

Motions of Molecules in Condensed Systems. II. The InfraRed Spectra for Benzene Solid, Liquid, and Vapor in the Range from 3 to 16.7 μ

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Motions of Molecules in Condensed Systems. II. The Infra-Red Spectra for Benzene Solid, Liquid, and Vapor in the Range from 3 to 16.7 μ

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Infra-red spectra are compared throughout the interval from 600 to 3300 wave numbers for the same amount of benzene existing separately as solid at 3°, liquid at 8°, and vapor at 20°C. The comparison demonstrates convincingly that (1) predictable selection rules for the solid are obeyed strictly, (2) there are no selection rules operating in the liquid phase, (3) the shift of molecular frequencies induced by successive stages of condensation is small and can be ignored in the approximation that regards the vibrations of an isolated molecule as harmonic ones, (4) the intensification of components of the spectrum accompanying changes of state proceeds as predicted qualitatively in an earlier paper, (5) all proposed complete assignments of the fundamental frequencies of benzene require revision. The components appearing in the several spectra are classified in accordance with a scheme suggested by the selection rules for the vapor and solid.

INTRODUCTION

INFRA-RED absorption bands are characterized by the locations of their centers on the frequency scale, by their fine structures or apparently continuous envelopes, and by their intensities. When a band is observed in the spectrum of a vapor its characteristics can be interpreted readily to a useful degree of approximation in terms of a molecular model wherein vibration and rotation are separable motions. The location of the band center measures the difference in energy between two vibrational states; the envelope¹ or fine structure, as the case may be, reveals information concerning the quantized rotational states; the integrated intensity,² when properly interpreted, measures the effective charges on vibrating parts of the molecule. When the molecule enters a condensed phase, its bands become altered; the location of a band is shifted, both the envelope or fine structure and the intensity are changed. Furthermore, new bands may develop in the spectrum of the condensed phase where none appear in the spectrum of the vapor. These phenomena are induced by intermolecular forces; they provide a little used and, in some respects, highly discerning method for studying matter in its condensed states. However, there are few data in the literature that are suitable for such an undertaking.

In order to avoid uncertainties arising from differences of either resolving power or calibration, it is necessary to compare spectra obtained for different states with the same instrument; also, for obvious reasons it is desirable to use always the same amount of absorbing material and to work at similar if not equal temperatures.

In this article we shall describe the results of a study of the infra-red spectra for benzene as vapor, liquid, and solid along with the procedures used for obtaining them. The results will be used to test the conclusion drawn in an earlier paper³ that the qualitative features of spectra in condensed phases can be interpreted by focusing attention upon the motions of one molecule. We shall show also that the vibrations of a molecule retain their individualities in the several phases within about the same degree of approximation that they may be regarded as harmonic in the isolated molecule.

Benzene was chosen for this study because of the ease with which it can be produced in all three states at similar temperatures and because its symmetry provides interpretable band envelopes in the vapor along with comparatively great promise of new developments accompanying condensation.

EXPERIMENTAL

Reagent grade, thiophene-free benzene was purified further by repeated fractional crystal-

¹S. L. Gerhard and D. M. Dennison, *Phys. Rev.* **43**, 197 (1933).

²A. J. Wells and E. B. Wilson, Jr., *J. Chem. Phys.* **9**, 659 (1941).

³R. S. Halford, *J. Chem. Phys.* **14**, 8 (1946).

lizations; the resulting specimen represented less than half of the original batch. Water, which influenced greatly the reflectivity of solid specimens, was removed by refluxing the recrystallized material with phosphorous pentoxide. The benzene was stored over this reagent and distilled into an absorption cell as required.

The absorption cells employed for study of liquid and solid specimens were each constructed from two disks, about 3 mm thick and 50 mm in diameter, of optical quality synthetic rocksalt. One disk, serving as a cover, was ground plane and given a high polish on both faces. The other disk was finished similarly on one face before it was attached with wax to a suitably constructed face plate with the rough surface exposed for machining on a lathe. Using a round-nosed tool to minimize marks, the surface was first machined until uniform; then, leaving a rim about 3 mm wide at the edge of the disk, a well was cut to the desired depth. The work was given a high polish before it was removed from the face plate. After dissolving the wax as completely as possible its thorough removal was accomplished by additional light polishing on both faces of the disk.

To assemble the cell, a thin layer of glycerine was applied on the outer portion of the rim, an excess of benzene was distilled into the well, and the cover was lowered, making contact first at one point on the edge, in a manner such that the excess liquid and all bubbles were forced out of the cell. The two disks were pressed tightly together and the upper one was rotated relative to the lower one in order to distribute the glycerine uniformly on the rim and to make a tight seal.

Cells prepared and filled in this way retain their contents indefinitely when stored in any position and can be taken apart only with difficulty. The glycerine does not dissolve appreciably in the benzene, remains confined to the rim, and has very slight action toward the rocksalt. During the course of this work we constructed and used several cells with wells varying from 20 to 100 microns in depth. After they had been in service for some time, two of them, assembled in the usual way, were calibrated by weighing their contents. The depths so determined

agreed* with the machining data within the precision of adjustment of the lathe.

The cell was supported rigidly in the light path by a holder consisting of threaded male and female parts arranged within a thermostating jacket. The female part was a shallow cylinder with a flange at the bottom whose aperture excluded the rim of the cell. The cell rested on the flange and was held in place by the male part with matching aperture. The male part advanced on fine threads so that the pressure on the cell was tolerably uniform. Cold air circulated intermittently through the jacket surrounding the cell holder. A thermocouple buried in the flange served to measure temperature and also, by activating a photo-switch in the power supply of a solenoid valve, to control the flow of cold air. The temperature at the site of the thermocouple was thus maintained constant within a range of about one degree. Observations of the melting point of benzene showed that the thermocouple reflected adequately the temperature of the specimen in the cell.

In order to prevent condensation of atmospheric moisture on the cold outer surfaces of the cell the jacketed holder was housed in a water-proofed wooden box fitted with rocksalt windows. The interior of the box was charged with fresh desiccant some hours prior to commencing operation of the cooler. In spite of these precautions occasional difficulties were experienced on excessively humid days and data were discarded routinely whenever subsequent dismantling of the apparatus disclosed any moisture on the cell.

Measurements were made with the automatic recording prism spectrophotometer⁴ placed at our disposal through the kindness of Professor Wilson. A polished disk of rocksalt in an identical companion holder, housed adjacent to the absorber in the same cooling jacket, served as the standard for photometry. The spectra were recorded a portion at a time. First, the liquid was brought to 8°C and its spectrum taken over a selected interval of frequencies. Then, after the specimen was frozen, it was annealed just below the melting point until it attained virtually

* We are indebted to Mr. Gene B. Carpenter for this information.

⁴ H. Gershinowitz and E. B. Wilson, Jr., *J. Chem. Phys.* 6, 197 (1938).

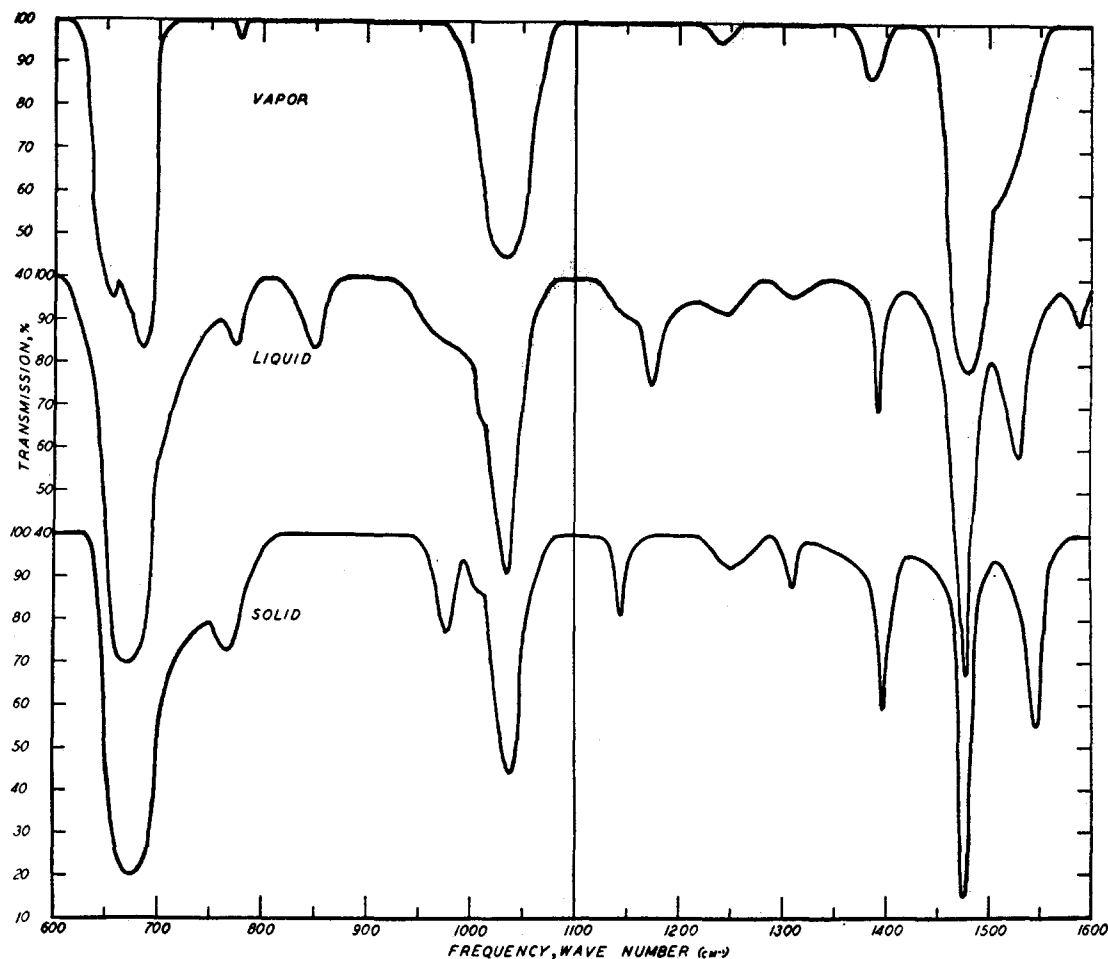


FIG. 1. Infra-red absorption spectra for equivalent absorbing paths of benzene vapor (48 mm in 30-cm cell at 20°C), liquid (0.065 mm thickness at 8°C), solid (same specimen at 3° C). Observations below 1100 wave numbers with rocksalt prism, others with fluorite prism.

constant transmission, the temperature was reduced to 3°C, and the spectrum of the solid was recorded over the same interval of frequencies. The cycle of operations was never repeated with the same specimen; instead, the apparatus was dismantled and inspected for evidences of moisture.

A liquid specimen that has not been frozen previously in the cell shows no evidence of contraction when it is cooled; it remains uniformly distributed over the whole cross section of the cell. Furthermore, rather drastic supercooling is

required to produce the solid which then forms suddenly. For this reason, the solid is also distributed uniformly over the cross section of the cell. *This fortuitous circumstance permits reasonably valid comparisons to be made between intensities of absorption by the same specimen in the two different states.* On the other hand, after regeneration from the solid, the liquid specimen exhibits an undesirable centered bubble of vapor. The bubble spans about 10 percent of the cross section and represents the space created by thermal contraction which occurs preferentially

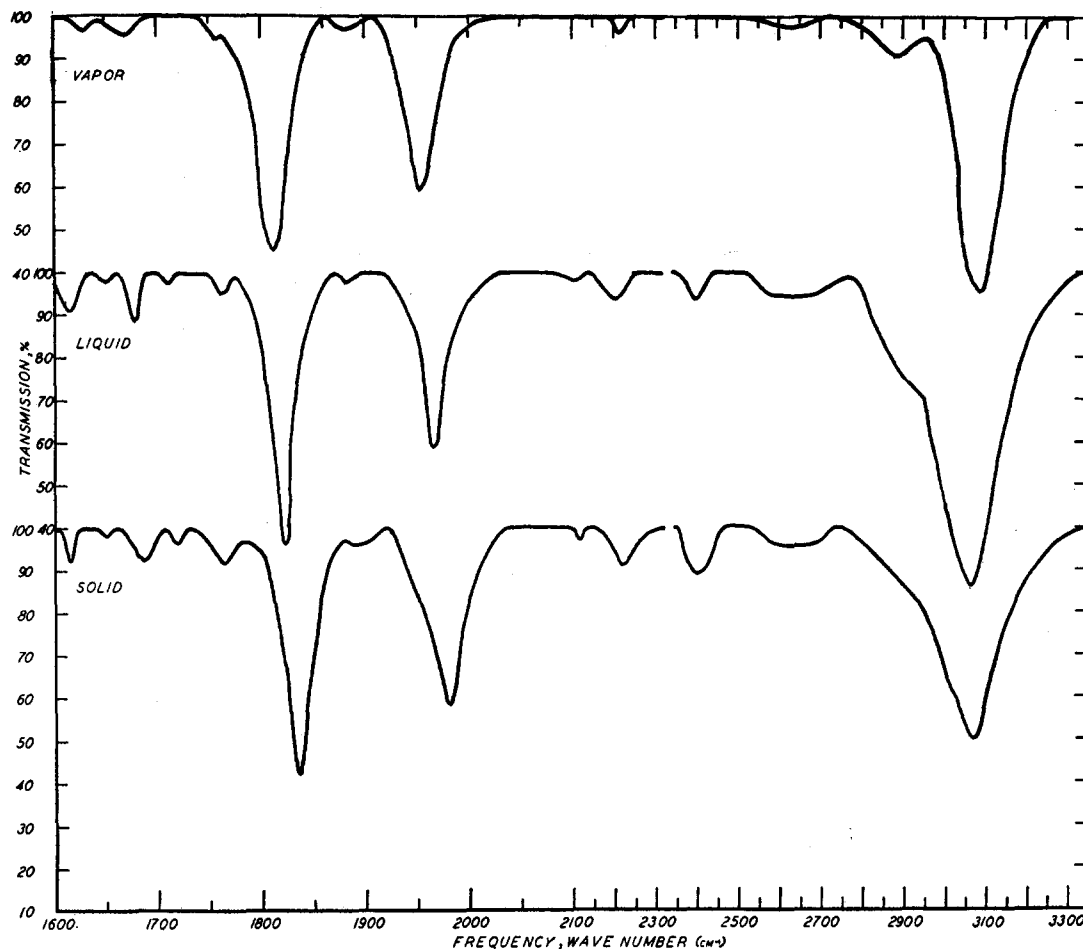


FIG. 2. Infra-red absorption spectra for equivalent absorbing paths of benzene vapor (48 mm in 30-cm cell at 20°C), liquid (0.065 mm thickness at 8°C), solid (same specimen at 3°C). All observations with fluorite prism.

in the cross section. Subsequent resolidification occurs gradually so that the specimen has an opportunity to redistribute itself in the cell. The resulting larger bubble contributes a disproportionate share of the transmitted radiation owing to the large reflection losses that occur elsewhere on the surface of the solid specimen. Consequently, comparisons of intensities of absorption by the two states are now rendered more than ordinarily suspect. The difficulty can be avoided

by warming the regenerated liquid until the bubble disappears.

The specimen of vapor was confined in a glass tube 30 cm long, closed at both ends with rock-salt windows; the photometric standard was an identical but empty cell. The pressure of the vapor was adjusted so that the ratio of densities for it and a liquid specimen was equal to the inverse ratio of the lengths of their absorbing paths.

RESULTS

Figures 1 and 2 depict the relative transmissions at different frequencies for the same amount of benzene when it exists separately as vapor, liquid, or solid. The spectra for both liquid and solid were examined with specimens approximately 40, 65, and 100 microns thick, in each case throughout all or part of the range from 600 to 3300 wave numbers. These variations of thickness produce little change in the spectra except for the expected one of uniform intensification. To avoid complicating the figures we have elected to reproduce only the most illuminating results. The spectrum of the vapor was examined with just one specimen, confined in our cell under a pressure of 48 mm Hg, which is equivalent to a liquid sample 65 microns thick. In all cases the spectra have been corrected for losses due to reflection. These were small for the vapor and liquid but ranged for the solid, depending upon its thickness and previous history, between 25 and 60 percent of the incident radiation. The correction was determined from the proportion of the incident light transmitted for frequencies that the specimen was evidently incapable of absorbing. The proportion of light lost by reflection was found to be the same within experimental error throughout the range of frequencies that we traversed with any one specimen but for the solid specimens it changed with age. Annealing produced initially a rapid increase of transmission that was followed by a slow, steady increase persisting over long periods of time. It was not feasible to wait for cessation of this latter effect; instead, the reflection loss was determined, always for the same standard frequency, at the start and at the end of each record made with the solid. The correction for reflection was applied as though its change had occurred linearly; because the increment was never more than a few units of percent this procedure was quite adequate.

Table I supplements Figs. 1 and 2 by showing for the band centers their locations on the frequency scale along with the corresponding measures of *absorption*. All data for liquid and solid were obtained with at least duplicate specimens. The locations of the band centers were reproduced in all cases within the precision afforded

by our instrument; this varies somewhat with the dispersion of a prism but is in the neighborhood of a few tenths of one percent of the value given for the frequency. The measures of absorption have not been corrected for stray light traversing the spectrometer. The amount of stray radiation was determined for a few frequencies selected at random and was found to constitute about ten percent of the incident radiation with some variation from place to place. The effective correction should be slightly larger for solid than for liquid specimens owing to some unavoidable inhomogeneity* in the crystalline material. In all other respects the measures of absorption are believed to be reliable for purposes of comparison. They were reproducible for different specimens in the same cell within a few units of percent and, most im-

TABLE I. The locations and the measures of absorption for the band centers in the spectra for vapor, liquid, and solid.

Vapor $\tilde{\nu}(\text{cm}^{-1})$	A(%)	Liquid $\tilde{\nu}(\text{cm}^{-1})$	A(%)	Solid $\tilde{\nu}(\text{cm}^{-1})$	A(%)	Type*
671	77	674	90	676	80	U
779	4	774	16	766	27	U
		849	16			G
		~ 980	<15	978	23	U'
		~1010	?	~1010	?	?
1032	55	1033	69	1037	56	U
		~1150	<10	1145	18	U'
		1175	25			G
1243	5	1247	8	1252	8	U
		1310	4	1309	12	U'
1385	13	1393	31	1396	41	U, U'
1483	82	1478	93	1485	85	U
~1526	<30	1530	42	1546	45	U
		1588	11			G
1615	4	1614	9	1616	8	U
1655	5	1650	3	1650	2	U
		1678	12	1686	8	U
		1712	3	1715	3	?
1755	5	1760	5	1764	9	U
1811	55	1822	64	1836	58	U
1880	3	1880	3	1890	4	U
1954	41	1965	41	1982	42	U
		2110	2	2110	3	?
2215	4	2210	6	2220	9	U
		2398	7	2400	11	U'
2620	3	2600	7	2600	4	U
		2690	7	2670	4	U
2880	10	~2880	?	~2880	?	U
		~2950	<30	~2950	<20	U'
3085	65	3065	74	3070	50	U, G

~ Indicates shoulder on adjacent band.

* See discussion.

* At 674 and 1480 the absorption is practically complete. At these locations the apparent transmissions are slightly greater for solid specimens than for liquid ones. The comparison permits one to judge the importance of this factor.

portant for the use we wish to make of them, fluctuations were uniform and parallel for both liquid and solid.

The intensities of absorption by vapor and liquid are comparable except in one respect. A spectrograph with limited resolving power, when viewing a sample of line absorptions, will average the transmissions through transparent regions with those through absorbing ones. If the breadth and spacing of the lines is altered, and this is undoubtedly the case upon passing from vapor to liquid, the averaged transmission will likewise be altered even though the true capacity for absorption remains unchanged. It is possible to correct² for this error, which could be a large one, but we have deemed it unnecessary to do so. Our present conclusions involving the vapor spectrum are derived solely from the presence or absence of a component there. Furthermore, there are some bands appearing in the spectra for all three states which are expected⁸ to have only slightly greater intensities in the condensed phases and this expectation is realized with the uncorrected data. For example, the integrated intensities for the band near 1950 are, in round numbers, 1700 in the vapor and 2200 in the liquid; for the band near 1820 they are 2200 in the vapor and 2700 in the liquid. These changes of approximately twenty percent in each case are not excessive and accordingly we believe that the intensities we have observed for the two states are comparable for our purposes without correction.

The fundamental molecular frequencies of benzene, with one exception, are believed generally to fall within the range we have been discussing. Indirect evidence⁵ supports the notion that the exception lies in the vicinity of 400 wave numbers. For sake of completeness we attempted to examine this region. A specimen of liquid was confined in a cell, similar otherwise to the ones we have described but constructed from KBr. The low intensity available from our source forced us to employ an exceptional gain in the amplifier and to work without the cooler in order to attain a maximum aperture. For the former reason, motions in the galvanometer suspension introduced an unusual amount of un-

certainty into the results. Furthermore, the results were complicated by a comparatively high proportion of stray radiation. Subject to these reservations, no absorption could be detected in the range from 380 to 450 wave numbers. We conclude that, if our specimen possessed an absorption band in this range, the associated intensity did not exceed fifteen percent. The extremely unfavorable conditions (smaller aperture, losses by reflection) that would attend examination of a solid specimen caused us to abandon the project.

The infra-red spectra of both vapor and liquid have been subjects for a number of prior investigations. Some of these were compared and discussed by Ingold⁶ *et al.*; others⁷ have been reported subsequently. When allowances are made for the varying resolving powers of different instruments and the influence of sample thickness upon resolution, no noteworthy discrepancies can be detected among the results, including our own, of recent studies with the liquid. We wish to emphasize particularly that the spectrum⁸ reported for a highly purified specimen of liquid benzene, NBS Standard 99.95 \pm 0.02 mole percent, is virtually identical with the one observed by us. Each spectrum contains two or three extremely weak components, all located above 1600 wave numbers, that do not appear in the other but these are the only respects in which they differ significantly. We conclude therefore that our own specimen was spectroscopically pure; it would also be rated pure if judged^{9,10} by other criteria. Different observers are not so well agreed concerning the spectrum of the vapor. Ingold *et al.* have reported weak components at 779, 807, 962, 1143, and 1240, all but one having counterparts in the spectrum of the liquid. We have found the first and last ones without difficulty but have been unable to detect any traces of the others in spite of careful searching.

⁶ C. R. Bailey, J. B. Hale, C. K. Ingold, and J. W. Thompson, *J. Chem. Soc.* 931 (1936).

⁷ A. P. I. Research Project No. 44, Spectrograms No. 122 and 307, available at National Bureau of Standards, Washington, D. C.

⁸ Reference 7, Spectrogram No. 307 contributed by U. S. Naval Research Laboratory, Washington, D. C.

⁹ F. S. Fawcett and H. E. Rasmussen, *J. Am. Chem. Soc.* 67, 1705 (1945).

¹⁰ G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.* 66, 2100 (1944).

⁵ R. C. Lord, Jr. and D. H. Andrews, *J. Phys. Chem.* 41, 149 (1937).

The spectrogram¹¹ reported for a vapor specimen of high purity, API-NBS Standard 99.94 ± 0.03 mole percent, shows only the first one among the list of components; however, the last one falls in a narrow region where, judging from the description provided by the Bureau of Standards, the otherwise powerful instrument employed is comparatively impotent. In our own studies the band at 1240 would escape notice with the rock-salt prism but could not be overlooked with the fluorite prism. The latter prism was used also by us in our unsuccessful search for a band at 1143. We hold no reservations concerning our conclusion that the spectrum of benzene vapor contains weak components near 780 and 1240 but no others in the intermediate range. There are other discrepancies in addition to the ones already noted; however, the only doubtful components in our list are weak ones at 1655 and 1880. Neither of these is likely to have any important role in the interpretation of the data as a whole and so we shall not offer further comments. We believe that ours is the first comprehensive study of the infra-red spectrum for solid benzene.

DISCUSSION

Theoretical principles appropriate for the interpretation of spectra observed with condensed systems were developed in the first paper³ of this series. In brief, selection rules, usually less strict than the ones governing the vapor spectrum, will operate in the crystalline phase; these are predictable from suitable knowledge of the crystal structure. No selection rules will operate in the liquid state. It is to be expected then that the spectrum for the crystal will be richer than the one for the vapor and that the one for the liquid may be richer still. A glance at the distribution of entries in Table I confirms that this expectation is realized in the case of benzene. Furthermore, the relaxation of selection rules is associated with the development of intermolecular forces; the absorptions that are peculiar to the condensed phases depend for their intensities upon these interactions. Intermolecular forces are more powerful and more concentrated in the

crystal than in the liquid; consequently, the components that are added by these forces commonly to the spectra of both states are likely to be more intense in the spectrum for the crystal. On the other hand, intermolecular forces are much weaker than intramolecular ones. Components of the vapor spectrum derive their intensities from the latter source. Therefore these are likely to be the most intense components in the spectra for all three states and, unless they are feeble in the spectrum for the vapor, their intensities should be altered less by changes of state. These predictions are well fulfilled by the data for benzene.

A knowledge of the selection rules for vapor and crystal is prerequisite for further discussion of the spectra. The thirty fundamental modes of vibration in an isolated benzene molecule, presumed to have the point symmetry D_{6h} , will produce twenty distinct frequencies. These are distributed¹² among the irreducible representations of D_{6h} in the pattern: $2A_{1g}$, A_{2g} , $2B_{2g}$, $4E_{2g}$, E_{1g} , A_{2u} , $2B_{1u}$, $2B_{2u}$, $2E_{2u}$, and $3E_{1u}$. Motions associated with A_{1g} , E_{1g} , and E_{2g} will contribute to the Raman spectrum, those associated with A_{2u} and E_{1u} to the infra-red spectrum. All other representations are inactive in both spectra and the two types of spectra are mutually exclusive.

Crystalline benzene is an example of the space group V_h ¹⁵ with four molecules per unit cell. This information suffices³ to show that in the crystal the molecules of benzene occupy sites having the symmetries C_i . The components of the spectrum for the crystal can be correlated with the modes of motion of one of its molecules; these are associated with the two irreducible representations A_g and A_u of the site group C_i . The representation A_g receives the lattice modes of rotatory origin and the fifteen molecular modes associated with the *gerade* representations of D_{6h} ; A_u receives the lattice modes of translatory origin and the fifteen molecular modes associated with the *ungerade* representations of D_{6h} . The modes associated with A_g contribute to the Raman spectrum, those with A_u to the infra-red spectrum; the two types of spectra continue to be mutually exclusive. In principle the fifteen molecular modes in each representation will pro-

¹¹ Reference 7, Spectrogram No. 122 contributed by The Texas Company, Beacon, New York.

¹² E. B. Wilson, Jr., Phys. Rev. **45**, 706 (1934).

duce fifteen distinct frequencies owing to the removal by intermolecular forces of degeneracies that prevail in the isolated molecule; in practice the resulting doublets will probably not be resolved and only ten frequencies will need to be considered.

All twenty resolvable fundamental frequencies can contribute to both types of spectra for the liquid. However, even though the two types of spectra are no longer mutually exclusive for this state, they will doubtless present contrasting intensity patterns.

The foregoing considerations suggest the utility of designating three types of components that may be encountered in the infra-red spectra for benzene in the three different states. Components of type *U* derive from the representations A_{2u} and E_{1u} of D_{6h} ; they will appear in the infra-red spectra for all three states and will usually show comparatively little intensification accompanying a change of state. Those of type *U'* will appear in the infra-red spectra for both condensed states but not in the spectrum for the vapor and will show comparatively great intensification accompanying solidification; they derive from the other *ungerade* representations of D_{6h} . Components of type *G* will appear in the infra-red spectrum for the liquid state only; they derive from the *gerade* representations of D_{6h} . The last type can be subdivided when discussing Raman spectra but the distinctions are without value except when implemented by more data than are now available. From the experimental point of view the distinction between types *U* and *U'* is not completely sharp since feeble components of the former type, if overlooked in the spectrum of the vapor, could be mistaken for ones of the latter type. However, it is to be hoped that the exceptions will not be too numerous. With this reservation the components observed by us have been classified according to types as shown in the last column of Table I.

Perhaps the most striking features that emerge from even a casual comparison of the spectra for the three states are the absorptions shown by the liquid, but not by either vapor or solid, in the vicinities of 849, 1175, and 1588. A thorough scrutiny of the figures shows that a similar pattern of behavior is exhibited also in the vicinities of 990 and 3060, accounting in the first

instance for the improved resolution achieved between the bands at 978 and 1037 in the spectrum of the solid and in the second instance for the unusual loss of intensity that accompanies solidification. The conclusions developed in the preceding paragraphs require unequivocally that these five locations must be associated with components of type *G*. The opportunity presents itself now to conduct a rather exacting test of the validity of our theoretical considerations. Potential components of type *G* will include the most prominent contributors to the Raman spectrum of liquid benzene. The latter are found¹³ at 606, 850, 992, 1178, 1586, 1604, 3048, and 3062 and account for all five of our locations. The result of this test is a spectacular success for the theory, showing in particular that the selection rules deduced for the crystal are indeed obeyed strictly and that there are no selection rules operating in the liquid phase. It is apparently true for benzene, and perhaps in general too, that prominent components in one type of spectrum are especially prone to enter the other type of spectrum whenever permitted to do so by relaxation of the selection rules. This empiricism is supported not only by the cases already cited but also by the apparent entry¹³ of components of type *U* into the Raman spectrum for the liquid.

All components observed in the spectrum of the vapor can be assigned to type *U* without further comment. The remaining bands, excluding those of type *G*, cannot be classified with the same degree of certainty. We have assigned them regularly to type *U'* except for the ones that failed to intensify upon solidification. Among the latter cases the shoulder near 2950 is almost certainly of type *U'* but its intensification is obscured by the behavior of the neighboring component of type *G*; the bands at 1678 and 2690 are assigned to type *U* because we can be certain in these instances that they are not intensified by the change of state; the others are too weak to justify any assignment and these have been left unclassified. Finally, we have indicated our belief that the component in the vicinity of 1390 may contain contributions of

¹³ N. R. Angus, C. K. Ingold, and A. H. Leckie, J. Chem. Soc. 925 (1936).

both types since the degree of its intensification by the changes of state seems somewhat unusual.

Almost all of the entries listed in Table I are shifted toward higher frequencies by the successive stages of condensation. However, even the most pronounced shift is not much greater than one percent of the value of the mean frequency. This is comparable with the error, deduced from applications of the product rule to the spectra¹⁴ of benzene and its deuterated derivatives, that results commonly from the assumption that the vibrations in the isolated molecule are harmonic. Also, the two errors are in opposed directions and tend to compensate. Therefore, shifts of frequency induced in molecular vibrations of benzene by intermolecular forces may be ignored to the degree of approximation that the motions of the isolated molecule are considered to be harmonic ones. Evidently the molecular vibrations retain their individualities in the condensed phases to a very high degree.

The resolving power of our instrument is apparently inadequate to exhibit the branched structure expected in the band envelopes for the vapor. Consequently we have been unable to

explore the status of molecular rotation in the condensed phases. The most fruitful objects for such a study would be the prominent bands of type *U* for which the structure is interpretable in the spectrum of the vapor. The basis for interpreting intensities in terms of intermolecular forces is insufficiently developed to permit of any conclusions. It is obvious, however, that such studies will be most productive when directed toward the components of types *G* and *U'* in the condensed phases.

FUNDAMENTAL MOLECULAR FREQUENCIES

Although it is incidental to our main purpose, we are aware that the new data reported here are capable, when properly interpreted, of contributing significantly to the identification of the fundamental frequencies of vibration in the benzene molecule. For example, our results invalidate, in one respect or another, all of the recently offered¹⁴⁻¹⁶ attempts to achieve a complete assignment of fundamental frequencies.

¹⁴ A. Langseth and R. C. Lord, Jr., Kgl. Danske Vid. Sels., Math.-Fys. Medd. [6] 16, 1 (1938).

¹⁵ W. R. Angus, C. R. Bailey, J. B. Hale, C. K. Ingold, A. H. Leckie, C. G. Raisin, J. W. Thompson, and C. L. Wilson, J. Chem. Soc. 971 (1936).

¹⁶ K. S. Pitzer and D. W. Scott, J. Am. Chem. Soc. 65, 803 (1943).