Contribution from the Department of Chemistry,
University of Wisconsin, Madison, Wisconsin 53706

The Geometry of CF_3PF_4 from Its Microwave Spectrum[1]

By Edward A. Cohen and C. D. Cornwell

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An investigation of the microwave rotational spectrum of CF_3PF_4 has been undertaken to determine the geometry of the molecule and the barrier to internal rotation of the CF_3 group. We wish to report our conclusions about the structure and a preliminary characterization of the barrier.

The plausible models of CF_3PF_4 would give rise to easily distinguishable rotational spectra. Each model may be classified by the symmetry of the PF_4 *framework*, which may be C_{2v}, C_{3v}, or C_{4v}. The first two are formed by equatorial and axial substitution in the PF_5 trigonal bipyramid. The last may be derived by distortion of the C_{2v} model or by axial substitution in a C_{4v} model of PF_5.

Symmetric rotor transitions $J \leftarrow J - 1$, accompanied by torsional and other vibrational satellites, were observed for $J = 4$, 6, 7, 8, 9, and 11. Lines from up to five excited torsional states were recorded. These had the nearly even spacing characteristic of transitions of excited states of a slightly anharmonic oscillator. The ground-state rotational constant and torsional frequency (the latter determined from relative intensities) are $B = 1183.026 \pm 0.001$ MHz and $\nu = 75 \pm 14\ \text{cm}^{-1}$.

The C_{2v} model or any other of lower framework symmetry cannot account for this spectrum, as it is certainly not that of an asymmetric rotor. The relative intensities and spacing of satellite lines are incompatible with the C_{4v} model: The latter would have a 12-fold barrier to internal rotation, and for the given torsional frequency only one excited state would be within the potential well.[2] The resulting satellite pattern would then not show the regularity in spacing found in the observed spectrum.

On the other hand, the spectrum is completely consistent with that expected[3] for the C_{3v} model with a threefold barrier to internal rotation of 5.0 ± 1.5 kcal/mole. Moreover, the rotational constant is in good agreement with that predicted for this model with parameters taken from CH_3PF_4[4] and CF_3I.[5]

We conclude that the CF_3PF_4 molecule which gives rise to the spectrum described has the C_{3v} structure. This is the structure favored by Muetterties, Mahler, and Schmutzler[6] on the basis of the nmr spectrum, although the latter does not provide definitive evidence, because of rapid averaging effects.

On the other hand, Griffiths,[7] from a study of the gas-phase infrared spectrum, has concluded that the framework symmetry is probably C_{2v}, and is certainly not C_{3v}. In order to see whether the discrepancy might be due to a difference in samples, we have examined both the microwave and the infrared spectra of a single sample of CF_3PF_4. The microwave spectrum was found to be the same as that described above. The gas-phase infrared spectrum of this sample, observed at 5 mm pressure over the range 500–1300 cm^{-1}, agrees completely with that reported by Griffiths. We must conclude that the apparent discordance between the infrared and microwave structural evidence is not due to a difference in samples.

Although it is clear that we have observed the microwave spectrum of a C_{3v} form of CF_3PF_4, we cannot rule out the possibility that other forms are present. The region searched was sufficient to include major features of the spectrum of any other plausible isomer. However, a C_{2v} form would be expected to have a low sixfold barrier, in which case its spectrum would be weakened by being split into a large number of lines, and so might have escaped detection.

Experimental Section

Most of the microwave measurements were made in this laboratory on a sample prepared by Dr. Mahler.[8] The sample was checked by mass spectroscopic analysis (CF_3^+, PF_4^+) after it had been received by us. The symmetric-top microwave lines attributed to CF_3PF_4 are fairly strong at −78°, the temperature at which the measurements were made.

We also observed a second set of lines, due to an asymmetric top, which grew slowly while the symmetric-top lines diminished in intensity. The asymmetric-top lines were shown to be due to CF_3POF_2, the identification being based on (1) mass spectroscopic analysis of a sample taken from the wave guide after it had reacted (CF_3^+, POF_2^+) and (2) comparison of the microwave spectrum with that of a known sample of CF_3POF_2. Preliminary analysis of the spectrum gave $A - [(B + C)/2] = 1064$ MHz, $(B - C) < 100$ MHz, consistent with model calculations for CF_3POF_2. With precautions taken to exclude moisture from the sample cell, the symmetric-top spectrum was stable for hours.

The additional observations made with the object of clarifying the discrepancy between the infrared and microwave results were performed by E. A. C. at the University of Southern California. The CF_3PF_4 sample for these observations was prepared by Dr. Sinclair and Professor Burg, and the known CF_3POF_2 sample was provided by Dr. Griffiths.

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(2) For an N-fold cosine barrier, the barrier height V_N is related to the zero-amplitude torsional frequency ν by $FV_N = (\nu/N)^2$ where F is the reduced reciprocal moment of inertia for the internal top, approximately 0.312 cm^{-1}. See eq 4, 5, and 12 of D. R. Herschbach, *J. Chem. Phys.*, **31**, 91 (1959). F, V_N, ν are in cm^{-1}.

(3) D. Kivelson, *ibid.*, **22**, 1733 (1954).

(4) L. S. Bartell and K. W. Hansen, *Inorg. Chem.*, **4**, 1777 (1965).

(5) J. Sheridan and W. Gordy, *J. Chem. Phys.*, **20**, 591 (1952).

(6) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).

(7) J. E. Griffiths, private communication.

(8) W. Mahler, *Inorg. Chem.*, **2**, 230 (1963).