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Raman Spectrum of Fluorobenzene*

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The Raman spectrum of fluorobenzene has been investigated with a Hilger E1 quartz spectrograph, the following frequency shifts being obtained: 241, 517, 613, 804, 829, 997, 1009, 1157, 1220, (1265), (1414), 1496, (1561), 1599, 3076 and 3677 cm^{-1} . Relative intensities were measured with a Zeiss three-prism glass spectrograph and a Moll microphotometer.

THE Raman spectrum of benzene has received much attention¹ and the spectra of chlorobenzene, bromobenzene and iodobenzene have been studied by several investigators.² At the time that the present work was undertaken, no data were available on the Raman spectrum of fluorobenzene. Recently, however, measurements on this compound have been reported by Pai³ and by Murray and Andrews.⁴

EXPERIMENTAL ARRANGEMENT

The experimental arrangement used was essentially that proposed by Wood.⁵ The primary light source was a 220-volt vertical quartz mercury arc backed by a reflector. A Pyrex tube, 25 mm in diameter and filled with a solution of 20 cm^3 of carbon tetrachloride to 1 cm^3 of a saturated solution of iodine in carbon tetrachloride, served as filter and condensing lens. It suppressed the continuous background from the mercury arc without reducing too greatly the intensities of the mercury lines between 3341Å and 4358Å. Because of the photochemical decomposition of the filter solution, it was renewed twice a day. An air blast was directed against the filter tube, the mercury tube being partially shielded. Screens of black paper kept unfiltered light from reaching the fluorobenzene; for,

though none of the mercury lines transmitted by the filter caused appreciable photochemical action, light filtered only through Pyrex glass produced a dark brown precipitate. The fluorobenzene, obtained from the Eastman Kodak Company, was distilled under normal pressure directly into the Wood's tube. This was surrounded by a water jacket, two-thirds of the exterior wall of which was covered by a closely fitting reflector. The scattered light passed through a plane Pyrex window and a totally reflecting prism and was focussed by a condensing lens on the 0.04 mm wide slit of a Hilger E 1 quartz spectrograph.

Four plates were taken with exposures varying from three to ten days. To enhance the weak Raman lines, enlargements were made on process plates. Contact prints were made of these enlargements and the wave numbers of the Raman lines were measured, linear interpolation from the closest known iron lines being used.

Since the configuration of the 3650Å group is readily recognized in the scattered spectrum, much aid in the assignment of the Raman lines was gained by including this group in the exciting light. Moreover, it is advantageous from the point of view of dispersion, scattering efficiency and photographic sensitivity to use as short wave-lengths as the absorptivity and photochemical stability of the irradiated substance permit.

In order to measure the relative intensities of the Raman lines, two plates were taken with a Zeiss three-prism glass spectrograph.⁶ The time of exposure of each plate was three days, the slit

* From a thesis submitted by F. W. Crawford to the Graduate Faculty of the University of Oklahoma in partial fulfillment of the requirements for the degree of Doctor of Philosophy. A report of this work was made before the Oklahoma Academy of Science on November 31, 1933.

¹ K. W. F. Kohlrausch, *Der Smekal-Raman-Effekt*, Springer, Berlin, 1931; P. Grassmann and J. Weiler, *Zeits. f. Physik* **86**, 321 (1933).

² K. W. F. Kohlrausch, ref. 1; W. D. Harkins and R. R. Haun, *J. Am. Chem. Soc.* **54**, 3920 (1932); J. W. Murray and D. H. Andrews, *J. Chem. Phys.* **1**, 406 (1932).

³ N. Gopala Pai, *Nature* **132**, 968 (1933).

⁴ J. W. Murray and D. H. Andrews, *J. Chem. Phys.* **2**, 119 (1934).

⁵ R. W. Wood, *Phil. Mag.* **6**, 729 (1928).

⁶ The intensity measurements were made at the Massachusetts Institute of Technology. We are indebted to Professor George R. Harrison who generously placed the facilities of the George Eastman Research Laboratory at the disposal of one of us (F. W. C.).

width being in one case 0.10 mm and in the other case 0.20 mm. A step-weakeners having ten steps, each 3 mm wide, was placed in contact with the exposed portion of the plate, which it covered completely. The central strip of the step-weakeners was removed with a sharp pointed knife, and the absorbing steps were staggered on either side. The step-weakeners was made from a photographic film by exposing adjacent strips for different times. The absorption of each step for the spectral region between 3600 and 5000 Å was measured with a Moll recording microphotometer, a Wratten No. 49 filter being placed in front of the thermocouple. The microphotometric record of a plate was made by recording step by step the complete Raman spectrum, as photographed through the step-weakeners, on a single light sensitive sheet. Ten curves, one below the other, were thus obtained. Only the upper six of these were found to be useful, however, since the four steps of greatest density absorbed so strongly that only the most intense lines produced appreciable blackening on the plates. The calibration curves for the plates were made from selected portions of these records. With a slit width of 0.20 mm, most of the Raman lines gave density curves with flat tops.

It was found unnecessary to correct for the small variation of plate sensitivity with wavelength. The loss of light due to reflection in the spectrograph was estimated for the cases of completely polarized and completely depolarized Raman lines, respectively, due regard being taken for the mode of illumination. The difference between the losses in the two cases was about 12 percent of the incident intensity. Since the degree of depolarization was not measured for the Raman lines, it was not possible to apply the proper correction to the individual Raman lines. The relative intensities, given in Table II, are, therefore, not very accurate, the greatest possible error being as much as 20 percent.

RESULTS

The Raman lines observed are listed in Table I in the order of decreasing wave numbers. The first column gives the ordinal numbers used to designate the lines. Three of the lines, indicated by a *z*, were observed only with the glass spectrograph with which more strongly exposed

plates were obtained than with the quartz instrument; because of the wide slit used with the glass spectrograph, the wave numbers of these three lines are accurate only to about $\pm 10 \text{ cm}^{-1}$. In the third column are listed the approximate intensities, estimated visually, of the Raman lines. Exceptionally broad lines are indicated by the letter *b*. The assignment of the lines is given in the fourth column, the incident mercury lines being designated by the letters used by Kohlrausch¹ and other authors; namely, *d* 20336, *e* 22938, *f* 22995, *g* 23039, *h* 24335, *i* 24516, *k* 24705, *l* 25098, *m* 25592, *o* 27293, *p* 27353 and *q* 27388 cm^{-1} . The mercury line 29919 cm^{-1} , not listed by Kohlrausch, is denoted by *r*.

Some of the Raman lines can be assigned in more than one way. In such cases the two or more possible assignments are enclosed together in brackets. The intensities of several of these lines are definitely greater than would be expected if they were due to a single Raman transition. Moreover, in two cases the merging of two or more Raman lines is clearly indicated by a broadening.

In computing the frequency shifts, the values listed above for the wave numbers of the incident mercury lines were used. It will be noticed that for the exciting line *o* the stokesian shifts have values somewhat larger than the average, whereas the one observed antistokesian line ascribed to this incident line gives a shift lower than the average. This irregularity is doubtless due to the fact that the exciting line *o* is really double, 3662.29 Å and 3663.28 Å, the long wave-length component being the more intense and sharper of the two.

In the case of the weak Raman lines 59, 61 and 63, no assignment can be made that is supported by the assignment of other lines. It is tentatively assumed, therefore, that these lines are excited by the strong mercury line *e*. These doubtful assignments are enclosed in parentheses.

Of the assignments not designated as doubtful, those of the lines 43 and 46, involving the large frequency shift 3677 cm^{-1} , are the least certain. These two Raman lines have the same separation as the mercury lines *q* and *p*. The line *o*—3677 does not appear, but, since *p*—3677 is very weak, the absence of *o*—3677 may well be due to underexposure. The Raman lines having the

TABLE I. Raman lines of fluorobenzene.

Designation	Wave number cm ⁻¹	Intensity	Assignment	Designation	Wave number cm ⁻¹	Intensity	Assignment
1	29112	(1)	$r-807$	37	24276	(6b)	$\begin{cases} i-240 \\ p-3077 \end{cases}$
2	28908	(1)	$r-1011$	38	24216	(6b)	$o-3077$
3	28881	(0)	$q+1493$	39	24186	(1)	$k-519$
4	28397	(0)	$q+1009$	40	24094	(0)	$k-611$
5	27629	(1)	$q+241$				
6	27594	(0)	$p+241$	41	23902	(10)	$\begin{cases} i-614 \\ k-803 \end{cases}$
7	27530	(0)	$o+237$	42	23877	(0)	$k-828$
8	27149	(4)	$q-239$				
9	27113	(3)	$p-240$	43	23711	(2)	$\begin{cases} i-805 \\ k-994 \\ q-3677 \end{cases}$
10	27047	(2)	$o-246$				
11	26873	(3)	$q-515$	44	23695	(8)	$k-1010$
12	26835	(2)	$p-518$	45	23685	(1)	$i-831$
13	26776	(3)	$\begin{cases} o-517 \\ q-612 \end{cases}$	46	23676	(1)	$p-3677$
14	26739	(0)	$p-614$	47	23549	(4)	$k-1156$
15	26668	(0)	$o-625$	48	23509	(0)	$i-1007$
16	26585	(10)	$q-803$	49	23486	(4)	$k-1219$
17	26559	(0)	$q-829$	50	22699	(4)	$e-239$
18	26548	(6)	$p-805$	51	22420	(3)	$e-518$
19	26483	(4)	$o-810$	52	22335 _z	(2)	$e-603$
20	26391	(1)	$q-997$	53	22180 _z	(0)	$f-815$
21	26381	(10)	$q-1007$	54	22132	(4)	$e-806$
22	26352	(0)	$p-1001$	55	21941	(1)	$e-997$
23	26345	(8)	$p-1008$	56	21929	(4)	$e-1009$
24	26280	(6)	$o-1013$	57	21781	(2)	$e-1159$
25	26231	(4)	$q-1157$	58	21721	(2)	$e-1217$
26	26197	(3)	$p-1156$	59	21675 _z	(0)	$(e-1265)$
27	26166	(3)	$q-1222$	60	21632	(10b)	$k-3073$
28	26135	(3)	$\begin{cases} o-1158 \\ p-1218 \end{cases}$	61	21524	(0)	$(e-1414)$
29	26072	(1)	$o-1221$				
30	26014	(0)	$e+3076$	62	21439	(2b)	$\begin{cases} e-1499 \\ g-1598 \\ i-3077 \end{cases}$
31	25790	(3b)	$q-1598$				
32	25753	(1b)	$p-1600$	63	21377	(0)	$(e-1561)$
33	25696	(0)	$o-1597$	64	21340	(1)	$e-1598$
34	24946	(2)	$k+241$	65	19863	(4)	$e-3075$
35	24462	(4)	$k-243$				
36	24313	(10)	$q-3075$				

shift 3677 cm⁻¹ and produced by other strong mercury lines would lie in the region of low photographic sensitivity. The frequency 3677 cm⁻¹ is undoubtedly a combination frequency, $\cong 613 + 3076$ cm⁻¹, similar in origin to the frequency 3680 cm⁻¹ found by Grassmann and Weiler¹ for benzene. The line 43 is made up of several Raman bands superposed on each other, as indicated in Table I. One might be tempted to interpret line 46 as $l-1422$ and identify the shift with that of 1414 cm⁻¹, tentatively assumed for line 61. However, the low intensity of the incident line l and the large difference between the frequency shifts speak strongly against this assignment.

The weighted averages of the Raman shifts obtained are listed in the first column of Table II. As in Table I, uncertain shifts are placed in parentheses. The accuracy is indicated in the case of each shift by giving an estimated upper limit for the error. In the second column are listed the photometrically determined intensities. For comparison, the Raman shifts reported by Pai³ and by Murray and Andrews⁴ are given in the third and fourth columns of the table. The intensity values, estimated visually by these authors, are listed in parentheses after the wave numbers.

It will be seen from Table II that with regard to the strongest frequency shifts there is good

TABLE II. Raman frequencies of fluorobenzene.

Crawford and Rud Nielsen Raman shift Intensity		Pai Raman shift	Murray and Andrews Raman shift
241 ± 2 cm ⁻¹	6	243 cm ⁻¹ (5) 424 (1)	244 cm ⁻¹ (8)
517 ± 2	3	521 (3)	502 (0) 520 (3)
613 ± 2	2	617 (3)	615 (2) (705) (1)
		757 (2)	755 (1)
804 ± 2	11	808 (5)	807 (9)
829 ± 2	0.5		830 (1) 883 (0)
997 ± 2	4		997 (2)
1009 ± 2	8	1012 (7)	1013 (10) (1025) (1)
		1065 (1)	1070 (1b)
1157 ± 2	3	1157 (4)	1159 (3)
1220 ± 2	2	1220 (4)	1222 (3)
(1265 ± 10)	0.5	1275 (1)	
			1302 (0)
(1414 ± 10)	—	1413 (1)	
1496 ± 3	1		1498 (1)
(1561 ± 3)	—		
1599 ± 2	1	1600 (5)	1601 (4b) (1625) (0)
			2615 (1) (2917) (1b) (2986) (1b)
			3027 (1)
3076 ± 1	14	3074 (7)	3075 (10) 3090 (1)
3677 ± 2	—		

agreement between the different observers. Although the agreement is within the experimental error, it may be noted that we find consistently somewhat lower values for the Raman shifts than do Pai and Murray and Andrews. As far as we know, Pai has not yet published a detailed account of his work. Murray and Andrews used a glass spectrograph whereas the present work was done with a quartz instrument. We have observed Raman lines over a wider spectral region and have worked with greater dispersion. On the other hand, it appears that Murray and Andrews obtained more strongly exposed plates, since they observed several weak Raman lines not found by us; yet they report no antistokesian lines.

Lines 59 and 61 are undoubtedly identical with two lines observed by Murray and Andrews. However, our assignment, in both cases indicated as doubtful, differs from theirs. There is little basis for preferring one assignment to the other. It would seem, however, that the large frequency shifts assumed by Murray and Andrews are less probable than the lower values assumed by us.

The shift 1414 cm⁻¹ agrees with Pai's value 1413 cm⁻¹, and the shift 1265 cm⁻¹, computed from the inaccurately measured line 59, may be identical with Pai's shift 1275 cm⁻¹.

Among the lines observed by Murray and Andrews but not by us, the lines 23,822 cm⁻¹ and 22,436 cm⁻¹, both of which are assumed to give shifts not otherwise found, may perhaps be more reasonably assigned as *h*—513 and *g*—1603, respectively.

Line 37 might have been assigned as *k*—429, in which case we should have obtained a frequency shift nearly equal to Pai's value 424 cm⁻¹. The double assignment given in Table I cannot well be in error, however, since 3077 cm⁻¹ is excited also by the other members of the 3650A group, and since 241 cm⁻¹ is a very intense Raman frequency.

Line 53 might be assigned as *e*—758, thus giving a shift practically equal to the value 757 cm⁻¹ reported by Pai. However, the assignment *f*—815 seems more reasonable in view of the great intensity of the 804 cm⁻¹ shift. The discrepancy between the values 815 and 804 cm⁻¹ is explained by the inaccuracy in the measurement of line 53 which was observed only with the glass instrument. The weak Raman line 23,950 cm⁻¹, reported by Murray and Andrews and interpreted by them as due to a shift of 755 cm⁻¹, was not observed by us.

DISCUSSION

It has been suggested by Mecke⁷ that the Raman frequencies 266 cm⁻¹, 317 cm⁻¹ and 420 cm⁻¹, represent the "valence vibrations" of iodobenzene, bromobenzene and chlorobenzene, respectively. On the assumption that this is correct, one may compute the frequency of the valence vibration of fluorobenzene approximately by plotting these frequencies against the reduced masses of the molecules, considered as quasi-diatomic, and extrapolating to the reduced mass of fluorobenzene. In this way a value of about 500 cm⁻¹ is obtained. Hence, it may be assumed that the Raman frequency 517 cm⁻¹ represents the valence vibration of the fluorobenzene molecule. On the other hand, Pai, on the basis of thermochemical data not given in his brief note, suggests

⁷ R. Mecke, *Leipziger Vorträge 1931*, p. 45.

that the frequency 1220 cm^{-1} is associated with the carbon-fluorine bond. This is not very likely to be correct, since all of the monohalides of benzene have frequencies in the neighborhood of 1200 cm^{-1} .

From the existing data, it is not yet possible to draw definite conclusions with regard to the structure of benzene and its monohalides. When an assumption is made as to the symmetry of the fluorobenzene molecule, it is possible, by the methods developed by Brester⁸ and Placzek,⁹ to make certain statements about the normal vibrations of the molecule. If it be assumed, for example, that the fluorobenzene molecule is plane and has the symmetry C_{2v} (i.e., one two-fold symmetry axis and a symmetry plane passing through the axis) there will be 11 normal vibrations that are symmetrical with respect to both symmetry elements. The strongest and most highly polarized Raman lines will belong to this group. In addition, there will be 3 normal vibrations which are symmetrical with respect to a rotation of π about the axis and antisymmetrical with respect to a reflection in the symmetry plane. This group of frequencies is

⁸ C. J. Brester, *Kristallsymmetrie und Reststrahlen*, Utrecht, 1923.

⁹ Cf. G. Placzek, *Rayleigh-Streuung und Raman-Effekt*, Marx: Handbuch der Radiologie, 2nd ed., Vol. 6, Part II, Braunschweig, 1934.

forbidden in the infrared absorption but will occur in the Raman effect as lines with a depolarization of $6/7$. Further, there are 6 normal vibrations that are antisymmetrical with respect to a rotation and symmetrical with respect to a reflection and, finally, 10 normal vibrations which are antisymmetrical with respect to both symmetry elements. Both of the last groups give Raman lines with a depolarization of $6/7$.

If, on the other hand, the benzene molecule has a three-fold rather than a six-fold symmetry axis, as indicated by the Kekulé formula and by recent work of Weiler,¹⁰ the fluorobenzene molecule would probably have at most just a single symmetry plane. The normal vibrations would then fall into two groups, 21 vibrations which are symmetrical with respect to a reflection in the symmetry plane and 9 that are antisymmetrical with respect to such a reflection. The symmetrical vibrations should, on the whole, be more intense in the Raman spectrum than the antisymmetrical vibrations.

The data on the Raman and infrared spectra of fluorobenzene and the other monohalides of benzene are not yet sufficiently complete to determine which, if either, of these models is the correct one.

¹⁰ J. Weiler, *Zeits. f. Physik* **89**, 58 (1934).

The Constancy of the Polarization of Non-Polar Molecules

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The dielectric constants of the vapors of *n*-hexane and *n*-heptane are measured over a range of temperature and used to show that the molecules of these substances have no detectable dipole moments. The constancy of the polarizations of non-polar vapors in contrast to the slight rise with

temperature of the polarizations of the same substances in the liquid state is attributed to the elimination of the intermolecular action which lowers slightly the polarizability of the molecules in the liquid state.

BECAUSE of the general use of hexane and heptane as solvents in dipole moment measurements, it was deemed desirable to check the zero values assigned to their moments from measurements upon the liquids by examination of the vapors. At the same time, it has been possible to obtain further information upon the

more general question of the constancy of the polarization of non-polar molecules.

The dielectric constants of the vapors were measured as before.¹ The polarization P at each absolute temperature T was calculated from the

¹ K. B. McAlpine and C. P. Smyth, *J. Am. Chem. Soc.* **55**, 453 (1933); *J. Chem. Phys.* **2**, 499 (1934).