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# Spectroscopic Studies of Rotational Isomerism. V. The Infra-Red Absorption Spectra of Six Solid Hydrocarbons in the Region 1600–650 $\text{cm}^{-1}$ \*

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The infra-red absorption spectra of six hydrocarbons have been measured at low temperatures. As with the Raman spectra, a considerable degree of simplification occurs on freezing, due to the existence of only one rotational isomer in the solid state. It has not proved possible to obtain accurate values of the energy differences between the isomers from this data. The possible ways of obtaining energy difference from spectroscopic data are discussed.

**T**HE detection of rotational isomerism in organic compounds by spectroscopic measurements was first proposed and investigated qualitatively by Kohlrausch<sup>1</sup> and Kohlrausch and Koppl.<sup>2</sup>

The first quantitative study of the phenomenon of rotational isomerism by means of the Raman effect was the work of Langseth and Bernstein<sup>3</sup> in which 1,1,2,2-tetrachloroethane was investigated. Mizushima, Morino and Nakamura<sup>4</sup> have investigated a number of hydrocarbons by obtaining Raman spectra in the liquid and solid states. Qualitatively the results of their researches show that the equilibrium concentration of the rotational isomers is temperature dependent.

Recently<sup>5-8</sup> in this laboratory the Raman spectra of a number of hydrocarbons have been investigated in the liquid and solid states. A quantitative study of the energy differences of the observed rotational isomers has been made.

Only a few investigations have been carried out to date on the infra-red spectra of organic compounds at low temperatures. Avery and Ellis<sup>9</sup> have studied ethane, propylene, and 2,2-dimethyl butane at liquid air temperatures and Halford and co-workers<sup>10,11</sup> have studied benzene and cyclohexane. More recently, Thompson and Richards<sup>12</sup> have studied a considerable number of compounds in the solid state.

Recently a paper<sup>13</sup> has appeared by Bernstein in which he has obtained quantitative measurements of the energy differences of the rotational isomers in 1-2 dichloroethane. This is the first demonstration of the spectroscopic method of investigating these isomers by means of infra-red absorption spectra. Gerding<sup>14</sup> has cast some doubt upon measurements of energy differences of rotational isomers by means of observations on spectra produced in the liquid state. To avoid these objections, which may or may not be valid, depending on the behavior of the material under investigation,

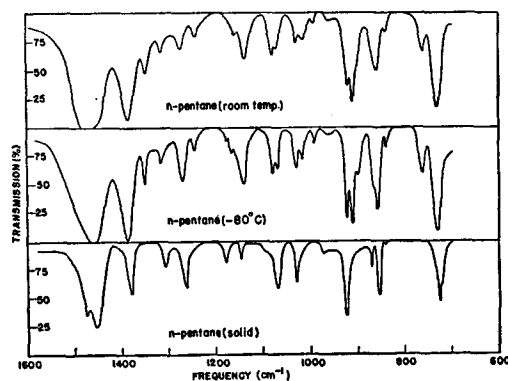


FIG. 1. The infra-red absorption spectrum of *n*-pentane at different temperatures. Cell thickness approximately 0.1 mm.

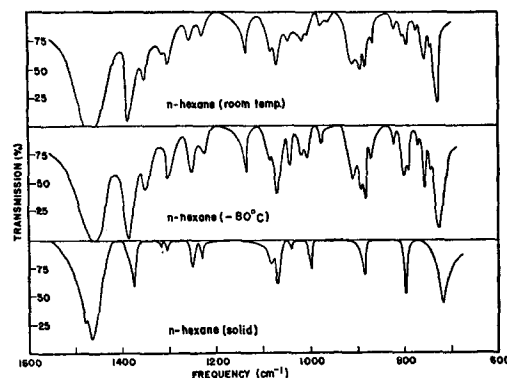


FIG. 2. The infra-red absorption spectrum of *n*-hexane at different temperatures. Cell thickness approximately 0.1 mm.

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<sup>1</sup> K. W. F. Kohlrausch, *Zeits. f. physik Chemie*, **B18**, 61 (1932).

<sup>2</sup> K. W. F. Kohlrausch and F. Koppl, *Zeits. f. physik Chemie*, **B26**, 209 (1934).

<sup>3</sup> A. Langseth and H. J. Bernstein, *J. Chem. Phys.* **8**, 410 (1941).

<sup>4</sup> Mizushima, Morino, and Nakamura, *Sci. Pap. Inst. Phys. Chem. Res. (Tokyo)*.

<sup>5</sup> Szasz, Sheppard, and Rank, *J. Chem. Phys.* **16**, 704 (1948).

<sup>6</sup> Rank, Sheppard, and Szasz, *J. Chem. Phys.* **17**, 83 (1949).

<sup>7</sup> N. Sheppard, and G. J. Szasz, *J. Chem. Phys.* **17**, 86 (1949).

<sup>8</sup> G. J. Szasz, and N. Sheppard, *J. Chem. Phys.* **17**, 93 (1949).

<sup>9</sup> W. H. Avery and C. F. Ellis, *J. Chem. Phys.* **10**, 10 (1942).

<sup>10</sup> R. S. Halford and G. B. Carpenter, *J. Chem. Phys.* **15**, 99 (1947).

<sup>11</sup> R. S. Halford and O. A. Schaeffer, *J. Chem. Phys.* **14**, 141 (1946).

<sup>12</sup> R. E. Richards and H. W. Thompson, *Proc. Roy. Soc. (London)* **195**, 1 (1948).

<sup>13</sup> H. J. Bernstein, *J. Chem. Phys.* **17**, 258 (1949).

<sup>14</sup> H. Gerding and P. G. Meerman, *Rec. Trav. Chim.* **61**, 523 (1942).

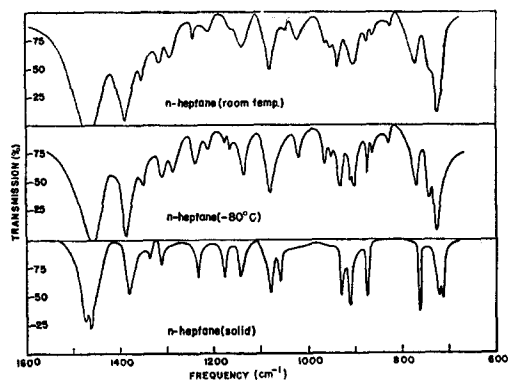


FIG. 3. The infra-red absorption spectrum of *n*-heptane at different temperatures. Cell thickness approximately 0.1 mm.

Bernstein has made his measurements in the vapor phase. It goes without saying that if it is possible to make measurements in the vapor phase, this method is very much more desirable than using measurements made in the liquid state. The complicating phenomena associated with the liquid state do not enter into the results of the experiments with the vapor.

The character of infra-red absorption bands in the gas phase for molecules of more than a very few atoms will often make the determination of energy differences of rotational isomers difficult or impossible when the study is made in the gas phase by means of infra-red absorption spectra. In general, the rotational structure of infra-red absorption bands in the gas phase is so widespread that anything approaching complete resolution of a pair of moderately close bands in the spectrum of even a simple molecule is relatively impossible.

In the Raman spectrum the situation is much more favorable since the bands in general are inherently very much sharper owing to the difference in selection rules for the rotational structure. However, a study of rotational isomerism by means of the variation in intensity of Raman lines obtained by excitation in the gas would be experimentally extremely difficult. With regard to the infra-red spectrum, the difficulties occasioned by rotational structure are not greatly diminished when one proceeds from the gas to the liquid at ordinary temperatures. However, at low temperatures, the bands will become very much sharper. This increased sharpness will allow at least a qualitative study of rotational isomerism. In the case of spectra which are produced by molecules somewhat larger than the molecules investigated by Bernstein, the complicating nature of the rotational structure may not permit quantitative determinations of energy differences of rotational isomers to be made even if temperatures are reduced, producing much sharper absorption bands. The purpose of this research is to investigate the possibility of obtaining energy differences of rotational isomers by means of the infra-red absorption spectra of some simple hydrocarbons. We have also investigated the discontinuous nature of the conversion of rotational isomers when the

material is transformed to the solid state, which phenomena has previously been observed in the Raman effect.

## EXPERIMENTAL

The absorption cell which was used in the present investigation was based on a design employed by Dr. R. C. Lord at the Massachusetts Institute of Technology. It consists of an ordinary infra-red absorption cell for liquids attached to the end of a copper tube which is sealed at the other end into a Pyrex tube and constitutes the bottom of a Dewar flask. This tube fits by means of a ground joint into an outer jacket with silver chloride windows which can be evacuated. The absorption cell was filled with the liquid under examination, and placed in the jacket which was then flushed with nitrogen. The liquid was then frozen by pouring liquid air into the Dewar flask and the cell evacuated by means of a Hyvac pump. Though the cell is best employed at liquid air temperatures, where it is possible to evacuate the outer jacket, it was found possible to

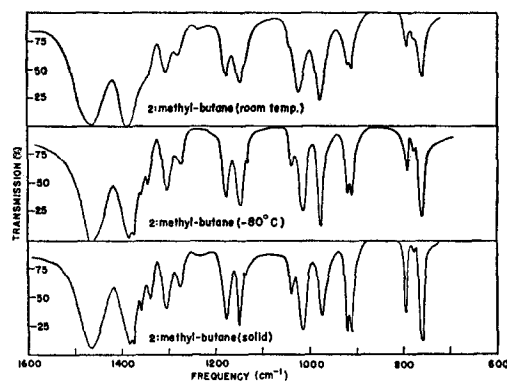


FIG. 4. The infra-red absorption spectrum of 2-methylbutane at different temperatures. Cell thickness approximately 0.1 mm.

get good traces at  $-80^{\circ}\text{C}$  using  $\text{CO}_2/\text{acetone}$  as a refrigerant, even though the jacket could not be evacuated at this temperature. The procedure for filling the cell and freezing the sample was straightforward except in the case of *n*-butane. The procedure with this compound has already been described.<sup>15</sup> All traces were run using a constant energy drive on the spectrometer, which was a standard Perkin-Elmer Model 12C instrument. This drive did not yield a perfectly flat  $I_0$  curve and the curves shown later have all been corrected so that they give percent transmissions accurate to approximately 5 percent. Calibration of the instrument and estimates of the scattered light correction were carried out in the usual way. The compounds studied here are the same as those used in the previous Raman investigations from this laboratory; namely: *n*-butane, *n*-pentane, *n*-hexane, *n*-heptane, 2-methylbutane (isopentane) and 2,3-dimethyl butane.

<sup>15</sup> D. W. E. Axford and D. H. Rank, J. Chem. Phys. 17, 430 (1949).

## RESULTS

The absorption curves obtained for the various substances are contained in Figs. 1-5. They show the absorption spectrum of each substance between 1600 and 650  $\text{cm}^{-1}$  at room temperature (approximately 25°C), -80°C, and when frozen at approximately liquid-air temperatures.

In Table I are listed the frequencies of absorption maxima observed in the straight-chain hydrocarbons at -80°C and in the solid state. The frequencies given are those quoted in the A.P.I. data on hydrocarbons.<sup>16</sup> They have not been corrected to vacuum. We have noted appreciable shifts in the positions of the maxima of some of the bands when the temperature is lowered, but these are not shown in the tables, which are the positions the bands would have at room temperature. In Table II are listed similar values for the two branched chain hydrocarbons studied.

All spectra become very much sharper on cooling, and accordingly certain bands which are diffuse at room temperatures are split at lower temperatures. This effect is very noticeable in the case of the branched hydrocarbons.

## DISCUSSION

We shall briefly discuss the spectrum of *n*-butane reported previously<sup>15</sup> since recently a paper by Gates<sup>17</sup> has appeared which somewhat supplements previous work. In any event *n*-butane is a small enough molecule so that it may be feasible in the near future to obtain a complete and unambiguous analysis of its vibrations.

Previously,<sup>5</sup> making use of available infra-red data and temperature classification and polarization data from the Raman spectrum, an attempt was made to analyze the vibrations of the *trans*-isomer of *n*-butane. At the time this work was done the authors were aware of the necessity for similar temperature classification data from the infra-red spectrum. We have recently obtained this data<sup>15</sup> and made certain changes in assign-

TABLE I. Observed frequencies in hydrocarbon spectra at -80°C and in the solid state.

<i>n</i> -Pentane		<i>n</i> -Hexane		<i>n</i> -Heptane	
-80°C	Solid	-80°C	Solid	-80°C	Solid
1464	1474	1467	1478	1470	1473
	1452		1456		1467
1379	1379	1379	1379	1377	1377
1342		1341		1342	1342
1308	1308		1307	1300	1300
1265	1265	1293	1293	1278	
1237		1246	1246	1232	1232
	1176	1219	1219	1204	
1162		1137		1176	1176
1138	1138	1066	1066	1166	
1072		1057	1057	1137	1137
1067	1067	1037	1037	1074	1074
1025	1025	1015			1055
1014		1005	1005	1020	
989		973		965	
965	965	905		945	
919	919	890		930	930
907		884	884	908	908
900		869		900	
868	868	825		875	875
861	861	804		863	
840		794	794	833	
763		773		773	773
728	728	759		739	
	721	726	726	723	724
					721

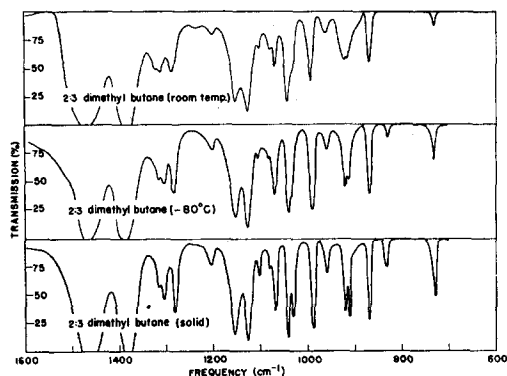


FIG. 5. The infra-red absorption spectrum of 2,3-dimethyl butane at different temperatures. Cell thickness approximately 0.1 mm.

<sup>16</sup> American Petroleum Institute Research Project No. 44.

<sup>17</sup> David M. Gates, J. Chem. Phys. 17, 393 (1949).

ment necessitated by this new experimental material. In our note mentioned above, owing to a typing error in comment (2), it was stated that both the band at 1340  $\text{cm}^{-1}$  and that at 795  $\text{cm}^{-1}$  disappear on cooling. Since as can be seen from the published curves, the 1340  $\text{cm}^{-1}$  band persists in the solid, the remarks in comment (2) obviously do not apply to this band. There is a reasonable probability that the 1340  $\text{cm}^{-1}$  frequency is a combination frequency of the 215  $\text{cm}^{-1}$  skeletal torsional vibration found by Gates<sup>17</sup> with one of the  $\text{CH}_3$  wagging vibrations around 1140  $\text{cm}^{-1}$ . It should be pointed out that from work on the Raman effect of *n*-butane<sup>5</sup> it seems extremely unlikely that the 325  $\text{cm}^{-1}$  Raman frequency belongs to the *trans*-isomer as suggested by Gates<sup>17</sup> in his recent assignment of the skeletal vibrations of *n*-butane. From our work it seems to be almost a certainty that the 432  $\text{cm}^{-1}$  frequency belongs to the *trans*-isomer and the 325  $\text{cm}^{-1}$  frequency belongs to the low energy form. It must be mentioned for the sake of completeness that the statement made by Gates<sup>17</sup> that the infra-red spectrum of *n*-butane gas can be interpreted in terms of only a single rotational isomer seems to rest on a rather insecure foundation in view of our present knowledge of the spectrum of gaseous, liquid, and solid *n*-butane. Furthermore, recent work on molecular vibrations tends to make it obvious that only when complete infrared and Raman spectra with polarizations are available is it possible to approximate correct assignments of molecular vibrations of even the more simple polyatomic molecules.

The traces for the straight-chain hydrocarbons show that there is a considerable degree of simplification on

TABLE II. Observed frequencies in hydrocarbon spectra at  $-80^{\circ}\text{C}$  and in the solid state.

2-Methylbutane		2,3-Dimethyl butane	
$-80^{\circ}\text{C}$	Solid	$-80^{\circ}\text{C}$	Solid
1462	1462	1459	1459
1381	1381	1381	1381
1368	1368	1308	1308
1352	1352	1297	1297
1337	1337	1280	1280
1299	1299	1196	1196
1269	1269	1153	1153
1176	1176	1129	1129
1149	1149	1106	1106
1135	1135	1083	1083
1043	1043	1066	1066
1014	1014	1038	1038
974	974	—	1028
920	920	991	991
910	910	958	958
796	796	921	921
779	779	910	910
764	764	870	870
		832	832
		728	728

cooling, paralleling their behavior in the Raman effect. A close study of our curves showed some significant shifts in the positions of the maxima of certain bands on freezing. At the present time we have not studied this effect closely, though its reality is convincing. Not all bands are shifted and one must conclude, as might in any case be expected, that certain vibrations are much more sensitive to change in environment than others.

Attempts to obtain values for the energy differences between the various rotational isomers from the data reproduced here were not very successful. There are variations in the relative intensities of certain line pairs in the straight-chain hydrocarbons, but the behavior is nowhere near as clean-cut as in the case of the Raman spectra. Few, if any, bands appear to decrease in absolute intensity on cooling, though in all cases, a number increase. This is probably because of the

greater importance of rotational structure in the case of absorption with its attendant overlapping of bands. No value could be obtained with *n*-butane as it proved too difficult with our cell to obtain a satisfactory spectrum of liquid *n*-butane at temperatures near that of the room.

It appears from our results that the Raman spectra in general are better than the infra-red for obtaining quantitative data on rotational isomerism. On the other hand, the infra-red spectrum shows the existence of the phenomenon convincingly in a relatively simple fashion and should prove of use in further investigations.

The results on the two branched-chain hydrocarbons 2-methylbutane and 2,3-dimethyl butane appear to confirm the results obtained from the Raman spectra. In neither case was there any simplification on freezing; in fact, owing to the sharpening of the bands, the solid spectra are actually more complex than those at room temperature.

There were no significant changes in the relative intensities of the bands on cooling. These branched-chain hydrocarbons showed considerably higher absolute transmissions at liquid-air temperatures than did the straight-chain compounds, though direct observation showed beyond doubt that these liquids were frozen. It seems possible in view of this high transmission, that the branched hydrocarbons formed glasses instead of crystallizing. The absence of changes in the relative intensities of the bands and the lack of simplification on cooling mean that it is still impossible to decide unambiguously between the cases of either a small or relatively large energy difference between the isomers.

#### ACKNOWLEDGMENT

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## Light Scattering Arising from Composition Fluctuations in Multi-Component Systems

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A general theory of Rayleigh scattering due to composition fluctuations in multi-component systems is developed with the aid of the grand canonical ensemble of Gibbs. It reduces to the usual expression for systems of two components, but contains previously neglected terms arising from thermodynamic interactions between solutes in systems of more than two components. The theory is used to interpret the turbidity measurements of polystyrene in benzene-methanol mixtures of Ewart, Roe, Debye, and McCartney.

### I

THE utility of light scattering measurements in the determination of molecular weights and in the study of thermodynamic interactions in solutions of macromolecules has been clearly demonstrated in recent

years. Correct theoretical interpretation of the measurements has been achieved for two-component systems composed of one macromolecular solute in a solvent of low molecular weight. However, attempts to extend the two-component theory to multi-component systems