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The $2\nu_1$, $2\nu_2$ and $2\nu_3$ overtones of $FClO_3$

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Abstract

The infrared spectra of the $2\nu_1$, $2\nu_2$ and $2\nu_3$ overtones of perchloryl fluoride, $FClO_3$, have been recorded at high resolution using monoisotopic pure samples. Four symmetric top species have been investigated: $F^{35}Cl^{16}O_3$, $F^{37}Cl^{16}O_3$, $F^{35}Cl^{18}O_3$ and $F^{37}Cl^{18}O_3$. The $v_i = 2$, $i = 1, 2, 3$ vibrationally excited states are totally symmetric, so these overtones correspond to parallel bands of medium/weak intensity, centered from 2010 to 2120 cm^{-1} ($2\nu_1$), from 1390 to 1430 cm^{-1} ($2\nu_2$) and from 1070 to 1100 cm^{-1} ($2\nu_3$). Most of the bands are unperturbed and their analysis was straightforward. The band origins, the rotational and centrifugal molecular constants in the $v_1 = 2$, $v_2 = 2$ and $v_3 = 2$ states have been determined, with standard deviations of the fits from 0.00024 to 0.00067 cm^{-1}. The $2\nu_1$ overtones of $F^{35}Cl^{16}O_3$ and $F^{37}Cl^{16}O_3$ are perturbed by an A_1/E Coriolis resonance between the $v_1 = 2$ state and one E component of the $v_4 = 1$, $v_6 = 2$ manifold. The $2\nu_2$ of $F^{37}Cl^{18}O_3$ is perturbed by the same kind of interaction involving the $v_1 = v_6 = 1$ (E) state, at about 1396 cm^{-1}. In these bands the resonance is localized on rotational levels with specific J and K values. As a consequence, a few transitions of the perpendicular bands involving the interacting levels could be identified in the spectra. A simultaneous fit of the transitions assigned to the dyads has been performed and the parameters of the excited states have been determined, including the high order Coriolis interaction coefficient C_{11}^{1}. The anharmonic constants x_{11}, x_{22}, x_{33} of all the studied isotopologues of $FClO_3$, x_{46} of $F^{35}Cl^{16}O_3$, $x_{46} + g_{46}$ of $F^{37}Cl^{16}O_3$ and x_{16} of $F^{37}Cl^{18}O_3$, have been derived.

Keywords: Perchloryl fluoride; Infrared spectrum; Rovibrational analysis; Anharmonic constants

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1. Introduction

Perchloryl fluoride, $FClO_3$, is a suitable benchmark for the spectroscopic analysis of rovibrational spectra of molecules with C_{3v} symmetry. It is a quite chemically stable compound, easy to handle, and is classified as a prolate symmetric rotor nearly spherical, since A_0 and B_0 differ by less than 10%. It has six normal modes, three totally symmetric (A_1), ν_1, ν_2 and ν_3, and three degenerate (E), ν_4, ν_5 and ν_6. The A_1 vibrations give rise to infrared parallel bands while the E vibrations to perpendicular fundamental bands. High resolution infrared spectra have been extensively recorded from 300 to 3000 cm^{-1}, the fundamental bands being observed from about 400 to 1400 cm^{-1}. All fundamentals, but ν_3, are intense, well separated and free from perturbations, apart ν_4. These favorable features are of great help in the analysis. The number of observed transitions is reduced to one-third since only levels of A symmetry with $k - l = 3p$ ($p = 0, 1, \ldots$) have non-zero statistical weights, owing to the zero value of the nuclear spin quantum number of $^{16/18}O$ atoms. Furthermore, to avoid the spectral congestion caused by the presence of $^{35/37}Cl$ isotopomers in the sample, monoisotopic species have been prepared. Four isotopically substituted symmetric top species have been synthesized: $F^{35}Cl^{16}O_3$, $F^{37}Cl^{16}O_3$, $F^{35}Cl^{18}O_3$ and $F^{37}Cl^{18}O_3$, indicated hereafter with the short notation (35,16), (37,16), (35,18) and (37,18).

The analysis of the spectra recorded using monoisotopic samples enables the study of all bands with comparable significance. Up to now the ground state [1] and all fundamental bands of the four symmetric species have been

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analyzed [2–9], with the exception of ν_4 of (35, 18) and (37, 18), whose analysis is in progress. Owing to the nearly spherical nature of perchloryl fluoride, different reduction of the rotational Hamiltonian have been tested in the ground state analysis [1]. In addition, the ν_6 and $2\nu_6$ bands have been studied using three different models of the Hamiltonian to compare their adequacy to the reproduction of the experimental data [8,9]. Recently, the equilibrium structure of perchloryl fluoride has been calculated from the A_e and B_e equilibrium constants of (35, 16) and (37, 16) species [6]. Our aim is the determination of the equilibrium structure of $FClO_3$, from the rovibration parameters of the four isotopologues.

The subject of the present investigation is the rovibration analysis of the first overtone bands $2\nu_1$, $2\nu_2$ and $2\nu_3$ of the four symmetric species from high resolution monoisotopic spectra. They are observed as parallel bands of medium/weak intensity, centered in the range 2010–2120 cm^{-1}, 1390–1430 cm^{-1}, and 1070–1100 cm^{-1}, respectively. The energy of most of them are far enough from those of fundamentals or combination bands not to interact significantly with them. Three localized A_1/E Coriolis perturbations have been identified. Two involve the $v_1 = 2$ state and one component of E symmetry of the $v_4 = 1$, $v_6 = 2$ manifold in (35, 16) and (37, 16), the third involves $v_2 = 2$ and the $v_1 = v_6 = 1$ state of E symmetry in (37, 18). The $2\nu_1$, $2\nu_2$ and $2\nu_3$ bands of (35, 16) have been already analyzed from medium resolution spectra recorded using a sample with $^{35/37}$Cl in natural abundance [2]. Owing to the higher resolution and the better quality of monoisotopic spectra, it is expected to extend the assignments and to enhance the precision of (35, 16) spectroscopic parameters of the $v_1 = 2$, $v_2 = 2$ and $v_3 = 2$ states. The corresponding constants will also be obtained for (37, 16), (35, 18) and (37, 18). Furthermore, the x_{11}, x_{22} and x_{33} anharmonic constants will be derived together with some x_{ij} from the perturbing degenerate states. These new parameters, together with those already reported [2,4,6,9], could be useful for the determination of the anharmonic force field for $FClO_3$. So far only the harmonic force field has been calculated [10].

2. Experimental

The details of the synthesis of the monoisotopic samples are reported in [1], where the recording conditions of FTIR spectra used in the present analysis have been listed in Tables 1 and 2, for $FCl^{16}O_3$ and $FCl^{18}O_3$. Spectra V and VI, in Table 1, have been used for the analysis of both $2\nu_2$ and $2\nu_3$, of (37, 16) and (35, 16), respectively, while spectra VII and X for $2\nu_1$ of (37, 16) and (35, 16), respectively. The three overtone bands of (37, 18) and (35, 18) are from spectra L and M of Table 2, respectively. To enhance the absorbance of the overtones the sample pressure was 5 mbar and the path lengths were 4.8 and 5.6 m in $FCl^{16}O_3$ and $FCl^{18}O_3$ spectra, respectively. The quoted resolution of all spectra is $4.4 \times 10^{-3}\ cm^{-1}$, the data precisions are estimated to be $3 \times 10^{-4}\ cm^{-1}$, in spectra V and VI, $2.5 \times 10^{-4}\ cm^{-1}$ in spectra VII and X, and $2.0 \times 10^{-4}\ cm^{-1}$ in L and M.

3. Spectra description

3.1. The $2\nu_1$ bands

The $2\nu_1$ parallel bands are fairly intense at the quoted experimental conditions and their overall shape is similar in the four isotopologues. The dense absorption maximum of the Q branch spreads over 3 cm^{-1} and is centered at 2120.5 cm^{-1} in (35, 16) while it is at lower wavenumbers in heavier species, i.e., at 2114.5 cm^{-1} in (37, 16), 2016.8 cm^{-1} in (35, 18) and 2009.5 cm^{-1} in (37, 18). The isotopic shift of about 100 cm^{-1} for the ^{18}O isotopologues is due to the fact that ν_1 corresponds mainly to the Cl–O stretching mode. The Q branch structure degrades to lower wavenumbers. The K-structure of the $P(J)$ and $R(J)$ subbranches are resolved except for $K = 0$ and 3 and degraded to lower wavenumbers (see Fig. 1). Weak extra lines, that belong to hot bands from the low energy modes ν_3, ν_5 and ν_6, are observed in the less congested part of the spectrum.

The $2\nu_1$ overtones are unperturbed in (35, 18) and (37, 18). A total of 1594 transitions with J'' and K'' up to 75 and 60 were assigned in (35, 18) while 1643 transitions with J'' and K'' up to 81 and 60 were assigned in (37, 18).

On the contrary, the effects of a localized perturbation originating from an A_1/E Coriolis interaction are observed above 2110 cm^{-1} in the $2\nu_1$ bands of (35, 16) and (37, 16). Transitions with $K'' = 9$ and $J'' = 30 \div 40$ in (35, 16) and $K'' = 15$, $J'' = 38 \div 45$, $K'' = 18$, $J'' = 62 \div 64$ in (37, 16)

Table 1
Ground state molecular constants (in cm^{-1}) of $FClO_3$[a]

Parameter	$F^{35}Cl^{16}O_3$	$F^{37}Cl^{16}O_3$	$F^{35}Cl^{18}O_3$	$F^{37}Cl^{18}O_3$
$A_0 \times 10^1$	1.871 217(42)	1.871 364(29)	1.663 254 17(100)	1.663 315 92(59)
$B_0 \times 10^1$	1.754 108 5(8)	1.753 265 6(6)	1.637 978 4(5)	1.637 481 9(4)
$D_{0J} \times 10^8$	4.997 9(9)	4.993 9(9)	4.271 6(7)	4.265 4(7)
$D_{0JK} \times 10^8$	5.534(5)	5.591(6)	3.937(4)	3.977(4)
$D_{0K} \times 10^8$	−7.6	−7.6	−5.915 99(142)	−6.288 44(104)
$\varepsilon_0 \times 10^9$	−3.07(60)	−3.20(64)	−5.31(8)	−5.47(9)

[a] From Table 4 [1]. Standard uncertainties (1σ) in parentheses refer to the least significant digits.