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RAMAN SPECTRUM OF FLUORENE

BY T. A. HARIHARAN
(Department of Physics, Indian Institute of Science, Bangalore-3)

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By using the technique of complementary filters, the Raman spectrum of fluorene is recorded at room temperature and the frequency shifts are compared with those of the earlier investigation. The Raman spectrum of fluorene dissolved in benzene is also obtained in the usual manner for liquids. Extra lines have been identified at 31, 67, 93, 356, 628, 875, 1266 and 1494 cm.$^{-1}$ and assignment of the Raman lines has been attempted.

1. INTRODUCTION

Fluorene or diphenylenemethane had been for a long time considered as nonplanar in its structure, the evidence being mainly from the doubtful existence of isomers of its unsymmetrically substituted derivatives. Recently however, Burns and Iball (1954) have made a detailed quantitative X-ray analysis of this compound and have definitely established the planar structure of the molecule. From the dipole moment measurements on pure fluorene as well as on substituted fluorenes Syrkin and ShottLvova (1944) arrive at the conclusion that the deviations from the planar structure is very small. The only earlier investigation on the Raman spectrum of this compound seems to be that of Manzoni-Ansidei (1937) who has also given a planar structure to the molecule with a symmetry C_{2v}. The infrared absorption spectrum has been reported by Lecomte and Lambert (1933) but only very few bands have been given. In view of the importance of the structure of this molecule, a detailed study of its Raman spectrum is considered worthwhile.

2. EXPERIMENTAL

The Raman spectrum of pure fluorene powder was obtained employing the technique of complementary filters of Ananthakrishnan (1937) with the difference that sodium nitrite solution was used in the path of the incident light and a dilute solution of iodine in CCl_4 in the path of the scattered light. The spectrum of the solution (15 gm. dissolved in 50 c.c. of benzene) was taken using a fairly concentrated solution of sodium nitrite as filter. A Hilger two-prism spectrograph of high light gathering power and having a dispersion of 27 A/mm. in the λ 4358 region is used to record the spectra. An iron arc comparison spectrum is superimposed on each plate for accurate measurement of frequency shifts.

3. RESULTS AND DISCUSSION

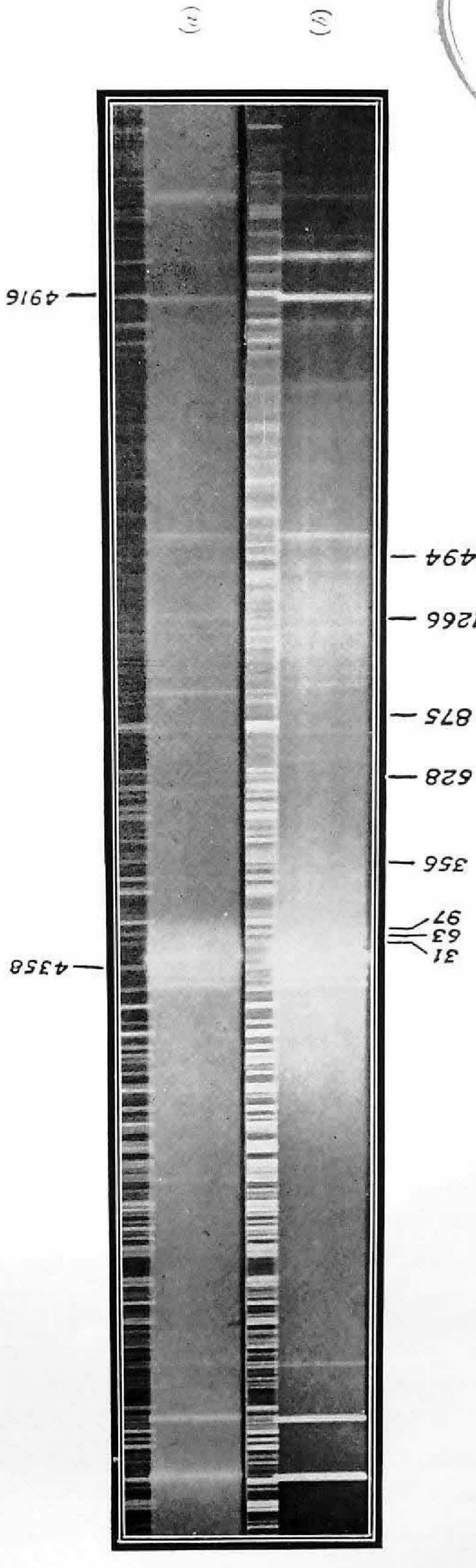
The Raman spectrum of pure fluorene and of its solution in benzene are reproduced in Plate XVII and the frequency shifts are given in Table I together with the results of Manzoni-Ansidei.

TABLE I

Raman Spectrum of Fluorene

Author $\Delta\nu$ cm.$^{-1}$	Manzoni-Ansidei (1937) $\Delta\nu$ cm.$^{-1}$	Author $\Delta\nu$ cm.$^{-1}$	Manzoni-Ansidei (1937) $\Delta\nu$ cm.$^{-1}$
31 (2)	..	1211 (1)	1210 (½)
67 (2)	..	1229 (5)	1228 (3½)
93 (3 *b*)	..	1266 (1)	..
141 (1)	140 (1)	1290 (1)	1291 (2)
279 (1)	277 (1)	1325 (1)	1325 (1)
356 (1)	..	1342 (2)	1344 (2)
392 (1)	394 (1)	1471 (3)	1476 (3)
566 (1)	567 (½)	1494 (1)	..
628 (0)	..	1574 (1)	1577 (1)
740 (3)	740 (3)	1610 (8)	1611 (7)
839 (3)	841 (3)	..	1639 (0)
875 (1)	..	2843 (1)	2840 (½)
1020 (5)	1018 (4)	2910 (1)	2909 (1 diff.)
1095 (1)	1096 (½)	3045 (4)	3049 (2)
1149 (2)	1151 (1)	3063 (2)	3064 (½)
1184 (2)	1185 (1)		

Excepting the line at 1639 cm.$^{-1}$ all the other lines reported by Manzoni-Ansidei have been observed in the present investigation. Additional lines have been observed at 31, 67, 93, 356, 628, 875, 1266, and 1494 cm.$^{-1}$ The low frequency shifts are fairly intense but the other new lines are faint. In



(*a*) Raman spectrum of solution of fluorene in benzene. (*b*) Raman spectrum of fluorene powder.

the spectrum of the solution in benzene the low frequency lines have been masked by the continuous wing but the other lines are present and no significant change in the positions or intensities of the lines could be observed.

Among the more prominent lines, those at 3063, and 3045 are the well-known C–H valence oscillation and the lines 2910, 2843, 1494, 1471 the valence and deformation vibrations of the CH_2 group. The Hydrogen bending vibration at 1178 cm.$^{-1}$ in the case of benzene is appearing as two lines at 1149 and 1184 cm.$^{-1}$. The lines between 800 and 1100 cm.$^{-1}$ can be assigned to the C–C vibrations. There is an intense line at 1229 cm.$^{-1}$ which may be assigned to the direct C-C linkage between the two benzene rings. In the case of diphenyl, Mukherji and Aziz (1938) and Fruhling (1951) have assigned a line at 1280 cm.$^{-1}$ to a similar linkage. The corresponding lines in the case of diphenylene oxide and diphenylene sulphide (Donzalot and Chaix, 1936) are perhaps at 1239 and 1233 cm.$^{-1}$ respectively. The frequencies corresponding to the C–C–C bending vibrations occurring in the region 200–500 cm.$^{-1}$ are very faint in this case, but the very low frequency shifts due to lattice oscillations at 31, 67 and 93 cm.$^{-1}$ are fairly intense, the first two being sharp and the third one slightly diffuse.

If the molecule is assumed to have a symmetry C_{2v}, it is expected to have 33 normal vibrations pertaining to the 13 skeletal carbon atoms of which 12 belong to the totally symmetric class A_1 and shall be polarised. An attempt was made to study the polarisation character of the Raman lines in the case of the solution in benzene and among the lines in the region 0–1300 cm.$^{-1}$, those at 1229, 1020, 875, 566 and 356 were observed to be polarised and hence belong to the totally symmetric class.

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