

Microwave spectrum of *cis* 3-fluorophenol

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Abstract. The microwave spectrum of *cis* 3-fluorophenol involving rotational states up to $J = 28$ has been observed and analysed in the frequency range 23–25 GHz in the ground vibrational state at room temperature. Analysis yields three rotational and five quartic centrifugal distortion constants. A tentative r_0 structure has been proposed satisfying the observed rotational constants. The small value of the inertia defect $\Delta = 0.07$ confirms the planarity of the conformer.

Keywords. Microwave spectroscopy; rotational isomer; *cis* 3-fluorophenol.

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1. Introduction

In the earlier communications (Jaman *et al* 1981, 1982) the analysis of the microwave spectrum of the parent and the deuterated species of *trans* 3-fluorophenol has been reported. 3-Fluorophenol, being an asymmetrically substituted fluorinated phenol, should exhibit another planar stable *cis* conformer. From a far IR spectrum analysis of 3-fluorophenol in the gas phase in the region $350\text{--}150\text{ cm}^{-1}$ Manocha *et al* (1973) have calculated the barrier hindering the internal rotation of the OH group around the C–O bond and concluded that the *cis* form is more stable by 84.5 cm^{-1} than its *trans* counterpart. However, dipole moment components obtained from bond moment calculations (Jaman *et al* 1981) indicated relatively smaller μ_a and μ_b values for the *cis* conformer. As a result, the transitions corresponding to the *cis* form are expected to be weaker. In the present communication, we report the results of the microwave spectroscopic investigation of the *cis* conformer of 3-fluorophenol in the ground vibrational state and propose a tentative r_0 structure satisfying the observed rotational constants.

2. Experimental

The spectrum was observed at room temperature with a conventional 100 kHz Stark modulated microwave spectrometer. Measurements were made at sample pressure around 10^{-2} mm Hg and Stark voltage around 200 V cm^{-1} with phase sensitive detection. The maximum experimental error in the frequency measurement was estimated to be around ± 0.2 MHz.

3. Assignment and results

The observed transition frequencies have been assigned using the same method described earlier (Jaman *et al* 1981, 1982). During the analysis the Watson (1967)

Hamiltonian in the I' representation has been used throughout. A total of 24 transitions involving rotational states up to $J = 28$ have been 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 (Kirchhoff 1972) comes out to be 0.25 which is of the order of experimental error. The observed transition frequencies are given in table 1. The associated rotational and centrifugal distortion constants, their respective error limits and the correlation matrix are listed in table 2. The small value of the inertia defect $\Delta = 0.07$ indicates that the *cis* conformer also behaves as a conventional planar molecule.

Table 1. Observed rotational transitions of *cis* 3-fluorophenol in the ground vibrational state (in MHz).

J'	Transitions					Observed frequency	Obs.-Cal.
	K'_{-1}	K'_{+1}	J	K_{-1}	K_{+1}		
8	1	7	7	1	6	23491.00	-0.38
8	3	6	7	3	5	24342.43	0.42
8	4	5	7	4	4	24732.35	0.24
8	5	3	7	5	2	24664.54	-0.23
8	6	3	7	6	2	24526.00	-0.03
8	6	3	8	5	4	24659.32	0.42
9	0	9	8	0	8	23162.86	-0.10
9	0	9	8	1	8	23134.10	0.15
9	2	7	8	3	6	23843.45	-0.05
10	6	5	10	5	6	24334.14	-0.41
11	1	10	11	0	11	24623.26	0.37
11	2	10	11	1	11	24707.02	-0.31
11	6	6	11	5	7	24163.86	-0.08
11	6	5	11	5	6	23486.36	-0.30
12	2	10	12	1	11	23077.29	-0.30
12	3	10	12	2	11	23713.24	-0.04
14	3	11	14	2	12	23378.78	0.32
14	6	9	14	5	10	24238.60	0.28
21	6	15	21	5	16	24049.57	0.01
21	8	13	21	7	14	24459.57	0.26
24	7	17	24	7	18	23494.71	-0.09
26	9	17	26	8	18	24088.57	-0.27
27	9	18	27	8	19	23701.57	-0.01
28	9	19	28	8	20	24585.99	0.14

Table 2. Rotational and centrifugal distortion constants of *cis* 3-fluorophenol (in MHz) and correlation matrix.

\bar{A}	3789.57 ± 0.06	1.000								
\bar{B}	1795.15 ± 0.06	0.816	1.000							
\bar{C}	1217.89 ± 0.05	0.974	0.852	1.000						
$d_J \cdot 10^3$	-3.68 ± 0.42	0.912	0.623	0.808	1.000					
$d_{JK} \cdot 10^3$	4.42 ± 2.31	0.282	0.389	-0.310	0.868	1.000				
$d_K \cdot 10^3$	11.00 ± 3.68	0.234	0.444	-0.339	0.978	0.433	1.000			
$d_{wJ} \cdot 10^7$	2.00 ± 1.00	0.300	0.902	0.361	0.981	0.949	-0.308	1.000		
$d_{wK} \cdot 10^6$	-3.20 ± 1.60	-0.279	-0.824	-0.392	0.315	-0.982	-0.983	-0.999	1.000	

4. Molecular structure

The analysis of the deuterated species was temporarily abandoned due to the very poor line intensities. Although no data are available for the isotopic species at present, a tentative r_0 structure can however be proposed. In order to do this, the ring geometry was assumed to be unchanged and its structural parameters as obtained for the *trans* conformer were held fixed. Since the dependence of the three rotational constants on the COH angle was not found to be pronounced, only the C–O bond length and the angle of tilt were adjusted until a best set of rotational constants resulted. The proposed structure is shown in figure 1. It is to be noted here that the C–O bond length and the angle of tilt comes out to be 1.344 Å and 3.2° respectively which are reduced by 0.02 Å and 0.4° from their respective *trans* conformer values. Table 3 lists the observed and calculated principal moments of inertia values.

Furthermore, from a consideration of the relative intensities of the transitions belonging to the *cis* and *trans* conformers the average energy difference between them was calculated to be around 92 cm^{-1} which is very near to its reported value of 84.5 cm^{-1} (Manocha *et al* 1973).

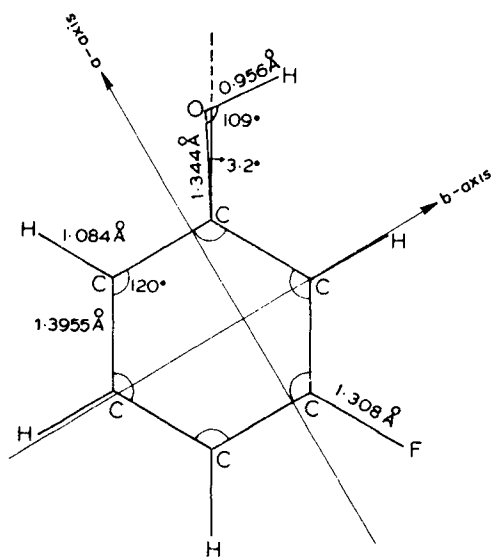


Figure 1. Tentative r_0 structure of *cis* 3-fluorophenol.

Table 3. Principal moments of inertia a of *cis* 3-fluorophenol ($\text{amu } \text{Å}^2$).

	Observed	Calculated	Obs.-Cal.
I_a	133.40	133.44	-0.04
I_b	281.61	281.57	0.04
I_c	415.08	415.01	0.07
Δ^b	0.07		

^a Conversion factor $505531\text{ MHz amu } \text{Å}^2$, ^b $\Delta = I_c - I_a - I_b$.

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