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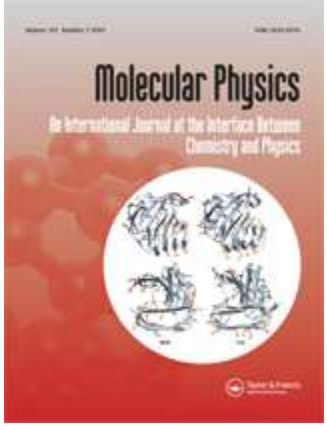

First analysis of the high resolution FTIR spectrum of the nu2 band of the FCO2 radical at 970.2 cm-1.

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Keywords:

fluoroformyloxyl radical, high resolution IR spectrum, rotational analysis, spin-rotation interactions, Fermi resonances.

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Abstract

The infrared spectrum of the fluorocarboxyl radical, FCO_2, was recorded at high resolution (0.0035 cm^{-1}) in the 600–1400 cm^{-1} region on a Bruker IFS 120 HR Fourier transform spectrometer of the University of Wuppertal. The analysis of the A-type ν_2 band of FCO_2 (CF stretching mode) centred at 970.208 cm^{-1} was performed taking use of the ground state parameters achieved by Kolesniková et al. [Kolesniková L, Varga J, Beckers H, Šimečková M, Zelinger Z, Nová Stříteská L, Kania P, Willner H, Urban Š. J. Chem. Phys. 128, 2008, pp. 224302-1-8]. For the FCO_2 radical, the ν_2 transitions are, in principle, splitted into two spin – rotation subcomponents corresponding to $J = N \pm 1/2$. However the spin- rotation parameters in the 2^1 vibrational state have values similar to those of the ground state, and spin-rotation doublings are observable only for the weaker transitions involving medium K_a or K_c values in the P and R branches. The ν_2 fundamental band is weakly perturbed by the $2\nu_5$ dark overtone band at 965.4 cm^{-1} and the 2^1 and 5^2 energy levels of FCO_2 are coupled through Fermi type resonances. The final energy level calculation was performed accounting both for the spin – rotation interaction within the 2^1 and 5^2 vibrational states, and the $2^1 \Leftrightarrow 5^2$ Fermi-type resonances.

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I Introduction

Recent interest on the fluorocarboxyl radical, FCO_2, is motivated because it is assumed to participate in atmospheric processes such as the degradation of hydrofluorocarbons that have been considered as chlorofluorocarbon substitutes [1-4]. On the other side, FCO_2 is isoelectronic to NO_3 and the spectroscopic and thermodynamic properties of these free radicals are expected to be governed by vibronic interactions to low lying electronic excited states [5-7]. Actually, the Born-Oppenheimer approximation breaks down for NO_3 [6,7], while there still exists rather little information on the spectroscopic properties of the FCO_2 radical.

Several results were achieved through *ab initio* calculations, like for example, the equilibrium structure of the FCO_2 radical which possesses C_{2v} symmetry in its ground state ($X\,^2B_2$) and in the next highest states [5, 8, 9]. Also the standard enthalpy of formation of FCO_2 was calculated [9]. The highly structured absorption in the visible originating at 13150 cm^{-1} was assigned, by comparison with *ab initio* calculations, to the $B\,^2A_1 \leftarrow X\,^2B_2$ electronic transition by Maricq et al. [5,10], and from the observed progressions of hot bands, the ν_3 vibrational mode of FCO_2 in the $X\,^2B_2$ ground state was measured at 520 cm^{-1}. From the study of photodetachment of the FCO_2^- ion, the ν_1, ν_2 and ν_3 mode of FCO_2 in $X\,^2B_2$ are measured at 1465, 950 and 500 cm^{-1}, respectively [11]. In addition, the visible spectrum and the IR spectrum of natural FCO_2, $FC^{18}O_2$ and $F^{13}CO_2$ isolated in noble gas matrices was reported [12]. In this study the free FCO_2 radical was prepared by vacuum flash pyrolysis of bis(fluoroformy1) peroxide, FC(O)OOC(O)F, diluted in N_2, Ar, or Ne and, the six fundamental vibrational states for FCO_2 in the ground X^2B_2 electronic state were assigned. For FCO_2 isolated in Ne the ν_1, ν_2 and ν_3 modes are at 1475, 960, and 519 cm^{-1} (A_1 symmetry), ν_4 and ν_5 at 1098 and 474 cm^{-1} (B_1 symmetry), and ν_6 at 735 cm^{-1} (B_2 symmetry). Table 1 and 2 give the symmetry properties of the FCO_2 radical and a short description of the vibrational modes in the ground state $X\,^2B_2$, respectively.

In Ref. [13] the first gas-phase detection of the FCO_2 radical by millimeter wave and high resolution infrared spectroscopy was performed guided by *ab initio* calculations. In this way the observed infrared bands ν_1 (1478 cm^{-1}), ν_2 (970 cm^{-1}) and ν_4 (1094 cm^{-1}) were identified. In this paper a detailed analysis of the FCO_2 radical was performed by microwave techniques, leading to a first set of ground state parameters including rotational, quartic centrifugal distortion, fine and hyperfine constants. Indeed FCO_2 is an open –shell molecular

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species, the coupling of the electron spin, with the rotation splits the rotational levels into two sublevels, and each of them is further split into a doublet by the hyperfine interaction due to the fluorine nuclear spin. The analysis of the millimeter wave measurements [13] was performed in the coupling scheme $\boldsymbol{J}=\boldsymbol{N}+\boldsymbol{S}$ and $\boldsymbol{F}=\boldsymbol{J}+\boldsymbol{I_F}$ between the rotational $\boldsymbol{N}$, electron spin $\boldsymbol{S}$, and ^{19}F nuclear spin $\boldsymbol{I_F}$ angular momenta. These ground state parameters were later improved by a subsequent millimeter wave analyses [14, 15]. Finally, the electron paramagnetic resonance spectra of the fluoroformyloxyl radical FCO_2 isolated in noble gas matrices have been investigated leading to the determination of principal *g* values and ^{19}F hyperfine coupling constants of FCO_2 [16].

Little information exists on gas phase infrared band analysis of FCO_2. To our knowledge, there is only one ongoing infrared study, which concerns the ν_4 band (antisymmetric CO stretching) centered at 1094.1492 cm^{-1} [17]. One surprising result of the analysis of this rather unperturbed *B*-type band are the significant differences between the spin rotational constants of the 4^1 and those of the ground state.

The present study concerns the ν_2 band, centered at 970.2086 cm-1 (CF stretching mode) using high resolution spectra recorded at Wuppertal. This *A*–type band is perturbed for the high N values due to Fermi resonances involving the 5^2 overtone state. Contrary to what is observed during the ν_4 band study, the spin –rotational constants in the 2^1 excited vibrational state differ only marginally from those of the ground state.

II Experimental details

FCO_2 radicals were generated in a flow system by pyrolysis of the peroxide FC(O)OOC(O)F at the entrance of a 1 m long White cell. The optical path length between the gold plated mirrors was adjusted to 36 m. The White cell was equipped at the entrance with the pyrolysis device consisting in a quartz tube (6 mm o.d.; 4 mm i.d.) with an electrical heating coil (Kantal wire) at the open end over a length of 20 mm. At the middle of the cell a capacitance pressure gauge (10 mbar MKS Baratron) and at the end a pump exit (flange diameter 40 mm) was attached. The cell was pumped through a 1 m long stainless steel bellow tube (40 mm i.d.) by a roots pump (500 m^3/h , Leybold Ruvac WS 501) to less than 10^{-3} mbar. At the pyrolysis device a cold U-trap containing the precursor and a needle valve for adjusting an

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argon gas flow was connected. Typical conditions for the generation of FCO_2 radicals were a flow rate of Ar of 30 to 100 mmol h^{-1} over the FC(O)OOC(O)F sample held at temperatures between –75 and –65°C.

During maximal pumping speed the resulting total pressure of the pyrolysis products together with excess of argon was in the range of 0.03 to 0.1 mbar inside the White cell. Under these conditions the residence time of the gas mixture in the cell is estimated to be about one second. It was found that pyrolysis temperatures of 300 to 350 °C resulted in the highest concentration of FCO_2. At lower temperatures less precursor were dissociated and at higher temperatures FCO_2 were depleted. It was not possible to increase the concentration of FCO_2 to saturate the most intensive IR bands. By reducing the pump speed with a valve, the pressure and residence time of FCO_2 in the White cell increased, but dimerization occurred and its unimolecular dissociation became more important.

During the measurements a few grams of FC(O)OOC(O)F were needed in one hour. FC(O)OOC(O)F was prepared by reacting a flow of a $F_2/O_2/CO$ (1 : 3 : 1) gas mixture at room temperature according to the literature procedures [12].

The IR spectra of FCO_2 were recorded on a Bruker HR 120 spectrometer at an apodized resolution (1/maximum optical path difference) of 0.003 cm^{-1} in the order of the Doppler width, and in the region 600 and 1400 cm^{-1}using a KBr beam splitter, an MCT600 detector, and an cut-off filter (>1400). Altogether 60 scans were co-added to obtain the final spectrum. The signal to noise ratio of the spectrum was ca. 20:1. Calibration was done by comparison with CO_2 lines [18].

III Analysis

The fluorocarboxyl radical, FCO_2, is a planar oblate asymmetric rotor molecule of C_{2V} symmetry. Its symmetry axis is the *a* inertial axis, and the ν_2 mode is of A_1 symmetry type (see Table 1). The total wavefunction (involving the electronic, vibrational, rotational and nuclear spin contributions) remains unchanged under symmetry operations equivalent to the permutation of the two oxygens (with a zero nuclear spin $I(^{16}O) = 0$), Due to the symmetry (X^2B_2) of the ground electronic state, the existing vibration-rotation energy levels $(v_1v_2\ldots v_6)[N\ K_a\ K_c]$ in the ground electronic state are K_a =odd if $(v_4+ v_5+v_6)$= even (resp. K_a = even for $(v_4+ v_5+v_6)$= odd). Therefore for the ground and the 2^1 vibrational states, only rotational levels with odd values of K_a are allowed [12, 15].

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As expected from symmetry considerations (see Table 1), the ν_2 band is an A –type band (see Fig. 1), and, as usual for planar oblate molecules, the P and R lines are grouped in clusters of lines keeping a constant value of ($2N$-K_c), the spacing between two successive clusters being of about $2C$. Examples of such clusters are given for a portion of the R branch on Fig. 2. Within these P and R clusters the strongest transitions which are those involving the low K_a values (starting from $K_a'' = 1$) are overlapping, and the assignments within these clusters are often difficult: this is evidenced on Figs. 2 and 3. In the Q branch, which is congested, the strongest transitions involve $K_a = J$ and very low K_c values. Series of $N_{N\,1,0} \leftarrow N_{N\,0,1}$ ($K_{c''} = 0$ and 1) transitions are easily observed on Fig. 4, from which $A' < A''$ can be inferred.

For the FCO_2 radical, each [N K_a K_c] energy levels are split by the electron spin – rotation interactions into two subcomponents corresponding to $J = N \pm 1/2$. However, the spin-rotation parameters in the 2^1 vibrational excited state differ only marginally from those of the ground state. As we are dealing with an A-type band, the spin-rotation splittings have similar values in the upper and lower levels for transitions involving energy levels in the symmetric top limit either for high K_a ($K_a \sim N$, $K_c << N$) or for high K_c ($K_a << N$, $K_c \sim N$) values. For this reason, the spin rotation splittings are not observable in the spectrum for strong lines of the P and R branches, or in the Q branch, since these transitions involve very low K_a (P and R branches) and very high K_a values (Q branch), respectively. This is clearly evidenced on Figs. (2-5). On the other hand, for weaker lines in the P and R branches involving medium K_a and K_c values ($1 << K_a << N$, and $0 << K_c << N$, respectively) the line doublings are clearly observable in the spectrum, since in this case the spin splittings in the upper and lower states differs significantly. Examples of these splittings are given on Figs 2, 3, and 5.

Finally, lets us mentioned that the hyperfine structure (of few megahertz, only) could not be observed during this infrared study. It is presumed that this hyperfine structure contributes to the apparent line width observed for the ν_2 transitions.

Some low and medium N and K_a transitions in the ν_2 band were first assigned. Then, using the ground state parameters of Ref. [15], the lower state spin – rotational energy levels were calculated and added to the newly observed line positions to get a list of experimental upper state energy levels. The upper state spin- rotational energy levels were inserted in a

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least squares fit to get an improved set of upper states parameters allowing better predictions and hence more assignments to be made.

This process was repeated iteratively until it appeared that several series were significantly perturbed for N≥ 40 values because of resonances involving the energy levels belonging to the 5^2 dark state located near 965 cm^{-1}. A model accounting for these resonances together with the spin-rotation interactions was then set up, which allowed more accurate predictions. To illustrate this point, Fig. 5 gives a portion of the R branch at 986.2 cm^{-1}: for the $(2N\text{-}K_c)$=40 stack, the line by line calculation is significantly improved when the $5^2 \Leftrightarrow 2^1$ Fermi type resonances are accounted for by the energy levels calculation. This iterative process was carried out until the ν_2 band was satisfactorily assigned. Table 3 gives an overview of the results of the present analysis. However, as the resonances coupling the 2^1 and 5^2 energy levels occur for rather high N values, the perturbed ν_2 lines are already weak and it was not possible to assign the resonating transitions belonging to the dark $2\nu_5$ band. Some remaining lines could not be assigned in the spectrum: it is presumed that these lines belong to hot bands: indeed since the ν_5 and ν_3 vibrational states are located near 474 and 519 cm^{-1}, respectively, the $\nu_2+\nu_5-\nu_5$ and $\nu_2+\nu_3-\nu_3$ are assumed to contribute for about 10 % and 8 %, respectively, to the total band intensity. However, the precise band head of these Q branch hot bands could not be located unambiguously.

IV Energy levels calculations.

In order to explain the perturbations which were observed during the analysis of the ν_2 band starting from N~40, one has to identify the dark states located in the vicinity of the 2^1 bright state. Indeed, the 5^2, 3^15^1 and 3^2 states of A_1, B_1 and A_1 symmetry type are crudely estimated near 948, 993 and 1038 cm^{-1}, respectively, by extrapolating from the values of the ν_3 and ν_5 vibrational frequencies issued from the Ne matrix measurements [12] (see Table 2). We tried several types of energy levels calculations depending on the symmetry type of the dark states which are assumed to be responsible of the observed resonances. Indeed, C-type Coriolis involving the $3^15^1 \Leftrightarrow 2^1$ resonating levels, Fermi resonances coupling either the $5^2 \Leftrightarrow 2^1$ or the $3^2 \Leftrightarrow 2^1$ resonating energy levels were considered for these test calculations. It appeared that the resonances are satisfactorily accounted for when considering only the $5^2 \Leftrightarrow$

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2^1 Fermi resonances, and this in agreement with the conclusions of the infrared investigation of the vibrational structure of FCO_2 in noble gas matrices performed by Argüello et al. [12].

The final calculation was performed considering in the v- diagonal part of the Hamiltonian both spin-rotation operators [19] and Watson 's type rotational operators written in I^R representation with an A-type reduction [20]. This choice of reduction and type of representation for the FCO_2 oblate asymmetric top is justified because it allows a straightforward comparison with the ground state parameters achieved in Refs. [13-15]. In addition this Hamiltonian involves Fermi type operators in the $5^2 \Leftrightarrow 2^1$ off diagonal blocks. The theoretical details are given in Ref. [21], and the final form of the Hamiltonian matrix is given in Table 4.

The experimental 2^1 spin-rotational energy levels obtained in this work were introduced in a least squares fit using this Hamiltonian model. Table 5 lists the Hamiltonian parameters (band centers, rotational, spin-rotation and coupling constants) resulting from the fit, together with their associated statistical uncertainties. Some constants were maintained at their ground state values [15], like for example the spin –rotation constants of the 5^2 dark state. For the 5^2 dark state we estimated the accuracy of the vibrational energy to be about 2 cm^{-1}, and the achieved rotational constants are rather effective ones: indeed, the resonances coupling the 5^2 and 2^1 energy levels begin to be significant only for N> 40, and it is difficult, at this stage, to predict accurately the position of the 5^2 resonating levels. In addition, it is not possible to estimate the rotational constants of 5^2 from those of 5^1 since no high resolution study exists so far for the ν_5 fundamental band.

Finally, as it can be seen in Table 5 the spin-rotation parameters in the 2^1 differ marginally from those of the ground state. To the contrary, an ongoing study of the ν_4 band [17] revealed a large vibrational dependence of the spin-rotation parameters, which probably can be traced back to a vibronic coupling to a nearby B^2A_1 electronic state via the ν_4 vibrational mode.

As far as the $5^2 \Leftrightarrow 2^1$ Fermi interaction constants are concerned, it was not possible to determine the zero order constants $h^{0F}_{55,2}$ which was maintained at zero during the calculations.

The results of the energy levels calculations proved to be rather satisfactory, as can be seen from the standard deviation and statistical analysis given in the lower part of Table 3.

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Finally, Figures 1 to 5 give detailed comparisons between the observed and calculated spectra in various spectral regions. For these comparisons, the relative line intensities of the spin-rotational sub-components were computed, using the tensorial method which is described in Ref. [22] to account for the spin-rotation interaction.

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Conclusion

The first high resolution analysis of the ν_2 band of the fluorocarboxyl radical, FCO_2, centred at 970.208 cm^{-1} was performed using spectra recorded at high resolution at Wuppertal. Because the spin-rotation parameters in the 2^1 upper state are similar to the ground state values, spin-rotation doublings for this *A*-type band are observable only for the weaker transitions involving medium K_a or K_c values in the *P* and *R* branches. The ν_2 fundamental band is weakly perturbed by a Fermi –type resonance coupling the 2^1 and 5^2 energy levels. The final energy level calculation was performed accounting both for the spin–rotation resonances within the 2^1 and 5^2 vibrational states, together with the $2^1 \Leftrightarrow 5^2$ Fermi-type interactions.

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Figure 1.

Overview of the 940-999 cm^{-1} spectral region with the ν_2 band of fluorocarboxyl radical, FCO_2.

Caption:

The lower trace corresponds to the experimental spectrum (T = 296 K). The upper trace is the line by line calculation for the ν_2 band of FCO_2.

Figure 2.

Part of R branch of the ν_2 band of FCO_2 near 976.3 cm^{-1}.

Caption:

Lower trace: experimental spectrum. Upper trace: calculated spectrum. Due to the values of the FCO_2 rotational constants (A ~B ~$2C$) the lines are grouped in stacks of lines corresponding to the same ($2N$-K_c) values (see text). The quoted assignments are given for the upper N', K'_a and K'_c values, with two stacks of lines corresponding to ($2N'$-K'_c) =14 and 15, respectively. For lines with medium K_a and K_c values, the spin-rotation splittings are observable and doublets of lines involving, J=N+1/2 and J=N-1/2 in the upper levels, are indicated by open triangles (△) and solid triangles (▲), respectively.

Figure 3.

Part of P branch of the ν_2 band of FCO_2 near 955.4 cm^{-1}.

Caption:

Lower trace: experimental spectrum. Upper trace: calculated spectrum. The quoted assignments are given for the upper N', K'_a, and K'_c values for lines belonging to the ($2N'$-K'_c) =33 stack, and for lines with medium K_a and K_c values. Only for the latter ones the spin-rotation splittings are observable and doublets of lines involving, J=N+1/2 and J=N-1/2 in the upper levels, are indicated by open triangles (△) and solid triangles (▲), respectively.

Figure 4.

Q branch of the ν_2 band of FCO_2 in the 970.2 cm^{-1} spectral region.

Caption:

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Several assignments (solid triangles ▲) are given for the degenerate ${}^{R}Q_{K_c''=0}$ and ${}^{P}Q_{K_c''=1}$ sub-branches, with $J = K_a$ ($\Delta J = \Delta K_a = 0$). In this case, the spin splittings are not observable.

Figure 5.

Part of R branch of the ν_2 band of FCO_2 near 986.3 cm^{-1}.

Caption:

The medium trace gives the experimental spectrum at the $(2N'-K'_c)$ =40 stack, and the upper and lower traces give the line by line model accounting and neglecting the $5^2 \Leftrightarrow 2^1$ Fermi resonances. Some transitions are assigned by the upper N', K'_a and K'_c values. The doublets of lines involving, $J=N+1/2$ and $J=N-1/2$ in the upper levels, are indicated by plus (+) and minus (-) signs, respectively.

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Table 1

Symmetry properties of FCO_2 in the X^2B_2 ground electronic state. Vibration-rotational levels $(v_1v_2\ldots v_6)[N\ K_a\ K_c]$ exist only are for K_a odd if $v_4+v_5+v_6$ = even (resp. K_a even for $v_4+v_5+v_6$ = odd).

Table 2

List of the vibrational modes for FCO_2 in the X^2B_2 ground electronic state.

Table 3

Range of the observed energy levels and the statistical analysis of the results of the energy level calculation.

Table 4

Hamiltonian matrix for the for the $\{2^1,5^2\}$ interacting vibrational states of FCO_2

Table 5

Vibrational energies, rotational, and spin-rotation constants, as well as coupling constants for the $\{2^1,5^2\}$ interacting vibrational states of FCO_2

Note: The results are in cm^{-1} and the quoted errors are one standard deviation. Constants marked with an # were fixed to the ground state values [15] during the least squares fit.

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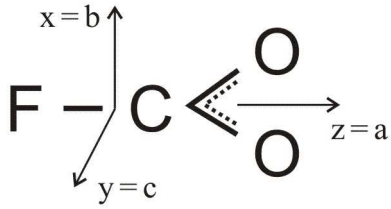
Table 1



	I	C_{2z}	σ_{xz}	σ_{yz}	Polar vector	Axial vector	Ground electronic state:	Vibration
A_1	1	1	1	1	T_z			ν_1, ν_2, ν_3
A_2	1	1	-1	-1		R_z		
B_1	1	-1	1	-1	T_x	R_y		ν_4, ν_5
B_2	1	-1	-1	1	T_y	R_x	X^2B_2	ν_6

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Table 2

Mode symmetry	Mode number		Experimental (Ne matrix)[a]	Experimental (gas phase)[b]
A_1	1	Symmetric CO stretch	1475	1478[c]
	2	CF stretch	960	970.2083 [e]
	3	OCO scissor	519	
B_1	4	Asymmetric CO stretch	1098	1094.42207[d]
	5	OCO rock	474	
B_2	6	OCO wagging	735	

[a] Fundamental vibration wavenumber (in cm^{-1}), Ref. [12]

[b] Band centers in cm^{-1}.

[c] Ref. [12]

[d] Ref. [17]

[e] This work

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Table 3

ν_2 band
2377 lines,
1141 levels
$N \leq 55$, $K_a \leq 39$

Statistical analysis of the results

Number of 2^1 spin-rotation levels:	1141
$0 \leq \delta < 0.001\,\mathrm{cm}^{-1}$	60.9 %
$0.001 \leq \delta < 0.002\,\mathrm{cm}^{-1}$	22.1 %
$0.002 \leq \delta < 0.004\,\mathrm{cm}^{-1}$	12.7 %
$0.004 \leq \delta < 0.008\,\mathrm{cm}^{-1}$	4.3 %

Standard deviation: $1.7\times10^{-3}\,\mathrm{cm}^{-1}$

$$\delta = |E_{obs} - E_{calc}|$$

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Table 4

Hamiltonian matrix

		J			
		2^1		5^2	
		N = J + 1/2	N = J – 1/2	N = J + 1/2	N = J – 1/2
2^1	N = J + 1/2	$H_{vv} + V_{vv}^{SR}$	V_{vv}^{SR}	$H_{vv'}^{F}$	
	N = J – 1/2	V_{vv}^{SR}	$H_{vv} + V_{vv}^{SR}$		$H_{vv'}^{F}$
5^2	N = J + 1/2	c.c.		$H_{vv} + V_{vv}^{SR}$	V_{vv}^{SR}
	N = J – 1/2		c.c.	V_{vv}^{SR}	$H_{vv} + V_{vv}^{SR}$

H_{vv}: Watson's A-type reduction, I^r representation Hamiltonian

$$H_{vv} = E_v + \left[A^v - \tfrac{1}{2}\left(B^v + C^v\right)\right]N_z^2 + \tfrac{1}{2}\left(B^v + C^v\right)\mathbf{N}^2 + \tfrac{1}{2}\left(B^v - C^v\right)N_{xy}^2$$

$$- \Delta_K^v N_z^4 - \Delta_{JK}^v N_z^2 \mathbf{N}^2 - \Delta_J^v \left(\mathbf{N}^2\right)^2 - \delta_K^v \left\{N_z^2, N_{xy}^2\right\} - 2\delta_J^v N_{xy}^2 \mathbf{N}^2$$

$$+ H_K^v N_z^6 + H_{KJ}^v N_z^4 \mathbf{N}^2 + H_{JK}^v N_z^2 \left(\mathbf{N}^2\right)^2 + H_J^v \left(\mathbf{N}^2\right)^3$$

$$+ h_K^v \left\{N_z^4, N_{xy}^2\right\} + h_{KJ}^v \left\{N_z^2, N_{xy}^2\right\}\mathbf{N}^2 + 2h_J^v N_{xy}^2 \left(\mathbf{N}^2\right)^2 + \ldots$$

Electron spin - rotation interaction in A-type reduction, I^r representation:

$$V_{vv}^{SR} = \varepsilon_{aa}^v S_a N_a + \varepsilon_{bb}^v S_b N_b + \varepsilon_{cc}^v S_c N_c +$$

$$\Delta_N^{vS} N^2 (N.S) + \frac{1}{2}\Delta_{NK}^{vS}\left\{N^2 N_z S_z + S_z N_z N^2\right\} + \Delta_{KN}^{vS}(N.S)$$

$$+ \Delta_K^{vS} N_z^3 S_z + \delta_N^{vS}\left(N_+^2 + N_-^2\right)(N.S) + \frac{1}{2}\delta_K^{vS}\left\{\left(N_+^2 + N_-^2\right)N_z S_z + N_z S_z\left(N_+^2 + N_-^2\right)\right\}$$

Fermi type interactions:

$$H_{vv'}^F = h_{vv'}^{0\,F} + h_{vv'}^{1F}\mathbf{N}^2 + h_{vv'}^{2\,F} N_{xy}^2 + \ldots$$

with: c.c.: complex conjugate, {A,B}=AB+BA and $N_{xy}^2 = N_x^2 - N_y^2$

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Table 5

Band centers and rotational constants

	0	**2^1**	**5^2**
E_v		970.20822(18)	965 ±2 cm^{-1}
A	0.4587249990	0.45791846(250)	0.460609(130)
B	0.3772716164	0.37618883(100)	0.379831(110)
C	0.2065695418	0.206146680(570)	0.20887147(910)
Δ_K	5.17792×10^{-7}	$4.2771(620)\times10^{-7}$	#
Δ_{NK}	-9.67002×10^{-9}	$97.94(450)\times10^{-9}$	#
Δ_N	2.60737×10^{-7}	$2.08360(400)\times10^{-7}$	$0.63592(260)\times10^{-6}$
δ_K	3.58732×10^{-7}	$3.8698(190)\times10^{-7}$	#
δ_N	1.12616×10^{-7}	$0.81826(300)\times10^{-7}$	#
H_K		$5.671(770)\times10^{-11}$	
H_{KN}		$-6.862(990)\text{x}10^{-11}$	
h_K		$-3.972(500)\text{x}10^{-11}$	

Spin-rotation constants

	0	**2^1**	**5^2**
ε^v_{aa}	-2.77982×10^{-3}	$-2.7732(160)\text{x}10^{-3}$	#
ε^v_{bb}	-2.65044×10^{-2}	$-2.73083(150)\ \text{x}10^{-2}$	#
ε^v_{cc}	-1.47348×10^{-3}	$-1.39817(670)\ \text{x}10^{-3}$	#
Δ^{vS}_K	5.2036×10^{-7}	#	#
$\Delta^{vS}_{KN} + \Delta^{vS}_{NK}$	-6.5979×10^{-7}	#	#
Δ^{vS}_N	1.3496×10^{-7}	#	#
Δ^{vS}_{NK}	0	#	#
δ^{vS}_K	-1.0064×10^{-7}	#	#

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δ_N^{vS}	6.6046×10^{-8}	#	#

Coupling constants

Fermi :	$5^2 \Leftrightarrow 2^1$
$\mathbf{J}^2$	$h^{1\ F}_{55,\ 2} = 1.8283(480)\text{x}10^{-4}$
J^2_{xy}	$h^{2\ F}_{55,\ 2} = 4.862(490)\text{x}10^{-5}$

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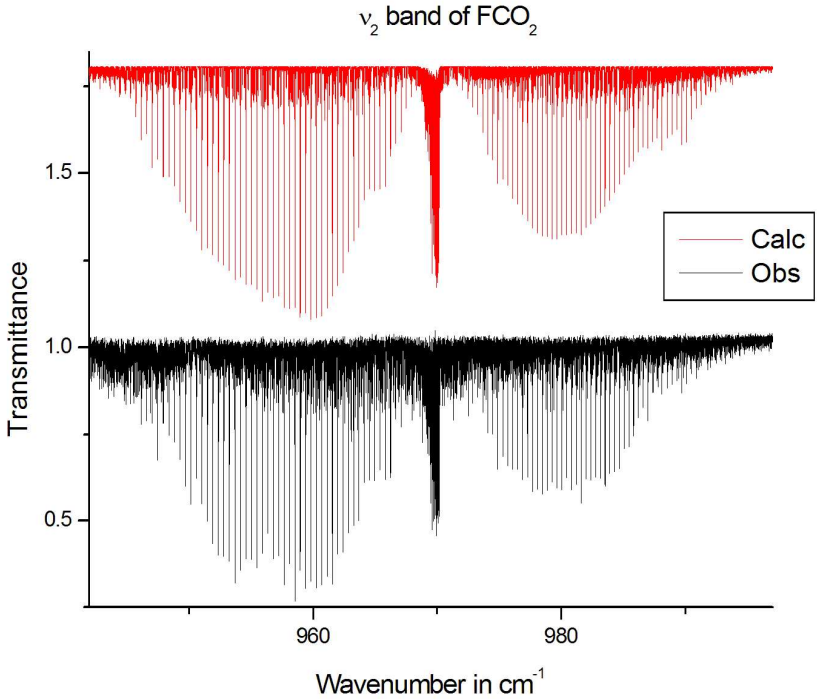

Overview of the 940-999 cm-1 spectral region with the nu2 band of fluorocarboxyl radical, FCO2.
279x215mm (150 x 150 DPI)

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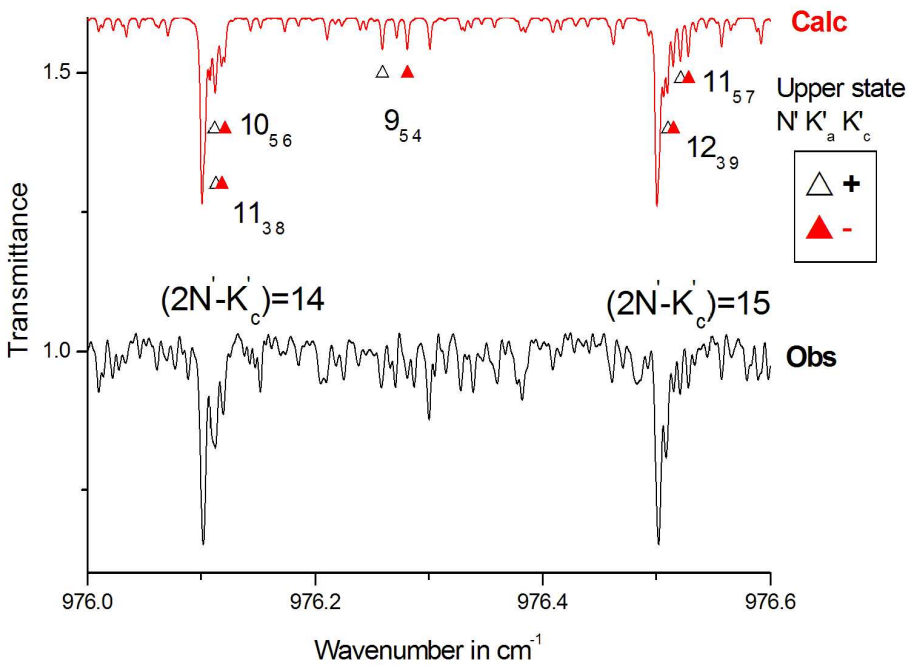

Part of R branch of the nu2 band of FCO2 near 976.3 cm-1.
279x215mm (150 x 150 DPI)

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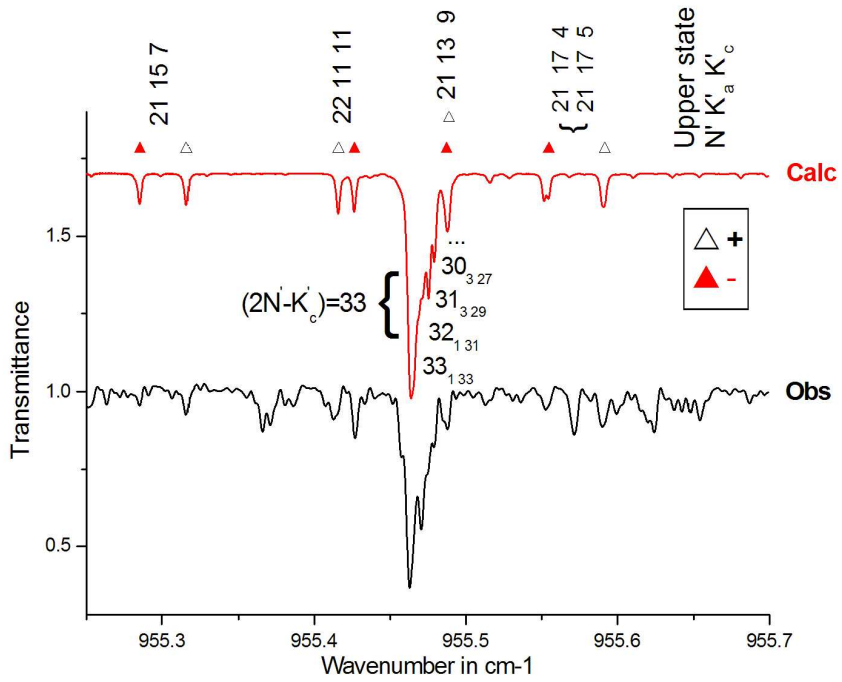

Part of P branch of the ν2 band of FCO2 near 955.4 cm-1.
279x215mm (150 x 150 DPI)

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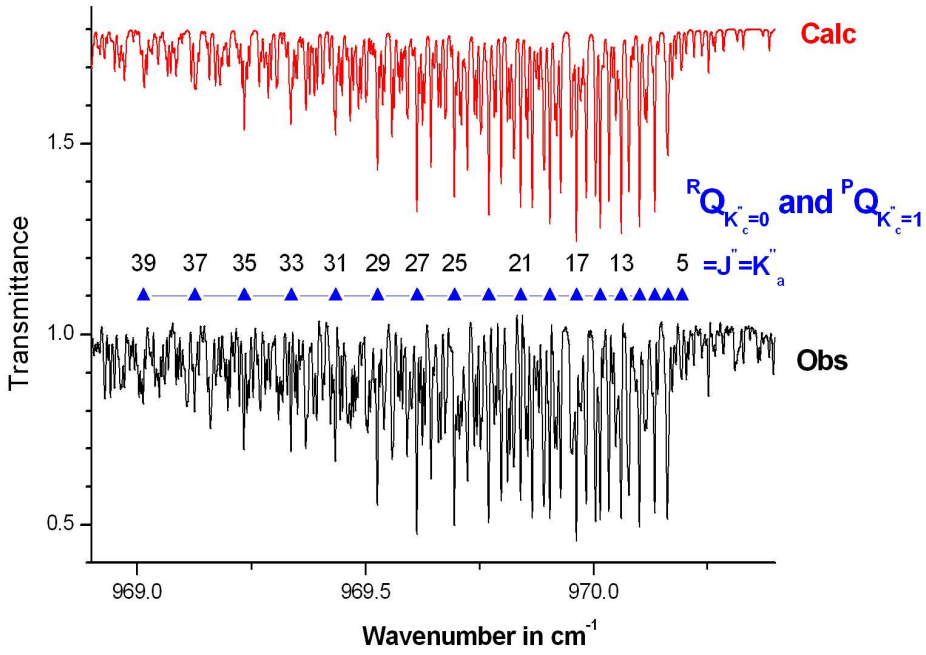

Q branch of the nu2 band of FCO2 in the 970.2 cm-1 spectral region.
279x215mm (150 x 150 DPI)

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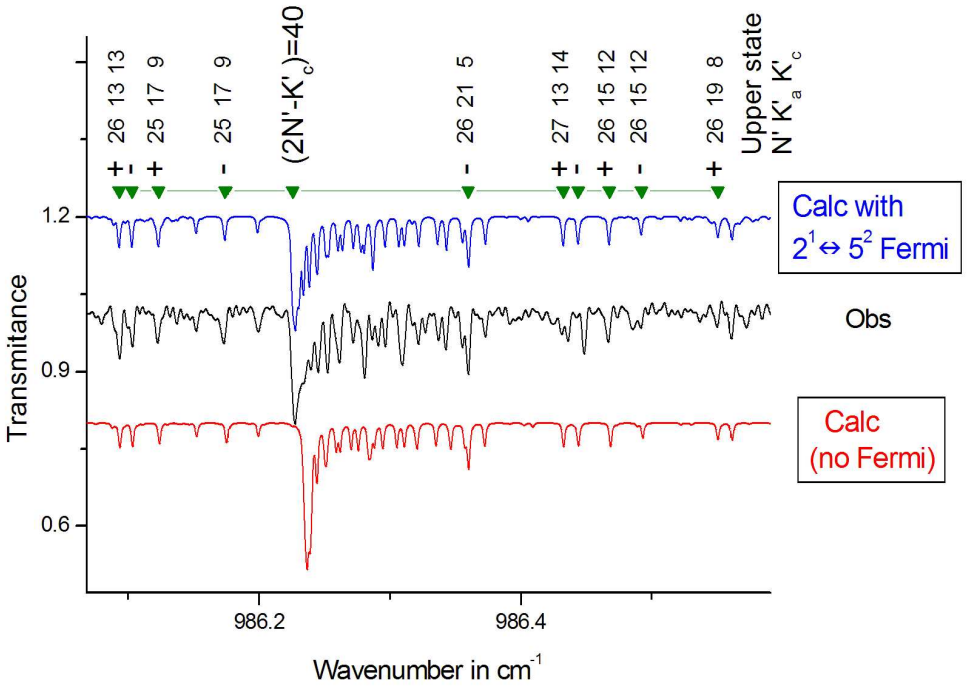

Part of R branch of the nu2 band of FCO2 near 986.3 cm-1.
279x215mm (150 x 150 DPI)

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