

## Microwave spectrum and dipole moment of pentafluorobenzene

S DORAISWAMY and S D SHARMA  
Tata Institute of Fundamental Research, Bombay 400005

MS received 1 October 1973; after revision 28 January 1974

**Abstract.** With the idea of evaluating the dipole moment of pentafluorobenzene from a low  $J$  transition, its microwave spectrum was investigated in the frequency region of 8,000 to 12,400 MHz. The spectrum had been earlier observed by the authors in the 12,400 to 18,000 MHz region which needs reassignment in the light of present investigations. The rotational constants are  $A = 1480.856 \pm 0.003$  MHz,  $B = 1030.066 \pm 0.003$  MHz and  $C = 607.496 \pm 0.002$  MHz. The dipole moment is  $1.44 \pm 0.05$  D.

**Keywords.** Microwave spectrum; pentafluorobenzene; dipole moment.

### 1. Introduction

The microwave spectrum of pentafluorobenzene was first reported in 1968 by the authors (Doraiswamy and Sharma 1968) in the frequency region of 12,400 to 18,000 MHz. At that time the dipole moment measurement from some convenient low  $J$  transitions was postponed because the set-up in the 8,200 to 12,400 MHz range, where those transitions are expected, was not available. Recently a search for the  $J = 3 - 2$  transitions in the lower frequency region was made and the lines could not be located at the positions predicted on the basis of the parameters reported earlier. This prompted us to reinvestigate the spectra.

Since very strong high  $J$  ( $J > 24$ ), Q-branch lines were few in the 8,000 to 10,000 MHz region, they were first identified using a computer programme (Sharma 1972). A search was later made for the low  $J$ , R-branch transitions from the expected spectrum by observing their Stark patterns. Unfortunately the lines were weak and the Stark effect was not helpful for identification. However, two R-transitions of sufficient intensity [ $7(0, 7) - 6(1, 6)$  and  $7(1, 7) - 6(0, 6)$ ] having a separation of 1.5 MHz provided the hint for a suitable identification. These two lines were first assigned after a careful search around the predicted region. Based on this assignment other R lines were readily identified.

### 2. The spectrum and rotational constants

It was possible to observe almost all the low  $J$  transitions of reasonable intensity. Some of the R and Q branch transitions are listed in table 1a along with the differences between the observed and calculated frequencies. The rotational constants and the corresponding moments of inertia are listed in table 2. A small

Table 1 b. Microwave spectrum of pentafluorobenzene

J	Transition		Observed frequency MHz	Calculated frequency MHz
	$K_{-1}$	$K_1$		
9	1	8	12759.68	12759.77
9	2	7	12764.84	12764.87
10	0	10	12757.70	12757.71
10	2	8	15188.75	15188.97
10	3	7	16219.50	16219.52
10	4	6	16758.72	16758.71
10	4	6	16060.00	16059.92
11	2	10	15190.20	15190.33
11	2	9	16411.76	16411.92
12	0	12	} 15187.80	15187.59
12	1	12		
12	2	10	} 12530.5	12529.70
12	3	10		
17	7	11	12869.6	12869.6
18	12	6	13033.9	13033.91
19	7	12	13677.7	13677.08
20	7	14	16670.4	16669.77
21	12	10	12565.8	12566.27
23	10	14	15663.2	15663.71
24	14	11	14540.5	14539.79
25	10	15	16324.7	16325.36
26	12	15	16151.6	16151.63
27	16	11	16102.7	16102.67
28	15	14	15364.6	15365.54
29	13	16	14965.0	14965.87
30	13	17	17042.8	17043.31
32	15	17	13878.6	13879.08
34	19	15	17503.6	17504.14
36	19	17	13981.3	13981.37

Table 1 a. Microwave transitions of pentafluorobenzene

J	Transition		Observed frequency (MHz)	$\nu_{\text{obs}} - \nu_{\text{calc}}$ (MHz)
	$K_{-1}$	$K_1$		
3	3	1	8134.62	0.10
3	3	0	8383.07	0.15
4	4	1	11179.34	0.10
4	4	0	11254.10	0.15
5	2	4	8215.18	0.07
6	2	5	9241.32	-0.05
6	3	4	11276.04	0.10
7	0	7	9112.39	-0.01
7	1	7	9113.95	-0.03
7	1	6	10303.52	-0.13
7	2	6	10373.07	-0.18
7	2	5	11118.03	0.07
8	1	7	8999.81	-0.07
8	0	8	10327.72	-0.07
8	2	7	11559.28	-0.01
9	2	7	8832.43	-0.02
9	3	7	8860.95	-0.10
9	8	2	9194.38	-0.01
9	8	1	9178.10	-0.11
9	0	9	11542.81	0.03
10	1	9	11439.63	0.03
10	2	8	10074.60	-0.03
10	3	7	8550.51	0.07
10	4	7	8686.76	-0.04
10	8	3	9035.64	0.02
10	8	2	8955.95	-0.01
10	9	2	10457.29	-0.03

Standard deviation  $\sigma=0.08$

inertia defect shows that the molecule is essentially planar. The presence of a  $C_{2v}$ -axis in the molecule is demonstrated by the fact that a number of closely spaced doublets showed an intensity ratio of 10:6 as demanded by the nuclear spin statistics (Townes and Schawlow 1955) for symmetric and antisymmetric rotational levels. The entire spectra generated by the rotational constants can be completely observed in both the 8,000 to 12,400 and 12,400 to 18,000 MHz regions. A few of the reassigned transitions reported earlier are shown in table 1 *b*. High  $J$  transitions have been assigned and the centrifugal distortion analysis is in progress. A number of transitions arising due to excited vibrational states have also been observed, and an attempt is being made to assign them.

### 3. Dipole moment

Most of the low  $J$  lines of the R-branch, which could be used for the dipole moment measurements were found in the congested regions of the spectrum. Many of them, as evident from their Stark coefficients, had negligible shift of their Stark lobes at reasonable field strengths. Fortunately  $M = 1$  lobe of the transition 3(3, 1) – 2(2, 0) at 8134.62 MHz happened to be quite convenient and was used to obtain the dipole moment. A molecular orbital calculation using INDO (Dobosh QCPE 142) programme with the molecular geometry of table 5 was also performed to obtain the dipole moment and the results are summarised in table 3. A comparison of the dipole moment of pentafluorobenzene and fluorobenzene shows that there has been an increase in  $\pi$  bond moment. The total dipole moment of 1.66 D of fluorobenzene (Kowalewski *et al* 1959) with its negative end at

Table 2. Rotational constants and moments of inertia of pentafluorobenzene

$A = 1480.856 \pm 0.003$ MHz	$I_a = 341.272_9 \pm 0.0007$ amu $\text{\AA}^2$
$B = 1030.066 \pm 0.003$ MHz	$I_b = 490.624_9 \pm 0.0014$ amu $\text{\AA}^2$
$C = 607.496 \pm 0.002$ MHz	$I_c = 831.900_1 \pm 0.0027$ amu $\text{\AA}^2$
$\kappa = -0.032326$	$\Delta = c - b - I_a = 0.0023$ amu $\text{\AA}^2$
Conversion factor : 505376 MHz amu $\text{\AA}^2$	

Table 3. Dipole moment of pentafluorobenzene (in debyes)

Microwave <sup>a</sup> spectroscopy	Molecular orbital calculations		Dielectric relaxation	
	INDO <sup>b</sup>	CNDO/2 <sup>c</sup>	Cyclo- hexane <sup>d</sup>	Carbon tetra- chloride <sup>e</sup>
$1.44 \pm 0.05^*$	1.94	1.70	1.43 } 1.42 }	1.34

\* Uncertainty is twice the standard deviation.

*a, b* : Present work

*c* : Davies D W 1967, *Mol. Phys.* 13 465

*d* : Farmer D B, Holt A and Walker S 1966 *J. Chem. Phys.* 44 4116

*e* : Smith T W 1966 Ph.D. Thesis and Private Communication from  
Dr G M Brooke

fluorine atom is supposed to consist of (see for example: Sutton 1955, Daudel *et al* 1959 and Emsley and Phillips 1966)  $\sigma$  bond moment (Lide and Mann 1958) of 1.96 D and an opposing  $\pi$  bond moment of 0.3 D. If we assume that the  $\sigma$  bond moments in pentafluorobenzene and fluorobenzene are equal, the total dipole moment of 1.44 D determined by this work leads to an opposing  $\pi$  bond moment of 0.52 D. This large increase in the  $\pi$  bond moment is due to the considerable  $\pi$  donor character of the fluorine atoms. Because of the large uncertainties in the  $\pi$  bond moments the per cent increase in the magnitude of the  $\pi$  bond moment may be different, but the increase of  $\pi$  bond moment is established showing a tendency on the part of fluorine atoms to donate electrons to the ring.

#### 4. Discussion

To our knowledge no work on the structural determination of pentafluorobenzene has been reported. Since the molecule is planar, only two moments of inertia can be used to get information about the structure of the molecule. Assuming that the ring skeleton forms a regular hexagon and the C—F and C—H bonds lie along the angle bisectors of this regular hexagon, there are three unknown parameters namely C—C, C—F and C—H bond lengths. Under this assumption, the

Table 4. Structural possibilities

Assumption	from eq (1)	Using values of cols (1) & (2) with eq (2)	Remarks
I $d_{CF} = 1.327$	$d_{CC} = 1.394$	$d_{CH} = 0.924$	C—H bond length is low compared to the normally accepted value of 1.084 Å
II $d_{CF} = 1.354$	$d_{CC} = 1.370$	$d_{CH} = 1.086$	C—C bond length in the ring is reduced by 0.024 Å
III A $d_{C_2F_2} = d_{C_3F_3} = 1.327$ $d_{CH} = 1.084$	$d_{CC} = 1.394$	$d_{C_4F_4} = 1.308$	Difference in CF bond lengths is high
B	Assuming $d_{C_2F_2} = d_{C_4F_4} \neq d_{C_3F_3} = d_{C_2F_3} \neq d_{C_4F_4}$		
$d_{CH} = 1.084$ $d_{CC} = 1.394$ (a) $d_{C_2F_2} = 1.354$	$d_{C_3F_3} = 1.291$	$d_{C_4F_4} = 1.287$	Difference in CF bond lengths is high
(b) $d_{C_2F_2} = 1.327$	$d_{C_3F_3} = 1.319$	$d_{C_4F_4} = 1.312$	
(c) $d_{C_2F_2} = 1.323$	$d_{C_3F_3} = 1.3225$	$d_{C_4F_4} = 1.3115$	Seems reasonable
C (a) $d_{C_4F_4} = 1.327$	$d_{C_2F_2} = 1.254$ $d_{C_3F_3} = 1.389$	(Solving the two equations simultaneously)	Difference in CF bond lengths is high
(b) $d_{C_4F_4} = 1.354$	$d_{C_2F_2} = 1.139$ $d_{C_3F_3} = 1.495$		
All $d$ values are in Å			

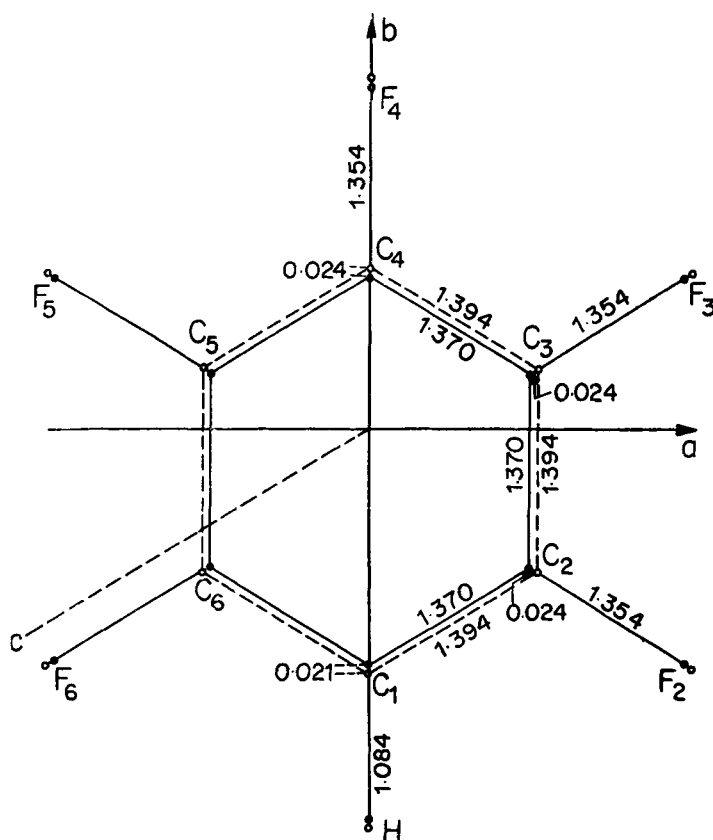


Figure 1. Pentafluorobenzene (dotted figure represents the undistorted benzene skeleton).

expressions for the two moments of inertia are:

$$I_b = 3 [M_c d_{cc}^2 + M_f (d_{cc} + d_{cf})^2] \quad (1)$$

$$I_a = I_b - M_f (d_{cc} + d_{cf})^2 + M_H (d_{cc} + d_{ch})^2 - [M_H (d_{cc} + d_{ch}) - M_f (d_{cc} + d_{cf})]^2 / M \quad (2)$$

where  $M_c$ ,  $M_f$  and  $M_H$  are respectively the masses of carbon, fluorine and hydrogen atoms,  $M$  is the total molecular weight,  $d_{cc}$ ,  $d_{cf}$  and  $d_{ch}$  are the bond distances. In the absence of data from the isotopic species, the structure of the molecule can be discussed only under some assumptions (figure 1). The electron diffraction results for hexafluorobenzene (Almenningen *et al* 1964) were available in 1964 and its structure has again been determined recently by x-ray analysis (Boden and Davis 1973). The results of electron diffraction studies on  $C_6F_6$  are;  $d_{cc} = 1.394 \pm 0.007 \text{ \AA}$  and  $d_{cf} = 1.327 \pm 0.007 \text{ \AA}$  whereas Nygaard *et al.* (1968) from their study on fluorobenzene have deduced that the normal C ( $sp^2$ )-F is around  $1.35 \text{ \AA}$ . (The actual  $d_{cf}$  value in fluorobenzene is  $1.354 \pm 0.006 \text{ \AA}$ ).

Table 4 summarises the various possibilities regarding the structure. Cases I and II assume that all the C—F bond length are equal, while case III assumes that all the C—F bond lengths need not be equal.

Table 5. Positional coordinates of pentafluorobenzene (in Å) in the benzene principal axes system\*

Atom	<i>a</i>	<i>b</i>
C <sub>1</sub>	0·0 (0·0)	-1·3720 (-1·3940)
C <sub>2</sub>	1·1868 (1·2072)	-0·6850 (-0·6970)
C <sub>3</sub>	1·1868 (1·2072)	0·6850 (0·6970)
C <sub>4</sub>	0·0 (0·0)	1·370 (1·3940)
C <sub>5</sub>	-1·1868 (-1·2072)	0·6850 (0·6970)
C <sub>6</sub>	-1·1868 (-1·2072)	-0·6850 (-0·6970)
H	0·0 (0·0)	-2·4560 (-2·4780)
F <sub>2</sub>	2·3594 (2·3798)	-1·3620 (-1·3740)
F <sub>3</sub>	2·3594 (2·3798)	1·3620 (1·3740)
F <sub>4</sub>	0·0 (0·0)	2·7240 (2·7480)
F <sub>5</sub>	-2·3594 (-2·3798)	1·3620 (1·3740)
F <sub>6</sub>	-2·3594 (-2·3798)	-1·3620 (-1·3740)

\* The coordinates in the brackets represent the undistorted benzene skeleton.

Since C—H bond length of 1·084 Å is more or less always constant the possibility II is acceptable where the C—C distance in the ring is reduced by about 0·024 Å. This idea agrees well with the result of Nygaard *et al* on fluorobenzene. The x-ray diffraction results on hexafluorobenzene also give the average C—C distance as  $1·36 \pm 0·02$  Å, much shorter than the electron diffraction value. However, their C—F bond length of  $1·32 \pm 0·017$  Å, although in agreement with the electron diffraction value, is shorter than the C—F value in fluorobenzene.

On the other hand if the C—F distances are assumed to be unequal the only reasonable result seems to be III B (c) of table 4 where the disparity between the various C—F distances is minimum.

If the possibility II of table 4 is agreed upon in which C—F and C—H are taken as 1·354 Å and 1·084 Å respectively then the positional co-ordinates of various atoms of pentafluorobenzene which give the best fit for the observed rotational constants are shown in table 5. Here all the carbon atoms are pushed inside the ring by about 0·024 Å except the C<sub>1</sub> atom which is pushed in by 0·021 Å

## References

- Almenningen A, Bastiansen O, Seip R and Seip H M 1964 *Acta Chim. Scand.* **18** 2115  
 Boden N and Davis P P 1973 *Mol. Phys.* **25** 81  
 Daudel R, Lefebvre and Moser C 1959 *Quantum chemistry, Methods and application* (New York: Interscience) p 211.

- Dobosh P A QCPE (142)  
Doraiswamy S and Sharma S D 1968 *Proc. Indian Acad. Sci. A* **68** 53  
Emsley J W and Phillips L 1966 *Mol. Phys.* **11** 443.  
Kowalewski de D G, Kokeritz P G and Selen H 1959 *J. Chem. Phys.* **31** 1438 L  
Lide D R and Mann D E 1958 *J. Chem. Phys.* **29** 914  
Nygaard L, Bojesen I, Pedersen T and Andersen J A 1968 *J. Mol. Structure* **2** 209  
Sharma S D 1972 *Microwave spectra of substituted pyridines*, Ph.D. thesis, Panjab University, Chandigarh  
Sutton L E 1955 *Determination of organic structures by physical methods*, Baude E A and Nachod F C (New York: Academic Press) pp. 392–396  
Townes C H and Schawlow A L 1955 *Microwave spectroscopy* (New York: McGraw Hill) p. 104

## ERRATUM

Pramāṇa Vol. 2, 62 (1974): Analysis of the neutral-current interaction in the inclusive neutrino reaction.

G Rajasekaran and K V L Sarma

1. The statement in section 2 to the effect that we cannot detect scalar or tensor parts of the neutral current by using the neutrinos or antineutrinos produced in the conventional charged-current decay modes is not correct, for the neutral-current interaction may flip the helicity of the incident neutrino. This does not affect our analysis of the hadronic neutral current however, although we now have to assume that the neutrino is a two-component field.

2. Equation (13 a) should read as

$$C = \frac{2}{\pi} m_u$$