

MICROWAVE SPECTRUM OF DEUTERATED *TRANS*-3-FLUOROPHENOL

A. I. JAMAN, N. CHATTERJEE and D. K. GHOSH

Saha Institute of Nuclear Physics, 92, Acharya Prafulla Chandra Road, Calcutta 700 009 (India)

(Received 23 July 1981; in final form 1 October 1981)

ABSTRACT

The microwave spectrum of deuterated 3-fluorophenol, 3-FC₆H₄OD, has been observed in the frequency ranges 12.5–18.0 GHz (*KU* band) and 21.5–25.0 GHz (*K* band) in the ground vibrational state at room temperature. Analysis yields three rotational and five quartic centrifugal distortion constants: $\bar{A} = 3742.943 \pm 0.029$, $\bar{B} = 1737.449 \pm 0.017$, $\bar{C} = 1186.728 \pm 0.016$, $d_J = (7.383 \pm 2.0) \times 10^{-4}$, $d_{JK} = (-13.756 \pm 3.191) \times 10^{-3}$, $d_K = (-17.814 \pm 4.298) \times 10^{-3}$, $d_{WJ} = (-4.0 \pm 1.0) \times 10^{-7}$, $d_{WK} = (9.3 \pm 2.2) \times 10^{-6}$ (in MHz). From a consideration of the r_s coordinate of the H atom in the OH group, the present analysis leads to the assignment of the observed spectrum to the *trans* conformer of the molecule. An r_0 structure satisfying the rotational constants of both the parent and the deuterated species is proposed. The small value of the inertia defect, $\Delta = -0.0368$, confirms the planarity of the molecule.

INTRODUCTION

Rotational isomers of organic compounds have been extensively studied by microwave spectroscopy leading to their conformational analysis, evaluation of barrier heights and energy differences. Investigations of the rotational spectra of phenol by Kojima [1], Forest and Dailey [2], Quade [3], Mathier et al. [4] and Larsen et al. [5] led to its substitution structure and revealed that the OH group undergoes hindered internal rotation with respect to the benzene ring. Hence, one would expect there to be two distinct conformers, *cis* and *trans*, in unsymmetrically substituted phenols due to the different positions of the H atom of the OH group relative to the substituted atom. Indeed, Pedersen et al. [6] showed the existence of two different rotamers in unsymmetrically substituted deuterated phenol. However, it was not possible for them to distinguish between the *cis* and *trans* conformers. Later, Larsen [7] solved the *cis/trans* problem with complete substitution studies and determined the absolute direction of the dipole moment.

Asymmetrically substituted fluorinated phenol should, in principle, behave as a mixture of two rotational isomers. A far-IR study [8] of *meta*-substituted fluorinated phenol predicted the existence of *cis* and *trans* conformers. Onda et al. [9, 10] have so far been able to detect the *cis* conformer of 2-chlorophenol. We have reported [11] an analysis of the microwave spectrum of the parent species of 3-fluorophenol in which we proposed

that the bands should be attributed to the *trans* conformer and showed that the compound behaves as a conventional planar molecule. In order to establish the planarity of the molecule and to remove the ambiguity in conformational analysis, an investigation of the deuterated species of 3-fluorophenol was undertaken. The microwave spectrum is analysed here. Using the r_s coordinate of the H atom in the OH group, the *trans* conformation of the molecule is confirmed. In addition, an r_0 structure of the *trans* conformer is proposed.

EXPERIMENTAL

Deuterated 3-fluorophenol was obtained by conventional exchanging of the normal sample (Aldrich Chemical Co.) with D_2O . The mixture was dried over anhydrous P_2O_5 for a few days after removing the excess D_2O and distilled under vacuum. Microwave spectra were observed with a 100-kHz Stark modulation microwave spectrometer in the frequency ranges 12.5–18.0 GHz (*KU* band) and 21.5–25.0 GHz (*K* band) at room temperature. D_2O vapour was injected into an absorption cell which was evacuated for several hours prior to injection of the sample. The sample pressure was maintained at around 10^{-2} mmHg during measurements and the Stark voltage at around 300 V cm^{-1} . The maximum experimental error in the frequency measurement was estimated to be ± 0.2 MHz.

RESULTS AND ASSIGNMENT

The expected absorption pattern of deuterated *trans* 3-fluorophenol was generated using the rotational constants given in ref. 11 with the exception that the H atom in the OH group was replaced by a D atom. The spectrum was expected to have both *b*-type *Q* branch and *a* and *b*-type *R* branch transitions.

The initial phase of the assignment involved the search for strong *b*-type *Q* branch lines (with high *J*) in the vicinity of the predicted frequencies. A least-squares analysis using different combinations of these lines was performed in order to obtain a set of $(A - C)/2$ and κ values. One such set using three of the most intense lines resulted in a fit which successfully predicted all other observed lines in the *KU* and *K* bands within experimental error. The intensities of the observed lines were consistent with the calculated transition strengths in both the *K* and *KU* bands. A least-squares analysis of all the observed *Q* branch lines gave a statistically meaningful estimate of $(A - C)/2$ and κ . The values of $(A - C)/2$ and κ predict the separation of the *R* branch lines at a given value of *J*. Selection of a sufficient number of *R* branch lines with the correct frequency separation completed the assignment.

In the above analysis the Watson [12] Hamiltonian in the I^F representation was used where $\mathcal{H}_0 = \tilde{A}P_x^2 + \tilde{B}P_y^2 + \tilde{C}P_z^2$ is the rigid-rotor Hamiltonian.

$$\mathcal{H} = \mathcal{H}_0 - d_J(J^2)^2 - d_{JK}J^2J_z^2 - d_KJ_z^4 - d_{WJ}\mathcal{H}_0J^2 - d_{WK}\mathcal{H}_0J_z^2$$

A total of 48 transitions involving rotational states up to $J = 28$ were measured and used in the least-squares analysis for evaluating the eight parameters \bar{A} , \bar{B} , \bar{C} , d_J , d_{JK} , d_K , d_{WJ} and d_{WK} . The standard deviation of the overall fit [13] was 0.31, similar to the experimental error. Most of the observed and calculated frequencies agreed to within ± 0.35 MHz. The contribution to the centrifugal distortion parameters was found to be significant for transitions involving rotational states $J > 11$. The observed transition frequencies, obs. — calc. values and centrifugal distortion corrections can be obtained from B.L.L.D. as Supplementary Publication No. SUP26213 (3 pages). The associated rotational and centrifugal distortion constants and their respective error limits are given in Table 1. The relatively large error limits for d_{WJ} and d_{WK} are due to the very slight dependence of these parameters on the measured transitions. It should be noted that the centrifugal distortion corrections obtained must be added to the rigid-rotor frequencies, with the sign convention shown in the supplementary material, to reproduce the observed transition frequencies.

MOLECULAR STRUCTURE

The small value of the inertial defect, $\Delta = -0.0368$, for the deuterated species of 3-fluorophenol confirms the planarity of the molecule. This value of Δ is more negative than that of the non-deuterated species (-0.0121), a feature which generally arises from an out-of-plane motion [14], in this case the OH torsion.

Using the rotational constants of the two measured species of the molecule, it is a straightforward matter to obtain the absolute values for the coordinates of the H atom of the OH group by application of Kraitchman's equations [15]. However, due to the lack of available data, we decided to propose an r_0 structure which would reproduce with reasonable accuracy both the derived rotational constants of the two species as well as the coordinates of the H atom, calculated as indicated above. Thus, we considered

TABLE 1

Rotational and centrifugal distortion constants of *trans*-3-FC₆H₄OD (in MHz)

\bar{A}	$= 3742.943 \pm 0.029$
\bar{B}	$= 1737.449 \pm 0.017$
\bar{C}	$= 1186.728 \pm 0.016$
d_J	$= (7.383 \pm 2.0) \times 10^{-4}$
d_{JK}	$= (-13.756 \pm 3.191) \times 10^{-3}$
d_K	$= (-17.814 \pm 4.298) \times 10^{-3}$
d_{WJ}	$= (-4.0 \pm 1.0) \times 10^{-7}$
d_{WK}	$= (9.3 \pm 2.2) \times 10^{-6}$

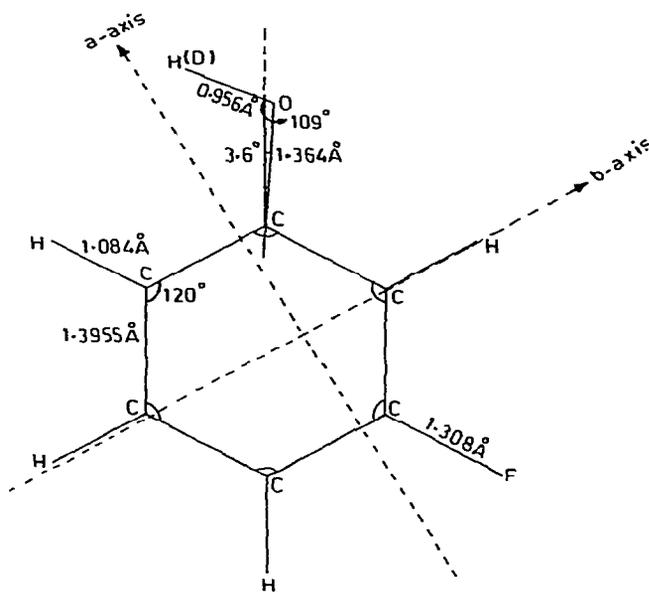


Fig. 1. r_0 Structure of *trans*-3-fluorophenol.

the r_0 structure proposed earlier for the parent species [11] and varied the COH angle and the angle of tilt of the CO bond until we found the best combination of these parameters. It was found, in practice, that only a small increase (0.1°) in the angle of tilt was required to obtain satisfactory reproduction of the rotational constants of the two species and reasonable coordinates for the H atom. The proposed structure is shown in Fig. 1. Table 2 lists the observed and calculated principal moments of inertia for both the parent and deuterated species. The principal axis coordinates of the H atom are given in Table 3. The agreement between the observed and calculated values provides strong evidence in favour of the *trans* conformer of the molecule.

TABLE 2

Principal moments of inertia^a (amu Å²)

	<i>trans</i> -3-FC ₆ H ₄ OH			<i>trans</i> -3-FC ₆ H ₄ OD ^c		
	Obs. ^b	Calc. ^d	Obs. - calc.	Obs.	Calc. ^d	Obs. - calc.
I_a	134.8627	134.8921	-0.0294	135.0624	135.1053	-0.0429
I_b	281.2079	281.1532	0.0547	290.9616	290.9686	-0.0070
I_c	416.0585	416.0453	0.0132	425.9872	426.0739	-0.0867
$\Delta = (I_c - I_a - I_b)$	= -0.0121			= -0.0368		

^aConversion factor 505 531 MHz amu Å². ^bRef. 11. ^cThis work. ^dCalculated using the r_0 structure shown in Fig. 1.

TABLE 3

Principal axis coordinates (A) of the substituted H atom

	Obs. ^a	Calc. ^b
a_H	3.124	3.164
b_H	0.462	0.473

^aObtained from Kraitchman's equations. ^bObtained from the r_0 structure shown in Fig. 1.

ACKNOWLEDGEMENTS

We thank Drs. A. Chatterjee and R. N. Nandi for helpful and stimulating discussions. One of us (A. I. J.) thanks the Director, S.I.N.P. for the award of a Research Fellowship.

REFERENCES

- 1 T. Kojima, *J. Phys. Soc. Jpn.*, 15 (1960) 284.
- 2 H. Forest and B. P. Dailey, *J. Chem. Phys.*, 45 (1966) 1736.
- 3 C. R. Quade, *J. Chem. Phys.*, 47 (1967) 1073.
- 4 E. Mathier, D. Welti, A. Bauder and Hs. H. Gunthard, *J. Mol. Spectrosc.*, 37 (1971) 63.
- 5 N. W. Larsen, E. Mathier, A. Bauder and Hs. H. Gunthard, *J. Mol. Spectrosc.*, 47 (1973) 183.
- 6 T. Pedersen, N. W. Larsen and L. Nygaard, *J. Mol. Struct.*, 4 (1969) 59.
- 7 N. W. Larsen, *J. Mol. Struct.*, 51 (1979) 175.
- 8 W. G. Fateley and F. A. Miller, 9th European Congress on Molecular Spectroscopy, Madrid, Spain, 1967, p. 131; A. S. Manocha, G. L. Carlson and W. G. Fateley, *J. Phys. Chem.*, 77 (1973) 2094.
- 9 M. Onda, Y. Oshima and I. Yamaguchi, *Bull. Chem. Soc. Jpn.*, 51(1) (1978) 65.
- 10 M. Onda and I. Yamaguchi, *Bull. Chem. Soc. Jpn.*, 51 (11) (1978) 3121.
- 11 A. I. Jaman, R. N. Nandi and D. K. Ghosh, *J. Mol. Spectrosc.*, 86 (1981) 269.
- 12 J. K. G. Watson, *J. Chem. Phys.*, 46 (1967) 1935.
- 13 W. H. Kirchhoff, *J. Mol. Spectrosc.*, 41 (1972) 333.
- 14 D. R. Herschbach and V. W. Laurie, *J. Chem. Phys.*, 40 (1964) 3142.
- 15 J. Kraitchman, *Am. J. Phys.*, 21 (1953) 17.