Microwave spectra of fluoroformyloxyl and fluorosulfate radicals

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***Abstract*—Rotational spectra of fluoroformyloxyl (FCO_2·) and fluorosulfate (FSO_3·) molecular free radicals were measured in millimetre wave region and analyzed in detail using matrix elements of rotational, centrifugal distortion, fine and hyperfine effective Hamiltonian terms. The microwave spectra of the FSO_3· free radical were observed, identified and analyzed for the first time.**

I. Introduction And Background

A participation of free radicals in atmospheric processes and in the interstellar medium is well known. Their analysed high resolution microwave spectra are desirable to enable monitoring of these species. The microwave data are also extremely useful to derive precise molecular parameters such as rotational constants, centrifugal distortion, fine and hyperfine parameters.

II. Results

Rotational spectra of fluoroformyloxyl (FCO_2·) and fluorosulfate (FSO_3·) radicals were measured using the Prague semiconductor millimeterwave spectrometer in the spectral range of 93 – 280 GHz. These radicals are of the atmospherical interest, for example the FCO_2· radical may be produced by stratospheric degradations of HCFCs and HFCs. Both radicals contain one unpaired electron that causes, above all, the fine splitting of the rotational levels into two sublevels.

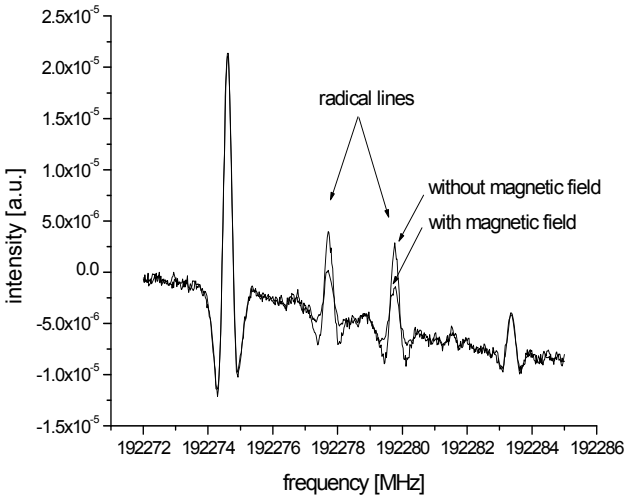

Figure 1: Two traces of measured spectra with and without magnetic field. The radical lines are broadened and lowered because of the molecular Zeeman effect.

Beside this, there are hyperfine interactions due to ^{19}F nucleus that can give rise to an additional hyperfine doubling of levels. The measured rotational spectra with resolved fine and hyperfine structures were analyzed in terms matrix elements of rotational, centrifugal distortion, fine and hyperfine effective Hamiltonians.

Since radicals are generally short-lived species, it is desirable to generate them inside the cell during spectroscopic measurements. In our experiment, the pyrolyses of suitable precursors were used:

$$FC(O)O\text{-}OC(O)F \rightarrow 2\ FCO_2\cdot$$
$$FSO_2O\text{-}OSO_2F \rightarrow 2\ FSO_3\cdot$$

Many transition lines of other molecular species nascent during the pyrolysis were also observed in our spectra. Therefore the identification of the radical lines was supported using an external magnetic field affecting only the radical species by the molecular Zeeman effect. Due to this phenomenon, the radical rotational levels are slightly split and this splitting causes a broadening of the radical line only. As a result of this broadening, the peak heights corresponding to the spectral lines measured using the frequency modulation in the second harmonic (approximately the second differentiation of the signal) are measurable decreased for the radical lines only while the non-radical lines are unaffected by the magnetic field (see Figure 1).

From measured and assigned transition frequencies, the several sets of rotational, centrifugal distortion, fine and hyperfine constants were derived for both the radicals. In the case of the fluoroformyloxyl (FCO_2·) radical, both reduction schemes of the rotation fine Hamiltonian were successfully tested [1] and the results obtained are in excellent agreement with theoretical considerations [2]. Although the asymmetry factor of the FCO_2· is $\kappa = 0.35$, the best fit of the experimental transition frequencies was obtained using the matrix elements derived from the ***s***-reduced Hamiltonian.

Both the radicals have identical oxygen nuclei, bosons, with the zero nuclear spin. Two as well as three 16 oxygen nuclei make possible only one the spin oxygen function and from this follows that the part of rotational states is forbidden by the Pauli Exclusion Principle. In the case of the FCO_2· radical, which is a C_{2v} asymmetric top with the B_2 rovibronic ground state, only the rotational states with the odd K_a (symmetries B_1 for K_c odd or B_2 for K_c even) are allowed in vibrational ground state. In the case of the C_{3v} symmetric top fluorosulfate (FSO_3·) radical, the rovibronic ground state has the A_2 symmetry and therefore only the rotational states of A_1

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or A_2 symmetries are allowed in vibrational ground state corresponding to $K = 0, 3, 6, \ldots$ states (see Fig. 2).

Spectral features observed for both the radical can serve as a textbook example of the spin statistic and the Pauli Exclusion Principle. From this point of view, the additional measurements of rotational transitions are extremely interesting in excited vibrational states of B_1 or B_2 and E symmetries for FCO_2· and FSO_3·, respectively, since the transitions excluded in the ground state are allowed in these excited states and oppositely, the observed ground state transitions are forbidden in these upper states.

An interesting feature observed in the fluorosulfate (FSO_3·) radical rotational spectra was a significant A_1-A_2 splitting that is manifested by a measurable doubling of $K = 3$ transitions. This relatively large splitting indicates that the fluorosulfate radical is most probably a quasispherical symmetric top. The analysis of the A_1-A_2 splitting made possible to determine the effective h_3 splitting constant and its N-dependence.

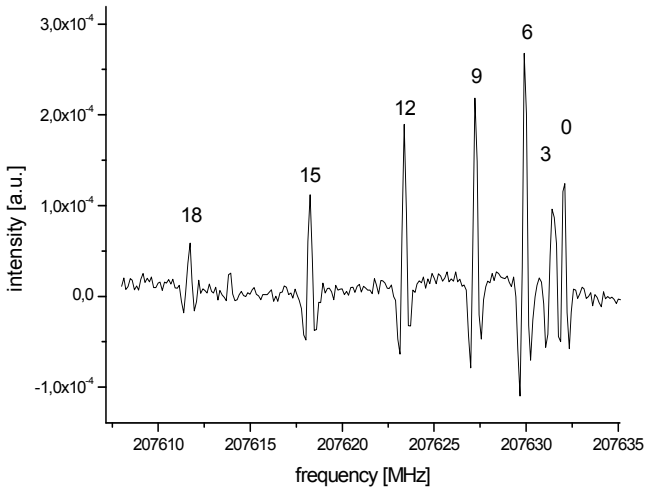

Figure 2: A rotational sequence for N" = 19 for the lower fine component (J = 19.5) of the fluorosulfate (FSO_3·) radical with rotational transitions with K=0, 3 6, …18. The K = 3 line is broadened because of the A_1-A_2 splitting (see text).

While the analysis of the FCO_2· radical frequencies enabled to determine a set of precise rotational, centrifugal distortion, fine and hyperfine parameters where the hyperfine part involves parameters of the ^{19}F nuclear spin-rotational and nuclear spin – electron spin (dipolar as well as Fermi contact term) magnetic interactions, in the case of the fluorosulfate radical the ^{19}F hyperfine effects are nearly negligible and only a nuclear spin – electron spin parameter was determined.

The microwave assignments and analysis of the fluorosulfate radical (FSO_3·) spectra were performed for the first time.

ACKNOWLEDGMENTS

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