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The ν_4 and $\nu_2 + \nu_5$ high resolution infrared bands of $F^{35}Cl^{18}O_3$ and $F^{37}Cl^{18}O_3$

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Abstract

The high resolution infrared spectra of monoisotopic $F^{35}Cl^{18}O_3$ and $F^{37}Cl^{18}O_3$ have been studied in the region of the ν_4 fundamentals, centered at 1278.3 and 1263.3 cm^{-1}, respectively. Large perturbations are observed in both bands due to a Fermi type anharmonic resonance with the $\nu_2 + \nu_5$ combination bands, centered at 1270.7 cm^{-1} in $F^{35}Cl^{18}O_3$ and 1257.3 cm^{-1} in $F^{37}Cl^{18}O_3$. In particular, they affect the $kl > 0$ levels of the $v_4 = 1$ and $v_2 = v_5 = 1$ states which cross at $kl \geqslant 18$ in $F^{35}Cl^{18}O_3$ and $kl \geqslant 3$ in $F^{37}Cl^{18}O_3$, due to the opposite values of $A\zeta_4^z$ and $A\zeta_{25}^z$. The $\Delta l = \Delta k = \pm 2$ and $\Delta l = 0$, $\Delta k = \pm 3$ essential resonances are also effective in the excited states of the dyad in $F^{35}Cl^{18}O_3$, while in $F^{37}Cl^{18}O_3$ only the $\Delta l = \Delta k = \pm 2$ one is active. In the spectrum of $F^{35}Cl^{18}O_3$ 3423 transitions have been assigned, 10% of them belonging to $\nu_2 + \nu_5$. The rovibrational parameters and the interaction constants between the $v_4 = 1$ and $v_2 = v_5 = 1$ levels have been obtained. The depertubed band origins of ν_4 and $\nu_2 + \nu_5$ are 1277.310567(165) and 1271.753733(195) cm^{-1}, respectively, and the anharmonic resonance constant W_{245}^F is 2.804416(153) cm^{-1}. For $F^{37}Cl^{18}O_3$, 3022 transitions have been assigned, 38% belonging to the $\nu_2 + \nu_5$ combination band. The depertubed band origins are 1260.856338(123) and 1259.872338(134) cm^{-1}, for ν_4 and $\nu_2 + \nu_5$ and the W_{245}^F constant is 2.9350669(405) cm^{-1}. The equilibrium geometry of perchloryl fluoride, r_e (ClO) = 139.7(3) pm, r_e (ClF) = 161.0(5) pm, and α_e (OClO) = 115.7(4) degree, has been determined using the A_e and B_e equilibrium constants of the four symmetric isotopologues of perchloryl fluoride, $F^{35/37}Cl^{16}O_3$ and $F^{35/37}Cl^{18}O_3$.
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Keywords: Perchloryl fluoride; High resolution infrared spectra; Fermi resonance; Rovibrational analysis; Fundamental band; Equilibrium geometry

1. Introduction

The vibrational levels of perchloryl fluoride, $FClO_3$, have been systematically explored in recent years and the rovibration analyses of fundamentals, overtones and combination bands have been reported on [1–11]. This molecule is interesting for many reasons: it is a C_{3v} prolate symmetric top with a quasi spherical character since its A_0 and B_0 constants are almost equal. The rovibrational levels can be characterized up to almost equally high J and K values, as the molecule is heavy and the difference between the molecular constants is small. The congestion of the spectra, also due to the presence of $^{35/37}Cl$ isotopically substituted molecules in the sample, is reduced since both the ^{16}O and ^{18}O atoms have nuclear spin quantum number $I = 0$. So, in the isotopologues with three identical oxygen atoms only one third of the rovibration levels are populated, those with $k - l = 3p$, where p is an integer.

Initially, $F^{35}Cl^{16}O_3$ and $F^{37}Cl^{16}O_3$ species have been studied, either in natural abundance or in isotopically pure samples [1–3]. The first paper [4] on $FCl^{18}O_3$ species referred on the analysis of the unperturbed ν_1 and ν_2 parallel bands from spectra of monoisotopic $FCl^{18}O_3$ with ^{35}Cl and ^{37}Cl in natural abundance (75.5/24.5). Using the ground state combinations differences (GSCD) from ν_1 and ν_2, the ground state constants, B_0, D_{0J}, D_{0JK}, H_{0J}, H_{0JK}, H_{0KJ} were obtained [4]. Later on, thank to the improvements in the synthesis of this molecule, four monoisotopic symmetric tops have been prepared, $F^{35}Cl^{16}O_3$,

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$F^{37}Cl^{16}O_3$, $F^{35}Cl^{18}O_3$ and $F^{37}Cl^{18}O_3$, indicated hereafter with the notation (35, 16), (37, 16), (35, 18) and (37, 18), and pure sample spectra have been recorded. As a consequence, the rovibrational analyses of ν_5 [5], ν_3 [6], ν_6 [7], $2\nu_6$ [9] and of the $2\nu_1$, $2\nu_2$, and $2\nu_3$ overtones [10], have been accomplished with comparable quality and the molecular parameters in the excited states have been obtained with similar precision in the four symmetric isotopologues. In the analyses [5–10] improved sets of the ground state constants were adopted resulting from the simultaneous fits of GSCD from ν_1, ν_2, and ν_5. Perturbation allowed transitions were found in the last band, so A_0, D_K and the coefficient of the $\Delta k = \pm 3$ interaction term, ε_0, were also derived for the four symmetric isotopologues [5].

The microwave spectra of (35, 16) and (37, 16) have been reported in [12] and extended to the asymmetric species $F^{35}Cl^{16}O_2^{18}O$ and $F^{37}Cl^{16}O_2^{18}O$ in [13]. The equilibrium geometry and the harmonic force field of perchloryl fluoride have been calculated [13].

This work presents the analyses of ν_4 for (35, 18) and (37, 18), the last fundamental to be studied in both isotopologues. The corresponding bands have been analyzed in [3] for (35, 16) and in [8] for (37, 16). Of the six infrared active vibrational modes only ν_4 is perturbed by the anharmonic interaction between the $v_4 = 1$ and $v_2 = v_5 = 1$ levels in all the symmetric species of $FClO_3$. From a simultaneous fit of ν_4 and $\nu_2 + \nu_5$, the deperturbed band centers, together with the rotational constants and the interaction constant W^F_{245}, will be determined. The vibrational dependence of the rotation parameters, α_i^A and α_i^B with $i = 1, 2 \ldots, 6$, will be calculated from the complete set of the molecular constants A_v and B_v, with $v = 0, 1, 2, \ldots, 6$, and the equilibrium values A_e and B_e will be derived. Using these data and those of (35, 16) and (37, 16) [8], the equilibrium geometry of perchloryl fuoride, i.e. the ClO and ClF bond lengths and the OClO angle, will be obtained.

2. Experimental

The synthesis of the monoisotopic (35, 18) and (37, 18) samples has been reported in [5], where the recording conditions of FTIR spectra are listed in Table 2, column C and D for (37, 18) and (35, 18), respectively. The resolution of both spectra is 2.2×10^{-3} cm^{-1}, the data precisions are estimated to be 1.0×10^{-4} and 1.5×10^{-4} cm^{-1}, for spectra of column C and D, respectively.

3. Spectra description

3.1. The $\nu_4/\nu_2 + \nu_5$ bands of $F^{35}Cl^{18}O_3$

The strong ν_4 perpendicular band extends from 1250 to 1300 cm^{-1}, the $^rQ_0$ branch being at ca. 1278.3 cm^{-1}. The weak $^rQ_0$ branch of the $\nu_2 + \nu_5$ combination band is observed at ca. 1270.7 cm^{-1}, partly overlapped by the stronger transitions to the $l = -1$ levels of the $v_4 = 1$ state. The overall shape of ν_4 is similar to that of the corresponding bands of (35, 16) and (37, 16). Adjacent sub-branches of the ^pQ and ^rQ branches are separated by about 0.4 cm^{-1} and extend to high and low wavenumbers, respectively, from the $^rQ_0$ position. They are intense and with J structures degraded to low wavenumbers. The P side of the band is easy to assign, each pattern comprising $^pP_K(J)$, $^pP_{K+3}(J+1)$, $^pP_{K+6}(J+2), \ldots$ or $^rP_K(J)$, $^rP_{K+3}(J-1)$, $^rP_{K+6}(J-2), \ldots$ transitions, which extend from low to high wavenumbers, see Fig. 1. Differently from (35, 16) and (37, 16) band heads do not show up for high J values. The structure of the R branches can be described as a succession of $^rR_K(J)$, $^rR_{K+3}(J+1)$, $^rR_{K+6}(J+2), \ldots$ or $^pR_K(J)$, $^pR_{K+3}(J-1)$, $^pR_{K+6}(J-2), \ldots$ transitions (see Fig. 2). The $^rR_K(J)$ sub-branches extend to low wavenumbers for $K'' = 0$ and 3 but reverse their direction for $K'' \geqslant 6$. Moreover, since the $kl > 0$ levels of $v_4 = 1$ and $v_2 = v_5 = 1$ cross for $kl \geqslant 18$ the $^rR_K(J)$ transitions of $\nu_2 + \nu_5$ become fairly apparent for $K'' \geqslant 18$. The corresponding transitions of ν_4 move to lower wavenumbers by about 5.6 cm^{-1}, among the strong ν_4 Q branches.

Most of the transitions assigned to $\nu_2 + \nu_5$ involve the $l = +1$ levels with $18 \leqslant K'' \leqslant 36$. Using the GSCD, from the strong $^rR_K(J)$ transitions the corresponding ^rQ and ^rP lines were found in congested regions of the spectrum. The $kl < 0$ transitions could be identified only in case they were not overlapped by stronger lines. Most of them belong to the $^pQ_K(J)$ sub-branches, with $K'' = 3 \div 9$. A total of 3423 transitions were assigned, 3064 to ν_4 with $J''_{\max}$ and $K''_{\max}$ equal to 70 and 359 to $\nu_2 + \nu_5$ with $J''_{\max}$ and $K''_{\max}$ equal to 70 and 36, respectively.

3.2. The $\nu_4/\nu_2 + \nu_5$ bands of $F^{37}Cl^{18}O_3$

The spectrum of the $\nu_4/\nu_2 + \nu_5$ dyad is different from that of (35, 18) for at least three aspects. The overall band intensity is weaker, even if the path length and the sample pressure in the spectrum recording were identical. The transitions to the $l = -1$ levels of $v_4 = 1$ are much stronger than those to the $l = +1$ levels, as it is evident comparing Fig. 3

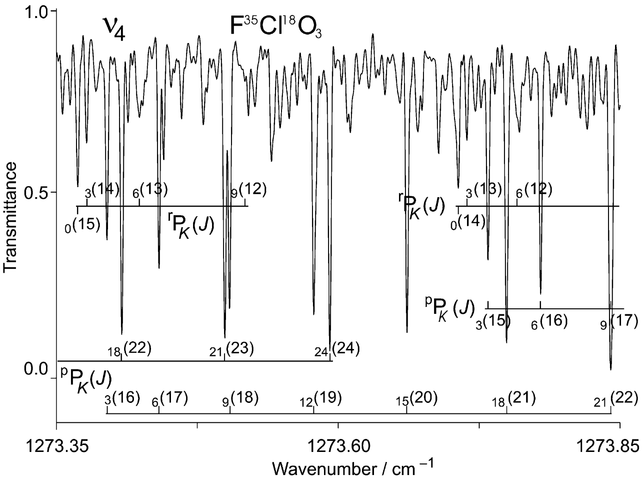

Fig. 1. Detail of the ν_4 band of the $F^{35}Cl^{18}O_3$ in the region of the $^pP_K(J)$ and $^rP_K(J)$ branches. The J and K assignments are indicated.

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