

## Absorption Spectrum of Fluorbenzene in the Near Ultraviolet

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variation is entirely too large to be accounted for by a change in density of condensed liquid. Also the condensation process cannot explain the disappearance of the discontinuity at 30°. Thus, the results obtained cannot be explained by the assumption of capillary condensation.

It might be assumed that a first-order change does not occur, but that the phenomena are due to the presence on the crystals of more than one type of surface, some of which are more effective than others. This can be shown to be improbable. Each surface would have its own isotherm. If the discontinuity were to take place on only one of the surfaces, then under equilibrium conditions a discontinuity would be observed as a mean of the effects. All of the experimental data, the constancy with time, and the reversibility indicate that the data are equilibrium values. Therefore, the observed discontinuity must be due to a discontinuity on at least *one* of the surfaces present. Therefore, the existence of different types of surfaces does not explain the observed discontinuity.

Other possible explanations are equally as im-

probable. Thus, the interpretation that the observed discontinuities are due to a first-order change appears certain. What has been designated as *stepwise adsorption* exhibits no obvious relationship to the change considered here.<sup>13</sup> (See Fig. 2.) The discontinuity in the low pressure region is the only one found, and the data do not indicate the presence of any other first-order change.

If the interpretation that the irregularities in stepwise adsorption are due to phase transitions, then it is possible to explain their existence in two ways. For a homogeneous surface each discontinuity would represent a new surface phase. This would lead to an inordinately large number of phases, so many that such an explanation is unreasonable. The other possible explanation from this point of view is that there are present a large number of individual surfaces for which the transitions take place at different pressures. However, the problem of stepwise adsorption has not been studied in sufficient detail to show what is involved.

<sup>13</sup> For a brief review, see: S. Brunauer, *The Adsorption of Gases and Vapors* (Princeton University Press, Princeton, New Jersey, 1943), pp. 346-348.

## Absorption Spectrum of Fluorobenzene in the Near Ultraviolet\*

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(December 28, 1945)

The absorption spectrum of  $C_6H_5F$  at 2750-2380Å was photographed in the first order of a three-meter grating spectrograph. As in  $C_6H_5Cl$  the band system corresponds to an electronic transition  $A_1, B_1$ . This is an allowed transition and the 0,0 band is stronger than in  $C_6H_5Cl$  because of the greater perturbation by the fluorine. Several progressions of totally symmetric vibrations are observed. The vibration whose excitation brings the corresponding benzene spectrum into appearance, and which shows up relatively intensely in  $C_6H_5Cl$ , appears in  $C_6H_5F$  but is not particularly prominent. In contrast to  $C_6H_5Cl$ , transitions to the carbon-halogen vibration in the upper electronic state are quite strong.

### INTRODUCTION

THE near ultraviolet absorption spectrum of chlorobenzene has been interpreted<sup>1</sup> as

\* Based on a portion of a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University, 1941.

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<sup>1</sup> H. Sponer and S. H. Wollman, *J. Chem. Phys.* **9**, 816 (1941).

having its origin in two types of transitions, each made possible by a different perturbation of the hexagonally symmetric potential field of benzene's planar carbon ring: a weak transition permitted because of the destruction of the sixfold symmetry by a non-totally symmetric vibration of symmetry  $\beta_1$ , and a somewhat stronger transition permitted because of the destruction of the sixfold symmetry by the presence of the electro-

negative atom of chlorine. A corresponding study has now been made for fluorbenzene to provide additional data to check the above interpretation.

The near ultraviolet absorption spectrum of fluorbenzene has been investigated by Henri;<sup>2</sup> but because of the incompleteness of the published results, it was necessary to rephotograph and remeasure the spectrum.

The analysis shows that the spectrum of fluorbenzene is similar to that of chlorbenzene, but that as might have been expected, the stronger perturbation of the carbon ring by the fluorine enhances the transitions forbidden in benzene but permitted in fluorbenzene because of the presence of the fluorine.

### EXPERIMENTAL DETAILS

The absorption spectrum of fluorbenzene was photographed in the near ultraviolet using a three-meter grating in Eagle mounting. The light source was a water-cooled hydrogen discharge tube of conventional design. It gave sufficient intensity to get a satisfactory density on a type II-0 Eastman spectrographic plate in from one and a half hours to three hours, depending on the intensity of the absorption bands.

Samples of pure fluorbenzene<sup>3</sup> were distilled into the absorption tube from an all-glass system. The quartz absorption tube used, 15 cm long, was provided with a side arm to hold the liquid sample. The temperature of the liquid and the vapor could be controlled independently. The vapor was always at room temperature; the temperature of the liquid, controlled by a dry ice and acetone bath, was varied from  $-55^{\circ}$  to  $28^{\circ}\text{C}$  depending on the desired pressure of vapor in the absorption path.

When the liquid was at room temperature the windows of the absorption tube became fogged gradually by photochemical decomposition products. The decomposition could have been predicted from examination of the absorption spectrum since some very diffuse bands (indicating predissociation) occur at the short wave-length end of the spectrum. The absorption of the fogged windows was tested and found to be uniform and continuous in the region of interest, and hence did not introduce any complications.

The bands were measured to the band head. The edges of the sharpest bands were measured to  $.2$  to  $.3\text{ cm}^{-1}$  while some of the diffuse bands could be measured only to the nearest two  $\text{cm}^{-1}$ .

Iron lines were used as the comparison spectrum.

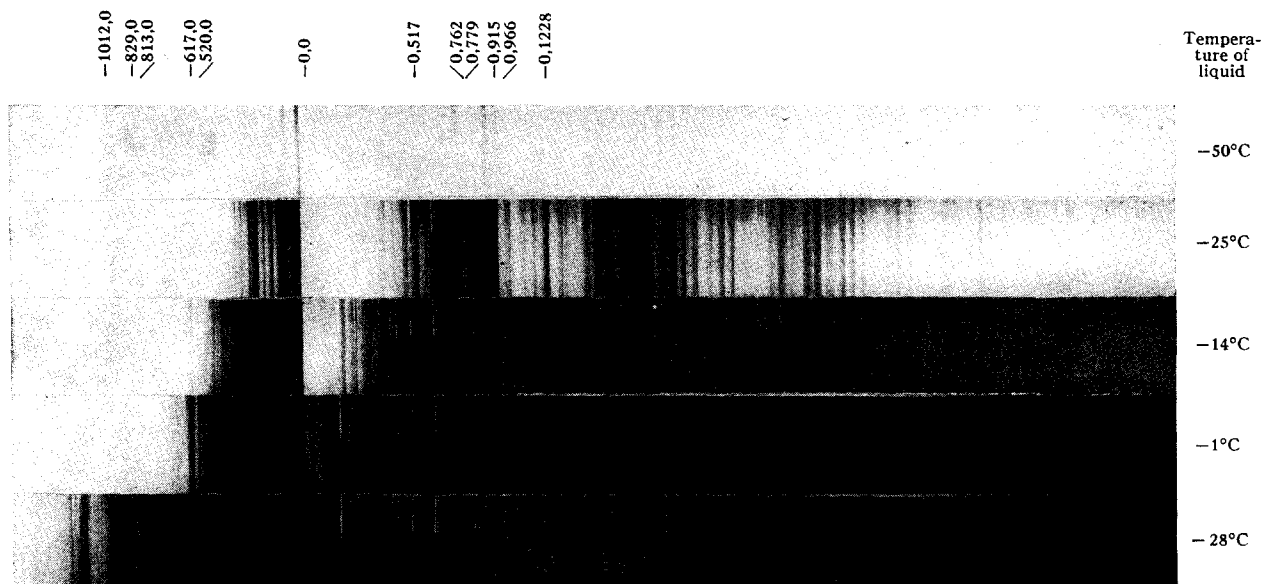


FIG. 1 Ultraviolet absorption spectrum of fluorbenzene vapor.

<sup>2</sup> V. Henri, *Structure des Molécules* (J. Henmann, Paris, 1925).

<sup>3</sup> We are indebted to Dr. Marcus Hobbs of the Chemistry Department for supplying the sample of fluorbenzene.

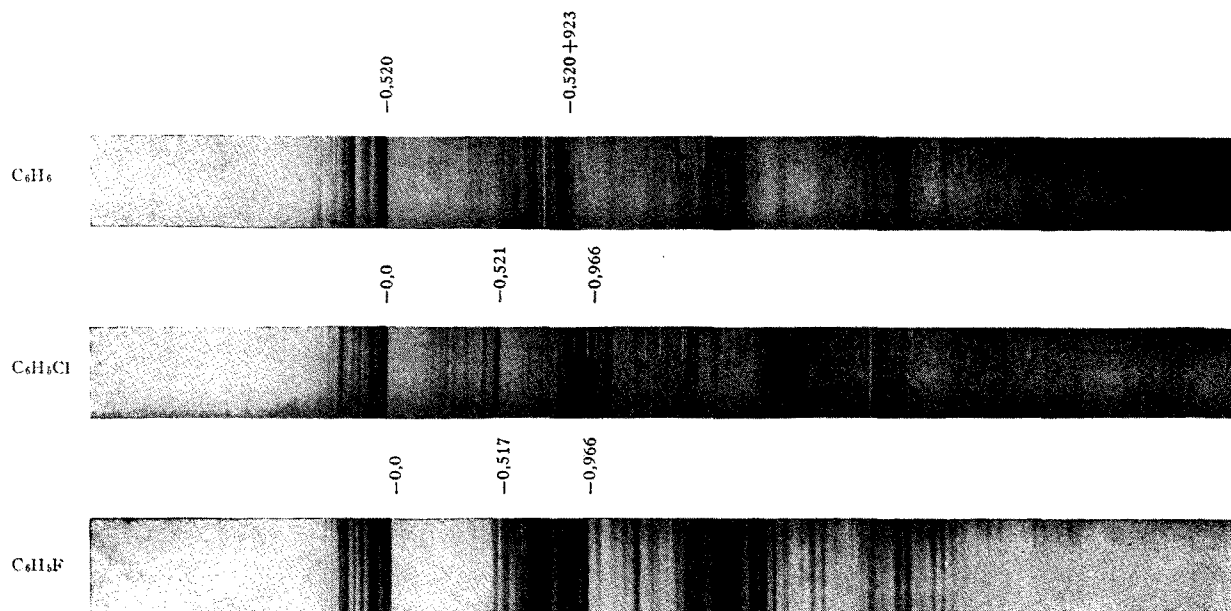


FIG. 2. Ultraviolet absorption spectra of benzene, chlorobenzene, and fluorobenzene.

### EXPERIMENTAL RESULTS

The part of the spectrum photographed lies in the region between 2750Å and 2380Å. A selection of the photographs of the spectrum taken at progressively higher pressures of vapor is shown in Fig. 1. As the pressure increases, more bands appear. Those at the extreme long wave-length end of the spectrum originate in transitions from excited vibrational levels in the ground electronic state.

All the bands are degraded to the red. Most of the band heads are doubled with a spacing of about  $2\text{ cm}^{-1}$ . The long wave-length head is the stronger and it seems probable that, if only a single head is observed, it is the long wave-length head. Hence all calculations of wave numbers are made relative to these strong heads.

The wave numbers, intensities, and some assignments of the observed bands are collected in Table I. Wave numbers in parentheses correspond to bands which were observed but not measured. Because of the wide range of intensities under various pressure conditions, the intensity classification refers to the experimental conditions in the remarks column. The notation in the intensity column means: *vw*=very weak, *w*=weak, *m*=medium, *st*=strong, *vst*=very strong, *d*=diffuse.

It is found that the vibrations are somewhat anharmonic, and, therefore, that the frequency of a particular vibration depends to a certain extent on its state of excitation, as well as on vibrations with which it is coupled. For example, the difference frequency,  $67\text{ cm}^{-1}$ , varies between  $65\text{ cm}^{-1}$  and  $70\text{ cm}^{-1}$ . Such fine distinctions have been ignored and a set of representative values has been chosen and listed throughout in the assignment column. The notation used to indicate transitions listed in the assignment column is as follows: Numbers to the left of the comma refer to the wave numbers of vibrations in the ground electronic state, those to the right to wave numbers of vibrations excited in the upper electronic state, except for those preceded by a minus sign which refer to the difference frequencies of 1,1 transitions.

### ANALYSIS OF THE SPECTRUM

The symmetry properties of fluorobenzene are the same as those of chlorobenzene.<sup>1</sup> The molecule is planar, with a twofold axis of symmetry through the fluorine atom, and belongs to the symmetry class  $C_{2v}$ . The lowest electronic state is totally symmetric as in benzene. It is assumed that the upper electronic state involved in the observed spectrum is of symmetry  $B_1$ . The

TABLE I. Bands of fluorbenzene.

Wave number (cm <sup>-1</sup> )	Intensity	Assignment	Remarks	Wave number (cm <sup>-1</sup> )	Intensity	Assignment	Remarks
36369	<i>vw</i>		Intensities were estimated from plates taken with liquid at 28°C	37721	<i>mstd</i>	0, -98	
36395	<i>vwd</i>			37733	<i>mstd</i>	0, -19-67	
36488	<i>vwd</i>			37749.4	<i>vst</i>	0, -67	
36513.5	<i>vw</i>	1218, -67		37752.0	<i>mst</i>		
36531.9	<i>w</i>			37758.5	<i>m</i>	0, -60	
36545	<i>vw</i>			37760.6	<i>w</i>		
36570.6	<i>m</i>	240-1012, 0		37799	<i>vst</i>	0, -19	
36577.3	<i>m</i>			37815.8	<i>vst</i>		
36590	<i>vwd</i>			37818.8	<i>vst</i>	0, 0	Main edge
36601	<i>m</i>	1012, -209; 1218, 0		37822.8	<i>mst</i>		
36603.3	<i>m</i>			37829.2	<i>vw</i>	758, 779	Intensities were estimated from plates taken with liquid at -14°C
36610.5	<i>w</i>	1012, -3×67		37839.4	<i>vw</i>		
36638	<i>vwd</i>	1012, -172		37846.5	<i>vw</i>		
(36662)	<i>vwd</i>	1457, 0		37865.7	<i>w</i>		
36677.2	<i>m</i>	1012, -2×67		37874	<i>vwd</i>		
36710	<i>md</i>	1012, -98		37883.7	<i>vw</i>		
(36725)	<i>vw</i>	1027, -67		37913	<i>w</i>		
36741.6	<i>st</i>	1012, -67		37929.3	<i>w</i>		
36780.5	<i>st</i>	829, -209		37931.7			
36792	<i>md</i>	1027, 0		37937.3	<i>vw</i>		
36807.0	<i>vst</i>	1012, 0		37950	<i>vwd</i>		Intensities were estimated from plates taken with liquid at -32°C
36809.6	<i>vst</i>			37959	<i>vwd</i>	0, 205-67	
36823	<i>md</i>	2×240-520, 0; 996, 0		37974	<i>vwd</i>	813, 966; 758, 915	
36841	<i>vwd</i>			38017.4	<i>w</i>	0, 332-2×67	
36858	<i>md</i>	829, -2×67		38023.5	<i>w</i>	0, 205; 758, 966	
36875	<i>md</i>	813, -2×67		38026.1	<i>w</i>		
36923.1	<i>m</i>	829, -67	Intensities were estimated from plates taken with liquid at 18°C	38083.9	<i>w</i>	0, 332-67	
36925.9	<i>m</i>			38128.7	<i>vw</i>	0, 517-209	
36939.8	<i>m</i>	813, -67		38137.6	<i>vw</i>	0, 517-3×67	
36942.3	<i>m</i>			38150.7	<i>w</i>	0, 332	
36951	<i>vwd</i>			38155.3	<i>vw</i>		
36990.2	<i>vst</i>	829, 0		38186.8	<i>w</i>		
36992.7	<i>vst</i>			38203.7	<i>w</i>	0, 517-2×67	
37006.1	<i>vst</i>	813, 0		38213.0	<i>vw</i>	520, 915	
37008.8	<i>vst</i>			38228.6	<i>w</i>	0, 410	
37021	<i>vwd</i>			38231.4	<i>vw</i>		
37036	<i>vwd</i>			38269.6	<i>w</i>	0, 517-67	
37061	<i>vwd</i>	240-520, 0; 758, 0		38278	<i>vwd</i>		
37071.8	<i>w</i>	617, -2×67		38320	<i>md</i>		
37093.8	<i>m</i>	520, -209		38335.6	<i>m</i>	0, 517	
37106.5	<i>vw</i>			38359.7	<i>vw</i>	240, 779	
37120	<i>vwd</i>			38375.7	<i>m</i>	0, 762-209	
37131	<i>vwd</i>			38383.6	<i>vw</i>	0, 762-3×67	
37136.9	<i>m</i>	617, -67		38391.0	<i>m</i>	0, 779-209	
37146	<i>vwd</i>			38393.3	<i>vw</i>		
(37165)	<i>vd</i>	520, -2×67		38410.0	<i>vw</i>	0, 205+517-2×67	
37196.3	<i>m</i>			38432	<i>m</i>	0, 205+410	Intensities were estimated from plates taken with liquid at -14°C
37202.1	<i>w</i>	617, 0	Intensities were estimated from plates taken with liquid at -14°C	38449.2	<i>m</i>	0, 762-2×67	
37221.8	<i>w</i>			38465	<i>m</i>	0, 779-2×67	
37232.9	<i>w</i>	520, -67		38478	<i>wd</i>	0, 205+517-67	
37241.6	<i>w</i>			38515	<i>st</i>	0, 762-67	
37248.3	<i>vw</i>			38530.9	<i>st</i>	0, 779-67	
37257	<i>vwd</i>			38532.9	<i>w</i>	0, 915-209	
37299.2	<i>st</i>	520, 0		(38541)		0, 205+517; 240, 966	
37301.3	<i>st</i>			38580.9	<i>vst</i>	0, 762	
37329	<i>md</i>	490, 0		38583.6	<i>m</i>	0, 966-209	
37350	<i>md</i>			38597.5	<i>vst</i>	0, 779	
37369.2	<i>m</i>			38600.0	<i>w</i>	0, 915-2×67	
37400.0	<i>st</i>	0, -2×209		38609.0	<i>w</i>		
37402.8	<i>st</i>			38616.3	<i>vw</i>		
37411.8	<i>m</i>			38665	<i>st</i>	0, 915-67	
37418.2	<i>m</i>			38674	<i>m</i>		
37421.1	<i>m</i>			38718.0	<i>vst</i>	0, 966-67	
37439	<i>vd</i>			38733.6	<i>vst</i>	0, 915	
37449	<i>wd</i>		Intensities were estimated from plates taken with liquid at -32°C	38738.3	<i>m</i>		
37460.4	<i>w</i>			38766.1	<i>m</i>	0, 966-19	
37470.2	<i>w</i>			38784.5	<i>vst</i>	0, 966	
37485.2	<i>w</i>			38787.0	<i>m</i>		
37501.9	<i>w</i>			38793.0	<i>vw</i>		
37512.2	<i>w</i>			38796.3	<i>vw</i>		
37517.7	<i>wm</i>	240, -67		38838.8	<i>w</i>	0, 1228-209	
37524.3	<i>vw</i>			38849.7	<i>m</i>		
37539.2	<i>vw</i>	813, 520		38852.3	<i>m</i>	0, 2×517	
37542.2	<i>m</i>	0, -67-209		38926.2	<i>w</i>		
37553.9	<i>w</i>			38935.9	<i>vw</i>		
37578.6	<i>m</i>	240, 0		38949.0	<i>vw</i>		
37581.1	<i>w</i>			38970	<i>wd</i>	0, 1218-67	
37609.7	<i>st</i>	0, -209		38978	<i>wd</i>	0, 1228-67	
37612.4	<i>m</i>			38985	<i>vwd</i>		
37619.0	<i>wm</i>	0, -3×67		38993	<i>vwd</i>	0, 410+762	
37629.9	<i>vw</i>	0, -19-172				0, 205+966	
37646.9	<i>m</i>	0, -172		39009	<i>vwd</i>	0, 410+779	
37649.0	<i>w</i>			39036.8	<i>mst</i>	0, 1218	
37656.4	<i>w</i>	0, -67-98		39043.8			
(37666)	<i>w</i>	0, -19-2×67		39046.8	<i>mst</i>	0, 1228	
37683.4	<i>st</i>	0, -2×67		39049.4	<i>vw</i>		
37685.8	<i>st</i>			39057.8	<i>vw</i>	0, 205+2×517	
37691.0	<i>w</i>					0, 517+779-67	
				39099.1	<i>w</i>	0, 517+762	

TABLE I.—Continued.

Wave number (cm <sup>-1</sup> )	Intensity	Assignment	Remarks	Wave number (cm <sup>-1</sup> )	Intensity	Assignment	Remarks
39115.7	<i>wm</i>	0, 517 + 779		40184	<i>vvd</i>	0, 517 + 762 + 966	
39119.7	<i>vw</i>			40218	<i>vvd</i>	0, 517 + 779 + 966	
39138	<i>wd</i>			40229	<i>vvd</i>	0, 517 + 915 + 966	
39150	<i>wd</i>			40234	<i>vvd</i>		
39172.3	<i>w</i>			40278	<i>wmd</i>	0, 2 × 1228	
39197	<i>wd</i>	0, 410 + 966				0, 517 + 2 × 966	
39230.7	<i>vw</i>			40300.7	<i>vw</i>		
39237.5	<i>vw</i>			40326	<i>vvd</i>	0, 762 + 779 + 966	
39245.3	<i>w</i>			40351	<i>vvd</i>	0, 2 × 779 + 966	
39251.6	<i>w</i>	0, 517 + 915		40370	<i>vvd</i>		
39257.6	<i>w</i>			40417.2	<i>m</i>	0, 762 + 2 × 915	
(39297)		0, 3 × 517 - 67		40433.6	<i>w</i>	0, 779 + 2 × 915	
39302.4	<i>m</i>	0, 517 + 966		40482.6	<i>m</i>		
39312.5	<i>m</i>	0, 2 × 779 - 67		40489.3	<i>m</i>		
(39342)	<i>vvd</i>	0, 2 × 762		40521	<i>vvd</i>	0, 762 + 2 × 966	
39359.3	<i>st</i>	0, 762 + 779		40537	<i>vvd</i>	0, 779 + 2 × 966	
39364.3	<i>wm</i>	0, 3 × 517		40546	<i>vvd</i>		
39381	<i>md</i>	0, 2 × 779		40557	<i>vvd</i>		
39405.3	<i>vw</i>			40568	<i>vvd</i>	0, 3 × 915	
39446	<i>wd</i>	0, 779 + 915 - 67		40622.2	<i>w</i>	0, 2 × 915 + 966	
39496	<i>md</i>	0, 762 + 915		40668.5	<i>w</i>	0, 915 + 2 × 966	
39502	<i>wmd</i>	0, 779 + 966 - 67		40675.6	<i>vw</i>		
39513	<i>md</i>	0, 779 + 915		40722	<i>wd</i>	0, 3 × 966	
39550	<i>md</i>	0, 762 + 966		40737	<i>vvd</i>	0, 2 × 517 + 915 + 966	
39569	<i>md</i>	0, 779 + 966		40814	<i>vvd</i>		
39588	<i>vvd</i>			40847	<i>vvd</i>		
39653.3	<i>m</i>	0, 2 × 915		40871	<i>vvd</i>		
39699	<i>md</i>	0, 915 + 966		40905.6	<i>vw</i>		
39707.0	<i>w</i>			40922	<i>vvd</i>	0, 915 × 966 + 1228	
39740	<i>wd</i>			40987.8	<i>vw</i>	0, 2 × 966 + 1228	
39753	<i>md</i>	0, 2 × 966		41132	<i>vvd</i>	0, 517 + 2 × 915 + 966	
39769	<i>vvd</i>	0, 2 × 517 + 915		41195	<i>vvd</i>	0, 915 + 2 × 1228	
39802	<i>wd</i>					0, 517 + 915 + 2 × 966	
39817	<i>wd</i>	0, 2 × 517 + 966				0, 517 + 3 × 966	
39825	<i>vvd</i>			41246	<i>vvd</i>		
39842	<i>vvd</i>			41335.1	<i>vw</i>		
39901	<i>vvd</i>			41385.0	<i>vw</i>		
39916	<i>vvd</i>			41401.2	<i>vw</i>		
39959	<i>wmd</i>	0, 915 + 1218		41449	<i>vvd</i>	0, 779 + 915 + 2 × 966	
39966	<i>wmd</i>	0, 915 + 1228		41534	<i>vvd</i>		
40014	<i>wmd</i>	0, 966 + 1228		41587	<i>vvd</i>	0, 2 × 915 + 2 × 966	
40054.6	<i>vw</i>	0, 3 × 779		41634	<i>vvd</i>	0, 915 + 3 × 966	
40084	<i>vvd</i>	0, 517 + 779 + 966		41689	<i>vvd</i>	0, 4 × 966	
40103	<i>vvd</i>			41741	<i>vvd</i>		
40118	<i>vvd</i>			41762	<i>vvd</i>		
40135	<i>vvd</i>			41835	<i>vvd</i>		
40166	<i>vvd</i>	0, 517 + 2 × 915		41898	<i>vvd</i>		
		0, 410 + 2 × 966		41947	<i>vvd</i>		

symmetry class  $B_1$  in the group  $C_{2v}$  corresponds to the class  $B_{2u}$  in the group  $D_{6h}$  of benzene, and arises when the sixfold axis of symmetry is destroyed by the substitution of a halogen atom for one of the hydrogens. In benzene the corresponding spectrum arises out of a transition to an upper electronic state of symmetry  $B_{2u}$ . Transitions between electronic states with symmetries  $A_1$  and  $B_1$  are allowed; the transition moment lies in the molecular plane perpendicular to the carbon-fluorine bond. Transitions with moments in the other two principal directions are "forbidden" unless permitted because of the accompanying transition of a vibration of suitable symmetry. When the transition moment is parallel to the carbon-fluorine bond the accompanying vibration is of symmetry  $\beta_1$ . Only one such vibration was found and it corresponds to the vibration of symmetry  $\epsilon_g^+$ , which permits the corresponding transition in benzene. When

the transition moment is perpendicular to the molecular plane, the accompanying vibration is of symmetry  $\alpha_2$ . A few such vibrations seem to be observed.

Since fluorobenzene and chlorobenzene have similar structures, it is to be expected that the absorption spectra will be similar. Comparison of the absorption spectra of fluorobenzene and chlorobenzene presented in Fig. 2 together with that of benzene shows that there is a strong resemblance. The pressure of the vapor and the length of the absorption path are 25 mm and 75 cm for benzene, 1.7 mm and 75 cm for chlorobenzene, and 3 mm and 15 cm for fluorobenzene, respectively. Examination of the spectra indicates that the absorption strength of fluorobenzene is about twice that of chlorobenzene and perhaps ten times that of benzene. Fluorobenzene has a greater absorption strength than benzene because the fluorine perturbs the hexagonal field

TABLE II. Wave numbers and symmetries of some vibrations in the ground electronic state of fluorbenzene.

Ultra-violet vapor	Raman liquid (reference 4)	Infra-red liquid (reference 5)	Depolarization factor (reference 4)	Symmetry (reference 4)	Symmetry (this paper)
240	241		.83	$\beta_2$	$\alpha_2$
520	519	518	.60	$\alpha_1$	$\alpha_1$
617	612	610	.92	$\beta_1$	$\beta_1$
813	807	802	.12	$\alpha_1$	$\alpha_1$
829	831			$\alpha_2$	$\alpha_1?$
996?	997	997			
1012	1010		.07	$\alpha_1$	$\alpha_1$
1027	1024				$\alpha_1$
(1157)	1157		.65	$\alpha_1$ or $\beta_1$	$\alpha_1?$
1218	1218		.15	$\alpha_1$	$\alpha_1$

of the carbon ring more than the chlorine does. Further evidence indicating that fluorbenzene has a ring field deviating more from hexagonal symmetry than that of chlorbenzene will be presented later in the discussion.

As in chlorbenzene,<sup>1</sup> it is postulated that the 0,0 transition is represented by the strongest band on the short wave-length end of the first strong group.

It is then possible to obtain the values of the wave numbers of vibrations in the ground electronic state by taking wave number differences between the 0,0 band and bands on its long wave-length side. The results, taken from Table I, are listed in Table II along with the corresponding values observed in the Raman effect<sup>4</sup> and the infra-red absorption spectrum<sup>5</sup> in the liquid state. In addition, depolarization factors<sup>4</sup> and symmetries assigned on the basis of Raman effect data<sup>4</sup> are listed as well as symmetries assigned on the basis of a combination of Raman and ultraviolet data.

The main portion of the spectrum, all the bands on the short wave-length side of the 0,0 band, arises from transitions to excited vibrational levels in the upper electronic state. The strongest bands involve totally symmetric carbon vibrations, singly or multiply excited, or excited in combination with other totally symmetric vibrations. The vibrations which are most strongly excited in the upper electronic state have the wave numbers 517, 762, 779, 915, 966, 1218, and 1228 cm<sup>-1</sup>.

<sup>4</sup> K. W. F. Kohlrausch and H. Wittek, *Monats. f. Chem.* **74**, 1 (1941). See this paper for earlier references.

<sup>5</sup> J. Lecomte, *J. de phys. et rad.* **8**, 489 (1937).

Reasonable assignments can be given for many of these vibrations in the ground and excited electronic states.

The 617 and the 520 frequencies in Table II are closely related to the carbon vibration 606 of symmetry  $\epsilon_g^+$  in benzene. When benzene has one hydrogen replaced by a halogen the degeneracy of the 606 vibration is removed and it is expected to split into a vibration of symmetry  $\beta_1$  with a frequency around 600 and a totally symmetric vibration with a somewhat lower frequency. This is observed: in fluorbenzene the frequencies are 617 and 520, respectively, and similarly, in chlorbenzene they are 615 and 418. Support for the assignment of the 520 is obtained from the value of the depolarization factor of the Raman scattering. Support for the assignment of the 617 is obtained from the following argument: The bands involving transitions from the singly excited 617 vibration, and bands involving transitions to the singly and possibly to the triply excited 517 vibration in the upper electronic state, have a sharpness similar to that of the corresponding bands in the near ultraviolet absorption spectrum of benzene. The 617 and 517 bands in fluorbenzene are significantly sharper than the bands corresponding to transitions involving only totally symmetric vibrations, including the case in which the 517 vibration is doubly excited. Moreover, in benzene, chlorbenzene, and fluorbenzene the difference in frequency of this vibration in the upper and lower electronic states is about the same. It therefore seems reasonable to assume that the 517 is related to the 617, and that the pair correspond to the 520 and the 606 in benzene, and to the 521 and the 615 in chlorbenzene, which show a similar sharpness. Now it is known from Raman spectra that the 606 in benzene is a carbon ring vibration. Hence it is expected that the 617 and 517 vibrations involve a carbon vibration rather than a hydrogen vibration. This interpretation is in contrast to that in a recent Raman study<sup>4</sup> where the 617 is assigned to a  $\beta_1$  vibration related to the  $\epsilon_u^-$  hydrogen vibration 1035 in benzene.

The transition of the form  $0, n \times 517, n = 2$ , increases in intensity relative to that with  $n = 1$  as the substituent changes from Br to Cl to F.<sup>6</sup>

<sup>6</sup> The fact that a band corresponding to  $0, n \times 517, n = 1, 2$  in fluorbenzene appears also in chlorbenzene and probably

This is an illustration of the decreasing importance of the vibration mechanism in making the transition allowed, or of the increasing perturbation of the ring field by the substituent in the order  $\text{Br} < \text{Cl} < \text{F}$ .

The structure of the 517 and the 617 seems to be characteristic not only of the particular vibrations but also of the direction of the transition moment of transitions permitted because of vibrations of symmetry  $\beta_1$ . This is indicated by the fact that the structure of the band corresponding to the transition  $0, 2 \times 517$  looks like that of a transition involving only totally symmetric vibrations. This is to be expected since the doubly excited vibration is totally symmetric. The dependence of band structure on the direction of the transition moment and hence on the symmetry class of an associated vibration is of help in determining the symmetry class of vibrations in these monosubstituted benzenes. Usually the depolarization factor of the Raman scattering can distinguish between totally symmetric and non-totally symmetric vibrations. If a vibration is non-totally symmetric and occurs in ultraviolet absorption in transitions of the form  $\nu, 0$  or  $0, \nu$  ( $\nu$  standing for an arbitrary vibration), it cannot be of symmetry  $\beta_2$ ; if the band is sharp and the presented discussion is correct, the transition moment is parallel to the carbon-fluorine bond and the symmetry is  $\beta_1$ ; in other bands the transition moment is perpendicular to the molecular plane and the symmetry is  $\alpha_2$ .

In connection with the vibrations with frequencies of about  $1000 \text{ cm}^{-1}$ , ultraviolet bands are observed at positions corresponding to the observation of vibrations of frequencies 996, 1012, 1027, (1157), and  $1218 \text{ cm}^{-1}$  in the ground electronic state. While a reasonable alternative assignment can be given for the band at  $36601 \text{ cm}^{-1}$ , *viz.* 1012, -209, it is fairly certain that 1218, 0 is also present since the weaker associated transition 1218, -67 is observed. The de-

polarization factor of the corresponding Raman band shows the vibration to be totally symmetric. There is no obvious assignment of a frequency in the upper electronic state to correspond to the 1218. The bands at 39037 and 39047 corresponding to the transitions 0, 1218, and 0, 1228, respectively, seem to be the best choice although they would involve frequency values equal or slightly higher than the one in the ground electronic state.

It is not certain that the 996 vibration is observed. The band at 36823 may not correspond to the transition 996, 0, since not only is an alternative assignment possible, but no transition of the form 996, -67 is observed.

The frequencies 1012 and 1027 in the ground state are probably carbon vibrations. Several totally symmetric carbon vibrations are to be expected in this region. If these vibrations are related to the 915 and the 966 in the upper electronic state which because of extensive strong progressions are certainly totally symmetric carbon vibrations, the recent assignment of the 1027 to a hydrogen vibration<sup>4</sup> is unlikely.

The 1157 is very probably a hydrogen vibration.

The 813 has been correlated with the carbon-fluorine vibration. The assignment<sup>4</sup> was made after comparison of Raman bands in monosubstituted benzenes. It was found that corresponding bands were strongly dependent on the mass of the substituent. Polarization measurements indicate that the vibration is totally symmetric.

The 829 has been assigned<sup>4</sup> to an out-of-plane vibration of the hydrogens because in a similar comparison the corresponding bands are largely independent of the substituent. It was assumed that the 829 represents the very closely neighbored components  $\alpha_2$  and  $\beta_2$  resulting mainly from  $850 \text{ cm}^{-1}$  in benzene. The ultraviolet absorption data do not indicate a confirmation of this assignment. The single excitation of a  $\beta_2$  vibration is a forbidden transition and the single excitation of an  $\alpha_2$  vibration should give rise to a relatively weak band. Contrary to these predictions the 829 is a strong band. Since the band appearance indicates that  $\beta_1$  symmetry is doubtful, the vibration is probably totally symmetric.

The 762 and the 779 frequencies in the upper

in brombenzene indicates that the transition from the ground state to the doubly excited vibration of symmetry  $\beta_1$  in the upper electronic state can occur, and that the band in chlorbenzene at  $38095 \text{ cm}^{-1}$  is probably  $0, 2 \times 521$ . The alternative explanation<sup>1</sup> (that the 1043 arises from an accidental degeneracy involving a doubly excited vibration with a fundamental frequency of  $525 \text{ cm}^{-1}$  and a totally symmetric carbon ring vibration) which was proposed because of the strong intensity of the band now seems doubtful.



electronic state probably correspond to the 813 and the 829 in the ground electronic state, although it is not clear which vibrations are to be paired. Either the 762 or the 779 represents the carbon-fluorine vibration in the excited electronic state. This is in contrast to results in chlorbenzene where the corresponding transition (to a state with a singly excited carbon-chlorine vibration) is not observed. A possible explanation of this difference may lie in the fact that the fluorine atom perturbs the carbon ring field more than a chlorine atom. It has been pointed out<sup>1</sup> that the transition moment may be dependent on the normal coordinate of a vibration. For transitions from the ground state to excited totally symmetric vibrations in the upper electronic state (in molecules in which the upper electronic state involved in the transition has a larger moment of inertia than the lower electronic state), the part of the transition moment independent of the displacement has a sign opposite to the part of the moment proportional to the first power of the displacement of the normal coordinate. In chlorbenzene these contributions probably cancel, since transitions from the ground state to a singly excited carbon-chlorine vibration in the upper electronic state do not seem to occur; in fluorbenzene as indicated by the over-all greater absorption strength, the constant term is larger than in chlorbenzene, and there is only partial cancellation. The transition from the ground state to a singly excited carbon-fluorine vibration in the upper electronic state is observed. The strong intensities of the 762 and the 779 bands and their way of combining with other vibrations suggests that they are both totally symmetric.

The 240 frequency in the ground electronic state is probably of symmetry  $\alpha_2$ . It has been assigned<sup>4</sup> to  $\beta_2$  symmetry related to the  $406\epsilon_u$  carbon vibration in benzene on the basis of Raman studies. However, the vibration appears

in a transition corresponding to 240,0 with moderate strength in studies on fluorbenzene, chlorbenzene, and brombenzene, and hence cannot be of symmetry  $\beta_2$ , as this transition would then be forbidden. Since the Raman scattering shows the vibration to be non-totally symmetric, and since the ultraviolet band appearance indicates that it is not of symmetry  $\beta_1$  it is probably of symmetry  $\alpha_2$ . The results do not permit a definite correlation of the 240 frequency to a particular mode of vibration.

In addition to the frequencies discussed, others occur, difference frequencies or  $n,n$  transitions, in bands to the long wave-length side of the more prominent bands. These difference frequencies have been identified by the fact that they are so low compared to the observed Raman frequencies and to the expected size of vibrational frequencies in this molecule. Confirmation could be obtained by studying the temperature dependence of the intensity of the bands involving them. The prominent difference frequencies are 20, 67, 98, 172, and 209  $\text{cm}^{-1}$ . Not much can be said about these difference frequencies at the present time. The 20, 98, and 172, which occur only once and not in progressions are probably to be associated with one of the higher ground-state frequencies. The 209 and the 67 which occur up to 2,2 and 3,3 transitions, respectively, are probably related to low frequencies, perhaps less than 400  $\text{cm}^{-1}$ . Probably none of the most prominent vibrations may be associated with the observed difference frequencies. The 98 agrees closely numerically with 617, 517 but the assignment is uncertain since the corresponding difference frequency does not appear in chlorbenzene.

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