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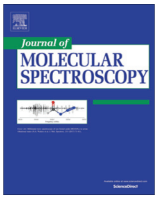

Resonance rotational level crossing in the fluorosulfate radical $FSO_3^{\bullet}$ and experimental determination of the rotational A and the centrifugal distortion D_K constants

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ABSTRACT

The resonance crossing of rotational levels with different fine-structure components and different k rotational quantum numbers was observed in the rotational spectra of the symmetric top fluorosulfate radical $FSO_3^{\bullet}$. Detailed measurements were performed to analyze these weak resonances as well as the A_1–A_2 splittings of the $K = 3$ and $K = 6$ transitions. The resonance level crossing enabled the experimental determination of "forbidden" parameters, the rotational A and the centrifugal distortion D_K constants as well as the corresponding resonance off-diagonal matrix element.

1. Introduction

In our previous study [1], the rotational line frequencies of the fluorosulfate radical were measured in the range of 93–281 GHz and assigned in the $^2A_2$ vibronic ground state for the first time. In this foregoing paper, it was experimentally proven that the $FSO_3^{\bullet}$ radical is a C_{3v} symmetric top molecule where only rotational states with the K quantum numbers 0, 3, 6, ... are permitted with nonzero statistical weights by the Pauli principle. The small difference between the rotational constants ($A - B$) of about 250 MHz qualifies the fluorosulfate radical as a quasi-spherical top where energy levels with different rotational quantum numbers K are close to each other. Moreover, the A_1–A_2 splittings of the $K = 3$ rotational levels were observed for N quantum numbers greater than 13. The transition frequencies were analyzed in terms of the A-reduced symmetric top effective Hamiltonian [2] using Pickett's SPFIT program [3]. This analysis of the transition frequencies provided the B rotational constant, quartic and sextic centrifugal distortion parameters, and fine-structure splitting constants. The value of the second rotational constant was only estimated from an empirical formula [4].

In the present study, the previous dataset has been extended up to 662 GHz to observe the presumed resonance crossing of rotational levels between the diverse fine-structure components with different values of the K rotational quantum numbers because the corresponding interaction can serve as a tool for the experimental determination of the A rotational constant.

Finally, the crossing of the energy levels with different quantum numbers K may lead to the failure of the reduction of the effective Hamiltonian [5], because the off-diagonal matrix elements cannot be successfully eliminated by a contact transformation.

2. Experiment

The experimental approach is described in detail in our previous studies of the radicals $FCO_2^{\cdot}$ and $FSO_3^{\bullet}$ [1,6,7]. The Prague millimeter-wave spectrometer was used to measure all the rotational spectra of the fluorosulfate radical. The experimental setup consists of a tunable microwave generator, semiconductor frequency amplifiers and multipliers, a measuring cell (a 2.3 m-long glass tube with an inner diameter of 100 mm) and detectors. The amplifiers, multipliers and detectors are based on Schottky diodes. The targeted rotational transitions for this study were in the frequency range of 400 GHz and higher. Due to the lower intensity of the incoming microwave radiation passing through the measuring cell, the optical length was not doubled, unlike in previous measurements [1].

The radical was prepared in situ by low pressure pyrolysis of its dimer (bis(fluorosulfuryl)peroxide) at a temperature of about 430 K. This precursor was prepared according to the procedure described by Zhang et al. [8]. The identification of the radical lines

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was enhanced by measurements with the local magnetic field generated by the Helmholtz coils, causing the Zeeman effect in the spectra [1].

3. Hamiltonian and matrix elements

The analysis of the transition frequencies were based on the Watson‘s rotational effective Hamiltonian [2] extended with the H_{fs} fine-structure terms:

$$H = H_{rot} + H_{fs}, \tag{1}$$

where H_{rot} is the C_{3v} symmetric top Hamiltonian [9]:

$$\begin{aligned}\hat{H}_{\mathrm{rot}} &= B\hat{N}^2 + (A-B)\hat{N}_z^2 - D_N\hat{N}^4 - D_{NK}\hat{N}^2\hat{N}_z^2 - D_K\hat{N}_z^4 + H_N\hat{N}^6 \\ &+ H_{NK}\hat{N}^4\hat{N}_z^2 + H_{KN}\hat{N}^2\hat{N}_z^4 + H_K\hat{N}_z^6 + L_N\hat{N}^8 + L_{NNK}\hat{N}^6\hat{N}_z^2 \\ &+ L_{NK}\hat{N}^4\hat{N}_z^4 + H_{KKN}\hat{N}^2\hat{N}_z^6 + L_K\hat{N}_z^8 + (\epsilon + \epsilon_N\hat{N}^2 \\ &+ \epsilon_{NN}\hat{N}^4)[\hat{N}_+^3 + \hat{N}_-^3, \hat{N}_z]_+ + (\epsilon_K + \epsilon_{NK}\hat{N}^2)[\hat{N}_+^3 + \hat{N}_-^3, \hat{N}_z^3]_+ \\ &+ \epsilon_{KK}[\hat{N}_+^3 + \hat{N}_-^3, \hat{N}_z^5]_+ + (h_3 + h_{3N}\hat{N}^2)(\hat{N}_+^6 + \hat{N}_-^6) \\ &+ h_{3K}[\hat{N}_+^6 + \hat{N}_-^6, \hat{N}_z^2]_+,\end{aligned} \tag{2}$$

where the brackets $[X, Y]_+$ denote the anticommutator of the X and Y operators. $\hat{H}_{\mathrm{rot}}$ provides the matrix elements diagonal in the rotational quantum number *k:*

$$\begin{aligned}\langle N,k|H_{rot}|N,k\rangle &= BN(N+1) + (A-B)k^2 - D_N N^2(N+1)^2 \\ &- D_{NK}N(N+1)k^2 - D_K k^4 + H_N N^3(N+1)^3 \\ &+ H_{NK}N^2(N+1)^2k^2 + H_{KN}N(N+1)k^4 + H_K k^6 \\ &+ L_N N^4(N+1)^4 + L_{NNK}N^3(N+1)^3k^2 \\ &+ L_{NK}N^2(N+1)^2k^4 + L_{KKN}N(N+1)k^6 + L_K k^8\end{aligned} \tag{3}$$

as well as the off-diagonal matrix elements. On the one hand, there are the $\Delta k = 3$ matrix elements:

$$\begin{aligned}\langle N,k|H_{rot}|N,k\pm3\rangle &= \{[\epsilon + \epsilon_N N(N+1) + \epsilon_{NN}N^2(N+1)^2](2k\pm3) \\ &+ [\epsilon_K + \epsilon_{NK}N(N+1)][k^3 + (k\pm3)^3] \\ &+ \epsilon_{KK}[k^5 + (k\pm3)^5]\}\cdot F_{\pm3}(N,k)\end{aligned} \tag{4}$$

where

$$F_{\pm n}(N,k) = \prod_{i=1}^{n}[N(N+1) - (k\pm(i-1))(k\pm i)]^{1/2} \tag{5}$$

and, on the other hand, there are also the $\Delta k = 6$ matrix elements

$$\langle N,k|H_{rot}|N,k\pm6\rangle = [h_3 + h_{3N}N(N+1)]F_{\pm6}(N,k), \tag{6}$$

where $F_{\pm6}(N,k)$ is defined in Eq. (5). In the symmetrized wavefunction bases $|N,\ K,\ A_\pm\rangle = \{|N,\ K\rangle \pm (-1)^K|N,-K\rangle\}/2^{1/2}$ where $K = |k|$, the off-diagonal matrix elements $\langle N, k = -3|H_{rot}|N, k = +3\rangle$ are becoming the diagonal matrix element:

$$\langle N, K=3,\pm|H_{rot}|N, K=3,\pm\rangle = \pm[h_3 + h_{3N}N(N+1)](\mathrm{N}+3)!/(\mathrm{N}-3)! \tag{7}$$

This diagonal matrix elements together with the off-diagonal term in Eq. (4) contribute to the A_1–A_2 splitting of the $K = 3$ levels.

The general form of the fine splitting Hamiltonian H_{fs} can be found in [10,11] and, for a prolate symmetric top, it reduces to [12]

$$\begin{aligned}\hat{H}_{\mathrm{fs}} &= \varepsilon_{aa}\hat{N}_z\hat{S}_z + \varepsilon_{bb}(\hat{N}_x\hat{S}_x + \hat{N}_y\hat{S}_y) + D_N^S\hat{N}^2(\hat{N}\hat{S}) \\ &+ \frac{1}{2}D_{NK}^S[\hat{N}^2, \hat{N}_z\hat{S}_z]_+ + D_{KN}^S\hat{N}_z^2(\hat{N}\hat{S}) + D_K^S\hat{N}_z^2\hat{N}_z\hat{S}_z \\ &+ (\epsilon^S + \epsilon_N^S\hat{N}^2)[([N_+^2, S_+]_+ + [N_-^2, S_-]_-), N_z]_+\end{aligned} \tag{8}$$

where the signs outside of the brackets $[A,B]_\pm$ denotes commutators $(-)$ and anticommutators $(+)$ of the A and B operators. This $\hat{H}_{\mathrm{fs}}$ operator provides also both the diagonal as well as off-diagonal matrix elements.

$$\begin{aligned}\langle N,K,S,J|H_{fs}|N,K,S,J\rangle &= -\left[\frac{N(N+1) + S(S+1) - J(J+1)}{2N(N+1)}\right] \\ &\times \{\varepsilon_{aa}K^2 + \varepsilon_{bb}[N(N+1) - K^2] \\ &+ D_N^S N^2(N+1)^2 \\ &+ (D_{NK+KN}^S)K^2N(N+1) + D_K^S K^4\}\end{aligned} \tag{9}$$

$$\begin{aligned}\langle N,K,S,J|H_{fs}|N-1,K,S,J\rangle &= -(K/2N)\{\varepsilon_{aa} - \varepsilon_{bb} + D_K^S K^2 + D_{NK}^S N^2\} \\ &\bullet [(N^2 - K^2)(N - J + S)(N + J + S + 1) \\ &\times (S + J - N + 1)\cdot(N + J - S)/(2N+1) \\ &\times (2N-1)]^{1/2}\end{aligned} \tag{10}$$

In addition to these matrix elements, there are also terms off-diagonal in the N and K quantum numbers that are crucial for the description of the crossing resonances:

$$\langle N,K,J|H_{fs}|N+1,K\pm3,J\rangle = \{[\epsilon^s + \epsilon_N^S N(N+1)](2k\pm3)\}F_{\pm3}(N,k) \tag{11}$$

where the $F_{\pm3}(N,k)$ function is defined in Eq. (5).

4. Analysis of spectra and results

The overall rotational spectra of the $FSO_3\cdot$ radical were measured in several regions in the frequency range of 93–662 GHz (N'' = 8–64). A total of 717 rotational transitions in the rovibronic ground state of the FSO_3 radical were analyzed. Only the rotational lines with the quantum numbers $K = 3n$ (n = 0, 1, 2, 3,. . .) are permitted in the ground state rotational spectra of the fluorosulfate radical as a consequence of the Pauli principle, which is applied to the C_{3v} molecule with three identical ^{16}O nuclei in the nondegenerate electronic state. Based on the previous analysis, the predictions were calculated step by step with Pickett's SPCAT program [3]. The other program, SPFIT, was used for spectral analysis. The analyses were performed using both the *A*- and *B*-reductions of the symmetric top Hamiltonian [13]. In the *A*-reduced Hamiltonian, all the terms providing $\Delta k = \pm3$ matrix elements are restricted to a fixed value, most often to zero [13]. The *A*-reduced Hamiltonian is suitable for molecules fulfilling an approximate relation for the rotational constants $A - B \sim B$ *or* A. The *B*-reduced Hamiltonian is designed mainly for the quasi-spherical molecules ($A - B \ll B$); in these cases, all the $\Delta k = \pm6$ matrix elements are usually constrained to zero.

Both the symmetric top reductions were employed in the analysis of the fluorosulfate radical rotational transition frequencies. The obtained parameters for both the reduced Hamiltonians, their estimated errors as well as the corresponding root-mean square deviation are listed in Table 1. Although the *B* rotational constant is about twenty times larger than the *A-B* difference and therefore the FSO_3 radical is more likely a near spherical top than a prolate molecule, a slightly better fit was obtained was obtained using the *A* reduced Hamiltonian. In order to visualize the crossing resonance areas (see below), a reduced-energy diagram ($E_{red}(N,k)$ versus J'') was created (see Fig. 1). The reduced energies were obtained by the subtraction of the purely *N*-dependent terms from the rotational energies involving the fine structure terms:

$$\begin{aligned}E_{red}(N,k,J) &= E_{rot,fs}(N,k,S,J) - BN(N+1) + D_N N^2(N+1)^2 \\ &- H_N N^3(N+1)^3 + LN_N^4(N+1)^4,\end{aligned} \tag{12}$$

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