



The $2\nu_4$ overtone bands of $F^{35}Cl^{16}O_3$

E. Cané^a, L. Fusina^{a,*}, K. Burczyk^b

^a Dipartimento di Chimica Fisica e Inorganica, Facoltà di Chimica Industriale, Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy

^b Anorganische Chemie, FB C Universität, 42097 Wuppertal, Germany

ARTICLE INFO

Article history:

Received 18 March 2010

Available online 27 April 2010

Keywords:

Perchloryl fluoride

High resolution infrared spectra

Fermi resonance

Overtone bands

Ro-vibration analysis

ABSTRACT

The high resolution infrared spectrum of the mono-isotopic species $F^{35}Cl^{16}O_3$ has been studied in the region of the $2\nu_4$ overtone, from 2560 to 2680 cm^{-1} . The $2\nu_4^{\mp 2}$ perpendicular component is strong and clearly observed while the $2\nu_4^0$ parallel component is very weak and almost completely hidden by the perpendicular one. Their origins differ by 12.6 cm^{-1} , the $2\nu_4^{\mp 2}$ being located at higher wavenumbers. The $2\nu_4^{\mp 2}$ band is perturbed by the anharmonic interaction between the $\nu_4 = 2$, $l_4 = \mp 2$ and $\nu_2 = \nu_4 = \nu_5 = 1$, $l_4 = l_5 = \pm 1$ excited states, both of E symmetry. In total 3157 transitions have been assigned, 83% of these to $2\nu_4^{\mp 2}$, 12% to $\nu_2 + \nu_4^{\pm 1} + \nu_5^{\pm 1}$, and 5% to $2\nu_4^0$. The three bands have been analyzed simultaneously, taking into account the Fermi resonance effective between the excited states of E symmetry. The ro-vibration parameters of the excited states have been obtained, including the deperturbed band origins of $2\nu_4^{\mp 2}$ and $\nu_2 + \nu_4^{\pm 1} + \nu_5^{\pm 1}$, at 2628.5890(4) and 2619.3342(5) cm^{-1} , respectively. The W_{245} anharmonic constant is equal to 4.0161(4) cm^{-1} . The $x_{44} + g_{44}$ and $x_{24} + x_{45} + g_{45}$ anharmonicity constants have been derived from the obtained band origins and those of ν_4 and $\nu_2 + \nu_5$.

© 2010 Elsevier Inc. All rights reserved.

1. Introduction

During the last 20 years perchloryl fluoride, $FCIO_3$, has been the subject of systematic investigations by high resolution infrared spectroscopy. This heavy molecule is a prolate quasi-spherical rotor of C_{3v} symmetry with six normal modes of vibration: ν_1 , ν_2 , and ν_3 , totally symmetric, ν_4 , ν_5 , and ν_6 , doubly degenerate. The great majority of spectroscopic studies have been carried out on spectra recorded using mono-isotopic samples, $F^{35}Cl^{16}O_3$, $F^{37}Cl^{16}O_3$, $F^{35}Cl^{18}O_3$ and $F^{37}Cl^{18}O_3$, to circumvent the spectral congestion due to the isotopic effect of chlorine. Moreover, the spectra of mono-isotopic samples containing ^{18}O have been analyzed to provide additional and accurate information for the determination of the anharmonic potential function and equilibrium structure of perchloryl fluoride. The spectroscopic parameters of the ground state [1] and the ro-vibration analyses of all fundamentals of the four species have been reported [2–9]. The A_e and B_e equilibrium rotational constants and the equilibrium geometry of perchloryl fluoride have been obtained [9].

The ro-vibration studies have been extended to the $2\nu_1$, $2\nu_2$, $2\nu_3$, $2\nu_5$ and $2\nu_6$ overtones [10–12] and to several combination and hot bands [2,4,6,8–10,13] of the four species. The excited vibrational states have been characterized and most of the anharmonicity constants have been derived. The conspicuous amount of experimental data has prompted also the calculation by ab initio method of the

anharmonic force field of $FCIO_3$ [13]. The comparison of the ab initio values of the molecular parameters and equilibrium geometry with the experimental ones is satisfactory [13].

With the aim of completing the study of the first overtones of $FCIO_3$ this work presents the analysis of the $2\nu_4$ band of $F^{35}Cl^{16}O_3$ centered at about 2630 cm^{-1} . Two bands are expected in this region: the parallel component $2\nu_4^0$ and the perpendicular one, $2\nu_4^{\mp 2}$. However, only the perpendicular band is strong and clearly apparent in the spectrum while the parallel one is so weak to be undetected at a first glance. This behavior is different from that observed in $2\nu_5$, where both components are of similar intensities and clearly seen [11], and in $2\nu_6$, where only the parallel $2\nu_6^0$ band has been detected [12]. Another peculiarity with respect to $2\nu_5$ and $2\nu_6$ is that the $2\nu_4$ overtone is expected to be perturbed, as observed in ν_4 [4]. In fact, the $\nu_4 = 1$ state is in anharmonic resonance with $\nu_2 = \nu_5 = 1$, owing to the cubic term of the anharmonic potential $\phi_{245}q_2q_4q_5$. This is also responsible of the interactions between the $\nu_4 = 2$, $l_4 = 0$ and $\nu_2 = \nu_4 = \nu_5 = 1$, $l_4 = \mp 1$, $l_5 = \pm 1$ states, of A_1 symmetry, and between $\nu_4 = 2$, $l_4 = \mp 2$ and $\nu_2 = \nu_4 = \nu_5 = 1$, $l_4 = l_5 = \pm 1$, of E symmetry.

The results of the rotational analysis of the $2\nu_4$ overtone and of the $\nu_2 + \nu_4^{\pm 1} + \nu_5^{\pm 1}$ combination band, which is in Fermi resonance with it, will be outlined in the following sections. The text is structured as follows. The experimental details and the description of the spectrum are given in Sections 2 and 3, respectively. The assignments, the theoretical model used in the analysis, and the fits are reported in Section 4. Section 5 outlines the results and draws some conclusion.

* Corresponding author. Fax: +39 051 209 3690.

E-mail address: fusina@ms.fci.unibo.it (L. Fusina).

2. Experimental

The synthesis of the $F^{35}Cl^{16}O_3$ mono-isotopic sample has been already reported [1]. In the same paper the recording conditions of the FTIR spectrum are listed in Table 1, column X. The spectral resolution is quoted $4.4 \times 10^{-3} \text{ cm}^{-1}$ (1/maximum optical path difference), the data precision is estimated to be $2.5 \times 10^{-4} \text{ cm}^{-1}$.

3. Description of the spectrum

The strong spectral feature centered at 2630 cm^{-1} is a perpendicular band that extends from 2560 to 2680 cm^{-1} . It is assigned as the $2\nu_4^{\mp 2}$ component of the overtone. The shape of the band is characterized by strong series of pQ_K and rQ_K branches that extend to low and high wavenumbers, respectively, from the rQ_0 position at 2630.4 cm^{-1} . The adjacent pQ_K and rQ_K sub-branches are separated by about 1 cm^{-1} , being almost equidistant. This separation is equal to three times $2(A' - 2A'\zeta - B')$ since only the sub-branches with K'' equal to 3, 6, 9, ..., are observed. In fact, the three identical oxygen atoms have nuclear spin quantum number $I = 0$, so only the rotational levels with $k - l = 3p$, where p is an integer, are populated. The J structure of the pQ_K and rQ_K branches degrades to low wavenumbers as J increases. The $\Delta K = +1$ side of the band is easy to assign, being essentially constituted by strong and regularly spaced patterns including ${}^rR_K(J)$, ${}^rR_{K+3}(J-3)$, ${}^rR_{K+6}(J-6) \dots$ transitions. They can be observed in the spectral detail reproduced in Fig. 1(a). In the $\Delta K = -1$ side of the band the strong and regularly spaced patterns are constituted by ${}^pP_K(J)$, ${}^pP_{K+3}(J-3)$, ${}^pP_{K+6}(J-6) \dots$ transitions as shown in Fig. 1(b). By inspection of this figure it is evident that the distance of the ${}^pP_{15}(J)$ lines from the adjacent ones is anomalous, suggesting the presence of a localized perturbation on the rotational levels with $K = 14$. The weak ${}^rP_K(J)$ and ${}^pR_K(J)$ transitions have been assigned by means of ground state combination differences (GSCD) from the positions of the strong ${}^pP_K(J)$, ${}^rR_K(J)$, ${}^pQ_K(J)$ and ${}^rQ_K(J)$ lines.

Even if at a first glance no other band is apparent in the spectrum, a more careful inspection evidences an anomalous enhancement of the line density at about 2616 cm^{-1} (see Fig. 2). The irregular shapes and positions of spectral features and the shift of the baseline suggest the presence of the very weak qQ branch of the $2\nu_4^0$ parallel band, almost completely hidden by the strong lines of $2\nu_4^{\mp 2}$. Moreover, after the assignment of the $2\nu_4^0$ transitions several ${}^pQ_K(J)$ and ${}^rQ_K(J)$ sub-branches of the perpendicular band $\nu_2 + \nu_4^{\pm 1} + \nu_5^{\pm 1}$, connected by Fermi resonance with $2\nu_4^{\mp 2}$, have been identified in the

range $2614\text{--}2620 \text{ cm}^{-1}$. These sub-branches are separated by about 0.4 cm^{-1} and the onset of the ${}^rQ_0(J)$ sub-branch is at 2617.9 cm^{-1} .

The same expanded portion of the spectrum from 2615.6 to 2616.4 cm^{-1} is illustrated three times in Fig. 2, to facilitate the identification of the assigned lines. In Fig. 2(a) the strong ${}^pP_K(J)$ transitions of $2\nu_4^{\mp 2}$ are evidenced. The ${}^pQ_9(J)$ and ${}^pQ_{12}(J)$ transitions of the $\nu_2 + \nu_4^{\pm 1} + \nu_5^{\pm 1}$ band and the ${}^pQ_K(J)$ transitions of $2\nu_4^0$, are identified in Fig. 2(b) and (c), respectively. Comparing Fig. 2 with Fig. 1 the abovementioned baseline shift, which highlights the presence of the weak bands hidden by $2\nu_4^{\mp 2}$, and the higher line density due to weak Q transitions severely overlapped are evident.

The transitions identified in Fig. 2(b) and (c) have been assigned thanks to GSCD. The assignments of $2\nu_4^0$ are limited only to the ${}^qQ_K(J)$ and ${}^qP_K(J)$ sub-branches, being the R branch too weak to be detected. The band origin has been located at 2616.0 cm^{-1} .

4. Analysis

The $2\nu_4^{\mp 2}$ band, that is characterized by regular and well-distinguishable features, was first analyzed. By means of GSCD, obtained from the precise ground state molecular constants [1], about 500 transitions with $J'_{\text{max}} = K'_{\text{max}}$ up to 30 were assigned. The initial rotational and centrifugal distortion parameters of the $\nu_4 = 2$, $l_4 = \mp 2$ state used in the fit were obtained from the ground state constants and their vibration dependences, α_4 and β_4 [4], according to the relations:

$$A_{\nu_4=2} = A_0 - 2\alpha_4^A; \quad B_{\nu_4=2} = B_0 - 2\alpha_4^B \quad (1)$$

$$D_{J\nu_4=2} = D_{0J} + 2\beta_4^D; \quad D_{JK\nu_4=2} = D_{0JK} + 2\beta_4^{DK}; \quad D_{K\nu_4=2} = D_{0K} + 2\beta_4^{DK} \quad (2)$$

$A\zeta$ was set equal to $0.0936986(8) \text{ cm}^{-1}$, corresponding to the value in the $\nu_4 = 1$, $l_4 = \pm 1$ state [4], and the band center was chosen as 2630.0 cm^{-1} , which is the rough average of the ${}^pQ_3(J)$ and ${}^rQ_0(J)$ sub-branch origins.

The term values of the excited ro-vibration levels have been obtained as:

$$E_v(J, K, l) / hc = E_v^0 + B_v[J(J+1) - k^2] + A_v k^2 - 2A\zeta_v k l - D_{vj}[J(J+1)]^2 - D_{vJK}[J(J+1)]k^2 - D_{vK}k^4 + \eta_{vj}[J(J+1)]kl + \eta_{vK}k^3 l + H_{vj}[J(J+1)]^3 + H_{vJK}[J(J+1)]^2 k^2 + H_{vKJ}[J(J+1)]k^4 + H_{vK}k^6 + \tau_{vj}[J(J+1)]^2 kl + \tau_{vJK}[J(J+1)]k^3 l + \tau_{vK}k^5 l + \tau_{vK}^* k^3 l^2 \quad (3)$$

Table 1

Spectroscopic parameters (cm^{-1}) for the ground, $\nu_4 = 1$, $\nu_2 = \nu_5 = 1$, $\nu_4 = 2$, $\nu_2 = \nu_4 = \nu_5 = 1$ states of $F^{35}Cl^{16}O_3$.^a

Parameter	Ground state ^b	$\nu_4 = 1$, $l_4 = \pm 1$ ^c	$\nu_2 = \nu_5 = 1$, $l_5 = \pm 1$ ^c	$\nu_4 = 2$, $l_4 = 0$	$\nu_4 = 2$, $l_4 = \mp 2$	$\nu_2 = \nu_4 = \nu_5 = 1$, $l_4 = l_5 = \pm 1$
E_v^0		1317.254153(28)	1305.61482(6)	2616.011845(278)	2628.589047(385)	2619.334208(458)
A	0.1871217(42)	0.18636261(7)	0.18684650(9)	0.186102800(775)	0.186148725(414)	0.185652722(997)
B	0.17541085(8)	0.17507300(3)	0.17489882(6)	0.174787037(816)	0.174788366(144)	0.174167607(630)
$D_J \times 10^7$	0.49979(9)	0.50071(6)	0.49196(16)	0.5168 ^d	0.516782(381)	0.61541(379)
$D_{JK} \times 10^7$	0.5534(5)	0.5529(4)	0.5982(5)	0.442 ^d	0.44184(138)	0.33717(934)
$D_K \times 10^7$	-0.76	-0.7630(4)	-0.7984(5)	-0.766 ^d	-0.766 ^d	-0.785 ^d
$A\zeta \times 10^1$		0.936986(8)	-0.684538(13)		0.9266345(420)	0.2504196(609)
$\eta_J \times 10^6$		-0.0686(7)	-0.2673(17)		0.63834(305)	3.5949(170)
$\eta_K \times 10^6$		0.01254(13)	-0.0855(23)		1.81505(529)	50.0356(271)
$\tau_K \times 10^{10}$		0.0	0.0		-0.28282(897)	0.0
$\varepsilon \times 10^8$	-0.307(60)	0.650(3)	1.790(9)		0.0	0.0
$q_l \times 10^6$		-0.3830(11)	0.758(6)		0.0	0.0
W_{245}		2.866485(27)			4.016058(390)	
No. of data		3669			2942	
$\sigma(\text{fit}) \times 10^3$		0.40			1.7	

^a Standard uncertainties (1σ) in parentheses refer to the least significant digits.

^b From Ref. [1].

^c From Ref. [4].

^d Fixed to the indicated value. See text.

Download English Version:

<https://daneshyari.com/en/article/5415245>

Download Persian Version:

<https://daneshyari.com/article/5415245>

[Daneshyari.com](https://daneshyari.com)