The Vibrational Spectra of Molecules and Complex Ions in Crystals. II. Benzene

Robert D. Mair and Donald F. Hornig

Additional information on J. Chem. Phys.

It should be noted, however, that the rotational constant shows that the $S-S-H$ angles must be near to 90° unless the $S-H$ distance is abnormally long. This fact offers very strong support for the chain structure, since such angles are rather improbable for any other structure.

4. CONCLUSION

As has been shown, the character of the hydrogen persulfide spectrum offers very strong support for a chain structure of the molecule, but gives no very direct information regarding the azimuthal angle, though the apparent hybrid character of the 2μ-over-tone band makes the cis-planar model quite improbable. The significant differences between the overtone $S-H$ band and the $O-H$ overtones of hydrogen peroxide are probably related to differences in the angle in these two molecules. It is hoped that a study of the fundamental of ν_4, the twisting vibration, may be made in the near future. The presence of this band in the infra-red spectrum would definitely exclude the cis-planar form. If the molecule has neither planar form the double minimum in the torsional potential would probably give rise to a detectable doubling of this band which would possibly permit an estimate to be made of the azimuthal angle.

The Vibrational Spectra of Molecules and Complex Ions in Crystals. II. Benzene*†

ROBERT D. MAIR** AND DONALD F. HORNIG

Metcalf Research Laboratory, Brown University, Providence, Rhode Island

(Received March 28, 1949)

The infra-red spectrum of crystalline benzene has been studied at -12°C, -65°C and -170°C as well as the liquid at 28°C. The lines are extremely sharp, the mean line width for fundamentals being 7 cm^{-1} in the crystal. In three cases, it is less than the spectral slit width. All out-of-plane degenerate modes are split by about 10 cm^{-1}. Selection rules are obeyed and agree with the reported x-ray structure. All ungerade fundamentals are observed directly, some for the first time. Fifty-two combination bands are observed. The frequency assignments of Ingold *et al.* are confirmed except for the B_{2u} species. Evidence is cited for re-assigning ν_{14} from 1648 cm^{-1} to 1310 cm^{-1} and ν_{15} from 1110 cm^{-1} to 1150 cm^{-1}. Ingold's isotopic data does not conflict with this change. Combination frequencies involving torsional lattice modes are apparently observed at -170°C.

I. INTRODUCTION

THE study of the infra-red and Raman spectra of crystals is a potentially powerful but as yet little used tool in the determination of molecular and crystal structure. In the first paper in this series[1] it was shown that in the harmonic approximation the spectrum of the crystalline solid (Raman or infra-red) should consist of only a relatively small number of extremely sharp lines, and that in this approximation the simple selection rules suggested by Halford[2] are correct. It was further pointed out that, particularly in the case of molecular crystals, this state of affairs should be most nearly approached at low temperatures.

The utility of the crystal in studying molecular vibrations arises, as has been pointed out by Halford,[2] from the fact that the crystalline field produces a new set of selection rules which are, in general, less strict than for the vapor. Some of the previously forbidden vibrations may become allowed, but their frequencies

will be shifted very little, if at all. In addition, the fact that the lines are usually very sharp, particularly at low temperatures, may be of considerable importance in dealing with a spectrum as complicated as that of benzene. The polarization properties of the lines may supply further information.

The determination of the normal vibrations of the benzene molecule has been the subject of a long series of investigations.[3]

The most successful attack has been the comprehensive study by Ingold and co-workers,[4] utilizing the infra-red and Raman spectra of benzene and five deutero-benzenes, together with the Redlich-Teller frequency product rule. Their frequency assignments appear to be largely correct.

Several attempts have been made to calculate the benzene frequencies from an assumed potential function.[5-8] In particular, Miller and Crawford have calcu-

---

[1] D. F. Hornig, J. Chem. Phys. **16**, 1063 (1948). Hereafter called I.

[2] R. S. Halford, J. Chem. Phys. **14**, 8 (1946).

[3] See G. Herzberg, *Infra-Red and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 362.

[4] C. K. Ingold *et al.*, Parts I–VIII, J. Chem. Soc., 912–987 (1936); Part IX, *ibid.*, 1210 (1936); Part X, *ibid.*, 1728 (1937); Parts XI–XXI, *ibid.*, 222–333 (1946). Hereafter designated simply by the part number.

[5] E. B. Wilson, Jr., Phys. Rev. **45**, 706 (1934).

[6] K. W. F. Kohlrausch, Zeits. f. physik. Chemie **308**, 305 (1935).

[7] R. C. Lord and D. H. Andrews, J. Phys. Chem. **41**, 149 (1937).

[8] W. G. Penney and J. Duchesne, Bull. Soc. Roy. Sci., Liege **11**, 514 (1939).

lated the frequencies of the out-of-plane vibrations with considerable success[9] and have recently given a similar treatment of the in-plane vibrations.[10]

In the present investigation the spectrum of crystalline benzene has been studied between $-12°C$ and $-170°C$. The spectrum of the liquid was also studied to provide auxiliary information useful in the interpretation of the solid spectra, since in the liquid all selection rules are relaxed. Halford and Schaeffer[11] had previously obtained the infra-red spectrum of solid benzene in the vicinity of its melting point, but with low resolving power. It was felt desirable to redetermine this spectrum with better resolution, particularly at low temperatures. This has been done, revealing a characteristic sharpness of bands and a wealth of detail, both of which have proved very useful in interpreting the data. The spectrum of the liquid, obtained under the same conditions, reveals more structure than was observed either by Ingold et al.[12] or by Halford and Schaeffer. It may be noted that it agrees in every detail with the spectrogram reported by the U. S. Naval Research Laboratories.[13]

Interpretation of these spectra has yielded information of several sorts. In particular, except for ν_{14} and ν_{15}, it has confirmed the assignments given by Ingold et al.[14] for the nine frequencies forbidden in the spectrum of the free molecule. Six of these have been observed directly and the others are upheld by combination bands. Secondly, it has demonstrated the chief features predicted in I for crystalline spectra. Selection rules appear to be strictly obeyed, for both internal and lattice modes as well as their combinations, and temperature effects, such as a general sharpening of lines at low temperatures, are plainly shown.

II. CRYSTALLINE BENZENE

It was shown in I that the symmetry properties of active fundamentals can be completely described by the factor group of the space group which is isomorphous with the crystallographic point group. It was shown further that selection rules could be obtained from the local symmetry of the molecule in the crystal, the site group of Halford. These same statements are approximately correct for combinations and overtones.

The x-ray structure of benzene has been determined most completely by Cox[15] who found the space group V_h^{15} with 4 molecules per unit cell. From the tables

published by either Niggli[16] or Halford,[2] the site symmetry of the benzene molecules is then C_i. The thirty modes of vibration should therefore result in 30 distinct frequencies as compared to twenty under D_{6h}, although the splitting due to removal of the degeneracies may not be resolved. The three rotations of the free molecule correspond to three torsional oscillations in the crystal whereas the three translations remain translations of the crystal.

The fifteen internal modes deriving from the gerade representations of D_{6h} plus the three torsional lattice modes belong to the species A_g of C_i. The fifteen deriving from the ungerade representations of D_{6h} belong to the species A_u of C_i. All A_g modes are allowed in the Raman spectrum and all A_u modes are allowed in the infra-red spectrum. All combinations are allowed, $A_g A_g$ and $A_u A_u$ in the Raman spectrum, and $A_u A_g$ in the infra-red spectrum. It is apparent that in crystalline benzene the mutual exclusion rule should apply rigorously. These selection rules apply without distinction to lattice as well as internal modes of vibration.

III. EXPERIMENTAL METHODS AND TECHNIQUES

The spectrometer used was a Perkin-Elmer Model 12B in which the single beam optical system had been replaced by a double-beam arrangement. By means of rotating sector mirrors, radiation from the source was sent into the monochromator alternately over one or the other of two optically identical paths. As used here, the instrument produced a point-by-point record of the transmission of the sample and the blank alternately. (These were placed one in each beam.) In addition, the instrument recorded the zero or base line after each transmission point. This very effectively eliminated errors due to drift, which is especially important in low temperature work where the base line may drift appreciably and irregularly. The records were reduced to superimposed base line, sample and blank curves by drawing smooth envelopes through the three sets of points.

Water and carbon dioxide were effectively eliminated by blowing dry nitrogen through the spectrometer housing. The strongest water band in the 6μ-region showed a maximum absorption of less than 30 percent and, in fact, only the stronger lines of this band could be detected.

The amount of stray radiation reaching the thermocouple was found to be appreciable only in the region near the cut-off of each prism. It was reduced by a factor ten by employing a scattering filter of the type described by McGovern and Friedel.[17] The filter used had a transmission of 4 percent at 2μ, 45 percent at 4μ, 75 percent at 6μ, and 85 percent at 7μ.

[9] F. A. Miller and B. L. Crawford, Jr., J. Chem. Phys. 14, 282 (1946).

[10] B. L. Crawford, Jr. and F. A. Miller, J. Chem. Phys. 17, 249 (1949).

[11] R. S. Halford and O. A. Schaeffer, J. Chem. Phys. 14, 141 (1946).

[12] See reference 4, Part IV.

[13] A. P. I. Research Project, 44, Spectrogram No. 307, contributed by the U. S. Naval Research Laboratory, Washington, D. C.

[14] See reference 4, Part XXI.

[15] E. G. Cox, Proc. Roy. Soc. 135A, 491 (1932).

[16] P. Niggli, Geometrische Kristallographie des Diskontinuums (Gebruder Borntraeger, Leipzig, 1919), Table IV, pp. 404–411.

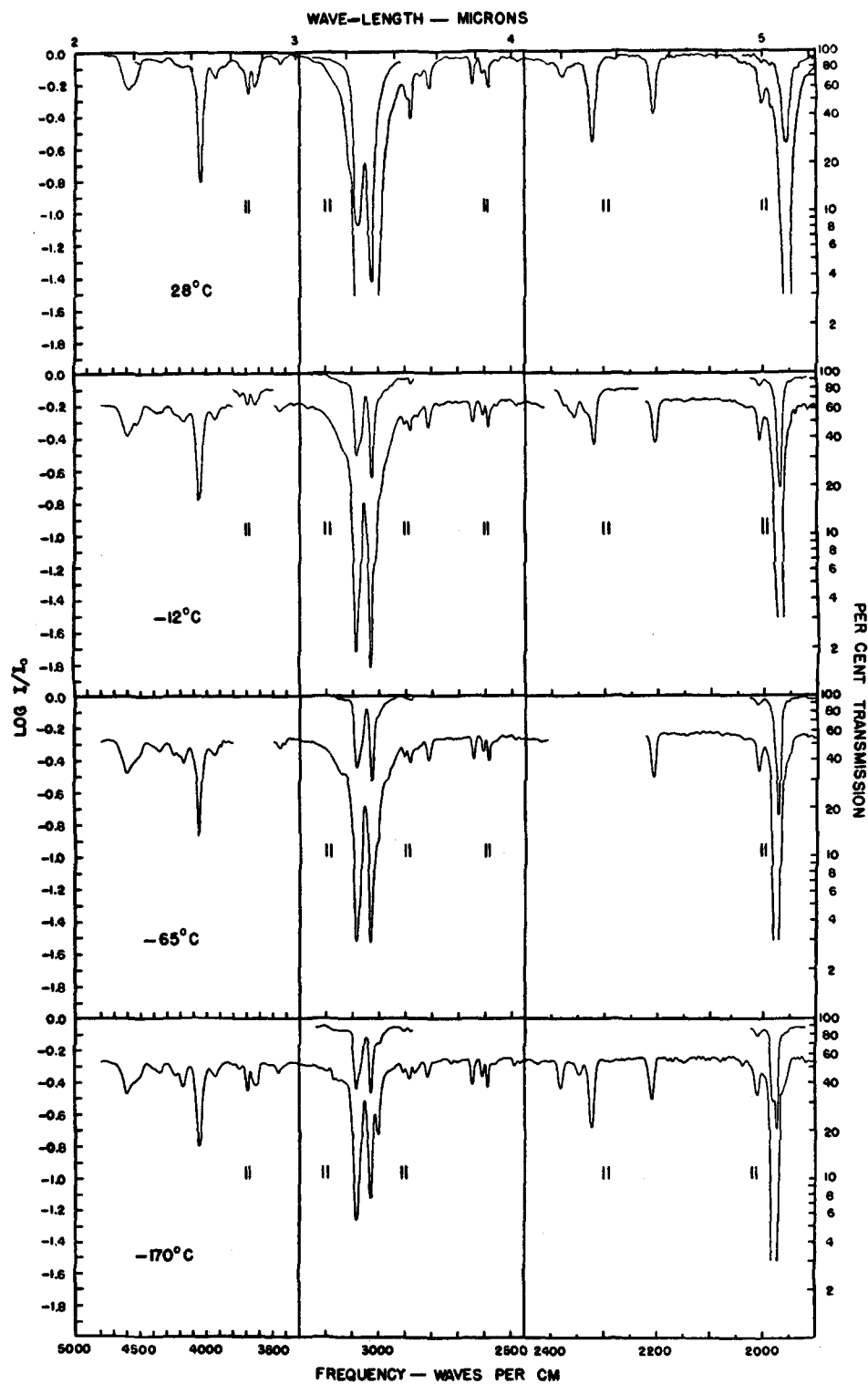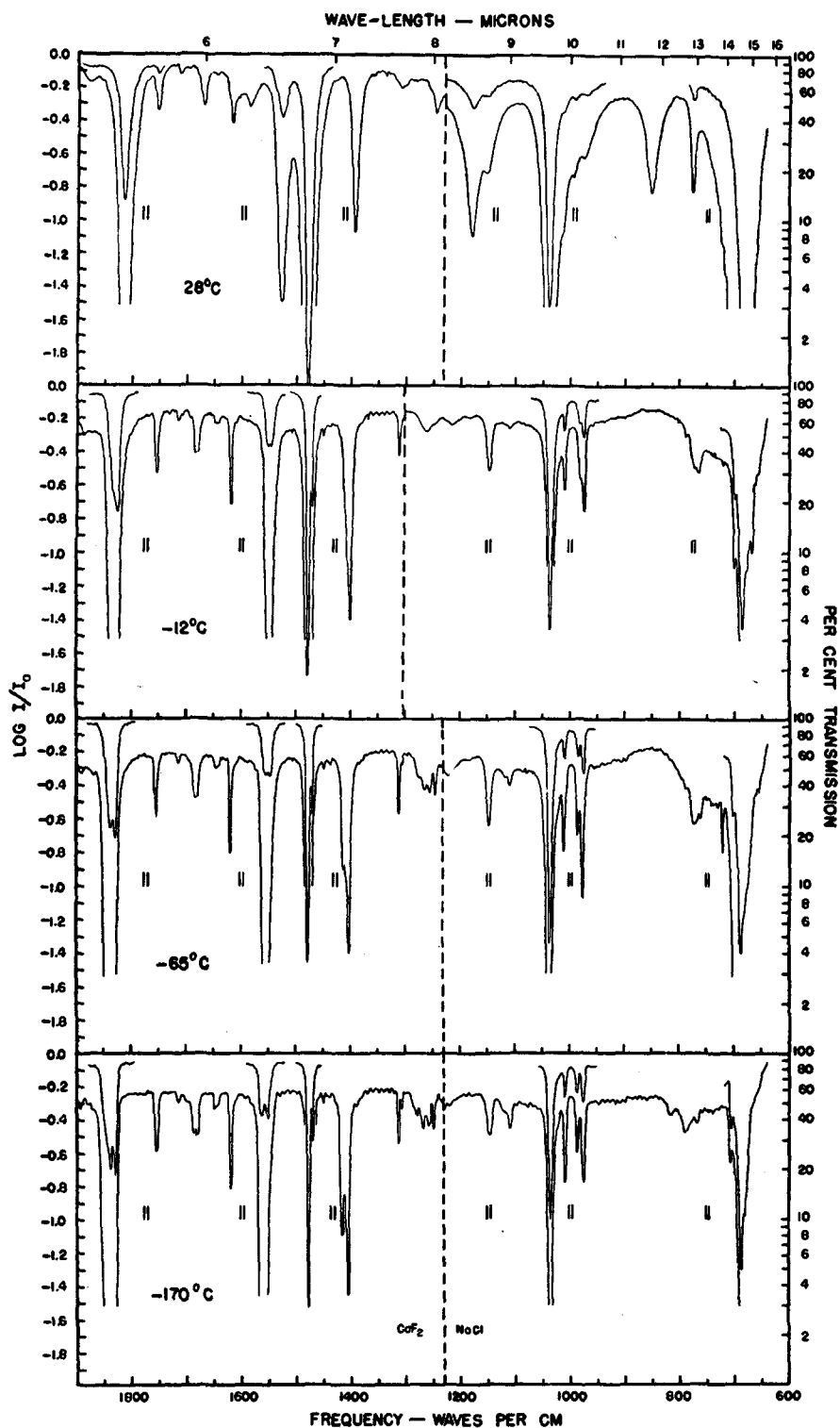[17] J. J. McGovern and R. A. Friedel, J. Opt. Soc. Am. 37, 660 (1947).

FIG. 1a. The infra-red spectrum of liquid and crystalline benzene between 5000 cm^{-1} and 1900 cm^{-1}. Spectral slit widths used in each region are indicated.

FIG. 1b. The infra-red spectrum of liquid and crystalline benzene between 1900 cm⁻¹ and 650 cm⁻¹. Spectral slit widths used in each region are indicated.

The absorption cell was of the transmission type similar to that described by Wagner[18] and could be directly inserted in the beam. It consisted of four main parts—the copper cooling block, the coolant reservoir to which the block was attached, the enveloping jacket, and the sample holder. The cooling block consisted of a piece of solid copper through which a rectangular hole had been machined. Two annular copper plugs kept the sample holder positioned in the block between them. One was soldered permanently in the opening while the other could be removed to introduce the

TABLE I. The infra-red frequencies of liquid and solid benzene.

Observed frequencies and intensities				Assignment	D_{6h} species	Calc. freq. Liq.	Calc. freq. Solid
28°C	−12°C	−65°C	−170°C				
~675 s	685 s	687 s	687 s	ν_{11}	A_{2u}	...	...
...	700 ww	702 ww	707 ww	...	...	...	...
776 mw	...	...	...	$\nu_9-\nu_{16}$	A_{2u}	773	759 / 769
...	769 mw	770 mw	769 / 788 mw / 816	ν_{11}+torsional lattice modes		...	768 / 785 / 811
852 m	...	...	...	ν_{10}	E_{1g}	849ª	854 / 864
975	975 / 982 mw	975 / 984 mw	975 / 987 mw	ν_{17}	E_{2u}	...	...
995	...	...	...	ν_5 or ν_1	B_{2g}, A_{1g}	...	...
~1013	1010 mw	1010 mw	1009 mw	ν_{12}	B_{1u}	...	...
1038 s	1036 s	1036 s	1035 s	ν_{18}	E_{1u}	...	...
...	1109 / 1117 ww	1109 / 1117 ww	1109 / ~1120 w	$\nu_{16}+\nu_4$	E_{1u}	1108	1108 / 1118
1150	1147 mw	1147 mw	1147 mw	ν_{15}	B_{2u}	...	...
1179 s	...	...	...	ν_9	E_{2g}	1178ª	...
...	1215 ww	1220 ww	1220 ww	$3\nu_{16}$	A_{2u}	1215	1215 / 1245
1246 mw	1245 / 1260 mw	1245 / 1255 / 1265 / 1275 mw	1249 / 1258 / 1267 / 1279 mw	$\nu_{16}+\nu_{10}$	E_{1u}	1255	1259 / 1269 / 1269 / 1279
...	1305	1305	1306	$\nu_{14}(C^{13}C_5{}^{12}H_6)$	B_{2u}	...	...
1310 w	1311 w	1311 w	1312 w	ν_{14}	B_{2u}	...	...
1394 ms	1401 ms	1402 / ~1412 ms	1405 / 1416 ms	$\nu_{16}+\nu_5$	E_{1u}	1400	1400 / 1410
...	1470 w	1470 w	1470 w	$\nu_{19}(C^{13}C_5{}^{12}H_6)$	...	...	...
1478 s	1478 s	1478 s	1478 s	ν_{19}	E_{1u}	...	...
1528 ms	1544 / 1551 ms	1547 / 1555 ms	1551 / 1563 ms	$\nu_{11}+\nu_{10}$	E_{1u}	1524	1551
1587 / ~1605 mw	...	...	...	ν_8 in res. with $\nu_1+\nu_6$	E_{2g} / E_{2g}	1596b / 1597	... / ...
1618 mw	1618 mw	1618 mw	1618 mw	$\nu_{12}+\nu_6$	E_{1u}	1616	1615
1647 ?	1644 ww	1644 ww	1645 ww	$\nu_{18}+\nu_6$	E_{1u}	1644	1642
1671 mw	1679 / 1684 mw	1680 / 1685 mw	1680 / 1687 mw	$\nu_{17}+\nu_4$	E_{1u}	1678	1678 / 1690
1713 ww	1715 ww	1714 ww	1714 ww	$\nu_{12}+\nu_4$	A_{2u}	1713	1713
1754 mw	1754 mw	1754 mw	1754 mw	$\nu_{15}+\nu_6$	E_{1u}	1756	1753
1815 s	1825 / ~1835 s	1828 / 1836 s	1829 / 1839 s / ~1850	$\nu_{17}+\nu_{10}$	E_{1u}	1824	1829 / 1839 / 1841 / 1851
1877 ww	1886 ww	1891 ww	1893 ww	$\nu_{18}+\nu_{10}$	A_{2u}	1886	1901
1959 s	1971 s	1973 s / ~1980 s	1974 s / 1986 s	$\nu_{17}+\nu_5$	E_{1u}	1970	1970 / 1982
1987 ww	...	...	...	$\nu_{12}+\nu_{17}$	E_{1g}	1985	...
2003 w	2008 w	2012 w	2011 w	{ $\nu_{16}+\nu_5$ or $\nu_{12}+\nu_5$ }	A_{2u} / A_{2u}	2001 / 2005	2011 / 2005
2208 mw	2206 mw	2210 mw	2210 mw	$\nu_{18}+\nu_9$	E_{1u}	2216	2210
2324 mw	2322 mw	...	2323 mw	$\nu_{18}+\nu_9$	E_{1u}	2328	2325
...	...	...	2347 ww	$\nu_{19}+\nu_{10}$	A_{2u}	2327	2342
2381 ww	2380 ww	...	2382 ww	$\nu_{18}+\nu_8$	E_{1u}	2378	2376
2591 / 2612 ww	2591 / 2610 ww	2588 / 2610 ww	2588 / 2608 ww	$\nu_{12}+\nu_8$c	E_{1u}	2597 / 2615	2597 / 2615
2648 ww	2648 ww	2647 ww	2647 ww	$\nu_{19}+\nu_9$	E_{1u}	2656	2652
2815 ww	2817 ww	2817 ww	2816 ww	$\nu_{19}+\nu_8$	E_{1u}	2818	2818
2845 ww	...?	...?	2862 ww	...	...	...	...
2883 w	2884 ww	2884 ww	2883 ww	...	...	...	...
2903 ww	2907 ww	2907 ww	2907 ww	$\nu_{14}+\nu_8$	E_{1u}	2906	2906
...	~2980 ?	~2990 ?	3000 w	...	...	...	...
3030 s / 3080 s	3030 ms / 3087 ms	3030 ms / 3086 ms	3030 ms / 3085 ms	ν_{20} in res. with $\nu_{19}+\nu_8$	E_{1u} / E_{1u}	3063 / 3074	3063 / 3074
...	~3070	~3070	~3070	ν_{13}	B_{1u}	...	...
...	~3140	3150 ww	3160 ww	...	...	...	...
3445 ww	3455 ww	3450 ww	3455 ww	$\nu_{16}+\nu_7$	A_{2u}	3452	3455
3645 w / 3695 w	3640 w / 3695 w	...	3630 w / 3688 w	ν_{20}d$+\nu_6$	E_{1u} / E_{1u}	3642 / 3696	3642 / 3696
3940 ww	3940 ww	3940 ww	3935 ww	$\nu_{20}+\nu_{10}$	A_{2u}	3912	3917
4050 m	4063 m	4063 m	4057 m	several possibilities	...	...	...
4200 ww	4180 ww	4177 ww	4177 ww	$\nu_{16}+\nu_7$	E_{1u}	4197	4187
...	~4240	4250 ww	4235 ww	$\nu_{13}+\nu_9$	E_{1u}	4248	4243
4350 ww	4360 ww	4360 ww	4355 ww	$\nu_{14}+\nu_7$	E_{1u}	4357	4352
~4560 m / 4600 m	4605 m	4605 m	4605 m	several possibilities	...	...	...

TABLE I. *Continued.*

ª Observed in Raman spectrum.
b Calculated from Raman doublet.
c Including resonance with $\nu_1+\nu_6$.
d Includes resonance with $\nu_{19}+\nu_8$.

sample holder. A thermocouple junction was soldered directly to the side of the block.

The sample holders were made from single crystal sheet silver chloride. This material has been described by Kremers.[19] Sample holders were constructed by placing a mica or silver chloride spacer between two rectangles of silver chloride, one 3 mm, the other 0.25 mm thick. The two pieces of silver chloride were then sealed around all sides with an electrically heated platinum wire loop, except for a minute opening left at one end for introducing the sample. When the sample holder had been filled, this opening was also sealed. The spacers used were either 50 microns or 250 microns thick.

Previous attempts to use potassium bromide were unsuccessful due to air bubbles being drawn in, and

[18] E. L. Wagner, thesis, Brown University, Providence, Rhode Island (1948).

[19] H. C. Kremers, J. Opt. Soc. Am. 37, 337 (1947).

cracking of the sample holder when it was cooled. In the silver chloride sample holders, the 3-mm layer provided both rigidity and heat conduction from the center of the film. The 0.25-mm layer, on the other hand, was flexible and yielded to atmospheric pressure when the volume decreased as the benzene solidified. This prevented the formation of vacuum pockets within the sample and was a major factor in minimizing scattering from the film.

The 0.25-mm silver chloride was found to cause pronounced interference bands throughout the sodium chloride and potassium bromide prism regions. The computed spacing of the interference peaks was $\Delta\nu = 9.7$ cm^{-1}. The observed value varied from 9.5 to 10 cm^{-1}. For the thick plate $\Delta\nu = 0.8$ cm^{-1} and the bands could not be detected. The interference bands were suppressed by rolling the silver chloride with a 35-mm glass tube on a glass plate so as to form shallow corrugations on the top surface. Thus a non-uniform thickness was obtained while the bottom surface remained essentially plane.

The temperatures attained by benzene films in this absorption cell were somewhat above those of the cooling block. This was demonstrated by embedding a thermocouple in a rectangle of 3-mm silver chloride of the same size as the sample holder, and measuring its temperature while the block was cooled. With the cooling block at $-15°C$, $-78°C$ and $-195°C$, equilibrium temperatures of the silver chloride plate were $-12°C$, $-65°C$, and $-170°C$. These probably correspond quite well to the film temperatures during absorption measurements.

The benzene was purified by the method of Kraus and Fuoss.[20] It was subjected to four successive fractional crystallizations, the resulting material freezing completely at the constant temperature of $5.51\pm0.01°C$. When care was taken to exclude moisture, it solidified to an ice-like mass composed of large single crystals. The benzene was stored over sodium-lead alloy in an all-glass still protected from atmospheric moisture.

The sample holder was filled by standing it vertically, with inlet downward, in a small bulb attached to a reservoir of dry, air-free benzene, thoroughly evacuating bulb and sample holder, condensing benzene vapor from the reservoir until the bottom of the holder was immersed in liquid, and then slowly admitting atmospheric pressure to the bulb. This last step forced liquid benzene through the tiny inlet, completely filling the space between the silver chloride plates. The sample holder was then removed from the bulb and the inlet sealed quickly with the hot platinum wire. If any benzene evaporated during this operation, so that an air bubble appeared in the film, the inlet was reopened and the sample holder refilled.

The behavior on freezing varied somewhat from film to film. If the sample holder had not been tightly sealed,

[20] C. A. Kraus and R. M. Fuoss, J. Am. Chem. Soc. 55, 21 (1933).

TABLE II. Fundamental benzene frequencies.

Active in D_{6h} model				Inactive in D_{6h} model			
Number and species	This research Liquid	Solid	Ingold et al.	Number and species	This research Liquid	Solid	Ingold et al.
$\nu_{11}(A_{2u})$	675*	687*	671§	$\nu_{12}(B_{1u})$	1010**	1010*	1010§§
$\nu_{18}(E_{1u})$	1038*	1036*	1037§	$\nu_{13}(B_{1u})$	3071†	3069†	3060§§
$\nu_{19}(E_{1u})$	1478*	1478*	1485§	$\nu_{14}(B_{2u})$	1310*	1312*	1648§§
$\nu_{20}(E_{1u})$	3063†	3063†	3073† 3080§§	$\nu_{15}(B_{2u})$	1150*	1147*	1110§§
$\nu_1(A_{1g})$	992§	990††	991.6§	$\nu_{16}(E_{2u})$	405**	405** 415**	405§§
$\nu_2(A_{1g})$	3062§	3060††	3061.9§	$\nu_{17}(E_{2u})$	975*	975* 987*	970§§
$\nu_6(E_{2g})$	606§	606**	605.6§	$\nu_3(A_{2g})$	1340**	1340**	1326§§
$\nu_7(E_{2g})$	3047§	3040††	3046.8§	$\nu_4(B_{2g})$	703§§	703**	703§§
$\nu_8(E_{2g})$	1596§§	1596**	1596§§	$\nu_5(B_{2g})$	995**	995**	985§§
$\nu_9(E_{2g})$	1178§	1174††	1178.0§				
$\nu_{10}(E_{1g})$	849§	854** 864**	848.9§				

* Observed, this research.
** Inferred, this research.
§ Observed, Ingold et al.
§§ Inferred, Ingold et al. Many of these values were confirmed by combinations observed here. See Table I.
† Assigned from Leberknight (see reference 23). 3073 cm^{-1} value is for benzene vapor.
†† Observed, Sirkar (see reference 21) Epstein and Steiner (see reference 22).

or if it contained a small air bubble or even a considerable amount of dissolved air, a cavity formed in the middle section of the film on solidification. If cooling was too rapid the supercooled benzene froze instantly to a translucent film which scattered incident radiation severely. All samples used for absorption measurements were observed, however, to crystallize slowly over a period of several seconds to a transparent continuous film. The 50μ-thickness, in particular, showed only slight visible indications of solidification and caused practically no scattering, as the experimental curves of Section IV indicate. The 250μ-films, on the other hand, scattered 40 to 50 percent of the incident radiation. As would be expected, the scattering increased as the temperature was lowered, and was slightly less at long than at short wave-lengths.

It seems possible that essentially non-scattering films of any thickness could be obtained by long periods of annealing at a temperature close to the melting point. For example, when a translucent 250μ-film was held at a temperature of 3 to 4°C for a period of two hours, a transparent spot appeared in the center and gradually enlarged toward the edges of the film, while the scattering decreased from 90 percent to 50 percent. It was observed that while a film was being cooled to low temperatures, scattering increased least when the cooling rate was very slow.

A careful analysis of errors arising in reading band centers, in calibration, in changing prisms and from

[21] S. C. Sirkar, Ind. J. Phys. 10, 109 (1936); 10, 189 (1936).
[22] H. Epstein and W. Steiner, Nature 133, 910 (1934); Zeits. f. physik. Chemie 26B, 131 (1934).
[23] C. E. Leberknight, Phys. Rev. 43, 967 (1933).

calibration drifts indicates that frequency assignments are good to within ±10 cm⁻¹ at 3μ and ±0.6 cm⁻¹ at 8μ with the calcium fluoride prism, and to within ±2.4 cm⁻¹ at 8μ and ±0.4 cm⁻¹ at 15μ with the sodium chloride prism. The reproducibility should be somewhat better since calibration errors are not involved.

IV. EXPERIMENTAL RESULTS

The absorption spectra of liquid benzene at room temperature, and of crystalline benzene at −12°C, −65°C and −170°C, in the wave-length region from 2μ to 15.6μ are presented in Figs. 1a and 1b. No scattering corrections have been made on these experimental curves, and the noise level has not been smoothed out. Table I lists the frequencies of the line centers as well as our assignments of the lines. The latter will be discussed in Sections VI and VII.

The data presented have been obtained with a calcium fluoride and a sodium chloride prism. The spectrum of the 15μ-region was obtained as well with a potassium bromide prism. Since it was identical with that obtained with the sodium chloride prism except for the effects of lower resolving power, it has not been reproduced here.

The spectra were obtained for a film thickness of approximately 250μ over the whole wave-length range, and of approximately 50μ in the vicinity of intense bands. The same thin film was used throughout the investigation, while three thick films were necessary. The complete solid spectra at −170°C and −65°C, and the spectrum from 2μ to 8μ at −12°C were determined from one such film. The remainder of the −12°C spectrum was obtained from another, and the liquid spectrum from a third. Although spacers of the same thickness were used for all three, it should be borne in mind that because of the low dimensional stability of the thin silver chloride sheet, the thicknesses of the three films were probably only approximately equal.

During the absorption runs at −65°C and −12°C the cell became contaminated with carbon dioxide gas and a trace of isopropyl alcohol. This invalidated portions of the spectra in the vicinity of 3750 cm⁻¹ and 2350 cm⁻¹. These portions were redetermined later on the same film used to complete the −12°C spectrum, but at this temperature only.

Although the sample holders were constructed so as to suppress interference effects, series of very weak bands, regularly spaced at ~10 cm⁻¹ apart, which must be residual interference bands, still occur throughout the spectra. Because of this, little significance can be attached to extremely weak bands of about the same intensity.

The spectrum of the liquid indicates that the benzene used in this research was of high spectroscopic purity. It is identical in every detail with that obtained by the U. S. Naval Research Laboratory, Washington, D. C.,[13] for a NBS Standard 99.95±0.02 mole percent specimen

except that the spectrum reported here is more completely resolved in some regions.

A striking feature of the solid spectra is the extreme sharpness of many of the bands, particularly of those assigned to the fundamental frequencies. Excluding the band system at about 3060 cm⁻¹ which involves two fundamentals plus a combination and the 685 cm⁻¹ band which is broadened for another reason, the seven remaining fundamentals at 1478, 1312, 1147, 1036, 1010, 987, and 975 cm⁻¹ have half-widths varying from 3.0 to 11 cm⁻¹ with an average of 7 cm⁻¹. This contrasts with widths of 13, 15, and 16 cm⁻¹ for the three corresponding bands in the liquid spectrum which are not overlapped by Raman-active fundamentals. The narrowness of these bands may be emphasized by remarking that the 1312 cm⁻¹ band at all three temperatures, and the 1478 and 1010 cm⁻¹ bands at the lowest temperature, are no wider than the spectral slit width. Their half-widths are 3, 5, and 5.5 cm⁻¹, respectively. These are among the narrowest infra-red bands ever reported.

A possible source of error in these measurements is the effect of reflection and scattering. They both depend upon the refractive index and the extinction coefficient at any wave-length. In the vicinity of a strong absorption band both quantities vary widely and may give rise to spurious peaks or shoulders, particularly on the high frequency side of the peak.[24] In the case of benzene the possible magnitude of reflection effects is negligible, but the presence of considerable scattering makes errors from this source possible, particularly in the 250μ-films. However, the thin film was essentially non-scattering, so that such effects should appear much more prominently in the thick film. Examination of Figs. 1a and 1b indicates that there are no significant scattering effects in the spectra presented here.

Comparison of the spectra at room temperature and at −12°C reveals all the changes generally observed to accompany transition from the liquid to the solid state. Most striking is the disappearance of two moderately strong bands at 850 cm⁻¹ and 1180 cm⁻¹ and a weaker band at 1585 cm⁻¹, as well as components at 995 cm⁻¹ and 1605 cm⁻¹. There is also a general pronounced sharpening of the remaining bands, disclosing in a number of cases a composite structure. In addition, frequency shifts of more than 5 cm⁻¹ are observed for nine bands, the largest being from 1527 cm⁻¹ to 1547 cm⁻¹. For all but the band at 776 cm⁻¹, these shifts are to higher frequencies.

A number of temperature effects are observed within the three solid spectra. One such is the improved characterization of band structure at lower temperatures. Single lines are more sharply defined, and the components of composite bands more clearly resolved. In fact, the double nature of the strong band at 1975 cm⁻¹ is revealed only at the lowest temperature. Apparent

[24] W. C. Price and K. S. Tetlow, J. Chem. Phys. 16, 1157 (1948).

changes in the integrated intensities of some of the strong bands are observed. Those at higher frequencies have essentially constant intensities, but the intensities of the three strong lower frequency fundamentals at 1478 cm^{-1}, 1036 cm^{-1}, and 687 cm^{-1} decrease with temperature in the respective ratios 100:82:64, 100:85:63, and 100:92:63. The combination band at about 1400 cm^{-1} maintains a constant intensity, however.

The band at 1110 cm^{-1} exhibits an unusual effect. As the temperature of the film is lowered, the intensity of this band increases manyfold. This is accompanied by a decrease in intensity of the neighboring band at 1147 cm^{-1}, which is identified as one of the B_{2u} fundamentals. The behavior appears to be due to an interesting case of Fermi resonance. It is discussed in Section VII.

Frequency changes are generally slight, being of about the order of the reproducibility, although in the case, for example, of the band at 1547 cm^{-1}, there is evidence of a real trend to slightly higher frequencies as temperature is decreased.

V. ASSIGNMENTS

Our assignments for the fundamental vibration frequencies are given in Table II, along with those obtained by Ingold et al. They have been obtained from a number of sources and represent what we believe to be the best choices available. Their origin is indicated in the table. They are classified according to their D_{6h} species, since this proves convenient in referring to the work of other investigators and in comparison with the free molecule. Wilson's number system[5] for the benzene fundamentals is used.

These assignments, with but two exceptions, agree with those of Ingold et al. to better than 1 percent. The other two, ν_{14} and ν_{15} of the species B_{2u}, were observed directly in the present investigation and differ from their earlier assignments by 20 percent and 3.2 percent, respectively. Since the evidence for these assignments is independent of that of Ingold et al., based on the Redlich-Teller product rule, it will be discussed in some detail.

VI. THE ACTIVE D_{6h} FUNDAMENTALS

A. The A_{2u} and E_{1u} Fundamentals, ν_{11}, ν_{18} and ν_{19}

Apart from shifts due to change of phase, the frequencies observed here agree closely with those obtained by Ingold et al. There is no indication of splitting of the degenerate E_{1u} mode, ν_{18}, in the solid. The very sharp but weak line at 1470 cm^{-1}, on the shoulder of ν_{19}, may possibly result from splitting of ν_{19} along with a crystal orientation effect but both the magnitude of the frequency shift and the intensity suggest strongly that it is due to $C^{13}C_5{}^{12}H_6$ which constitutes 6.6 percent of the sample.

B. The E_{1u} Fundamental, ν_{20}

The best data available for the assignment of this mode are the high resolution studies of gaseous, liquid, and solid benzene in the 3μ-region made by Leberknight.[24] In the vapor he found two strong perpendicular bands whose Q-branches lay at 3100 and 3046 cm^{-1} as well as a weak maximum at 3074 cm^{-1}. In the liquid and solid he observed three strong components at 3091, 3071, and 3036 cm^{-1}. In both cases the lowest frequency was most intense. In addition a weak component appeared in the solid at 3055 cm^{-1}.

Ingold et al. interpreted the corresponding doublet in their vapor spectrum as due to Fermi resonance between ν_{20} and $\nu_{19}+\nu_8$. This interpretation is probably valid. In the vapor three components may result from resonance between ν_{20}, $\nu_{19}+\nu_8$ and $\nu_{19}+\nu_1+\nu_6$, all at about the doublet mean of 3073 cm^{-1}.†† In the liquid and solid, both strong branches drop by about 10 cm^{-1} and the mean is at 3063 cm^{-1}. The middle member at 3071 cm^{-1} in the liquid, and 3069 cm^{-1} in the solid, may be assigned to the B_{1u} fundamental, ν_{13}, which is allowed in these spectra. It had been estimated by Ingold et al. to lie at 3060 cm^{-1}. The bands in Fig. 1a agree with Leberknight's spectra except for the lower resolution.

The resonating doublet just described appears to enter into a combination with the Raman active fundamental ν_6 to produce the doublet observed in both liquid and solid at 3645 and 3695 cm^{-1}. Ingold attributed this doublet to $\nu_{20}+\nu_6$ and $\nu_{13}+\nu_6$, but the present explanation seems preferable.

C. The A_{1g}, E_{2g}, and E_{1g} Fundamentals,
ν_1, ν_2, ν_6, ν_7, ν_8, ν_9, ν_{10}

None of these Raman active fundamentals have been observed in the solid. On the other hand, ν_9 and ν_{10} are both observed in the liquid, as is the doublet due to Fermi resonance between ν_8 and $\nu_1+\nu_6$ first explained by Wilson.[25] This appearance of Raman frequencies in the liquid spectrum and their complete absence from the spectrum of the crystal has been pointed out by Halford and Schaeffer[11] as a striking demonstration that the selection rules for the crystal are strictly obeyed.

The behavior of the combination bands which involve the fundamental $\nu_{10}(E_{1g})$ in the infra-red spectrum of the crystal is very interesting. They indicate strongly that in the solid state this fundamental is split into two components, separated by 10 cm^{-1} and whose frequencies lie about 5 and 15 cm^{-1} higher than those of the liquid. For instance, the strong band at 1528 cm^{-1} in the liquid can be assigned only to the combination $\nu_{11}+\nu_{10}$. In the solid it becomes a doublet at 1544,

---

†† The rather large splitting, 54 cm^{-1}, and the extent to which intensity is partitioned suggests a rather close coincidence of levels. Since the lower branch is more intense, ν_{20} may be slightly lower than the assigned frequency.

[25] E. B. Wilson, Jr., Phys. Rev. 46, 146 (1934).

1551 cm^{-1} (at $-12°C$), 1547, 1555 cm^{-1} (at $-65°C$) and 1551, 1563 cm^{-1} (at $-170°C$). Even with the higher ν_{11} value observed in the crystal it is necessary, in order to get reasonable agreement between calculated and observed values, to split ν_{10} and raise the frequency of its components. The suggested shift of ν_{10} is the minimum which can be tolerated.

The strong band at about 1830 cm^{-1}, and the much weaker one at about 1250 cm^{-1}, both support this splitting convincingly. They are due to the combinations $\nu_{17}+\nu_{10}$ and $\nu_{16}+\nu_{10}$, respectively, involving the pair of degenerate E_{2u} fundamentals. The latter plainly exhibits four components and the shoulders on the former suggest more than two. They require the frequencies previously chosen for ν_{10}. They will be considered in greater detail in the discussion of ν_{16} and ν_{17}.

On the other hand, the evidence from three very weak combination bands, all of species A_{2u}, is less definite. $\nu_{20}+\nu_{10}$, at 3940 cm^{-1}, shows only one component, but in this region the resolution was inadequate to resolve two components 8 cm^{-1} apart. $\nu_{19}+\nu_{10}$ was observed at 2347 cm^{-1} in the solid at $-170°C$. It also shows but one maximum although, again, the resolution may have been inadequate. $\nu_{18}+\nu_{10}$ is observed in both liquid and solid, and although structure appears to be exhibited at $-170°C$, the band is too weak to reach definite conclusions.

The conclusions reached about the behavior of ν_{10} in the crystal await direct confirmation in the Raman spectrum. That some splitting and frequency shift takes place seems inescapable.

VII. INACTIVE FUNDAMENTALS

A. The E_{2u} Fundamentals, ν_{16} and ν_{17}

The value of about 405 cm^{-1} for ν_{16} in the liquid and in the vapor is by now firmly established. Although it was not found in this research, Plyler[26] has recently observed it at 403 cm^{-1} in the infra-red spectrum of liquid benzene. It has also been obtained from the Raman spectrum of the liquid,[27] from partially deuterated benzene,[4] from the ultraviolet absorption spectrum[28] and from the fluorescence spectrum.[29] The last two have shown this frequency to be degenerate, and since all other degenerate vibrations are known, it is positively assigned to the E_{2u} class.

Ingold's assignment of ν_{17} to about 970 cm^{-1} was based on two independent values of the frequency product $\nu_{16}\times\nu_{17}$, together with the frequency of ν_{16}. It is certainly firm. We have observed ν_{17} directly in both the liquid and solid spectra. The 985 cm^{-1} shoulder found by Ingold et al. in the liquid has been resolved into two definite lines, one of which, at 975 cm^{-1}, can

only be ν_{17}. In the crystal it appears plainly and the splitting of this degenerate fundamental is striking, a second component appearing at a frequency 12 cm^{-1} higher.

The strong combination line, $\nu_{17}+\nu_5$ (ν_5 is the non-degenerate B_{2g} mode), at about 1970 cm^{-1}, mirrors almost exactly the behavior of the fundamental. Although single in the liquid, the splitting is resolved at $-170°C$ in the crystal, the two peaks being separated by 11 cm^{-1}. As in the fundamental, the higher frequency branch appears less intense.

The strong combination, $\nu_{17}+\nu_{10}$, which we have previously mentioned, is also fruitful. Using the observed ν_{17}-frequencies and the postulated ν_{10}-frequencies, components are predicted at 1829, 1839, 1841, and 1851 cm^{-1}. The observed structure with sharp peaks at 1829 and 1839 cm^{-1} and a shoulder at approximately 1845 cm^{-1} ($-170°C$) agrees well with this prediction.

Still another weaker combination band, $\nu_{17}+\nu_4$, involving the other inactive B_{2g} mode, is split at all three temperatures. At $-170°C$ the splitting is 7 cm^{-1}.

Let us now consider ν_{16} further. Like ν_{17} it is associated in three bands with the fundamentals ν_5, ν_{10}, and ν_4. The behavior of the two sets is so similar that a splitting and upward shift of one branch of ν_{16} is obvious. The moderately strong combination, $\nu_{16}+\nu_5$, at 1410 cm^{-1} is fully resolved at $-170°C$ and the splitting is 10 cm^{-1}. As with ν_{17}, the high frequency branch is definitely the weaker. We must accordingly conclude that in the crystal the two components of ν_{16} lie at 405 and 415 cm^{-1}.

We have previously mentioned the weaker combination $\nu_{16}+\nu_{10}$. Using the postulated splitting, we predict components at 1259, 1269, 1269, and 1279 cm^{-1}. In fact, all four components are resolved. The resemblance between the outlines of this band and the corresponding $\nu_{17}+\nu_{10}$ is marked, although the resolution is somewhat better in this region.

In the case of the third band, $\nu_{16}+\nu_4$ (species E_{1u}), a shoulder is almost resolved at $-170°C$. It is at a frequency 7 cm^{-1} higher than the peak. This band is quite unusual in that as the temperature is lowered, its intensity shows a remarkable increase, accompanied by a decrease in the intensity of the neighboring fundamental, $\nu_{15}(B_{2u})$. This interesting effect, attributed to Fermi resonance, is considered further under ν_{15}.

These fundamentals are also observed in the very weak combinations $\nu_{16}+\nu_7$, $\nu_{17}+\nu_7$, $\nu_{16}+\nu_8$ and $\nu_{17}+\nu_8$. None of these are resolved, however.

B. The B_{1u} Fundamentals, ν_{12} and ν_{13}

The carbon bending frequency, ν_{12}, has been firmly established at about 1010 cm^{-1}. It is observed here for the first time as a sharp line at 1010 cm^{-1} in the solid at all three temperatures. We have assigned the hydrogen stretching frequency, ν_{13}, to the middle component of the 3.25μ-band in Leberknight's data.[24] In this research it is present as a shoulder only.

[26] E. K. Plyler, J. Chem. Phys. 16, 1008 (1948).
[27] R. C. Lord and D. H. Andrews, J. Chem. Phys. 41, 149 (1938).
[28] H. Sponer et al., J. Chem. Phys. 7, 207 (1939).
[29] See reference 4, Part XXI.

C. The A_{2g} Fundamental, ν_3

Ingold *et al.* placed this vibration firmly in the vicinity of 1330 cm^{-1} by means of the frequency product rule. They then assigned it to the extremely weak Raman line at 1326 cm^{-1} observed only by Grassmann and Weiler.[30] In support they cite the Raman frequency 2925 cm^{-1} which they ascribe to $\nu_3+\nu_8$, and a "rather prominent" infra-red band at 2356 cm^{-1}, which they assign to $\nu_{18}+\nu_3$. This investigation shows that the 2356 cm^{-1} band has three components, a prominent one at 2323 cm^{-1}, a weaker one at 2380 cm^{-1} and a very weak third already mentioned in connection with ν_{10}. The first must involve ν_{15}, as will be shown, but the second is probably the $\nu_{18}+\nu_3$ combination. Figure 1a also shows a weak but definite band at 2816 cm^{-1} which may be attributed to $\nu_{19}+\nu_3$.

Both of these infra-red combinations as well as the Raman combination cited by Ingold indicate a fundamental frequency of about 1340 cm^{-1}, and if the Raman value for the fundamental proved spurious, this higher value would be preferred.

D. The B_{2g} Fundamentals, ν_4 and ν_5

Ingold *et al.* have placed these two puckering vibrations in the vicinity of 700 and 990 cm^{-1}, respectively, using two independent values of the frequency product $\nu_4 \times \nu_5$. They then assigned ν_5 to a shoulder which they had observed in the infra-red spectrum of liquid benzene. The shoulder observed by Ingold has been resolved into two distinct bands at 975 cm^{-1} and 995 cm^{-1}. The first we have assigned to ν_{17} and the other, since it is present in the liquid spectrum alone, must be either ν_5 or ν_1. This value is also obtained from the two strong combination bands, $\nu_{16}+\nu_5$ and $\nu_{17}+\nu_5$ which were discussed previously. These bands might also involve ν_1, but this seems unlikely because of the parallelism between them and the combination bands involving ν_4. Moreover, if ν_1 were involved these would be the only combination bands observed in which the D_{6h} selection rules were violated. No other combination lines involving ν_5 are observed in the infra-red spectrum except that $\nu_{12}+\nu_5$, which is predicted at 2005 cm^{-1}, is one of two possibilities for the line observed at 2011 cm^{-1} and $\nu_{13}+\nu_5$ is a possible candidate for the band at 4060 cm^{-1}.

ν_4 has not been observed directly, but Ingold's value of the fundamental frequency is supported by three combination bands, $\nu_{16}+\nu_4$ which is a weak temperature-dependent band at 1110 cm^{-1}, $\nu_{17}+\nu_4$ which is the weak band at 1680 cm^{-1} and $\nu_{12}+\nu_4$ which is an extremely weak but definite band at 1715 cm^{-1}. All have been discussed previously. On the other hand, it appears to us that the Raman line at 2294 cm^{-1} which Ingold *et al.* have used to support this same assignment is in fact $2\nu_{15}$.

[30] P. Grassmann and J. Weiler, Zeits. f. Physik **86**, 321 (1933).

E. The B_{2u} Fundamentals, ν_{14} and ν_{15}

One of the most striking results of the study of the benzene crystal is that it appears likely that the B_{2u} carbon stretching frequency, ν_{14}, occurs at 1311 cm^{-1}, a frequency almost 200 cm^{-1} lower than the lowest value that has been obtained theoretically, and 338 cm^{-1} lower than that obtained by Ingold *et al.*[31]

Ingold *et al.* have pointed out, however, that since ν_{14} should have very nearly the same frequency in all of the isotopic benzenes, the frequency product ratios give practically no information regarding it. On the other hand, their deductions regarding the hydrogen frequency, ν_{15}, are certainly sound.

Ingold *et al.* indicated a frequency of 1110 cm^{-1} for ν_{15}. In the infra-red spectrum of the crystal, where ν_{15} is allowed, one is struck by the presence of the weak but fairly sharp line at 1147 cm^{-1} at all three temperatures. It has no possible interpretation as a combination frequency, so its assignment to ν_{15} is clearly indicated. In the liquid spectrum, it is present as a band just resolved at 1152 cm^{-1} on the shoulder of an adjacent moderately strong Raman-active frequency.

There is strong support for this assignment among the combination bands. A weak but sharp line at 1754 cm^{-1} in all four spectra can have no interpretation other than $\nu_{15}+\nu_6$ with a calculated value of 1753 cm^{-1}. Similarly, the fairly prominent band at 2323 cm^{-1} in both the liquid and the crystal must be attributed to $\nu_{15}+\nu_9$. In addition, the Raman line at 2294 cm^{-1}, already mentioned, agrees well with the interpretation $2\nu_{15}$ although in this case the alternative $\nu_4+\nu_8$ is also a possibility.

It is also satisfying that the Raman line and infra-red vapor band used by Ingold *et al.* in arriving at the 1110 cm^{-1} value for ν_{15} can be simply interpreted. The former, at 2128 cm^{-1}, fits the combination $\nu_{15}+\nu_{17}$ (calculated 2125 cm^{-1}). A higher resolution study of benzene vapor[32] has shown that the band observed by Ingold at 2288 cm^{-1} has components at 2220 and 2340 cm^{-1}, the latter having a pronounced shoulder at about 2400 cm^{-1}. These all correspond to lines in the liquid and solid spectra; in particular, that at 2340 cm^{-1} corresponds to the 2323 cm^{-1} band $\nu_{15}+\nu_9$. It is interesting to note that the other ν_{15} combination appears at 1770 cm^{-1} in this vapor spectrum compared with 1754 cm^{-1} in the liquid and solid. These data indicate that ν_{15} has a somewhat higher frequency in the vapor, tentatively estimated to be about 1160 cm^{-1}.

The band which does in fact occur in the vicinity of 1110 cm^{-1} (which we have assigned to $\nu_{16}+\nu_4$) shows a peculiar temperature dependence. As the temperature is lowered its intensity shows a manyfold increase, accompanied by a steady decrease in the intensity of ν_{15}. Whereas a variety of factors can explain a decrease in intensity in the spectrum of the solid, only one, Fermi

[31] See reference 4, Part XXI.
[32] A.P.I. Research Project 44, Spectrogram No. 122, contributed by the Texas Company, Beacon, New York.

resonance, can account for such an increase. The difference in symmetry species of fundamental and combination, B_{2u} and E_{1u}, offers no fundamental difficulty since in the benzene crystal, vibrations, strictly speaking, belong only to the two representations, A_g and A_u of the point group C_i. On the other hand, it is surprising to find appreciable interaction when it is not allowed by the gas symmetry. The intensity change may be explained in this way if the separation between the two levels decreases somewhat as the temperature is lowered and intensity is increasingly "borrowed" from the fundamental by the combination. In this regard, it is noteworthy that the sum of the two intensities is very nearly constant.

In order to preserve Ingold's frequency products, the suggested change in ν_{15} would fix ν_{14} in the vicinity of 1600 cm^{-1}. Its assignment to the weak but extremely sharp line at 1618 cm^{-1} is a possibility since it is generally observed that fundamentals are particularly sharp in crystalline spectra. Only one line in the entire spectrum is narrower than the 1618 cm^{-1} line. There is, however, an alternative assignment to this line, namely, the combination $\nu_{12}+\nu_6$ which is allowed in the vapor spectrum, and has been observed by Ingold et $al.$, Halford and Schaeffer and others. This would appear to make the fundamental assignment unlikely except for a discrepancy in the gas spectra in that the spectrum of the vapor obtained by the Texas Company[32] with the highest resolution yet used on benzene vapor, and a sample of exceptional purity, does not show the 1617 cm^{-1} band. In the same spectrum, nevertheless, the weak band at 779 cm^{-1} shows a peak absorption of about 15 percent as compared to less than 5 percent found by Ingold, et $al.$ It is perhaps revealing that the sample pressure used in this instance was 24.1 mm, compared to 40 mm employed by Ingold, et $al.$ and 48 mm by Halford and Schaeffer. This suggests that the line in the gas may be due to benzene adsorbed on the cell windows so that this assignment for ν_{14} is at least tenable. However, it has practically no support from combination frequencies. The very weak line at 2610 cm^{-1} which has already been assigned to $\nu_{12}+\nu_8$ might be assigned to $\nu_{14}+\nu_1$, but in that case it would be the only combination observed which is not allowed in the vapor spectrum.

However, if this assignment is accepted for ν_{14}, there is no reasonable assignment for the very sharp line which appears at 1311 cm^{-1}. Its extreme sharpness suggests that it may be a fundamental. It fits the forbidden combination $\nu_4+\nu_6(E_{1g})$ very well, but if it were indeed this forbidden transition it would be the more surprising since not only would it be the only such case observed but, in fact, the only combination observed which is not allowed in the vapor. We suggest that it is the fundamental, ν_{14}.

A variety of evidence supports this assignment. Ingold, et $al.$ have observed Raman lines which they consider of anomalous intensity for combination fre-

quencies at 2618 cm^{-1} in C_6H_6, 2590 cm^{-1} in C_6H_5D, 2583 cm^{-1} in 1,4-$C_6H_4D_2$ and 2571 cm^{-1} in C_6D_6. They have also found a weak Raman line at 2581 cm^{-1} in 1,2,4,5-$C_6H_2D_4$.[33]

It seems likely that these are all first overtones of ν_{14} (and ν_{14}-like vibrations of the less symmetrical benzenes). They also observe a Raman fundamental at 1292 cm^{-1} in C_6H_5D which they assign to the B_1 species of C_{2v}. This species includes B_{2u} of D_{6h}. Similarly, their infra-red curves for C_6H_5D show a shoulder at about 1295 cm^{-1}.

Using these frequencies we can recalculate some of the product ratios used by Ingold. For example, using one-half the Raman frequencies for ν_{14} in the isotopic benzenes we obtain:

$$\frac{\prod B_{2u}(C_6H_6)}{\prod B_{2u}(C_6D_6)} = \frac{1310\times1150}{1285\times825}$$

$$= 1.421 \text{ (harmonic value 1.414)}.$$

$$\frac{\prod B_{2u}\cdot E_{1u}(C_6H_6)\cdot}{\prod B_{3u}(1,4\text{-}C_6H_4D_2)} = \frac{1310\times1150\times1037\times1478\times3080}{1292\times1106\times814\times1413\times3079}$$

$$= 1.405 \text{ (harmonic value 1.396)}.$$

We have used Ingold's frequencies in these products except for ν_{14} and ν_{15}. It is apparent that the agreement is good. This is not surprising since the ratios are almost independent of the choice of ν_{14}, although it is interesting that the new choice of ν_{14} apparently compensates the shift in ν_{15} adequately.

The strongest support in our own data lies in the sharp but extremely weak peak at 1305 cm^{-1} which can be ascribed to the ν_{14}-like vibration of $C^{13}C_5{}^{12}H_6$. ν_{14} is one of the three fundamentals in these spectra in which this isotope shift might be observed and the shift is just that expected. The combination band at 2907 cm^{-1}, to which no other binary combination can be assigned, may result from $\nu_{14}+\nu_8$ (calculated, 2908). Finally, the line at 4355 cm^{-1} can be assigned to $\nu_{14}+\nu_7$ (calculated 4359 cm^{-1}) and in this case, too, no other binary combination will fit. This assignment obviously demands further examination, but the evidence for 1310 cm^{-1} seems stronger than for any frequency previously proposed.

VIII. COMBINATION BANDS

Most of the bands arising from binary combinations have been discussed in preceding sections. Details of others are given in Table I. A number, however, deserve further consideration.

The sharp band appearing in the liquid at 776 cm^{-1} and present as an apparently real component of the vapor spectrum at 779 cm^{-1} has been attributed by Ingold et $al.$ to the difference band $\nu_9-\nu_{16}$ (A_{2u}, calculated 773 cm^{-1}). The corresponding band system appear-

[33] Personal communication.

ing in the solid cannot possibly be explained by the difference frequency alone. The intensities of the difference band at $-12°C$, $-65°C$, and $-170°C$ would have to be in the ratio $100:57:3$ while the bands in Fig. 1b show little, if any, total intensity change. It should be noted, however, that the shape of the band does change markedly with temperature. Another explanation for this absorption region may be suggested in the case of the crystal, namely, a combination between ν_{11} and certain torsional lattice modes which have been observed in the Raman spectrum of solid benzene.[22,34] If the $\nu_9 - \nu_{16}$ assignment is valid for liquid and vapor, the solid band must result from a superposition of the two effects.

If the $\nu_9 - \nu_{16}$ assignment is correct for this reasonably strong band, it seems surprising that the corresponding summation band does not appear at all at about 1583 cm^{-1}. There is certainly no trace of it in the solid spectra. The validity of this assignment could readily be tested by measuring the temperature dependence of its intensity in the liquid. The expected intensity increases by 51.2 percent in going from 6°C to 75°C.

Several lines can be interpreted only as ternary combinations. Such possible combinations are very numerous and may be responsible for some of the very weak bands which we have assigned otherwise. Because of the large number of possibilities no assignment has been attempted for these lines.

Gross and Vuks[34] and Sirkar[22] have investigated the Raman spectrum of crystalline benzene in the vicinity of the exciting line. The former, using single crystals of unspecified orientation, found intense Raman lines at 63 and 108 cm^{-1} when the specimen was at 2°C to 3°C. The latter, using translucent, multicrystalline masses, found three intense lines at 81, 98, and 124 cm^{-1} with the specimen at liquid air temperature. He also found that the frequencies are strongly temperature dependent.

According to I, three lattice modes of the crystal, corresponding to in-phase libration of all benzene molecules about the three Cartesian axes, may be active in the Raman spectrum. It seems likely that the observed frequencies are those modes.[35] In that case it is possible that Gross and Vuks failed to observe the third component because of the orientation of their crystal. These modes may combine with any infra-red active modes. If we assign the three observed components at $-170°C$, as combinations with ν_{11}, the lattice frequencies are approximately 82 cm^{-1}, 101 cm^{-1} and 128 cm^{-1}. The agreement with the Raman data taken at the same temperature is surprisingly good.

At the two higher temperatures, it appears that, in accordance with the Raman data, the lattice frequencies become lower. The simultaneous increase in the intensity of the superimposed difference band makes a detailed analysis impossible. That ν_{11} couples with lattice modes is made more probable by the fact, also, that the line width is more than twice as great as for any other fundamental. Furthermore, the line is not symmetrical and it appears to have considerable structure.

IX. ORIENTATION EFFECTS

It is possible to obtain still further information by considering the effect of crystal orientation in unpolarized light, or better, in polarized light. According to the x-ray structure of Cox,[15] the plane of the benzene molecule is approximately parallel to the b-axis of the crystal and approximately bisects the angle between the a and c axes. The three axes are all orthogonal and the a and c axes are nearly equal.

On this basis we can predict that the dipole moment vector of all out-of-plane vibrations (A_{2u} and E_{2u} modes) will lie in the ac plane. Hence they should be observed with infra-red radiation polarized in the ac plane but not if the electric vector is parallel to the b-axis of the crystal. In the case of unpolarized light no orientation effects may be expected.

In the case of non-degenerate in-plane modes (B_{1u} and B_{2u} modes), we can only say that the dipole moment change lies in a plane containing the b-axis. Using light polarized perpendicular to and along the b-axis would allow the determination of the direction of the dipole moment change when these modes are made allowed in the crystal.

In the case of the E_{1u} modes, which may be split by the crystalline field, we expect that one of the components will be polarized along the b-axis and one perpendicular to it. Hence they can be plainly distinguished in polarized light. Further than that, one of the components should not be observed in unpolarized light directed along the b-axis of the crystal. This last is the only such effect we might have observed. Except for ν_{19} we found no indication of splitting of these modes, and in the case of ν_{19} the sharp peak on its low frequency side appears to be due to isotopic carbon. The absence of any observable splitting of these modes leads to two possible conclusions: either the films were highly oriented with the b-axis perpendicular to the surface and one component was completely suppressed, or the splitting of the E_{1u} modes does not exceed 2 or 3 cm^{-1}. The same reasoning applies to E_{1u} combinations involving the Raman active E_{2g} fundamentals. Since no splitting of any of these lines was observed, we are left with the same alternative conclusions.

[34] E. Gross and M. Vuks, Nature 135, 100 (1935); J. de phys. et rad., series 7, 7, 113 (1936).

[35] A. Kastler and A. Rousset, Phys. Rev. 71, 455 (1947).