Vol 18 No 7, July 2009
1674-1056/2009/18(07)/2724-05

Chinese Physics B

© 2009 Chin. Phys. Soc.
and IOP Publishing Ltd

Isotopic effect of Cl_2^+ rovibronic spectra in the A–X system*

Wu Ling(吴 玲)[a)c)], Yang Xiao-Hua(杨晓华)[b)†], and Chen Yang-Qin(陈扬骎)[b)]

[a)] *Institute of Materials Physics, Hangzhou Dianzi University, Hangzhou* 310018, *China*
[b)] *State Key Laboratory of Precision Spectroscopy and Department of Physics, East China Normal University, Shanghai* 200062, *China*
[c)] *State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan* 430071, *China*

(Received 27 June 2008; revised manuscript received 10 December 2008)

This paper studies the isotopic effect of Cl_2^+ rovibronic spectra in the $A^2\Pi_u$ ($\Omega = 1/2$) – $X^2\Pi_g$ ($\Omega = 1/2$) system. Based on the experimental results of the molecular constants of $^{35}Cl_2^+$, it calculates the vibrational isotope shifts of the (2, 7) and (3, 7) band between the isotopic species $^{35}Cl_2^+$, $^{35}Cl^{37}Cl^+$ and $^{37}Cl_2^+$, and estimates the rotational constants of both $A^2\Pi_u$ and $X^2\Pi_g$ states for the minor isotopic species $^{35}Cl^{37}Cl^+$ and $^{37}Cl_2^+$. The experimental results of the spectrum of $^{35}Cl^{37}Cl^+$ (3, 7) band proves the above mentioned theoretical calculation. The molecular constants and thus resultant rovibronic spectrum for $^{37}Cl_2^+$ were predicted, which will be helpful for further experimental investigation.

Keywords: Cl_2^+, isotope shifts, molecular constants
PACC: 3310J, 3520P

1. Introduction

The element chlorine (Cl) has two natural isotopes, ^{35}Cl and ^{37}Cl, and the ^{35}Cl almost occupies 75%. Therefore, Cl_2 molecule has 3 kinds of isotopes,$^{35}Cl_2$, $^{35}Cl^{37}Cl$ and $^{37}Cl_2$.

The spectra of the two lighter isotopes$^{35}Cl_2^+$ and $^{35}Cl^{37}Cl^+$ have been studied widely.[1−5] There are a large number of red-degraded bands extending from about 640 to 340 nm which were assigned to the $A^2\Pi_u - X^2\Pi_g$ transition. This system has two components: $^2\Pi_{1/2} - ^2\Pi_{1/2}$ and $^2\Pi_{3/2} - ^2\Pi_{3/2}$. However, the vibrational bands were congested because of the overlapping isotopic bands and high rotational temperature, and furthermore, the excited electronic state is known to be severely perturbed. It causes the analysis to be ambiguous both for the assignment of the vibrational quantum numbers of the bands and for the identity of the bands as belonging to the $\Omega = 1/2$ or $\Omega = 3/2$ component.

In 1984, the extensive rotational envelope of each (v', v'') vibrational band is effectively removed in the supersonic expansion (rotational temperature is ∼20 K), which was made by Tuckett and Peyerimhoff.[6] One hundred vibrational bands have been fitted into two Deslandres tables (one for $\Omega = 1/2$ and the other for $\Omega = 3/2$). A graph of isotopic splitting $\Delta\nu$ against frequency of the $^{35}Cl_2^+ A - X$ vibronic band has been made. Only by correlating the photoelectron spectrum with this optical emission spectrum, van Lonkhuyzen and de Lange[7] could assign vibrational quantum numbers to these tables.

In 1989, Λ-doubling were observed in a jet-cooled $A - X$ emission spectrum by Choi and Hardwick.[8] They confirmed the identity of some of the bands as belonging to the $\Omega = 1/2$ bands. Later, they reported more bands of the $\Omega = 3/2$ component and first rotationally analysed the bands of the minor isotope $^{35}Cl^{37}Cl^+$.[9] Nearly at the same time, Bramble and Hamilton[10] observed laser-induced fluorescence excitation spectrum of Cl_2^+ and analysed many bands of the (v', 0) progression of the $\Omega = 3/2$ component and some extra bands arising from the perturbation

*Project supported by the National Natural Science Foundation of China (Grant Nos 10434060 and 10574045), the National Key Basic Research and Development Program of China (Grant No 2006CB921604), the Basic Key Program of Shanghai Municipality (Grant Nos 07JC14017 and 07dz22025), State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics of China (Grant No T152616), State Key Laboratory of Precision Spectroscopy and Department of Education of Zhejiang Province of China (Grant No Y200701718).
†E-mail: xhyang@phy.ecnu.edu.cn

of both $^{35}Cl_2^+$ and $^{35}Cl^{37}Cl^+$.

Most recently, the absorption spectra of $^{35}Cl_2^+$ and $^{35}Cl^{37}Cl^+$ have been observed by employing optical heterodyne detected velocity modulation spectroscopy enhanced by magnetic rotation (OH-MR-VMS) in our previous publication.[11] Rotational analysis of the (2, 7) and (3, 7) bands of $^{35}Cl_2^+$ and the (3, 7) band of $^{35}Cl^{37}Cl^+$ were reported. The little magnetic enhancement of the lines confirms the identity of these bands as due to the $\Omega = 1/2$ component of the electronic transition in spite of the paramagnetic feature of Cl_2^+ molecule itself.

The spectrum of the least abundant isotopic species $^{37}Cl_2^+$ has not yet been observed. The relative abundances of the $^{35}Cl_2$,$^{35}Cl^{37}Cl$ and $^{37}Cl_2$ are 9.53:6.17:1.00. The spectral intensity of $^{37}Cl_2^+$ is, thus, considerably weaker than those of the two lighter isotopes.

In order to help the seeking of the spectrum due to $^{37}Cl_2^+$, we studied the isotope effect of Cl_2^+ in the present paper. Using the isotopic effect, we calculated the vibrational isotope shifts of the (2, 7) and (3, 7) band between the isotopic species $^{35}Cl_2^+$, $^{35}Cl^{37}Cl^+$ and $^{37}Cl_2^+$ and obtained the molecular constants of $^{35}Cl^{37}Cl^+$ and $^{37}Cl_2^+$ based on the experimental results of the most abundant one $^{35}Cl_2^+$. The calculated rovibronic spectrum of $^{35}Cl^{37}Cl^+$ (3, 7) band was proved in comparison with the experimental result. Therefore, the theoretical predicted rotational constants and resultant spectrum for $^{37}Cl_2^+$ will be helpful for further work.

2. Spectra of Cl_2^+

The absorption spectra of Cl_2^+ have been recorded at high resolution in the region 16820–17350 cm^{-1}.[11] The experimental details were described in Refs.[11] and [12]. The I_2 absorption spectrum[13] was simultaneously recorded to calibrate the absolute wavelength of each observed spectral line with the uncertainty ranging from 0.005 to 0.01 cm^{-1} depending on its signal-to-noise ratio.

The P and R branches are observed while the Q branches are absent, which is consistent with the character of the $^2\Pi - {}^2\Pi$ transition. We employ the Faraday effect to tell the spectrum observed due to $\Omega = 1/2$ or $3/2$ component because the spectral signal will linearly increase the applied longitudinal magnetic field if the states are paramagnetic.[14] Comparing the two sets of spectrum with the magnetic field ON or OFF, we find that some lines keep unchanging, presenting a weak Zeeman effect.[15] It confirms that they arise from the essentially diamagnetic state $^2\Pi_{1/2}$.[16] Thus, they were picked out and assigned to the (2, 7) and (3, 7) bands of $^{35}Cl_2^+$ and (3, 7) band of $^{35}Cl^{37}Cl^+$ in the $A^2\Pi_{1/2} - X^2\Pi_{1/2}$ system. It extends the range of vibrational assignments considerably in both the ground and the excited states. By the vibrational and rotational analyses of these two isotopic species, we derived precise molecular constants.[11] Unfortunately, the spectrum due to the least abundant isotope $^{37}Cl_2^+$ failed to be observed.

3. Theory

For isotopic molecules, the formulae for the vibrational energy levels are in a very good approximation[17]

$$G^{\mathrm{i}}(\upsilon) = \rho\omega_{\mathrm{e}}\left(\upsilon+\frac{1}{2}\right) - \rho^2\omega_{\mathrm{e}}x_{\mathrm{e}}\left(\upsilon+\frac{1}{2}\right)^2 + \rho^3\omega_{\mathrm{e}}y_{\mathrm{e}}\left(\upsilon+\frac{1}{2}\right)^3 + \dots, \quad (1)$$

where $\rho^2 = \mu/\mu^{\mathrm{i}}$ and μ is the mass of molecules. 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. Neglecting the higher order correction term of $\omega_{\mathrm{e}}y_{\mathrm{e}}$, we find that the vibrational isotopic shift of two isotopic molecules is

$$\Delta\nu = \nu_0 - \nu_0^{\mathrm{i}} = K - (1-\rho)\omega_{\mathrm{e}}''\left(\upsilon''+\frac{1}{2}\right) + (1-\rho^2)\omega_{\mathrm{e}}''x_{\mathrm{e}}''\left(\upsilon''+\frac{1}{2}\right)^2, \quad (2)$$

where

$$K = (\nu_{\mathrm{e}} - \nu_{\mathrm{e}}^{\mathrm{i}}) + (1-\rho)\omega_{\mathrm{e}}'\left(\upsilon'+\frac{1}{2}\right) + (1-\rho^2)\omega_{\mathrm{e}}'x_{\mathrm{e}}'\left(\upsilon'+\frac{1}{2}\right)^2.$$

Here ν_{e} is the difference of the two electronic potential curves involved, which is the same as a very good approximation for the two isotopic molecules.

For isotopic molecules, the rotational constants are given to a very good approximation[17]

$$B^{\mathrm{i}} = \rho^2 B_{\mathrm{e}} - \rho^3\alpha_{\mathrm{e}}\left(\upsilon+\frac{1}{2}\right) \quad (3)$$

and

$$D^{\mathrm{i}} = \rho^4 D_{\mathrm{e}} + \rho^5\beta_{\mathrm{e}}\left(\upsilon+\frac{1}{2}\right). \quad (4)$$

Therefore, the rotational isotopic shift of the band lines is,

$$\begin{aligned}\Delta\nu_{\rm r} = \nu_{\rm r} - \nu_{\rm r}^{\rm i} &= (1-\rho^2)[B'_{\rm e}J'(J+1) \\ &- B''J''(J''+1)] \\ &- (1-\rho^3)\left[\alpha'_{\rm e}\left(\upsilon'+\frac{1}{2}\right)J'(J'+1)\right. \\ &\left.- \alpha''_{\rm e}\left(\upsilon''+\frac{1}{2}\right)J''(J''+1)\right] \\ &- (1-\rho^4)[D'J'^2(J'+1)^2 \\ &- D''J''^2(J''+1)^2]. \qquad (5)\end{aligned}$$

4. Results and discussion

The band origins obtained in our work provide additional entries to the Deslandres table of the $\Omega = 1/2$ component of Tuckett and Peyerimhoff.[6] Thus the improved values of the vibrational constants of the upper and lower states were obtained by using the band origins in our work[11] together with those of (8, 1), (8, 2), (11, 1), (11, 2) and (12, 1) bands in Ref.[8]. The derived constants are listed in Table 1. The standard deviation ($\sigma = 19$ cm^{-1}) is mainly due to the irregular vibrational intervals caused by the perturbations, however, it means that we have got a relative accuracy at the order of 1.0×10^{-3}. The perturbations also affect precisely predicting the position of the bands of $^{35}Cl^{37}Cl^+$ or $^{37}Cl_2^+$ based on that of the most abundant isotope $^{35}Cl_2^+$. Nevertheless, the analyses of the isotope effects are helpful for searching isotopic bands in the experiment and further assigning the observed lines because 19 cm^{-1} is acceptable.

Table 1. Summary of the molecular constants (in cm^{-1}) of $^{35}Cl_2^{+a,b}$.

	$\nu_{\rm e}$	$\omega_{\rm e}$	$\omega_{\rm e}x_{\rm e}$	$\sigma^{\rm e}$
$A^2\Pi_{\rm u}$	20640(25)[c]	390.4(64)[c]	2.52(42)[c]	19
$X^2\Pi_{\rm g}$	0	643.6(59)[c]	2.62(81)[c]	
	$B_{\rm e}$	$\alpha_{\rm e}$	$\sigma^{\rm e}$	
$A^2\Pi_{\rm u}$	0.1971(16)[d]	0.00226(17)[d]	0.0012	
$X^2\Pi_{\rm g}$	0.26893(15)[d]	0.001346(32)[d]	0.00015	

[a] Values belonging to the $\Omega = 1/2$ component.

[b] Numbers in parentheses denote one standard deviation in units of the last two digit.

[c] Estimated values using vibrational numbering from Refs.[6, 8, 11].

[d] Estimated values using rotational constants from Refs.[8, 11].

[e] σ represents the standard deviation of the fitting.

The vibrational isotopic shifts were calculated regarding Eq.(2). For the pair $^{35}Cl_2^+$ and $^{35}Cl^{37}Cl^+$, it gives $\Delta\nu$(cal) = −43.9 cm^{-1} which is in good agreement with $\Delta\nu$(obs) = −41.32 cm^{-1} for the (3, 7) band. The difference between the calculated value and the observed value is mainly caused by the fairly precise vibrational constant caused by the perturbations. Meanwhile, $\Delta\nu$(cal) of the (2, 7) band is predicted to be –48.8 cm^{-1} and the band origin of the (2, 7) band of $^{35}Cl^{37}Cl^+$ is obtained, in accordance with the tendency of Fig.2 in Ref.[6]. These values are listed in Table 2.

The matrix elements reported by Amiot *et al*[18] of the effective Hamiltonian of Brown *et al*[19] were used to determine the molecular constants as Choi and Hardwick did in Ref.[8]. The derived rotational constants and those of (8, 1), (8, 2), (11, 1), (11, 2) and (12, 1) bands in Ref.[8] were used to fit $B_{\rm e}$ and $\alpha_{\rm e}$ of the upper and lower states by using the expression $B_\upsilon = B_{\rm e} - \alpha_{\rm e}\left(\upsilon+\frac{1}{2}\right)$. Here the centrifugal distortion constants D' and D'' were neglected since the value of D'' was fixed at 1.8×10^{-7} for the least-squares fit in Ref.[8]. The derived constants are also listed in Table 1. They are more precise than the derived vibrational constants. It agrees with the result of Ref.[6] that the perturbations between the states, which are very close in energy, were likely to be vibrational in nature and it will cause vibrational shifting and remain the rotational structure.

Therefore, using Eq.(3), we have calculated the rotational constants of the upper and lower states of the isotopic species $^{35}Cl^{37}Cl^+$. A comparison between calculated and experimental values is also listed in Table 2. The spectrum of $^{35}Cl^{37}Cl^+$ (3, 7) band is calculated and compared with the experimental one. There is a root-mean-square (rms) deviation of 2.8 cm^{-1}. The relatively large deviation is mainly due to the fairly precise vibrational constant caused by the perturbations mentioned above. Therefore using the experimental vibrational constant and calculated rotational constants, we have calculated the spectrum again with an rms deviation of 0.3 cm^{-1}. It proves the reliability of the theoretical calculation.

Table 2. Molecular constants and isotopic shifts (in cm^{-1}) for the $\Omega = 1/2$ component of $A-X$ of $^{35}Cl^{37}Cl^+$.

	$v''=7$	$v'=2$	$v'=3$	σ^c
B	0.252070(19)[a]		0.184335(20)[a]	0.0041[a]
B(cal)	0.25198	0.1864	0.1842	
		(2, 7)	(3, 7)	
ν_0		16962.4	17323.2867(10)[a]	
$\Delta\nu$(obs)			–41.32	
$\Delta\nu$(cal)		–48.8	–43.9	

[a] Values of Ref.[11].

[b] Numbers in parentheses denote one standard deviation in units of the last two digit.

[c] σ represents the standard deviation of the fitting.

As to the isotopic species $^{37}Cl_2^+$, molecular constants and the isotope shifts $\Delta\nu(\text{cal}) = \nu_0(^{35}Cl_2^+) - \nu_0^i(^{37}Cl_2^+)$ were predicted and listed in Table 3. Furthermore, the spectrum of $^{37}Cl_2^+$ (3, 7) band was predicted and listed in Table 4.

Table 3. Molecular constants and isotopic shifts (in cm^{-1}) for the $\Omega = 1/2$ component of $A-X$ of $^{37}Cl_2^+$.

	$v''=7$	$v'=2$	$v'=3$
$B(^{37}Cl_2^+)$	0.24511	0.1813	0.1792
		(2, 7)	(3, 7)
$\nu_0(^{37}Cl_2^+)$		17012.0	17370.4
$\Delta\nu$(cal)		–98.4	–88.5

Table 4. The predicted rotational lines for the $\Omega = 1/2$ components of (3, 7) band of $^{37}Cl_2^+$(in cm^{-1}).

J	$P(J)$	$R(J)$
0.5		17370.8059
1.5	17369.5326	17370.9666
2.5	17368.8443	17370.9953
3.5	17368.0242	17370.8922
4.5	17367.0721	17370.6572
5.5	17365.9883	17370.2903
6.5	17364.7725	17369.7916
7.5	17363.4250	17369.1611
8.5	17361.9458	17368.3988
9.5	17360.3347	17367.5048
10.5	17358.5920	17366.4791
11.5	17356.7177	17365.3218
12.5	17354.7117	17364.0328
13.5	17352.5743	17362.6123
14.5	17350.3053	17361.0604

Table 4. (*Continued*).

J	$P(J)$	$R(J)$
15.5	17347.9049	17359.3770
16.5	17345.3731	17357.5622
17.5	17342.7101	17355.6162
18.5	17339.9159	17353.5390
19.5	17336.9905	17351.3306
20.5	17333.9341	17348.9912
21.5	17330.7467	17346.5209
22.5	17327.4285	17343.9197
23.5	17323.9795	17341.1877
24.5	17320.3999	17338.3250
25.5	17316.6897	17335.3318
26.5	17312.8490	17332.2082
27.5	17308.8781	17328.9542
28.5	17304.7769	17325.5700
29.5	17300.5456	17322.0558
30.5	17296.1844	17318.4115
31.5	17291.6933	17314.6375
32.5	17287.0725	17310.7337
33.5	17282.3222	17306.7004
34.5	17277.4425	17302.5377
35.5	17272.4335	17298.2457
36.5	17267.2954	17293.8246
37.5	17262.0284	17289.2746
38.5	17256.6326	17284.5958
39.5	17251.1082	17279.7884
40.5	17245.4553	17274.8525

5. Conclusion

In this paper the isotope effect in the $A^2\Pi_u(\Omega = 1/2) - X^2\Pi_g$ ($\Omega = 1/2$) spectra of Cl_2^+ is reported. Based on the experimental molecular constants of $^{35}Cl_2^+$, the vibrational isotope shifts of the (2, 7) and (3, 7) bands for the pairs $^{35}Cl_2^+$ and $^{35}Cl^{37}Cl^+$, and $^{35}Cl_2^+$ and $^{37}Cl_2^+$ are derived, and the rotational constants of both $A^2\Pi_u$ and $X^2\Pi_g$ states are calculated for the minor isotopic species $^{35}Cl^{37}Cl^+$ and $^{37}Cl_2^+$. Then the spectrum of $^{35}Cl^{37}Cl^+$ (3, 7) band is calculated and compared with the experimental one. The agreement between the experimental and theoretical values proves the reliability of the theoretical calculation. Therefore the rovibronic spectrum for $^{37}Cl_2^+$ is predicted to help the seeking of experimental lines.

References

[1] Elliot A and Cameron W H B 1937 *Proc. Roy. Soc.* A **158** 681

[2] Elliot A and Cameron W H B 1938 *Proc. Roy. Soc.* A **164** 531

[3] Haranath P B V and Rao P T 1958 *India J. Phys.* **32** 401

[4] Rao V V and Rao P T 1958 *Can. J. Phys.* **36** 1557

[5] Huberman F P 1966 *J. Mol. Spectrosc.* **20** 29

[6] Tuckett R P and Peyerimhoff S D 1984 *Chem. Phys.* **83** 203

[7] van Lonkhuyzen H and de Lange C A 1984 *Chem. Phys.* **89** 313

[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] Bramble S K and Hamilton P A 1990 *J. Chem. Soc., Faraday Trans.* **86** 2009

[11] Wu L, Yang X, Guo Y, Zheng L, Liu Y and Chen Y 2005 *J. Mol. Spectrosc.* **230** 72

[12] Wang R, Chen Y, Cai P, Lu J, Bi Z, Yang X, and Ma L 1999 *Chem. Phys. Lett.* **307** 339

[13] Gerstenkorn S and Luc P 1978 *Atlas du Spectra d'Absorption de la Molecule d'Iodine* (ORSAY: Laboratoire Aime - Cottou CNRS)

[14] Yang X, Chen Y, Cai P, Wang H, Chen J and Xia C 1998 *Appl. Opt.* **37** 4806

[15] McCarthy M C and Field R W 1992 *J. Chem. Phys.* **96** 7237

[16] Tamassia F and Brown J M 1999 *J. Chem. Phys.* **110** 7273

[17] Herzberg G 1950 *Molecular Spectra and Molecular Structure* I: *Spectra of Diatomic Molecules* (New York: van Nostrand)

[18] Amiot C, Maillard J P and Chauville J 1981 *J. Mol. Spectrosc.* **87** 196

[19] Brown J M, Kaise M, Kerr C M L and Milton D J 1978 *Mol. Phys.* **36** 553