with the experiments, the present results are both reliable and accurate.

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