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# The high resolution infrared bands $\nu_1$, $\nu_2$, $\nu_4$ and $\nu_2 + \nu_5$ of $F^{37}Cl^{16}O_3$

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Dedicated to Prof. Hans Bürger on the occasion of his 70th birthday.

**Abstract**

The high resolution infrared spectrum of mono-isotopic $F^{37}Cl^{16}O_3$ has been studied in the regions of $\nu_1$, $\nu_2$, $\nu_4$ and $\nu_2 + \nu_5$ bands, centered at 1060.20, 707.16, 1301.71 and 1292.15 $cm^{-1}$, respectively. The $\nu_1$ and $\nu_2$ parallel bands are unperturbed so their analysis was straightforward and 3355 and 2433 transitions were assigned, respectively. The band origins, the rotational and centrifugal molecular constants in the $v_1 = 1$ and $v_2 = 1$ states have been determined, with standard deviation of the fits $\sigma = 0.00019$ and 0.00018 $cm^{-1}$. The $\nu_4$ fundamental is affected by an anharmonic resonance with the $\nu_2 + \nu_5$ combination band. The $kl > 0$ sublevels cross at $kl \geqslant 27$ because of the opposite values of $A\zeta_4^z$ and $A\zeta_{25}^z$. The anharmonic resonance constant $W_{245}^F = 2.7991246(358)\ cm^{-1}$ has been derived. The $\Delta l = \Delta k = \pm 2$ and $\Delta l = 0$, $\Delta k = \pm 3$ essential resonances have been found to be effective in $\nu_4$, while in $\nu_2 + \nu_5$ only the $\Delta l = \Delta k = \pm 2$ one was active. A total of 5721 transitions have been assigned, 25% of them belonging to $\nu_2 + \nu_5$. The rovibrational parameters and the interaction constants of $F^{37}Cl^{16}O_3$ have been obtained. The standard deviation of the fit is 0.0006 $cm^{-1}$, six times the estimated data precision. The equilibrium geometry of perchloryl fluoride has been determined from the $A_e$ and $B_e$ constants of $F^{35}Cl^{16}O_3$ and $F^{37}Cl^{16}O_3$. Using the $A_0$ and $B_0$ constants of all the symmetric species the $r_0$ geometry has also been derived.

*Keywords:* Perchloryl fluoride; High resolution infrared spectra; Rovibrational analysis; Equilibrium geometry of $FClO_3$

## 1. Introduction

Perchloryl fluoride, $FClO_3$, has been the subject of several spectroscopic investigations. The molecule is chemically stable and can be prepared in four isotopically substituted symmetric top species, $F^{35}Cl^{16}O_3$, $F^{37}Cl^{16}O_3$, $F^{35}Cl^{18}O_3$ and $F^{37}Cl^{18}O_3$, indicated hereafter with the short notation (35,16), (37,16), (35,18) and (37,18). Earlier spectra were recorded using samples in natural abundance and, more recently, pure mono-isotopic forms were employed.

These isotopologues have $C_{3v}$ symmetry and six infrared active vibrations: $\nu_1$ (Cl–O stretching), $\nu_2$ (Cl–F stretching), $\nu_3$ ($ClO_3$ deformation), of $A_1$ symmetry, observed as parallel bands, and $\nu_4$ (Cl–O stretching), $\nu_5$ ($ClO_3$ deformation) and $\nu_6$ ($ClO_3$ rocking), of *E* symmetry, observed as perpendicular ones. The fundamental bands are in the region between 400 ($\nu_6$) and 1330 ($\nu_4$) $cm^{-1}$. Almost all of them, with the exception of $\nu_3$, are intense and well separated. Only $\nu_4$ is perturbed by the anharmonic interaction effective between the states $v_4 = 1$ and $v_2 = v_5 = 1$.

$FClO_3$ is a prolate symmetric rotor that behaves as a quasi-spherical one, with spherical factor $\gamma = (A_0 - B_0)/1/2\ (A_0 + B_0) = 0.0646$, 0.0652, 0.0153 and 0.0157 in the (35,16), (37,16), (35,18) and (37,18) isotopologues, respectively, the spherical character being more pronounced in the heavier ones. So perchloryl fluoride represents a well suited testing ground for theoretical models.

Owing to the small *B* value, about 0.175 $cm^{-1}$, rotational levels with *J* up to 100 may be populated at room temperature. Thanks to the small difference $A-B$, about

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$0.01\ \mathrm{cm}^{-1}$, levels with high $K$ values, up to 90, can be probed. However, the congestion of the spectral lines is reduced to 1/3 since rotational levels of $E$ symmetry are missing. In fact, both $^{16}$O and $^{18}$O atoms have nuclear spin quantum number $I = 0$, so levels with $|k-l| = 3p$ or $\neq 3p$, with $p = 0, 1, 2, 3, \ldots$, respectively, have statistical weight equal to 1 or 0.

The first rovibrational studies of perchloryl fluoride were based on spectra recorded in the gas phase at medium resolution, about $0.04\ \mathrm{cm}^{-1}$, using samples of $\mathrm{FClO_3}$ in natural abundance (the $^{35}$Cl/$^{37}$Cl isotopic ratio being 75.5/24.5), or the (35,16) mono-isotopic species [1]. The parallel fundamental bands $\nu_1$, $\nu_2$ and $\nu_3$ of (35,16), together with their overtones and combination bands, were analyzed, while for (37,16) the analysis was limited to $\nu_1$ and $\nu_2$. In 1990 Heldmann and Dreizler reinvestigated the microwave (MW) spectrum of $\mathrm{FClO_3}$ by microwave Fourier transform spectroscopy and determined precise $B$, $D_J$, quadrupole coupling and spin rotation constants of (35,16) and (37,16), together with the dipole moment of the molecule [2 and references therein]. Infrared spectra of the $\nu_2$, $\nu_3$, $\nu_5$ and $\nu_6$ bands of (35,16) were later recorded at high resolution (0.003–$0.004\ \mathrm{cm}^{-1}$). A set of more precise ground state molecular constants was obtained by adding to the MW data new rotational transitions measured in the millimeter wave region and ground state combination differences (GSCD) from the $\nu_2$ and $\nu_5$ infrared bands [3]. Owing to the identification in $\nu_5$ of perturbation allowed transitions, due to $\Delta k = \pm 3$ resonance effects, the $A_0$ rotational constant of (35,16) was determined. The equilibrium structure of perchloryl fluoride was also presented for the first time [3]. The analyses of the unperturbed $\nu_1$ and of the $\nu_4/\nu_2+\nu_5$ dyad completed the characterization of the fundamental bands of (35,16) [4]. The de-perturbed band centers of $\nu_4$ and $\nu_2+\nu_5$, together with the interaction constant $W^F_{245}$ were determined. The equilibrium rotational constants were derived from the complete set of vibration rotation constants.

The first study on $\mathrm{FCl^{18}O_3}$ species concerned the rovibrational analysis of the $\nu_1$ and $\nu_2$ unperturbed bands of (35,18) and (37,18). GSCD from these bands were used to derive the ground state molecular constants, with the exception of the $K$-dependent parameters [5]. Complete and improved sets of ground state parameters for all symmetric isotopomers were derived from the analysis of the $\nu_5$ fundamentals, recorded using mono-isotopic samples [6]. Perturbation allowed transitions observed in $\nu_5$ for the $^{18}$O species allowed the determination of both $A_0$ and $D_K$ while for (35,16) and (37,16), $D_K$ was fixed to a value derived from a harmonic force field calculation. Two different models of the rotational Hamiltonian were adopted: one contained only diagonal terms up to sextic order, the other included the off-diagonal $\Delta k = \pm 3$ term, leading to the evaluation of the $\varepsilon_0$ coefficient. The parameters of the latter model resulted statistically better determined and more suitable to fit the experimental data. The analyses of $\nu_3$, $\nu_6$ and $2\nu_6$ bands of the four isotopologues were reported in [7–9], and the results were used to test different reductions of the Hamiltonian for the analysis of the $v_t = 1$ isolated states of $\mathrm{C_{3v}}$ molecules [10 and references therein]. The anomalous intensity of the $\nu_3$ band, which is weak in $\mathrm{FCl^{16}O_3}$ spectra but completely disappears in the spectra of $\mathrm{FCl^{18}O_3}$, has been theoretically explained [11]. The study of the ground vibrational state of perchloryl fluoride was extended to the asymmetrically substituted $\mathrm{F^{35}Cl^{16}O_2{}^{18}O}$ and $\mathrm{F^{37}Cl^{16}O_2{}^{18}O}$ isotopologues by Müller and Gerry [12]. They used the ground state rotational data to evaluate geometrical parameters of $\mathrm{FClO_3}$ and refined the harmonic force field of the molecule.

We present here the analyses of the high resolution spectra of the $\nu_1$, $\nu_2$, $\nu_4$ and $\nu_2+\nu_5$ bands of (37,16), to complete the study of the fundamentals of this species. The results for $\nu_1$ and $\nu_2$, observed as unperturbed parallel bands at about 1060 and $707\ \mathrm{cm}^{-1}$, respectively, are more precise and complete than previous ones [1]. The analysis of the $\nu_4/\nu_2+\nu_5$ dyad is presented for the first time, to be compared with the results on (35,16) [4]. The vibration–rotation interaction constants, $\alpha_i^A$ and $\alpha_i^B$ with $i = 1, 2, \ldots, 6$, are calculated from the complete set of the molecular constants $A_v$ and $B_v$, with $v = 0, 1, 2, \ldots, 6$, and the equilibrium rotational constants $A_e$ and $B_e$ are derived. Using these data, together with those of the (35,16) species, the equilibrium geometry of perchloryl fluoride, i.e. the ClO and ClF bond lengths and the OClO angle are calculated. Finally, the $r_0$ geometry is also calculated, using the values of $A_0$ and $B_0$ in [6].

## 2. Experimental

Details of the synthesis of (37,16) sample are described in [6] where the recording conditions of FTIR spectra were listed in Table 1, column I, for $\nu_2$ and columns II and V for $\nu_1$, $\nu_4$ and $\nu_2+\nu_5$ bands, respectively. The quoted spectral resolutions are $2.8\times10^{-3}$, $2.2\times10^{-3}$ and $4.4\times10^{-3}\ \mathrm{cm}^{-1}$, the data precisions are estimated to be $1.5\times10^{-4}$, $1.0\times10^{-4}$ and $3.0\times10^{-4}\ \mathrm{cm}^{-1}$, for spectra of column I, II and V, respectively. The last spectrum has been used to extend the $\nu_1$ analysis to higher $J$ values.

## 3. Description of the spectra

### 3.1. The $\boldsymbol{\nu_1}$ band

The intense $\nu_1$ parallel band is centered at $1060.20\ \mathrm{cm}^{-1}$, with a dense $Q$ branch spreading over $3\ \mathrm{cm}^{-1}$ and degrading to low wavenumbers (see Fig. 1). The $K$ structures of $P$ and $R$ sub-branches are resolved except for $K = 0$ and 3. The $J$ patterns of $R$ and $P$ branches are $K$-degraded to low wavenumbers. A large number of weak extra lines, corresponding to hot band transitions associated to $\nu_1$ from the low energy modes $\nu_3$, $\nu_5$ and $\nu_6$, is scattered all over the spectral range. The results of the analysis of the $\nu_1+\nu_3-\nu_3$ hot band have been reported in [7]. The hot bands from $\nu_5$ and $\nu_6$ have not been analyzed here. Since $\nu_1$ is unperturbed, the rotational analysis was