Study on the $A^2\Pi_{3/2u}$, $B^2\Delta_{3/2u}$, and $X^2\Pi_{3/2g}$ states of Cl_2^+ including its isotopologues*

Wu Ling(吴 玲)[a], You Su-Ping(尤素萍)[a], Shao Xu-Ping(邵旭萍)[b], Chen Gang-Jin(陈钢进)[a], Ding Ning(丁 宁)[a], Wang You-Mei(汪友梅)[a], and Yang Xiao-Hua(杨晓华)[b]†

[a] *School of Science, Hangzhou Dianzi University, Hangzhou* 310018, *China*
[b] *School of Science, Nantong University, Nantong* 226019, *China*

(Received 1 February 2015; revised manuscript received 30 March 2015; published online 20 June 2015)

Adopting the experimentally available vibrational constants in a recent analysis of the strong perturbation between the $A^2\Pi_{3/2u}$ and $B^2\Delta_{3/2u}$ states of Cl_2^+ in the A–X band system [Gharaibeh *et al.* 2012 *J. Chem. Phys.* **137** 194317], an unambiguous vibrational assignment of the bands reported previously is carried out. The equilibrium rotational constants B_e and α_e of the $X^2\Pi_{3/2g}$ and $A^2\Pi_{3/2u}$ states for $^{35}Cl_2^+$ and $^{35}Cl^{37}Cl^+$ and those of the $B^2\Delta_{3/2u}$ state for $^{35}Cl_2^+$ are obtained by fitting the experimental values of B_υ. In addition, the values of B_e and α_e of these three states for the minor isotopologues $^{35}Cl^{37}Cl^+$ and $^{37}Cl_2^+$ are predicted by employing the isotopic effect. The values of equilibrium internuclear distance R_e of the three states for the three isotopologues are calculated as well.

Keywords: Cl_2^+, isotopic effect, molecular constants

PACS: 33.15.Mt, 33.20.Vq **DOI:** 10.1088/1674-1056/24/8/083301

1. Introduction

The highly perturbed $A^2\Pi_u$–$X^2\Pi_g$ system of the chlorine cation (Cl_2^+) has been investigated for nearly one century, however, knowledge about the structure of the electronic states, $A^2\Pi_u$ and $X^2\Pi_g$, is still limited. This system has two components: $A^2\Pi_{1/2}$–$X^2\Pi_{1/2}$ and $A^2\Pi_{3/2}$–$X^2\Pi_{3/2}$. Initial spectroscopic data came from a series of dispersed emission studies.[1–5] It is difficult to assign the absolute vibrational quantum numbers to the observed bands because of the irregular vibrational internals and non-systematic chlorine isotopic effects resulting from the severely perturbed excited electronic state $A^2\Pi_u$. In addition, since the spin–orbit splitting for the $X^2\Pi_g$ state is found to be very close to the vibrational energy spacing, the spin–orbit resolved vibrational bands have been analyzed ambiguously. In 1966, Huberman[6] studied the Cl_2^+ emission spectrum and made the most comprehensive rotational assignment of the observed. In 1989, Tuckett and Peyerimhoff[7] observed the Cl_2^+ emission spectrum in the supersonic expansion, which allowed them to make a fuller analysis due to the cold Doppler-free spectrum. One hundred vibronic bands were fitted into two Deslandres tables (one for $A^2\Pi_{1/2}$–$X^2\Pi_{1/2}$, and the other for $A^2\Pi_{3/2}$–$X^2\Pi_{3/2}$). Still, they could not assign vibrational quantum numbers to the Deslandres tables. *Ab initio* calculations show that $A^2\Pi_u$ is crossed near its origin by some states arising from $\ldots\sigma_g^2\pi_u^4\pi_g^{*2}\sigma_u^{*1}$, i.e. $^2\Sigma_u^+$ and $^2\Delta_u$.

In 1989, the Λ-doublets was first observed in a jet-cooled A–X emission spectrum by Choi and Hardwick,[8] and four bands were unambiguously assigned as $A^2\Pi_{1/2}$–$X^2\Pi_{1/2}$. Later in 1991, they[9] reported more bands of the $\Omega = 3/2$ component. Among those, 10 bands were assigned to the $A^2\Pi_{3/2}$–$X^2\Pi_{3/2}$ system, which had been rotationally analyzed by Huberman earlier. These measurements improved the accuracy of the rotational constants for this system. Additionally, five bands were assigned to a new system of $B^2\Delta_{u3/2}$–$X^2\Pi_{g3/2}$, and they, for the first time, rotationally analyzed the bands of the minor isotopologue $^{35}Cl^{37}Cl^+$. They agreed with Huberman on vibrational numbering of the ground state, and their analyses were also in agreement with a new analysis by Gharaibeh *et al.*[10] However, the vibrational numbering of the excited state seems to be modified. In 1990, Bramble and Hamilton[11] reported the first laser-induced fluorescence spectra of Cl_2^+ and analyzed many bands of the (υ', 0) progression of the $\Omega = 3/2$ component together with some extra bands arising from the perturbation.

In 2012, Gharaibeh *et al.*[10] studied the laser-induced fluorescence spectrum of jet-cooled Cl_2^+ with high sensitivity and rigorous vibrational and spin–orbit cooling. A full understanding of the $A^2\Pi_{3/2}$–$X^2\Pi_{3/2}$ band system was presented, including a complete treatment of the interaction between the $A^2\Pi_{u3/2}$ and $B^2\Delta_{u3/2}$ states, based on the experimental spectrum and *ab initio* calculations. The (0, 0) band was identified for the first time. They studied two bands at high-resolution and obtained the accurate B values. For most of the low-resolution bands, they listed approximate upper state B values as well.

*Project supported by the Natural Science Foundation of Zhejiang Province, China (Grant Nos. Y6110524 and Y1111085), the Scientific Research Foundation of the Department of Education of Zhejiang Province, China (Grant No. Y201430970), the National Nature Science Foundation of China (Grant No. 11247007), and the QingLan Project of Jiangsu Province, China.

†Corresponding author. E-mail: xhyang@ntu.edu.cn

© 2015 Chinese Physical Society and IOP Publishing Ltd

More information about the electronic states of Cl_2^+ has been derived from the photoelectron spectroscopy (PES).[7,12,13] In 2007, Li *et al.*[12] studied the isotopomer-resolved vibrational and spin–orbit energy structures of $Cl_2^+(X^2\Pi_g)$ by one-photon zero kinetic energy (ZEKE) photoelectron spectroscopy. The precise values of the spin–orbit splitting for $X^2\Pi_g$ were reported. Most recently, Mollet and Merkt[13] studied the $X^2\Pi_g$, $A^2\Pi_u$, $B^2\Delta_u$, and $a^4\Sigma_u^-$ states of Cl_2^+ by partially rotationally resolved pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectroscopy. A large number of Franck–Condon-forbidden transitions to vibrational levels of the $X^2\Pi_g$ ($\Omega = 3/2$, 1/2) were observed. The potential energy function of $Cl_2^+(X^2\Pi_g)$ was determined in a direct fit to the experimental data. Transitions to vibrational levels of the $A^2\Pi_{u3/2}$, $B^2\Delta_{u3/2}$ states were identified by using the results of Ref. [10] and transitions to the upper spin–orbit component $A^2\Pi_{u1/2}$ ($\upsilon = 2$–6) were detected. Additionally, the $A^2\Pi_{u1/2}$ state was found to be perturbed by the $^2\Sigma_{u1/2}$ state. Unfortunately, their data were too scarce to model this interaction.

In the present work, we study the rotational structure of the $\Omega = 3/2$ component of the $X^2\Pi_g$, $A^2\Pi_u$, and $B^2\Delta_{u3/2}$ states. Aiming to obtain the equilibrium rotational constants B_e and α_e of these states based on the experimental data, we reassign the vibrational quantum numbers for the previously observed bands and subsequently fit the rotational constants. Using the isotopic effect, the rotational spectroscopic constants for the minor isotopologues $^{35}Cl^{37}Cl^+$ and $^{37}Cl_2^+$ are predicted.

2. Theoretical details

Two methods are used to calculate the values of origin T_0 for vibrational bands of the $A^2\Pi_{3/2}$–$X^2\Pi_{3/2}$ system of Cl_2^+. The first method is to use the effective Hamiltonian matrix. The form of the matrix is shown in Fig. 8 of Ref. [10]. The diagonal energy terms are $E_\upsilon = T_e + G_\upsilon$, where

$$G_\upsilon = \omega_e\left(\upsilon+\frac{1}{2}\right) - \omega_e x_e\left(\upsilon+\frac{1}{2}\right)^2 + \omega_e y_e\left(\upsilon+\frac{1}{2}\right)^3 + \omega_e z_e\left(\upsilon+\frac{1}{2}\right)^4 + \cdots.$$

The off-diagonal terms are $H_{SO}^{AB}\langle\chi_{\upsilon A}^d|\,\chi_{\upsilon B}^d\rangle$, where the first term is the electronic spin–orbit interaction matrix element and the second term is a vibrational overlap.[14] The vibrational overlaps are calculated by using LeRoy's RKR1 2.0 and LEVEL 8.0 programs.[15,16] Additionally, for calculating the matrix elements, we adopt the reported vibrational constants and also the spin–orbit coupling term H_{SO}^{AB}.[10] The matrix is diagonalized and the eigenvalues are stored for calculating the values of origin $T_0(\upsilon',\upsilon'') = E_{\upsilon'} - E_{\upsilon''}$ of vibrational bands. Note that the adopted vibrational constants and the interaction constant are fitted by using the band heads rather than band origins in Ref. [10], because the band origins cannot be determined accurately without full rotational analysis. However, it was argued that this introduces a little error (only 0.3 cm^{-1}–0.5 cm^{-1}), which is well within the overall standard error for the least square analysis. As to the vibrational assignment, it is accurate enough. Moreover, the band heads replace the band origins in the second calculation method.

The second method is much simpler: there is no need to calculate the vibrational overlaps nor to diagonalize the matrices. Using the experimentally observed positions of the band heads, such as $T_0(\upsilon',0)$ of the $(\upsilon',0)$ bands, the values of band origin T_0 (υ',υ'') can be evaluated by using the following formulas:

$$T_0(\upsilon',\upsilon'') = E_{\upsilon'} - E_{\upsilon''}, \tag{1}$$

$$T_0(\upsilon',0) = E_{\upsilon'} - E_{\upsilon''=0}, \tag{2}$$

and

$$T_0(\upsilon',\upsilon'') = T_0(\upsilon',0) + E_{\upsilon''=0} - E_{\upsilon''}. \tag{3}$$

The vibrational constants ω_e'' (645.6 cm^{-1}) and $\omega_e\chi_e''$ (2.98 cm^{-1}) of $^{35}Cl_2^+(X^2\Pi_{3/2})$[13] are adopted. In Ref. [10], 70 band heads of the $^{35}Cl_2^+$ species are listed, which all originate from the $\upsilon'' = 0$ level of the $X^2\Pi_{3/2}$ state. The relevant upper levels are $A^2\Pi_{3/2}(\upsilon' = 0$–$39)$ and $B^2\Delta_{u3/2}(\upsilon' = 0,\ 1,\ 3$–$8,\ 10$–$12,\ 14$–$19,\ 21$–$26,\ 28$–$29,\ 31,\ 32)$. The extent of the upper levels and the accuracies of the band heads are sufficient for the purpose of this work.

Molecular chlorine has three isotopologues, $^{35}Cl_2$, $^{35}Cl^{37}Cl$, and $^{37}Cl_2$ with relative abundances of 57.41%, 36.72%, and 5.87%, respectively.

The spectroscopic constants for two different isotopologues i and j have the following relationships:[17]

$$\omega_e^{(j)} = \rho_{ij}\omega_e^{(i)}, \tag{4}$$

$$\omega_e x_e^{(j)} = \rho_{ij}^2\omega_e x_e^{(i)}, \tag{5}$$

$$\omega_e y_e^{(j)} = \rho_{ij}^3\omega_e y_e^{(i)}, \tag{6}$$

$$B^{(j)} = \rho_{ij}^2 B_e^{(i)} - \rho_{ij}^3\alpha_e^{(i)}\left(\upsilon+\frac{1}{2}\right), \tag{7}$$

and

$$D^{(j)} = \rho_{ij}^4 D_e^{(i)} + \rho_{ij}^5\beta_e^{(i)}\left(\upsilon+\frac{1}{2}\right), \tag{8}$$

with

$$\rho_{ij} = \sqrt{\frac{\mu_i}{\mu_j}}, \tag{9}$$

where μ_i and μ_j are the reduced mass values for isotopologues i and j. The values of ρ for the pairs $^{35}Cl_2$ and $^{35}Cl^{37}Cl$, and $^{35}Cl_2$ and $^{37}Cl_2$ are 0.98640 and 0.97261 respectively. The investigations of the isotopic effect in electronic band spectra lead to the determination of the correlated constants[18] and are helpful for discovering the new isotopologues of very small abundance.[19]

3. Results and discussion

The vibrational band origins of the $A^2\Pi_{3/2}$–$X^2\Pi_{3/2}$ and $B^2\Delta_{u3/2}$–$X^2\Pi_{3/2}$ are calculated by using the above two methods respectively and subsequently the observed bands reported in Refs. [6], [7], and [9] are reassigned. Listed in Table 1 are the origins with the vibrational assignments in a Deslandres table for the $A^2\Pi_{3/2u}$–$X^2\Pi_{3/2g}$ system of $^{35}Cl_2^+$. The vibrational assignments for the emission spectra of $^{35}Cl_2^+$ and $^{35}Cl^{37}Cl^+$ observed by Choi and Hardwick[9] are listed in Table 2. We agree on their ground state vibrational assignments but modify the vibrational numbering of the excited state $A^2\Pi_{3/2}$. Moreover transitions to the $B^2\Delta_{u3/2}$ state have also been assigned, and they are also listed in Table 2.

Table 1. Deslandres table for $^{35}Cl_2^+$ $A^2\Pi_{3/2u}$–$X^2\Pi_{3/2g}$. All data are in units of cm^{-1}.

	υ''					
υ'	0	1	2	3	4	5
5		21557[a]	20926.30[b]	20298.58[b]	19676.74[b]	19060.7[b]
6		21857[a]	21222.091[c]	20594.394[c]	19972.61[b]	19356[a]
7		22301.97[b]	21668.33[b]	21040.62[b]	20419.4[b]	
8		22609.345[c]	21975.704[c]	21347.975[c]	20727[a]	20109[a]
9		22910.86[b]	22277.20[b]	21647[a]		
10	23966[a]	23326.99[b]	22693.378[c]	22066[a]		
11	24263[a]	23623.26[b]	22989.512[c]	22360[a]	21740.056[c]	21120[a]
12	24564.25[b]	23924.63[b]	23292[a]			
13	24947.52[b]	24307.94[b]	23674.199[c]			
14	25235.98[b]	24596.41[b]	23966[a]		22713.040[c]	
15						
16	25882.50[b]	25242.94[b]				
17	26166.25[b]	25526.65[b]	24893[a]			
18						
19	26773.31[b]					
20	27051.61[b]					

[a]From Ref. [7], [b]from Ref. [6], [c]from Ref. [9].

Table 2. Vibrational assignments for the emission spectra of $^{35}Cl_2^+$ and $^{35}Cl^{37}Cl^+$ observed by Choi and Hardwick[9].

	Band origins/cm^{-1}	Upper state	(υ', υ'')	
			This work	Ref. [9]
$^{35}Cl_2^+$	21222.091	$A^2\Pi_{3/2u}$	(6, 2)	(5, 2)
	20594.394	$A^2\Pi_{3/2u}$	(6, 3)	(5, 3)
	22609.345	$A^2\Pi_{3/2u}$	(8, 1)	(7, 1)
	21975.704	$A^2\Pi_{3/2u}$	(8, 2)	(7, 2)
	21347.975	$A^2\Pi_{3/2u}$	(8, 3)	(7, 3)
	22693.378	$A^2\Pi_{3/2u}$	(10, 2)	(9, 2)
	22989.512	$A^2\Pi_{3/2u}$	(11, 2)	(10, 2)
	21740.056	$A^2\Pi_{3/2u}$	(11, 4)	(10, 4)
	23674.199	$A^2\Pi_{3/2u}$	(13, 2)	(12, 2)
	22713.040	$A^2\Pi_{3/2u}$	(14, 4)	(13, 4)
	21513.817	$B^2\Delta_{u3/2}$	(4, 2)	(x, 2)
	20886.082	$B^2\Delta_{u3/2}$	(4, 3)	(x, 3)
	23035.716	$B^2\Delta_{u3/2}$	(7, 1)	(y, 1)
	22402.080	$B^2\Delta_{u3/2}$	(7, 2)	(y, 2)
	24036.785	$B^2\Delta_{u3/2}$	(11, 1)	(z, 1)
$^{35}Cl^{37}Cl^+$	21217.479	$A^2\Pi_{3/2u}$	(6, 2)	(5, 2)
	20598.076	$A^2\Pi_{3/2u}$	(6, 3)	(5, 3)
	22584.246	$A^2\Pi_{3/2u}$	(8, 1)	(7, 1)
	21959.075	$A^2\Pi_{3/2u}$	(8, 2)	(7, 2)
	21339.656	$A^2\Pi_{3/2u}$	(8, 3)	(7, 3)
	22671.110	$A^2\Pi_{3/2u}$	(10, 2)	(9, 2)
	22960.571	$A^2\Pi_{3/2u}$	(11, 2)	(10, 2)
	23887.800	$A^2\Pi_{3/2u}$	(12, 1)	(11, 1)
	22390.594	$B^2\Delta_{u3/2}$	(6, 2)	(y, 2)

Based on the unambiguous vibrational assignments of the states, some vibrational quantum numbers υ with the rotational constants B_υ are modified consequently, such as B'_υ in Ref. [9]. The rotational constants of the $X^2\Pi_{3/2g}$, $A^2\Pi_{3/2u}$, and $B^2\Delta_{3/2u}$ states for $^{35}Cl_2^+$ and $^{35}Cl^{37}Cl^+$ in the previous work are listed in Table 3. The constants B_e and α_e are fitted according to $B_\upsilon = B_e - \alpha_e(\upsilon + 1/2)$. The derived values of B_e and α_e of the $X^2\Pi_{3/2g}$ and $A^2\Pi_{3/2u}$ states for $^{35}Cl_2^+$ and $^{35}Cl^{37}Cl^+$ and those of the $B^2\Delta_{3/2u}$ state for $^{35}Cl_2^+$ are listed in Table 4. The values of equilibrium internuclear distance R_e for those three states of all the three isotopologues are determined from the values of B_e and listed in Table 4. The derived rotational constants of the $X^2\Pi_{3/2g}$ and $A^2\Pi_{3/2u}$ state are in good agreement with those from the *ab initio* PECS in Ref. [10]. For $^{35}Cl_2^+$ ($B^2\Delta_{3/2u}$), the derived value of B_e is 0.1746 cm^{-1} in comparison with the theoretical value of 0.1617407 cm^{-1}.[10]

Using Eq. (7), the rotational constants of the minor isotopologues $^{35}Cl^{37}Cl^+$ and $^{37}Cl_2^+$ are predicted and listed in Table 4 as well.

It should be mentioned that according to the calculated vibrational band origins, the bands at 16913, 17030, 17282, and 17323 cm^{-1} would be assigned as (1, 6) (3, 7) and (2, 6) of $^{35}Cl_2^+$ and (2, 6) of $^{35}Cl^{37}Cl^+$ of the $A^2\Pi_{3/2}$–$X^2\Pi_{3/2}$ sub-system instead, which are tentatively assigned as (2, 7), (3, 7), and (4, 8) of $^{35}Cl_2^+$ and (3, 7) of $^{35}Cl^{37}Cl^+$ of the $A^2\Pi_{1/2}$–$X^2\Pi_{1/2}$.[20,21] When modifying the vibrational quantum numbers of the bands, the experimental rotational constants in Refs. [20] and [21] are in good agreement with those in Ref. [10].

Table 3. Experimentally determined rotational constants of the $X^2\Pi_{3/2g}$, $A^2\Pi_{3/2u}$, and $B^2\Delta_{3/2u}$ states. All data are in units of cm^{-1}.

	$X^2\Pi_{3/2g}$		$A^2\Pi_{3/2u}$				$B^2\Delta_{3/2u}$	
	v''	B'	v'	B'	v'	B'	v'	B'
$^{35}Cl_2^+$	0	0.2686(8)[a]	0		16	0.1607[a]	0	0.179[c]
	1	0.267309(39)[b]	1	0.19123[c]	17	0.1622[a]	1	0.170[c]
		0.2670(4)[a]	2	0.18929[c]	18	0.157[c]	3	0.171[c]
	2	0.265639(35)[b]	3	0.186[c]	19	0.1588[a]	4	0.166859(60)[b]
		0.2654(0)[a]	4	0.179[c]	20	0.1568[a]		0.161[c]
	3	0.263893(33)[b]	5	0.1788[a]	21	0.148[c]	5	0.161[c]
		0.2637(6)[a]	6	0.173284(35)[b]	22	0.155[c]	6	0.160[c]
	4	0.26234(22)[b]		0.1729[a]	23	0.150[c]	7	0.165263(48)[b]
		0.2621(2)[a]	7	0.1749[a]	25	0.149[c]		0.161[c]
			8	0.174426(33)[b]	26	0.149[c]	8	0.161[c]
				0.1742[a]	27	0.145[c]	10	0.156[c]
			9	0.1691[a]	28	0.143[c]	11	0.158755(88)[b]
			10	0.168992(40)[b]	30	0.140[c]		0.157[c]
				0.1694[a]	31	0.140[c]	12	0.157[c]
			11	0.170458(42)[b]	32	0.135[c]	14	0.156[c]
				0.1702[a]	33	0.124[c]	17	0.146[c]
			12	0.1664[a]	34	0.121[c]	21	0.138[c]
				0.1659[c]	35	0.124[c]	22	0.138[c]
			13	0.163750(54)[b]	36	0.120[c]	23	0.145[c]
				0.1641[a]			25	0.133[c]
			14	0.16689(22)[b]			26	0.134[c]
				0.1665[a]			28	0.129[c]
							29	0.129[c]
							32	0.123[c]
	$X^2\Pi_{3/2g}$		$A^2\Pi_{3/2u}$				$B^2\Delta_{3/2u}$	
	v''	B'	v'	B'			v'	B'
$^{35}Cl^{37}Cl^+$	0	0.26139(10)[c]	1	0.18611(9)[c]			6	0.159453(82)[b]
		0.26145(14)[c]	2	0.18430(12)[c]				
	1	0.260135(50)[b]	6	0.169733(51)[b]				
		0.26[a]	8	0.169842(46)[b]				
	2	0.258471(52)[b]	10	0.16319(78)[b]				
		0.2585[a]		0.1644[a]				
	3	0.256789(53)[b]	11	0.166336(62)[b]				
				0.1663[a]				
			12	0.164038(54)[b]				

[a]From Ref. [6], [b]from Ref. [9], [c]from Ref. [10].

Table 4. Fitted rotational constants, the predicted rotational constants (in cm^{-1}), and the equilibrium internuclear distances of the $X^2\Pi_{3/2g}$, $A^2\Pi_{3/2u}$, and $B^2\Delta_{3/2u}$ states.

		$^{35}Cl_2^+$		$^{35}Cl^{37}Cl^+$			$^{37}Cl_2^+$	
		This work	Previous work	This work	This work	Previous work	This work	Previous work
$X^2\Pi_{3/2g}$	B_e	0.269791(85)[a]	0.26950[b] 0.2707(11)[c]	0.262648(14)	0.262503[e]		0.255216[e]	
	α_e	0.001665(27)	0.00164[b] 0.0012(4)[c]	0.0016730(52)	0.001598[e]		0.001532[e]	
	σ	0.00006		0.0000073				
	R_e	1.891 Å		1.890 Å	1.891 Å		1.891 Å	
$A^2\Pi_{3/2u}$	B_e	0.1903(14)	0.1897495[d]	0.1878(24)	0.1852[e]	0.1846241[d]	0.1800[e]	0.1794985[d]
	α_e	0.001770(63)	0.001375892[d]	0.00208(28)	0.0016988[e]	0.001320652[d]	0.001629[e]	0.001265973[d]
	σ	0.0038		0.003				
	R_e	2.251 Å	2.25 Å[d]	2.235 Å	2.251 Å	2.254 Å[f]	2.251 Å	2.254 Å[f]
$B^2\Delta_{3/2u}$	B_e	0.1746(12)	0.1617407[d]		0.1699[e]	0.1573721[d]	0.1652[e]	0.1530031[d]
	α_e	0.001561(69)	0.001193303[d]		0.001498[e]	0.001146015[d]	0.001436[e]	0.001098608[d]
	σ	0.003						
	R_e	2.350 Å	2.44 Å[d]		2.350 Å	2.442 Å[f]	2.350 Å	2.442 Å[f]

[a]Numbers in parentheses are in the units of the last quoted digits. [b]From Ref. [6], [c]from Ref. [13], [d]from Ref. [10].

[e]Predicted using the isotopic effect. [f]Calculated based on the constants of the previous work.

However there is less experimental information about the A state $\Omega = 1/2$ levels than about the $\Omega = 3/2$ levels. Theoretically, the $A^2\Pi_{1/2u}$ levels above $\sim \upsilon = 4$ will be perturbed by levels of the $C^2\Sigma^+_{1/2u}$ state.[10] In the experiment, the jet-cooling only allows the $\Omega = 3/2$–$\Omega = 3/2$ transitions to be observed.[10] If more bands of the other half transitions $\Omega = 1/2$–$\Omega = 1/2$ could be observed, combined with the data reported in previous work, the data could be fitted to understand the whole structure of Cl_2^+ and the spin–orbit coupling constant A for the $A^2\Pi_u$ state would precisely be obtained.

4. Conclusions

The vibrational and rotational structures of the $A^2\Pi_{3/2}$, $B^2\Delta_{u3/2}$, and $X^2\Pi_{3/2}$ states of the three isotopologues of Cl_2^+ ($^{35}Cl_2^+$, $^{35}Cl^{37}Cl^+$, $^{37}Cl_2^+$) are studied. Using the previous experimentally observed positions of the band origins and the vibrational constants,[10,13] we calculate the vibrational band origins of the $A^2\Pi_{3/2}$–$X^2\Pi_{3/2}$ and $B^2\Delta_{u3/2}$–$X^2\Pi_{3/2}$ systems and reassign the observed bands reported in Refs. [6], [7], and [9]. Some vibrational quantum numbers of the states are modified, and thus the experimental rotational constant B_υ are modified accordingly.

Based on the unambiguous vibrational assignments of the states, the values of B_υ reported in previous investigations are used to derive the constants B_e and α_e of the $X^2\Pi_{3/2g}$ and $A^2\Pi_{3/2u}$ states for $^{35}Cl_2^+$ and $^{35}Cl^{37}Cl^+$ and those of the $B^2\Delta_{3/2u}$ state for $^{35}Cl_2^+$. Then the rotational constants of the minor isotopologues $^{35}Cl^{37}Cl^+$ and $^{37}Cl_2^+$ are predicted based on the isotopic relations. Additionally, the values of equilibrium internuclear distance R_e for those three states of all the three isotopologues are calculated.

References

[1] Uchida Y and Ota Y 1928 *Jpn. J. Phys.* **5** 53
[2] Elliot A and Cameron W H B 1937 *Proc. Roy. Soc. A* **158** 681
[3] Elliot A and Cameron W H B 1938 *Proc. Roy. Soc. A* **164** 531
[4] Haranath P B V and Rao P T 1958 *India J. Phys.* **32** 401
[5] Rao V V and Rao P T 1958 *Can. J. Phys.* **36** 1557
[6] Huberman F P 1966 *J. Mol. Spectrosc.* **20** 29
[7] Tuckett R P and Peyerimhoff S D 1984 *Chem. Phys.* **83** 203
[8] Choi J C and Hardwick J L 1989 *J. Mol. Spectrosc.* **137** 138
[9] Choi J C and Hardwick J L 1991 *J. Mol. Spectrosc.* **145** 371
[10] Gharaibeh M A, Clouthier D J, Kalemos A, Lefebvre-Brion H and Field R W 2012 *J. Chem. Phys.* **137** 194317
[11] Bramble S K and Hamilton P A 1990 *J. Chem. Soc., Faraday Trans.* **86** 2009
[12] Li J, Hao Y, Yang J, Zhou C and Mo Y 2007 *J. Chem. Phys.* **127** 104307
[13] Mollet S and Merkt F 2013 *J. Chem. Phys.* **139** 034302
[14] Lefebvre-Brion H and Field R W 2004 *The Spectra and Dynamics of Diatomic Molecules* (Amsterdam: Elsevier)
[15] Le Roy R J 2004 *RKR1* 2.0*: A computer program implementing the first-order RKR method for determining diatomic molecule potential energy functions* (University of Waterloo Chemical Physics Research Report No. CP-657R)
[16] Le Roy R J 2007 *LEVEL* 8.0*: A computer program for solving the radial Schrödinger equation for bound and quasibound levels* (University of Waterloo Chemical Physics Research Report No. CP-663)
[17] Herzberg G 1950 *Molecular Spectra and Molecular Structure I: Spectra of Diatomic Molecules* (New York: van Nostrand)
[18] Shao X, Wang Q, Wu Y, Wu L and Yang X 2014 *Chin. Phys. Lett.* **31** 113301
[19] Wu L, Yang X and Chen Y 2009 *Chin. Phys. B* **18** 2724
[20] Wu L, Yang X, Guo Y, Zheng L, Liu Y and Chen Y 2005 *J. Mol. Spectrosc.* **230** 72
[21] Wu L, Yang X and Chen Y 2008 *J. Quantum Spectros. Radiat. Transfer* **109** 1586