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Spectroscopic Studies of Rotational Isomerism. I. Liquid *n*-Butane and the Assignment of the Normal Modes of Vibration*

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The Raman spectrum of *n*-butane has been investigated over the temperature range 147°K to 305°K. The results clearly show the presence of two rotational isomers in the liquid. These are the planar, *trans*-form (symmetry C_{2h}) and probably the gauche form obtained by a rotation of 120° about the central C—C bond (symmetry C_2). The photoelectric spectrograph was used for quantitative intensity measurements on the line pair at 432 cm^{-1} and 325 cm^{-1} over the temperature range studied. These lines belong to the two rotational isomers and the results were used to give a value of 770 ± 90 cal. mole⁻¹ for the energy difference, $-\Delta H$, between the two forms of *n*-butane in the liquid phase. This result is shown to be in good agreement with a value assumed by Pitzer in his treatment of long chain paraffins. A detailed assignment has been made of the vibrational spectrum of the *trans*-rotational isomer.

I. INTRODUCTION

THE first spectroscopic evidence for the existence of rotational isomers in liquids was obtained by Kohlrausch^{1,2} in his study of the Raman spectrum of 1,2-dichloroethane and other halogenated ethanes. Such rotational isomers are possible when different stable configurations can be obtained by rotation of the groups at either end of a single bond. This will be true when, as for example in 1,2-dichloroethane, the C_2 symmetry of both end groups is destroyed.

As normal butane is the simplest hydrocarbon in which such a situation occurs, a detailed understanding of its vibrational spectra is necessary before complete interpretations can be made of the spectra of more complex hydrocarbons. For this reason we undertook a detailed re-investigation of its Raman spectrum.

The first investigation of this nature was carried out by Kohlrausch and Köppl³ who favored the existence of more than one rotational isomer for normal butane on the basis of their study of the Raman spectrum. However, they pointed out that the infra-red spectrum could apparently be interpreted in terms of one form

only. Mizushima, Morino, and Nakamura⁴ also favored the presence of more than one form, and showed that several weak lines in the Raman spectrum of the liquid disappeared on solidification—presumably corresponding to a reversion to the single isomeric (*trans*) form in the crystal. Although their work seemed to be well substantiated from studies of this and related molecules, the determination of weak lines in the Raman spectrum of a solid is usually a hazardous procedure in view of the increased scattering background. Other investigations of the Raman spectrum of normal butane at room temperature have been made by Bhagavantam,⁵ Ananthakrishnan,⁶ and Murray and Andrews.⁷ These are in substantial agreement with the work discussed above. The infra-red absorption spectrum of gaseous normal butane was originally obtained by Coblenz,⁸ and has been studied more recently by several laboratories under the auspices of the American Petroleum Institute.⁹ Pitzer¹⁰ has obtained good agreement with the measured ther-

⁴ S. Mizushima, Y. Morino, and S. Nakamura, Sci. Pap. Inst. Phys. Chem. Res. (Tokyo) **37**, 208 (1940).

⁵ S. Bhagavantam, Ind. J. Phys. **6**, 595 (1932).

⁶ R. Ananthakrishnan, Proc. Ind. Acad. Sci. **5**, 285 (1937).

⁷ J. W. Murray and D. H. Andrews, J. Chem. Phys. **1**, 406 (1933).

⁸ W. W. Coblenz, *Investigations of Infrared Spectra* (Carnegie Institute of Washington, D. C.), No. 17, **35**, Part I (1905).

⁹ American Petroleum Institute Research Project 44. Spectrogram No. 438, contributed by the Shell Development Company, Emeryville, California.

¹⁰ K. S. Pitzer, J. Chem. Phys. **8**, 711 (1941).

* This research was carried out on Contract N6onr269, Task V, of the Office of Naval Research.

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

² K. W. F. Kohlrausch, "Ramanspektren," *Hand und Jahrbuch der Chemischen Physik; Akademische Verlagsges* (Leipzig, 1943), pp. 234 *et seq.*

³ K. W. F. Kohlrausch and F. Köppl, Zeits. f. physik. Chemie **B26**, 209 (1934).

modynamic properties of the gas by making certain assumptions with respect to the amounts of different isomers present, whereas Aston, Isserow, Szasz, and Kennedy¹¹ were able to obtain similar results on the assumption of a single molecular species.

This research was thus undertaken with the following objectives:

(i) To determine whether or not there is more than one rotational isomer present in normal butane at room temperature. This was investigated by comparing the Raman spectra of liquid normal butane at room temperature with that near, but above, the freezing point. Any lines due to less stable (higher energy) rotational isomers should decrease in intensity on going to the lower temperature.

(ii) If rotational isomers were found to be present, to determine the energy difference between them by the method of Langseth and Bernstein.¹² This involves measuring the relative intensities of pairs of Raman lines caused by two molecular species, over a range of temperatures.

(iii) To determine as far as possible the symmetries of the separate isomers and to assign the lines caused by the separate isomers to their respective modes of vibration. The low temperature spectrum obtained as described in (i) will distinguish between lines caused by the different isomers; the usual selection rules, polarizations, etc., can then be used to attempt an answer to question (iii).

II. EXPERIMENTAL

Both of the spectrographs used in this investigation have already been adequately described.^{13,14} The photoelectric recording Raman spectrograph of Rank and Wiegand was found to be almost ideal for a study of the relative intensities of line pairs in the Raman spectrum. Its main drawback lies in the strong secondary excitation of the 4358Å Hg line of the source. In making these quantitative studies of individual lines, use was made of the best combina-

tion of speed, time constant, and amplification ratio available in this instrument. At the speeds used, it took approximately 45 minutes to scan the spectral region of the line pair used.

The prism spectrograph, together with our new, recently described,¹⁵ low background sources, was used to obtain complete Raman spectra in the various temperature ranges investigated.

In both spectrographs sodium nitrite solutions were used both as filters and as condensing lenses. Praseodymium nitrate solutions were used to reduce the background intensity in the neighborhood of the exciting line. In the photographic work Eastman-I plates were used after suitable backing with Fe₂O₃ paste to reduce halation caused by Rayleigh scattering. Exposure times ranged from two to eight hours. The microphotometer traces were made with the Leeds and Northrup recording microphotometer.

The *n*-butane used was made by The Ohio Chemical Company and was obtained from the Petroleum Refining Laboratory of this College. It was stated to be 99+ percent pure. The material was handled in a high vacuum system and was dried by passing over phosphorus pentoxide. At temperatures in the neighborhood of the freezing point the small amount of impurity present froze out of the liquid. However, it formed relatively few large particles and did not interfere appreciably with the measurements.

The low temperature measurements were made by placing the sample tube in a Dewar vessel and cooling it with cold air. The temperature in the Dewar was measured by the indications of a single junction copper-constantan thermocouple, and the sample was kept at a constant temperature by proper adjustment of the flow of cold air. The Dewar was an unsilvered Pyrex glass vessel, with two plane glass windows on the bottom, of 38-mm and 48-mm diameter, respectively. It was evacuated to a high vacuum and sealed off. The system was closed by a rubber stopper, with a center hole for the sample tube and appropriate small openings for air inlet, air outlet, and thermocouple. The source of dry air was a liquid air boiler of 20-liter capacity, made of steel, insulated by rock wool, and housed in a wooden box. A resistance heater of

¹¹ J. G. Aston, S. Isserow, G. J. Szasz, and R. M. Kennedy, *J. Chem. Phys.* **12**, 336 (1944).

¹² A. Langseth and H. J. Bernstein, *J. Chem. Phys.* **8**, 410 (1941).

¹³ D. H. Rank and R. Wiegand, *J. Opt. Soc. Am.* **36**, 325 (1946).

¹⁴ D. H. Rank, R. Scott, and M. R. Fenske, *Ind. Eng. Chem. Anal. Ed.* **14**, 816 (1942).

¹⁵ D. H. Rank, N. Sheppard, and G. J. Szasz, *J. Chem. Phys.* **16**, 698 (1948).

TABLE I. Observed Raman and infra-red frequencies in *n*-butane (below 1500 cm^{-1}).

Raman lines (cm^{-1})		Infra-red frequencies (cm^{-1})
Low energy form	High energy form	
1455 (<i>dp</i>)	(1455)	1466 (<i>S</i>)
(1370)		1390 (<i>S</i>)
1304 (<i>p</i>)	1282	1340 (<i>W</i>)
		1297 (<i>S</i>)
1148 (<i>p</i>)	1167	1244 (<i>W</i>)
1058 (<i>p</i>)	1077 (<i>p</i>)	1134 (<i>M</i>)
	981 (<i>p</i>)	
		970 (<i>S</i>)
956 (<i>dp</i>)		959 (<i>S</i>)
835 (<i>p</i>)	789 (<i>p</i>)	
		795 (<i>W</i>)
		751 (<i>M</i>)
		734 (<i>M</i>)
432 (<i>p</i>)	325 (<i>p</i>)	

45 ohms was wound on the outside of the boiler to make controlled rates of flow possible. The boiler required about six liters of liquid air to cool it down, and the rate of evaporation thereafter was found to be less than one liter per hour. The evaporated air was cooled by passage through a coil immersed in liquid air, before entering the Dewar. All lines conducting cold air were insulated with felt and thus the temperature of the air entering the Dewar was probably close to 100°K.

III. THE RESULTS AND THEIR INTERPRETATION

A. The Raman Spectra at 302° and 147°K

In Fig. 1 are shown the Raman spectra below 1500 cm^{-1} for the higher and lower temperatures, respectively. These have been traced directly from the microphotometer curves except that short range fluctuations caused by grain on the original plate have been smoothed out. It can be seen at once that a considerable number of the lines have decreased in intensity relative to the others. The most notable changes are the apparent disappearance, at the low temperature, of the 325- cm^{-1} line and the reversal in intensity of the 956- cm^{-1} and 981- cm^{-1} lines, presumably due to the weakening of the latter. If one takes a line of medium strength, such as those at 956 cm^{-1} or 1148 cm^{-1} as a standard, it is an easy matter to pick out those lines which

have weakened considerably at the low temperature. These are presumably the lines due to the less stable (high energy) rotational isomer, as the concentration of the latter will decrease with temperature. The fact that each strong line of the stable isomer is accompanied by only one such weak companion is evidence for the presence of a single high energy form. In Table I are listed the Raman spectra due to the two forms, together with the observed infra-red bands.

The weak Raman line near 730 cm^{-1} , which is not listed in Table I is caused by triple excitation of the 835- cm^{-1} line. The broad, ill defined line near the 1370- cm^{-1} line may also be due to multiple excitation or may be a weak line of the stable isomer. It is inserted in brackets in Table I. The ease with which the two sets of lines can be separated is indisputable evidence for the existence of two rotational isomers in liquid *n*-butane.

Our Raman spectra are in good agreement with those of Mizushima *et al.*,⁴ and we used their exact wave numbers throughout. In separating the Raman lines belonging to the two forms, our results again agree with those of the Japanese investigators, with the exception of their erroneous assignment of the 956- cm^{-1} line to the high energy isomer. Careful examination of our plates shows that the very strong 1450- cm^{-1} band splits into two components at the low temperature, in agreement with Mizushima's analogous observation on the solid spectrum.

The polarization data listed in Table I are those of Ananthakrishnan,⁶ as given by Kohlrausch.² We redetermined the polarization of the 1304- cm^{-1} line, however, because it seemed difficult to assign this shift to a depolarized

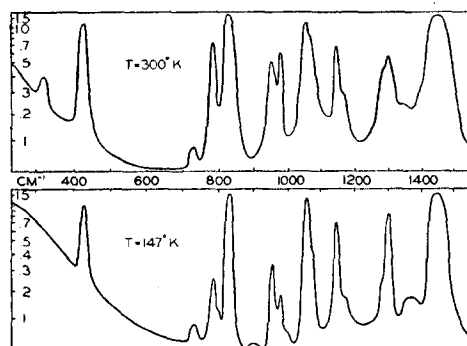


FIG. 1. Smoothed microphotometer curves of the Raman spectrum of liquid *n*-butane at 300°K and at 147°K.

mode. We found the correct depolarization to be about 0.6. The lines at 1167 cm^{-1} and 1282 cm^{-1} were too weak for polarization measurements.

The infra-red spectrum was obtained from the American Petroleum Institute's compilation of infra-red spectra.⁹ These data refer to *n*-butane in the vapor phase. The infra-red bands are generally broad because of their rotational structure and this probably obscures the doubling of lines due to the two forms in most cases. Except where otherwise stated we have quoted the center of the band, and further subdivision must await the determination of the infra-red absorption spectrum of liquid *n*-butane at low temperatures. The infra-red band near 965 cm^{-1} has a complex contour and we have assumed that there are two separate frequencies of the same isomer corresponding to the differently shaped peaks at 970 cm^{-1} and 959 cm^{-1} . The infra-red band near 740 cm^{-1} also has two separate peaks at 751 cm^{-1} and 734 cm^{-1} . These are both of similar shape and therefore probably correspond to frequencies of the same general type. We have assumed them to be related frequencies of the two rotational isomers, and have arbitrarily assigned the 751- cm^{-1} frequency to the *trans*-form.

B. The Determination of the Energy Difference between the Rotational Isomers

A choice was made of well separated line pairs which probably correspond to related vibrations of the two isomers, with the purpose of carrying out quantitative measurements on their relative intensities at several temperatures according to

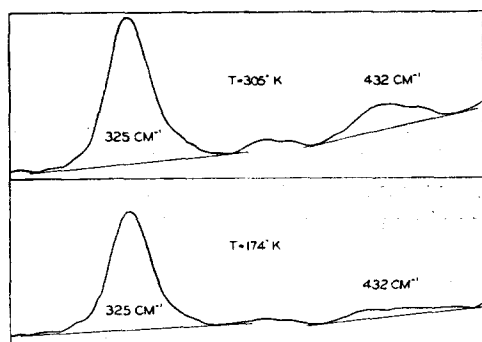


FIG. 2. Photoelectric intensity recording of the 325- cm^{-1} and 432- cm^{-1} Raman shifts in liquid *n*-butane at 305°K and at 174°K.

TABLE II. The intensity ratio of the 432- cm^{-1} to 325 cm^{-1} line pair as a function of temperature.

$T^{\circ}\text{K}$	174	184	184	217	301	301	305
I/I'	14.60	14.70	14.10	10.00	6.05	6.50	5.92
$(1/T) \times 10^3$	5.75	5.43	5.43	4.61	3.32	3.32	3.28
$\log I/I'$	1.164	1.167	1.149	1.000	0.782	0.813	0.772

the method of Langseth and Bernstein.¹² Most of the line pairs are unsuitable because of the relatively small separation between the two components, and the consequent failure of the photoelectric spectrograph to resolve them. With these considerations in mind the most profitable pairs to study appeared to be those at 325 and 432 cm^{-1} , and 789 and 835 cm^{-1} . The study of the 325- and 432- cm^{-1} line pair proved to be a straightforward matter, and a typical pair of curves obtained at the lower and higher temperatures is given in Fig. 2. On the other hand, it was found to be impossible to utilize the line pair at 789 and 835 cm^{-1} as a quantitative check on our results with the lower line pair, because the secondary excitation of the stronger 835- cm^{-1} line almost obliterates the 789- cm^{-1} line at low temperatures. Quantitative measurements on this line pair were finally abandoned, although it was concluded that within the large limits of error introduced by this difficulty the behavior of this line pair was consistent with the result obtained from the 432- and 325- cm^{-1} line pair.**

The quantitative results are summarized in Table II where the first row lists the temperatures and the second row gives the corresponding intensity ratios, intensity of 432- cm^{-1} line/intensity of 325 cm^{-1} line.

The equation used to determine the difference in energy between the two forms was the integrated form of the standard Van't Hoff equation $\log(K_1/K_2) = (\Delta H/2.303R)[(1/T_2) - (1/T_1)]$ (1) with the usual assumptions. The observed intensity of a line is given by $I = C\alpha$, where C is the concentration of molecules and α is the line intensity per molecule.

Thus

$$K_1 = (C/C')T_1 = ((I/I') \cdot (\alpha'/\alpha))T_1, \quad (2)$$

** Note added in proof: Recently we have been able to obtain a quantitative value for the energy difference from the 835- and 789- cm^{-1} line pair by using the low pressure source described in reference 15. The value obtained was 800 ± 150 cal. mole⁻¹.

TABLE III. Designation, character, species, and activity of the normal vibrations of *n*-butane.

Description / C_{2h}	$A_g(R.p)$	$A_u(I.R.)$	$B_g(R.dp)$	$B_u(I.R.)$	Expected freq. range	Reference
CH ₃ stretching	ν_1	ν_{12}	ν_{20}	ν_{27}	2800–3000 cm ⁻¹	17
CH ₃ non-symm. stretching	ν_2	ν_{13}	ν_{21}	ν_{28}		
CH ₃ symm. stretching	ν_3	—	—	ν_{29}		
CH ₃ bending	ν_4	—	—	ν_{30}	ca. 1450 cm ⁻¹	18
CH ₃ non-symm. deformation	ν_5	ν_{14}	ν_{22}	ν_{31}		
CH ₃ symm. deformation	ν_6	—	—	ν_{32}	ca. 1370 cm ⁻¹	18
CH ₃ wagging	ν_7	—	—	ν_{33}	1290–1340 cm ⁻¹	19
CH ₃ twisting	—	ν_{15}	ν_{23}	—	1100–1350 cm ⁻¹	19
C—C (skeletal) stretching	$\nu_{8,9}$	—	—	ν_{34}	800–1200 cm ⁻¹	19
CH ₃ rocking	ν_{10}	ν_{16}	ν_{24}	ν_{35}	900–1200 cm ⁻¹	18
CH ₃ rocking	—	ν_{17}	ν_{25}	—	720–760 cm ⁻¹	19
Skeletal bending	ν_{11}	—	—	ν_{36}	<650 cm ⁻¹	19
Skeletal torsion	—	ν_{18}	—	—		
Methyl torsion	—	ν_{19}	ν_{26}	—		
C _{2v}	$A_1(R.p;I.R.)$ $A_2(R.dp)$ $B_1(R.dp;I.R.)$ $B_2(R.dp;I.R.)$					
C ₂	$A(R.p;I.R.)$ $B(R.dp;I.R.)$					

and assuming α'/α to be independent of temperature

$$K_1/K_2 = (I/I')T_1/(I/I')T_2. \quad (3)$$

The experimental results are shown in Fig. 3 in which $\log I/I'$ is plotted against $1/T$. In accordance with Eq. (1) the best straight line is drawn through the points, and its slope determines ΔH . The scattering of the points is an indication of the consistency of our results. It will be noticed that the scattering is somewhat greater for the points at the lowest temperatures, as in these cases the accuracy of measurement of the weak line is considerably reduced (cf. Fig. 2).

From the slope of the straight line the value of $-\Delta H = 770 \pm 90$ cal. mole⁻¹ was obtained. In estimating our error we have allowed for the spread of values that could be obtained by taking extreme slopes of the line between the upper and lower temperatures. No explicit correction has been made for the variation with temperature of the relative distribution of molecules between

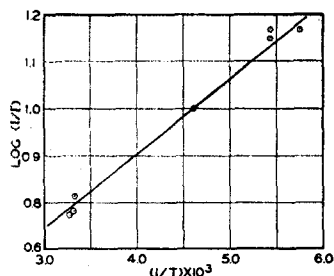


FIG. 3. Plot of intensity ratio of the 325-cm⁻¹ and 432-cm⁻¹ Raman shifts in liquid *n*-butane vs. temperature.

the ground state and the vibrational state studied in each molecular species. Calculations showed that such a correction would be but a fraction of our experimental error.

In his discussion of the partition function for long chain hydrocarbons Pitzer¹⁰ assumed the presence of rotational isomers. He calculated the fraction of a particular isomer (1) from the expression $a_1 \exp(-E_1/kT) \sum_{i=1}^n a_i \exp(-E_i/kT)$ where n is the total number of isomeric species. The various a 's are statistical factors determined by the geometry of the molecule, and the E 's are the appropriate integral multiples (including zero) of 800 cal. mole⁻¹. In the case of normal butane this 800 cal. mole⁻¹ was regarded as the energy difference between the two rotational isomers. Our value of $-\Delta H = 770$ cal. mole⁻¹ could be directly compared with the above value of 800 cal. mole⁻¹ if the assumption were made, with Pitzer, that the products of the remaining partition functions for the two isomers are identical, and further that there is little change in this value in passing from the liquid to the vapor phase. Although these assumptions are not strictly correct the agreement can be taken as good confirmation of Pitzer's treatment.

C. The Symmetry of the Rotational Isomers and the Assignment of Their Spectra

1. The Symmetry of the Isomers

If the assumption is made that the configuration of the rotational isomers is determined by

TABLE IV. Assignment of the normal vibrations of the *trans*-isomer of *n*-butane.

CH ₂ stretching	$\nu_1 = 2860 \text{ cm}^{-1}$,	$\nu_{12} = (2935)$,	$\nu_{20} = 2934$,	$\nu_{27} = (2860)$,
CH ₂ non-symm. stretching	$\nu_2 = (2950)$,	$\nu_{13} = (2960)$,	$\nu_{21} = 2964$,	$\nu_{28} = (2950)$,
CH ₂ symm. stretching	$\nu_3 = 2880$,	$\nu_{29} = (2880)$,		
CH ₂ bending	$\nu_4 = 1455$,	$\nu_{30} = 1466$,		
CH ₂ non-symm. deformation	$\nu_5 = (1455)$,	$\nu_{14} = (1466)$,	$\nu_{22} = (1455)$,	$\nu_{31} = (1466)$,
CH ₂ symm. deformation	$\nu_6 = 1370$,	$\nu_{32} = 1390$,		
CH ₂ wagging	$\nu_7 = 1304$,	$\nu_{33} = 1297$,		
CH ₂ twisting	$\nu_{15} = 1244$,	$\nu_{23} = (1250)$,		
CH ₂ wagging	$\nu_{10} = 1148$,	$\nu_{25} = 1134$,	$\nu_{16} = 959$,	$\nu_{24} = 956$
CH ₂ rocking	$\nu_{17} = 751$,	$\nu_{25} = (740)$,		
Skeletal stretching	$\nu_8 = 1058$,	$\nu_9 = 835$,	$\nu_{34} = 970$,	
Skeletal bending	$\nu_{11} = 432$,	$\nu_{26} = (365)$,		
Skeletal torsion	$\nu_{18} = ?$			
Methyl torsion	$\nu_{19} =$	or $\nu_{26} = (200?)$,		

repulsion between the groups at either end of the central C—C bond of butane, the most likely configurations are an essentially *trans*-(C_{2h}) form and two optically isomeric (and therefore spectroscopically identical) C₂ forms. On the other hand, if the restricted rotation is caused by attraction between the groups at either end, we would expect three "eclipsed" forms, one of symmetry C_{2v} (*cis*) and two optical isomers of symmetry C₂. An analogous discussion is given by Herzberg¹⁶ for the 1,2-dichloroethane molecule.

n-Butane will have 36 normal modes of vibration and these can be further subdivided as shown in Table III. In this table the selection rules and symmetry types are given for the different possible molecular configurations, together with the regions of the spectrum where the various molecular vibrations will probably occur. These rules are derived from several sources and an appropriate reference is given in each case.¹⁷⁻¹⁹ Table III has been further subdivided into broad frequency ranges which can be investigated fairly independently from the point of view of the number of observed vibrations. The most interesting regions are those lying between 1500 cm⁻¹ and 700 cm⁻¹ and <650 cm⁻¹.

First of all let us consider the spectrum of the most stable isomer whose Raman lines below 1500 cm⁻¹ are given in the first column of Table I.

If this molecule has the symmetry C_{2h} (*trans*), C_{2v} (*cis*) or C₂ (*gauche*) it will have, respectively, 11, 21, and 21 allowed Raman fundamentals in the region 1500–650 cm⁻¹. Although all the Raman lines may not have been detected, it should be noticed that the observation of the triple excitation of the 835-cm⁻¹ line on both microphotometer traces, at *ca.* 730 cm⁻¹, shows that a line of one-hundredth of the strength of the strongest line of the more stable isomer could be observed. Table I shows that, at the most, eight distinct lines can be detected in the Raman spectrum of this region and this is clearly strong evidence for the C_{2h} (*trans*) configuration for the molecule. In the infra-red spectra the number of allowed lines for the C_{2h}, C_{2v}, and C₂ configurations are 10, 17, and 21, respectively, whereas there are only nine well established lines, including several weak ones. This again is very good evidence for the C_{2h} symmetry and we can thus conclude that the more stable rotational isomer has undoubtedly the *trans*-configuration. In the region below 650 cm⁻¹ the isomeric configurations C_{2h}, C_{2v}, and C₂ would require 2, 5, and 5 Raman lines, and if we exclude the restricted rotation of the methyl groups, which, in general, seem to be difficult to observe in Raman scattering, the above would reduce to 1, 3, and 3, respectively. The fact that a single line at 432 cm⁻¹ is observed in the Raman spectrum of the more stable isomer is therefore further evidence for the C_{2h} (*trans*) configuration. The infra-red spectrum has not so far been examined in this region.

With regards to the configuration of the other rotational isomer we cannot reach any very

¹⁶ G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 347.

¹⁷ J. J. Fox and A. E. Martin, Proc. Roy. Soc. London **A175**, 208 (1940).

¹⁸ G. Herzberg, reference 16, p. 195, and discussions of individual hydrocarbon spectra.

¹⁹ N. Sheppard, J. Chem. Phys. **16**, 690 (1948).

definite conclusions, as all the Raman lines observed have been relatively weak. These presumably correspond to the most symmetrical modes and it is clear that the small concentration of this isomer is such that we cannot expect to detect the weaker lines caused by the less symmetrical vibrations. However, as there is no doubt about the *trans*-configuration of the more stable isomer, it is probable that the other rotational isomer has also a "staggered" configuration, which will be of symmetry C_2 .

2. General Methods of Assignment

In Table IV an assignment has been made of the observed vibrational frequencies of the *trans* form of *n*-butane to the normal modes of vibration. In drawing up this assignment the following points have been taken into account.

(a) Polarization data on the Raman lines can be used to distinguish between A_g and B_g type vibrations.

(b) Infra-red active frequencies of symmetry A_u give rise to a change in electric moment during the vibration which is perpendicular to the plane of symmetry, i.e., along the greatest axis of inertia. They should thus have band contours exhibiting a Q branch under conditions of sufficiently high resolution. Vibrations of type B_u will have "hybrid" contours which cannot be easily predicted.

(c) Many assignments can be made with the help of the correlation rules listed in Table III. These have been derived from the study of series of related molecules.

(d) Because of the center of symmetry in the molecule, closely related stretching and bending modes of the CH_2 and CH_3 groups occur in pairs, one being active in infra-red absorption and the other in Raman scattering. In several cases the application of rules (a)–(c) show that these occur with very similar frequencies in the two types of spectra, and this fact has been used to assign approximate values to non-observed members of other frequency pairs.

(e) A Raman active skeletal stretching mode, on the other hand, will probably not have any such corresponding frequency in the infra-red spectrum, and vice-versa.

When the above points are taken into account

the reasons for many of the assignments are clear, but some less evident points are discussed below.

3. The Spectrum in the Region of 3000 cm^{-1}

The frequencies in this region are caused by C—H stretching modes of vibration. Fox and Martin¹⁷ have shown, from a study of infra-red spectra, that CH_2 groups have symmetric and non-symmetric CH stretching modes near 2850 and 2925 cm^{-1} , respectively, and that CH_3 groups have corresponding symmetric and non-symmetric modes near 2870 and 2960 cm^{-1} . They also showed that an overtone of the hydrogen deformation frequency near 1450 cm^{-1} occurs near 2900 cm^{-1} . In the Raman spectrum, Mizushima and his co-workers⁴ give the following frequencies for liquid and solid *n*-butane:—liquid; 2667(2,*p*), 2703(3,*p*), 2733(4,*p*), 2860(10,*p*), 2880(10,*p*), 2909(8,*p*), 2937(10,*p*), 2964(9,*dp*?); solid 2703(1), 2725(1), 2853(8), 2872(8), 2896(10), 2912(4), 2931(1), 2950(4), 2965(9). The polarization data on the room temperature spectrum were taken from Ananthakrishnan's work.⁶

The assignments given in Table IV have been made with the help of Fox and Martin's rules, and taking into account the polarization data and the persistence of frequencies in the spectra of both liquid and solid butane. The infra-red frequencies have been assigned in a schematic fashion with the help of the Raman assignments and the correlation rules.

4. The Spectrum in the Region 1500–650 cm^{-1}

The polarized Raman lines in the region 1500–1300 cm^{-1} can be assigned with the help of the correlation rules, and there remains only the identification of the 1148-, 1058- and 835- cm^{-1} lines to be made to one or the other of the modes ν_8 , ν_9 , or ν_{10} . It seems likely that the 1148- cm^{-1} frequency corresponds to the only hydrogen deformation frequency of the three, *viz.*, an in-plane CH_3 wagging mode, as there is a corresponding infra-red band at 1134 cm^{-1} (see C 2 d). We therefore assign $\nu_{10} = 1148$ cm^{-1} (and $\nu_{35} = 1134$ cm^{-1}), and thus the 1058- and 835- cm^{-1} lines are, respectively, ν_8 and ν_9 . These seem to be very reasonable values for C—C stretching modes, and obey point C 2 e, in

that there are no neighboring frequencies in the infra-red spectrum. The single observed depolarized Raman line in this region at 954 cm^{-1} can be assigned to ν_{24} , an out-of-plane CH_3 wagging mode, on the basis of the correlation data. Nearly all the strong lines in the infra-red spectrum of this region can be immediately assigned with the help of the correlation rules and the previous interpretation of the Raman frequencies. The exceptions are bands at 1340 cm^{-1} (weak), 970 cm^{-1} (strong), 795 cm^{-1} (weak), and 734 cm^{-1} (medium). The 734-cm^{-1} line is probably the analogue of the 751-cm^{-1} frequency in the spectrum of the less stable rotational isomer. The 970-cm^{-1} frequency corresponds to the strongest band left and is almost certainly the remaining C—C stretching mode, ν_{34} . It is possible that the 1340- and 795-cm^{-1} bands correspond to the less stable isomeric form, or, on the other hand, they may be summation or difference bands. If they are summation bands, the 795-cm^{-1} frequency can be most easily explained as $\nu_{11} + \nu_{36}$, giving $\nu_{36} = 365\text{ cm}^{-1}$. This is in satisfactory agreement with Pitzer's calculation¹⁰ of 380 cm^{-1} for this mode, but must await confirmation from the infra-red spectrum before being accepted. The 1340-cm^{-1} line seems to be rather anomalous with respect to the correlation rules, and hence can also be most probably explained as a combination level. It is, however, difficult to assign this band satisfactorily with the help of fundamentals that have already been identified. The most likely explanation would appear to be a combination level involving either ν_{10} or ν_{35} near 1140 cm^{-1} together with a frequency near 200 cm^{-1} (ν_{18} , ν_{19} , or ν_{22}). Such a frequency, if it were assigned to the methyl torsion modes ν_{19} or ν_{26} , would give a reasonable

value for the barrier to rotation of the methyl groups of between 2000 and 3000 cal. mole⁻¹.

5. The Spectrum in the Region below 650 cm^{-1}

Unfortunately, the infra-red data in this region are not available. The polarized Raman line at 432 cm^{-1} is clearly the bending mode, ν_{11} .

6. The Spectrum of the C_2 Isomer

Only a few of the strongest Raman lines of the molecule have been observed and they have been listed earlier in Table I. In most cases they occur as weaker satellites to strong Raman lines of the *trans*-isomer and can be assigned to the same vibrations of the less symmetrical molecule (see Table I). The line at 981 cm^{-1} of the less stable (C_2) isomer is anomalous in that its polarization is different from that of the neighboring 956-cm^{-1} line of the *trans*-form, and it is more intense than the latter. It seems probable that it corresponds to a different mode of vibration in the less stable rotational isomer, and it may be the third C—C stretching mode, ν_{34} , which is allowed in the Raman spectrum of this molecule and occurs at 970 cm^{-1} in the infra-red spectrum of the *trans*-molecule.

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