

Fourier Transform Microwave Spectroscopy of CF<sub>3</sub>SF<sub>5</sub>  
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We have investigated trifluoromethylsulfur pentafluoride CF<sub>3</sub>SF<sub>5</sub> by Fourier transform microwave spectroscopy in order to determine the twelve-fold potential barrier to internal rotation in this molecule and have found the  $V_{12}$  value to be close to zero. Relaxation among internal-rotation and overall-rotation levels was found inhomogeneous, resulting in distributions quite different from thermal in low-temperature molecular beam, much affecting thermodynamic properties of the molecule. Spectra of the <sup>13</sup>C and <sup>34</sup>S species were also observed in natural abundance, leading to the  $r_s$  C-S bond length of 1.8808 (7) Å.

### 1. Introduction

CF<sub>3</sub>SF<sub>5</sub> has been attracting much attention because of its unusually large global warming potential. It was subjected by Kisliuk and Silvey to a microwave spectroscopic study to confirm that the molecule was really a symmetric top with the rotational constant  $B = 1097.6$  (4) MHz.<sup>1)</sup> Infrared and Raman spectroscopic investigations and electron diffraction experiments all indicated that the internal rotation was of low barrier, as presumed by the potential function being of as high symmetry as 12-fold. The present study primarily aims at detailed clarification of the internal rotation in CF<sub>3</sub>SF<sub>5</sub>.

### 2. Experimental

A sample of CF<sub>3</sub>SF<sub>5</sub> was purchased from SynQuest Labs. Inc. and was used without any further purification. CF<sub>3</sub>SF<sub>5</sub> was diluted with either Ar or Ne to 0.5% and was introduced in the chamber of a FTMW spectrometer through a pulsed nozzle at the backing pressure of approximately 100 kPa. The relative intensities of the rotational transitions of CF<sub>3</sub>SF<sub>5</sub> diluted by Ar were not much different from those recorded using Ne in place of Ar.

### 3. Observed spectra, assignment, and analysis

We have scanned the frequency regions where we expected to observe  $J+1 \leftarrow J$  rotational transitions of  $J = 1$  to 9, based upon the  $B$  rotational constant reported by Kisliuk and Silvey, and have observed a large number of lines centered at multiples of  $2B$ . Most of them form series, as shown in Fig.1 by the observed frequencies divided by  $2(J+1)$  and plotted against  $J$ . We have noticed that there are three pairs of prominent lines, two component lines of which are nearly symmetrically displaced each other from the central clusters of lines; the three pairs are identified by A, B, and C.

We have employed a symmetric-top rotational Hamiltonian with some Kivelson's centrifugal terms: Eqs. (1) and (2) and products of free internal-rotation  $|m\rangle$  and symmetric-top rotational  $|J, k\rangle$  wavefunctions as bases [abbreviated as  $(m, k)$ ]. We have taken into account interaction Hamiltonians Eqs. (3)-(5), as shown below, and have assigned A series to  $(m, k) = (3, 1)_{\pm}$  [ $B_1/B_2$  symmetry] and B series to  $(m, k) = (3, -1)_{\pm}$  [ $A_1/A_2$  symmetry], and tentatively ascribed C series to  $(m, k) = (6, 0)_{\pm}$  [ $B_1/B_2$  symmetry]. These three series are split in the first order. The C series showed anomalous  $J$  dependence of the intensity, which is probably

caused by relaxation inhomogeneously taking place among internal-rotation and overall-rotation energy levels. The Hamiltonians used are

$$H_0 = BJ^2 + (A - B)J_z^2 + F(p - \rho J_z)^2 + \frac{V_{12}}{2}(1 - \cos 12\alpha) \quad (1)$$

$$H_1 = J^2[G(p - \rho J_z)^2 + L(p - \rho J_z)J_z - D_{JK}J_z^2 - D_JJ^2 + U_{12}(1 - \cos 12\alpha)] \quad (2)$$

$$H_3 = U_3[e^{3i\alpha}J_{g+} + e^{-3i\alpha}J_{g-}] \quad (3)$$

$$H_6 = e^{6i\alpha}[U_{6A}J_{g+}^2 + U_{6B}J_{g-}^2] + e^{-6i\alpha}[U_{6B}J_{g+}^2 + U_{6A}J_{g-}^2] \quad (4)$$

$$H_{12} = i[V_{12a} + U_{12a}J^2](e^{12i\alpha} - e^{-12i\alpha})J_z \quad (5)$$

It is quite difficult to assign the central cluster lines. Most of the “lines” probably consist of several component lines barely resolved one another. We have noticed that the frequencies of the series labeled as c-h, c-l, 3l1, 3l2, and 2l1 in Fig.1 are closely fit to the expression:  $f_0 + f_1 n^2$ , where  $n = 0, 1, 2, 3$ , and 4, respectively, and the running number  $n$  may be identified as either  $k$  or  $m$ ,  $k$  being more reasonable than  $m$ .

We have also searched and assigned spectra of  $^{13}\text{C}$  and  $^{34}\text{S}$  isotopic species in natural abundance. The rotational constants thus determined for the two isotopic species are 1093.6564 (37) and 1095.4166 (9) MHz, which lead to the  $r_s$  value of C-S: 1.8808 (7) Å. This value may be compared with the  $r_a$  1.887 (8) Å reported by Marsden *et al.*<sup>2)</sup>

The present study determined the internal-rotation potential barrier  $V_{12}$  to be small: -0.211 (97)  $\text{cm}^{-1}$ ; the internal rotation in  $\text{CF}_3\text{SF}_5$  is essentially free, as expected. The negative sign of  $V_{12}$  means that the equilibrium conformation is staggered. The DFT molecular parameters obtained by present quantum chemical calculations, agreed with those reported previously.<sup>3)</sup> Molecular constants calculated were compared with the present results. The  $V_{12}$  obtained by MP2/6-311++G(d, p) was in much closer agreement with the observed than those by DFT.

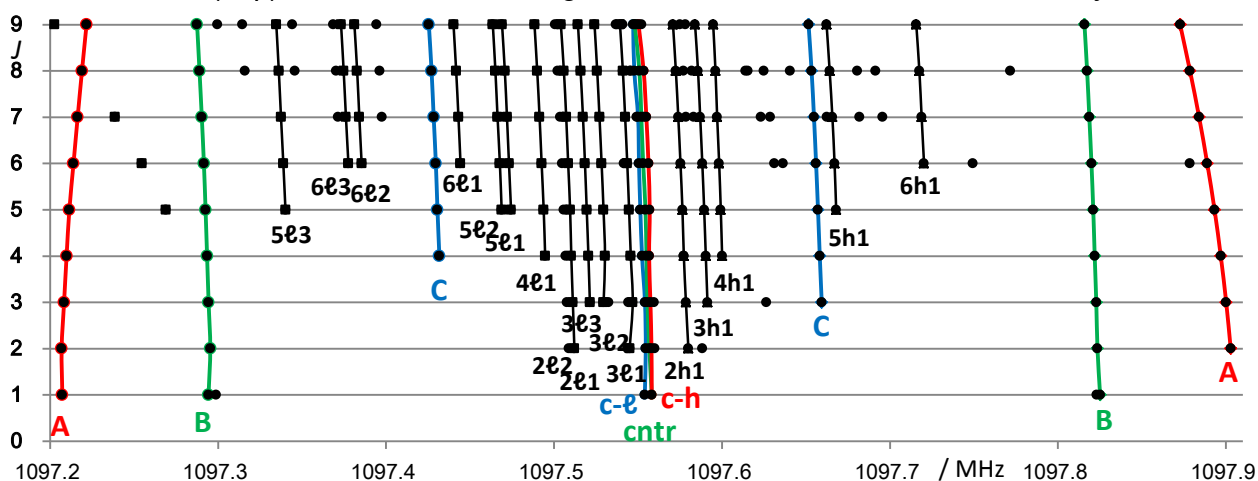


Fig. 1 Observed frequencies of the transitions from  $J = 2 \leftarrow 1$  up to  $10 \leftarrow 9$ , divided by  $2(J+1)$   
References <sup>1)</sup> P. Kisliuk and G. A. Silvey, *J. Chem. Phys.* 20 (1952) 517. <sup>2)</sup> C. J. Marsden, *et al. J. Mol. Struct.* 131 (1985) 299. <sup>3)</sup> W. Xu, *et al. Mol. Phys.* 102 (2004) 1415.