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Infra-red spectra are compared throughout the interval from 650 to 3300 wave numbers for the same amount of cyclohexane when it exists separately as vapor at 20°, liquid at 10°, and solid I at 3°C, likewise in the intervals from 700 to 1600 and 2500 to 3300 wave numbers when it exists as solid I at −75° and solid II at −100°C. The four spectra obtained with the condensed phases are quite similar and differ only slightly from the one for the vapor. These results contrast sharply with ones reported previously for a similar study of benzene and indicate that there is a greater semblance of order in liquid cyclohexane than in liquid benzene. The spectra are consistent with, but yield no constructive evidence to confirm or deny the notion that molecules of cyclohexane are able to rotate freely in solid I. Developments attributable to intermolecular forces, although not spectacular, contain new information about the numbers and positions of bands which may prove useful toward assigning frequencies to normal modes of vibration in the isolated molecule of cyclohexane. The results of this study do not contradict any of the principles set forth in the first paper of this series.

INTRODUCTION

MUCH information pertaining to condensed phases might be obtained from the infra-red absorption spectra of liquids and solids if the theoretical treatment were as complete as that for the spectra of vapors. The first paper[1] of this series described some useful simplifications of the theoretical problem whereby the spectrum of a molecular crystal is interpreted in terms of the motions of an isolated molecule. This approach makes possible the prediction of approximate selection rules for such crystals and indicates also that there are no selection rules operating in the liquid state.

This treatment was tested by application to benzene, reported in the second paper,[2] and was found capable of explaining all the important new features of the spectra of liquid and solid.

The present paper compares the infra-red absorption spectra of cyclohexane in the vapor, liquid, and two solid forms over the range from 650 to 3300 wave numbers. The results are examined in the light of the principles set forth in I.

The infra-red spectra of the two solid forms have not been reported previously, although the vapor and liquid have been examined by other workers.[3a, b] It was, however, necessary to re-examine these states in order to avoid comparison difficulties arising from different resolutions, sample thicknesses, etc., in the various published results.

Cyclohexane was chosen for examination because of its convenient physical characteristics, being easily produced in vapor, liquid, and two solid states; the higher temperature solid is of interest in that probably its molecules rotate in the crystal lattice. In addition, the substance is well suited for comparison with results reported previously for benzene.

EXPERIMENTAL

The cyclohexane was Standard Sample 209 obtained from the National Bureau of Standards, Washington, D. C. Although no assay was furnished with the individual sample, a prospectus advertised it to be 99.98±.02 percent pure. After opening, the original ampule was stored in a

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[1] R. S. Halford, J. Chem. Phys. 14, 8 (1946), hereafter referred to as I.
[2] R. S. Halford and O. A. Schaeffer, J. Chem. Phys. 14, 141 (1946), hereafter referred to as II.

[3] a. C. F. Kettering and W. W. Sleator, Physics 4, 39 (1933); P. Lambert and J. Lecomte, Ann. de physique 18, 329 (1932); R. S. Rasmussen, J. Chem. Phys. 11, 249 (1943); b. A. P. I. Research Project No. 44: Spectrograms 16 and 17, contributed by Shell Development Company, Emeryville, California, and Spectrogram 116, contributed by University of Oklahoma Research Institute, Norman, Oklahoma. All spectrograms available at National Bureau of Standards, Washington, D. C.
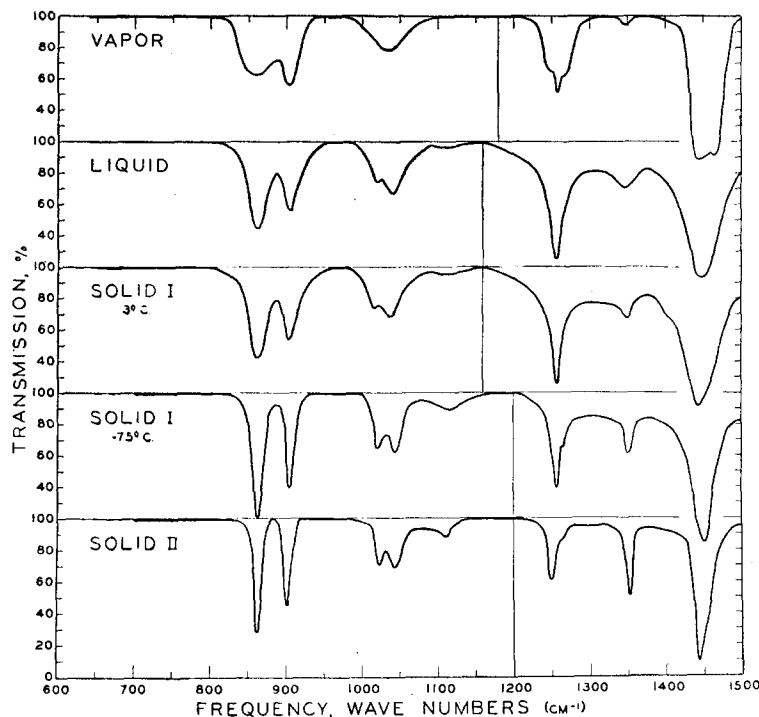
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FIG. 1. Infra-red absorption spectra for equivalent absorbing paths of cyclo-hexane vapor (42 mm in a 30-cm cell at 25°C), liquid (0.065 mm thickness at 10°C), solid I (same specimen at 3°C), solid I (same specimen at −75°C), solid II (same specimen at −100°C). Observations below 1150–1200 cm^{-1} with rocksalt prism, others with fluorite prism. Results for lowest two temperatures not strictly comparable to others.

small outer container in an atmosphere of dry air, and the contents were used without further treatment.

The absorption cell for the vapor specimen was of conventional design, a glass tube 30 centimeters long sealed at both ends with rocksalt windows. An otherwise identical, evacuated cell was employed for the photometric standard ("blank" cell).

The rocksalt (or potassium bromide) absorption cells for the condensed samples at 10° and 3°C were made, filled, supported, and thermostated as described in II. Glycerin, used to seal the edges of these cells, is not appreciably soluble in cyclohexane. As in II, a single piece of polished rocksalt (or potassium bromide) was used as the blank, since the reflection at the two air-salt interfaces is the chief variable for which the blank must compensate.

The absorption cell thermostat for the solid samples at −75° and −100°C was that described by Halford and Karplus,[4] with the following modification. The arrangement of cooling coils around the sample and the connected flexible metal tubing was retained, but the system for pumping a cooling liquid through the coils was not used because of the lack of such a liquid which would flow also through coils in a bath of liquid nitrogen—the most convenient cooling agent. Instead, the liquid nitrogen was poured intermittently into a funnel sealed to one end of the flexible tubing leading to the coils around the cell; a stopper was placed loosely into the top of the funnel so that the pressure developed by the evaporated nitrogen forced the remaining liquid through to the coils. The liquid nitrogen was added necessarily in small increments and the frequency of addition determined the temperature obtained. The heat capacity of the coils was sufficiently large that no great changes of temperature could occur in the sample in this procedure. The rocksalt (or potassium bromide) cell for the sample was the same as in runs made at higher temperatures.

All observations were made with an automatic recording prism spectrophotometer;[5] for the privilege of using this apparatus, we are indebted to Professor Wilson.

The vapor sample was observed at room temperature. Each liquid specimen was cooled to

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[4] R. S. Halford and R. Karplus, in preparation.

[5] H. Gershinowitz and E. B. Wilson, Jr., J. Chem. Phys. 6, 197 (1938).

about 10°C and maintained at that temperature while its spectrum was recorded. It was then frozen (6.6°C) and subsequently held at about 3°C while the corresponding spectrum of the solid was recorded. Solidification of the cyclohexane specimen in the cell occurred abruptly but without drastic supercooling, in contrast to the earlier experience with benzene (II). The resulting solid was almost perfectly transparent; only the presence of faint, seemingly parallel striations, which formed on cooling and disappeared on rewarming through the melting point, revealed its crystalline nature. A slight but easily detectable decrease of transmission was observed with the spectrophotometer as an accompaniment to solidification and served to confirm the change. The transmission of the solid did not increase appreciably on standing, as did that of solid benzene, but was quite high from the instant of freezing. This solid (hereafter called solid I) is stable between the freezing point and −87.0°C, at which point transition[6] to a different crystal structure takes place. The spectrum of solid I was observed also at −75°C. The same sample was then cooled to −100°C and held there as the spectrum was recorded. The occurrence of the change in crystal structure was evidenced by an abrupt drop in the transmission of the sample as it was cooled; this is presumably due to the formation of numerous small cracks resulting from the contraction in volume at the transition.

In the interval between the observations at higher and lower temperatures, modifications were made in the spectrophotometer which resulted in a substantial increase of resolving power. For this reason the two sets of spectra are not strictly comparable.

RESULTS

Figures 1 and 2 show the relative transmissions as a function of frequency in wave numbers, in the range from 650 to 3300 wave numbers, for the same amount of cyclohexane when it exists separately as vapor, liquid, solid I at 3° and −75°C, and solid II. The high temperature form, solid I, was examined near both ends of its range of stability in order to facilitate comparison with adjacent states. The entire range of frequencies was examined with liquid and solid samples approximately 65 microns thick, and with a vapor

FIG. 2. Infra-red absorption spectra for equivalent absorbing paths of cyclohexane vapor (42 mm in a 30-cm cell at 25°C), liquid (0.065 mm thickness at 10°C), solid I (same specimen at 3°C), solid I (same specimen at −75°C), solid II (same specimen at −100°C). All observations with fluorite prism. Results for lowest two temperatures not strictly comparable to others.
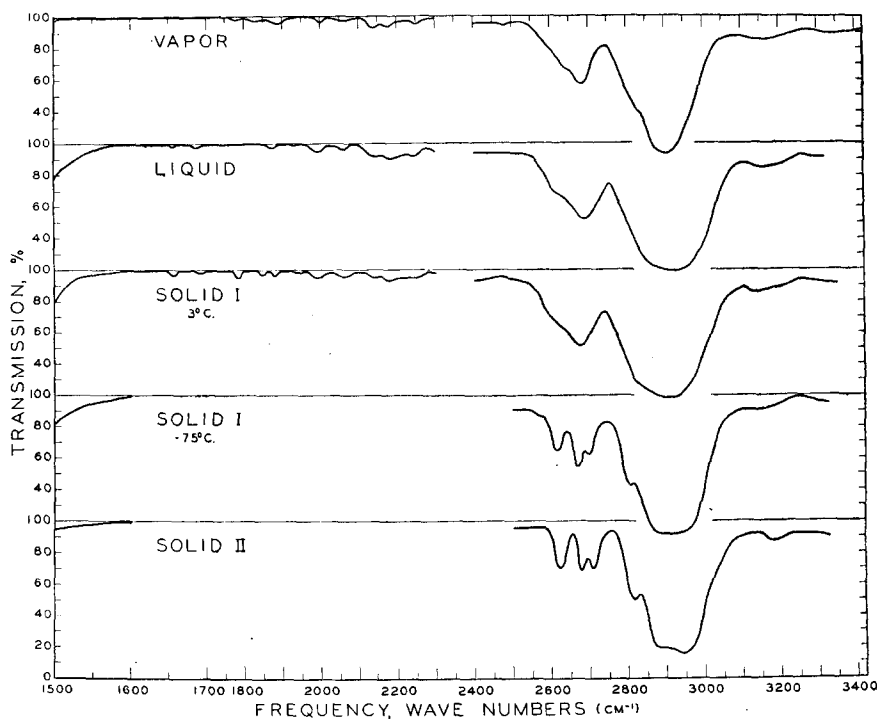
[6] J. G. Aston, G. J. Szasz, and H. L. Fink, J. Am. Chem. Soc. 65, 1135 (1943); R. A. Ruehrwein and H. M. Huffman, J. Am. Chem. Soc. 65, 1620 (1943).

TABLE I. The locations and absorptions of the centers of prominent bands in the infra-red spectra of cyclohexane in different states.

Vapor $\tilde{\nu}$ (cm⁻¹)	$A(\%)$	Liquid $\tilde{\nu}$ (cm⁻¹)	$A(\%)$	Solid I (3°) $\tilde{\nu}$ (cm⁻¹)	$A(\%)$	Solid I (−75°) $\tilde{\nu}$ (cm⁻¹)	$A(\%)$	Solid II $\tilde{\nu}$ (cm⁻¹)	$A(\%)$
527*	(8)*								
862	37	862	55	862	57	861	79	862	71
905	44	904	44	903	46	905	59	901	55
		1021	25	1019	26	1020	35	1024	30
1037	21	1041	33	1038	31	1043	37	1045	31
		1112	(3)	1112	(4)	1113	(10)	1113	(11)
1260	48	1258	73	1258	73	1258	60	1251	38
						1266	(10)	1265	(8)
1348	(5)	1352	(30)	1351	(33)	1353	38	1354	49
1457	92	1449	87	1447	88	1451	95	1444	91
2630s	(10)	2610s	(10)	2610s	(10)	2620	(35)	2624	29
2685	43	2695	48	2680	48	2670	(45)	2680	30
						2695	(30)	2710	(18)
2810s	(5)	?		?		2810s	(12)	2820	(25)
2905	87	2915	81	2910	82	2920	88	2920	84
3135	(10)	3170	(10)	3165	(10)	3160	(8)	3180	(10)

* Observed with 100-mm Hg pressure of vapor.

sample contained in our cell under a pressure of 42 millimeters of mercury, which provides the number of molecules equivalent to a 65-micron thickness of liquid or solid. In addition, samples of condensed states 20 and 170 microns thick were observed less intensively as an aid to interpretation of the spectra. In the interest of clarity, the figures include only the observations made on the intermediate thickness, but with refinements verified by the additional information: the thinnest sample served to verify the resolution shown for the more intense absorptions, while the thickest one confirmed the reality of the weaker components. For all condensed states, wherever there was any doubt as to the result, or where the spectrum seemed to be of special significance, observations were repeated as required to establish the results.

The low temperature results are somewhat less extensive than those for higher temperatures because of the difficulty in carrying out these observations. The data extend down to 700 wave numbers, and the relatively unimportant region between 1600 and 2500 wave numbers is not reported since our data here are sufficient only to show that there are no large changes from the results obtained at higher temperatures. In all spectra, no accurate data were obtained in the vicinity of 2350 wave numbers because of the presence of the extremely strong absorption by the carbon dioxide in the atmosphere. This cuts down the incident light intensity to values too

low for accurate work; we may, however, report that there are no intense bands in this region.

The curves for the lowest two temperatures are not completely comparable with those at higher temperatures because the resolving power of the spectrophotometer was increased between the determination of the latter and the former. Part of the obvious sharpening of bands in the low temperature spectra then is caused by increased resolution, and the remaining sharpening is to be attributed to the temperature effect.

In Table I are listed the positions of the band centers for the more important bands of cyclohexane, together with the corresponding measures of absorption, which are the depths of the band centers measured in percent of light transmitted. Table II gives the same information, where it is available, for the weaker bands which appear in regions where no fundamentals are expected. The absorption values in Table II are for a 170-micron sample, in order that the relative values be significant. The measurement of position of a band center is reproducible to within a few tenths of one percent of the value quoted for its frequency. We believe that the accuracy is about the same. The measures of absorption have been corrected for losses by reflection but not for stray light passing through the spectrophotometer. The former corrections were small but variable from state to state. The latter ones may amount to as much as ten percent of the incident radiation in the worst case, are variable from place to place

on the frequency scale, but enter all three spectra similarly, and hence do not affect a comparison at the same frequency of the relative intensities of absorption by cyclohexane in the four states. Less reliable measurements are enclosed in parentheses.

Table I also includes a very weak band at 527 wave numbers which was observed with a vapor sample in our cell under a pressure of 100 millimeters of mercury. It is certainly too weak to detect in a cell containing much less cyclohexane. Data have not yet been obtained in this region for the other states.

The spectra observed by us for the vapor and liquid are for the most part in excellent agreement with those reported by others.[3] We believe that ours is the only comprehensive study of the spectra for the solid forms of cyclohexane.

The most notable discrepancy between our observations and prior ones occurs in the region just below 700 wave numbers. Whereas we find this region to be transparent for vapor, liquid, and solid I, Lambert and Lecomte[3] report absorption by the liquid at 678; Kettering and Sleator,[3] by the vapor at about 670; Rasmussen,[3] by the vapor at 673 wave numbers; the other investigators cited did not examine this region. In our first observation with the vapor, we encountered a weak band with P-, Q-, and R-branches, centered at about 670 wave numbers. However, when careful attention was given to sources of contamination in the cell and accessories for filling it, this band disappeared. It never appeared in the other states. We have reason to believe that, in our case, the spurious absorption was caused by a well-known and extremely intense component of the spectrum for benzene. It seems likely that this contaminant might have been present in the specimens examined by those other workers‡ who found a band in the same vicinity. We have not yet sought this absorption in solid II, but it is difficult to see how it could appear there if it does not also appear in the liquid.

We attach no significance to the indentation shown on the bottom of the intense band at 1457 in the spectrum of the vapor as our observations

‡ E. K. Plyler, in a private communication to F. G. Brickwedde, M. Moskow, and J. G. Aston, J. Research Nat. Bur. Stand. **37**, 263 (1946), states that there is no band at 673 in the spectrum of pure cyclohexane.

with this part of the vapor spectrum were not sufficient to establish its reality.

The region between 1500 and 2500 wave numbers shows numerous weak absorptions. We have confirmed those shown for the liquid and solid I by noting that they intensify with increasing sample thickness. Although the absorption of the atmospheric water vapor in the light path complicates measurements throughout a large part of this region by causing sharp fluctuations in the intensity of the incident light, the blank compensates for this difficulty. Our results concerning the spectrum for the liquid here agree with independent observations[7] made by means of a spectrophotometer with an evacuated light path and consequent freedom from atmospheric complications. Our data alone do not prove beyond doubt the existence of the corresponding bands in the vapor spectrum, but the necessary confirmation can be found in other observations. We conclude that most, if not all, of these numerous weak absorptions are actually present in vapor, liquid, and solid I, although the shapes of the band envelopes are often somewhat altered by the changes of state.

DISCUSSION

The spectra observed with all four phases are interpretable, according to the principles developed in I, in terms of the motions of an isolated molecule. A cyclohexane molecule has forty-eight fundamental internal modes of vibration. Some of these are expected to have frequencies below

TABLE II. The locations and absorptions of the centers of the less prominent bands in the infra-red spectra of cyclohexane liquid and solid I (170 micron sample).

Liquid		Solid I (3°C)	
$\bar{\nu}$ (cm⁻¹)	A(%)	$\bar{\nu}$ (cm⁻¹)	A(%)
1648	8	1649	8
1685	12	1685	13
1695s	(5)	1695s	(6)
1780	11	1780	13
1832	5	1832	7
1874	12	1875	14
1932	3	1934	4
1989	16	1990	17
2059	11	2062	14
2136	21	2139	22
2182	23	2183	24
2214s	(8)	2218s	(8)
2247	23	2249	25
2494s	(11)	2495s	(12)

[7] Spectrogram 16, reference 3b.

the range of our observations, but their number is small. Therefore, the comparative scarcity of components in the infra-red spectrum of the vapor is presumptive evidence that rather strict selection rules are operating in the isolated molecule. This assertion is supported by the appearance of the Raman spectrum. The totality of evidence[8] along these lines, including depolarization factors and Raman effect, weighs heavily in favor of the "chair" structure, with symmetry D_{3d}. This form differs from the "boat" structure mainly in that rotation to the "opposed" configuration has taken place about two of the six carbon-carbon single bonds. From an order-of-magnitude estimate of 3000 calories per mole for the height of the potential barrier restricting rotation about such a bond, and from the assumption that the "staggered" configuration represents the minimum potential energy, one can use the Boltzmann distribution to estimate that the portion of molecules in the boat form is perhaps of the order of 0.01 percent: utterly negligible for our considerations.

Comparison of Vapor and Liquid

It was predicted generally in I, and confirmed for the case of benzene in II, that there are no selection rules operating in the liquid phase, although the intensities of bands which appear only in the liquid spectra are relatively lower than those of bands which appear also in the vapor. One would expect therefore that the infra-red spectrum of cyclohexane should be enriched by a large number of weaker components as a result of its condensation, whereas upon first examination of the spectra, it may appear that such is not the case. There are, however, a number of changes induced by condensation: the doublet structure which develops around 1030, the shallow band at about 1115, the broad shoulder on the low frequency side of the band near 1260, the intensification of the 1350 band, and the pronounced broadening of absorption occurring in the vicinity of 2900 wave numbers. These changes are fairly numerous although they are in no way spectacular. They are probably accompanied by other changes too small to be detected.

These developments attending condensation of cyclohexane, as summarized in the preceding paragraph, are in distinct contrast to those observed with benzene. With the latter substance, a number of components, forbidden in the spectrum of the vapor, achieve some prominence in the spectrum of the liquid. Outstanding are a group of bands, the centers of which correspond to all the principal frequencies in the Raman spectrum of benzene. Now for cyclohexane, the more important contributions to the Raman spectrum are found[9] at 802, 1029, 1158, 1267, 1348, 1445, and between 2854 and 2935 wave numbers, excluding ones that fall outside the range of available infra-red data. At some of these locations, weak developments in the infra-red spectrum of the liquid might be obscured by the more intense absorption carried over from the spectrum of the vapor, but not so at 802 and 1158, and possibly also at 1029 and in the neighborhood of 2900 wave numbers. Indeed, developments are found around 1029, 1348, and 2900 which might, however, originate in modes of vibration other than the ones concerned in the Raman spectrum. At 802 we detected, with a 170 micron sample thickness, a possible faint trace of absorption, so weak (not more than 2 percent) that it remains uncertain; at 1158, similarly, we found no absorption whatever. It is for frequencies in these latter regions that the most spectacular changes take place for benzene.

This dissimilarity between the two substances seems somewhat surprising when one considers that the intensity of developments of the kind in question are dependent on the intermolecular forces for which the gross measures, such as the heat of vaporization and the boiling point, are quite similar for benzene and cyclohexane. One hypothesis will be offered for consideration. The intermolecular potential energy arises from the instantaneous polarization of a molecule by its neighbors, and accordingly is determined in part by the molecular polarizability. To a fair approximation, the latter is an additive property of the various structural features, and is numerically very similar for benzene and cyclohexane. For benzene, however, the principal contribution arises from the electrons in the ring, whereas in

[8] This evidence is summarized by K. W. F. Kohlrausch and W. Stockmair, Zeits. f. physik. Chemie B31, 382 (1935), and R. S. Rasmussen, reference 3.

[9] A. Langseth and B. Bak, J. Chem. Phys. 8, 403 (1940).

cyclohexane, it arises from the electrons shared by hydrogen and carbon. Thus we should expect that the "ring modes" in benzene and the "hydrogen modes" in cyclohexane will be, in each case, the ones more strongly influenced by the perturbing effect of the molecular environment. For both molecules, the ring modes lie mostly below 1350, while the hydrogen modes fall mostly above 1200 wave numbers. The observed developments are most prominent with benzene in the former range, and with cyclohexane in the latter range.

Any such hypothesis which serves only to emphasize one region of the spectrum relative to another seems incapable of accounting completely for the generally lesser intensity of developments throughout the spectrum of cylohexane, especially at 802 and 1158 wave numbers. For this reason, it appears necessary to suppose that there is more semblance of orderly arrangement in liquid cyclohexane than in liquid benzene. The minimum symmetry of the environment of an arbitrary molecule which provides for mutually exclusive Raman and infra-red spectra possesses a center of inversion; the arrangement of molecules in liquid cyclohexane must approximate this symmetry. Furthermore, since the absorption process is practically instantaneous, relative to nuclear motions, this approximation must apply at any instant rather than merely as a time-average. A similar conclusion is indicated also by the observation that the x-ray diffraction pattern of liquid cyclohexane is somewhat sharper than the one of liquid benzene.[10]

Whatever may be the proper interpretation for the dissimilarity between benzene and cyclohexane, we regard the fact itself, because it seems surprising, as strong encouragement for our belief in the discriminatory powers of the line of investigation we have been following in these studies.

In addition to the Raman-active frequencies, there should appear also in the infra-red spectrum of the liquid frequencies which are prohibited from appearing in either spectrum for the vapor state. There are five such inactive fundamentals, all in the region from 700 to 1350 wave numbers,[11] of which only one has been estimated to more

than one significant figure. This is the inactive ring mode which Saksena[12] calculated to be near 1110 wave numbers, on the basis of a very simple model of the cyclohexane molecule. (This absorption could appear in the spectrum of the liquid even if the latter had an actual center of symmetry.) We find that a weak band does appear at 1112 wave numbers in the liquid spectrum. We cannot say, however, that this band might not originate in some other mode or combination of modes.

Comparison of Liquid and Solid I

The striking similarity of the spectra for the liquid and the high temperature form of the solid must be regarded as indicating a corresponding similarity in structure of the two phases. Again this is in marked contrast with the state of affairs in the benzene spectra where some of the bands which appear first in the liquid disappear on freezing due to the increased symmetry in the crystal. But in the case of cyclohexane, once the spectrum of the liquid had been examined, we could expect no result other than the one obtained; no large bands emerge in the liquid, so none of them can disappear on passing to the solid. Beyond this, however, we notice that those small changes which developed in the liquid remain also in solid I.

A facile explanation of the difference in behavior of the two substances is that the molecules of cyclohexane probably rotate in the crystal lattice of the high temperature form (solid I), while those of benzene do not rotate in the solid. This is, however, unsatisfactory, because no abrupt changes occur on passing through the solid I–solid II transition point, where rotation is presumed to stop.

We may conclude that the intermolecular forces in cyclohexane are changed less than those of benzene on passing from liquid to solid, from the observation[13] that the decrease in volume on freezing for the former is only half that for the latter. Therefore we do not even find appreciable changes of band envelopes or of positions of band

[10] H. K. Ward, J. Chem. Phys. **2**, 153 (1934).
[11] R. S. Rasmussen, reference 3.

[12] B. D. Saksena, Proc. Ind. Acad. Sci. **12A**, 321 (1940). The calculations reported in this paper have been checked by one of us; the value of 208 for the doubly degenerate ring distortion appears to be in error, the correct value being 330.
[13] D. Rozental, Bull. Soc. Chim. Belg. **45**, 585 (1936).

centers on freezing cyclohexane, whereas both types of changes were found in benzene (II).

One small difference between liquid and solid is observed: the band at 1350 wave numbers becomes somewhat narrower and deeper in the solid. This is probably one of the hydrogen modes, which we expect to be more strongly affected by slight changes in the molecular environment than the ring modes.

Two workers[14] have examined the Raman spectrum of solid I, but the slight changes which they report are not in sufficiently good agreement to permit much discussion.

Comparison of Solid I and Solid II

Since the effect of a large change in temperature is quite noticeable, it was necessary to repeat the measurement of the spectrum of solid I at a temperature just above the transition point (-87C) in order to be able to compare it with that of solid II just below the transition. The low temperature required in these observations (to-

[14] S. M. Mitra, Phil. Mag. **25**, 895 (1938) and A. I. Siderova, Acta Physiochimica U. S. S. R. **7**, 193 (1937).

gether with the increased resolving power of the spectrophotometer) causes the sharpening of the bands. We attribute to these factors alone the alterations produced in the appearance of the spectrum through the higher range of frequencies.

Here too the changes are slight, being found chiefly in the intensities of several bands. Most of the statements made in the preceding section concerning the similarity of structure and the slight changes of intermolecular forces accompanying the change of state are applicable here also.

An interesting feature of the spectra measured at low temperatures is that they show conclusively the presence of several shoulders and small bands, the existence of which was uncertain before: ~ 1022, ~ 1113, ~ 1266, ~ 2622, ~ 2675, ~ 2703, and ~ 2815.

The scarcity of developments accompanying condensation dissuades us from attempting any detailed analysis in terms of crystal structures. The spectra do indicate, however, that cyclohexane occupies in both solid forms a site[1] possessing a center of symmetry.