

The Interpretation of the Infra-Red and Raman Spectra of the n-Paraffins

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THE INTERPRETATION OF THE INFRA-RED AND RAMAN SPECTRA OF THE *n*-PARAFFINS

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Infra-red spectra of a series of crystalline *n*-paraffins containing an odd number of carbon atoms have been obtained. The spectrum of oriented crystals of *n*-nonadecane has also been examined. These new experimental results have been combined with the earlier data on the crystalline *n*-paraffins containing an even number of carbon atoms, and many series of absorption bands have been identified in the complete set of spectra. These regularities, as well as those present in the Raman spectra, have been interpreted in terms of CH_2 , CH_3 , and C—C stretching vibrations. Very regular distributions of frequencies have been found between 720 and 1030 cm^{-1} and between 1200 and *ca.* 1370 cm^{-1} , which are assigned to CH_2 rocking and wagging vibrations, respectively. The majority of the absorption bands between 1150 and 880 cm^{-1} can be attributed to C—C stretching or CH_3 rocking modes, and assignments are suggested for the principal series observed in this region.

INTRODUCTION

The vibrational spectra of the *n*-paraffins show marked variations with change in state. As liquids, they have complex spectra, but in the crystalline form the number of frequencies observed is much smaller. The explanation of this phenomenon is that in the liquid state these flexible molecules exist in a number of 'staggered' configurations arising from restricted rotation about internal single bonds (Pitzer 1940); each type of configuration has its own set of vibrational frequencies. In the crystalline solid state only one form is stable and consequently the number of frequencies is greatly reduced. The investigations of Müller (1928) have shown that for the long-chain *n*-paraffins the stable form in the

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crystal above and below the transition temperature corresponds to a planar zigzag structure. This same configuration has been assumed to occur in crystals of the shorter-chain molecules studied in the present work. It will be seen that the selection rules predicted on this assumption are in excellent agreement with observation for the whole set of crystalline *n*-paraffins; it is therefore considered to be a very reasonable one. Earlier investigations of the Raman spectra of the crystals (Mizushima, Morino & Takeda 1941; Rank, Sheppard & Szasz 1949; Sheppard & Szasz 1949; Mizushima & Simanouti 1949) have shown that because of experimental difficulties only a few strong series of frequencies

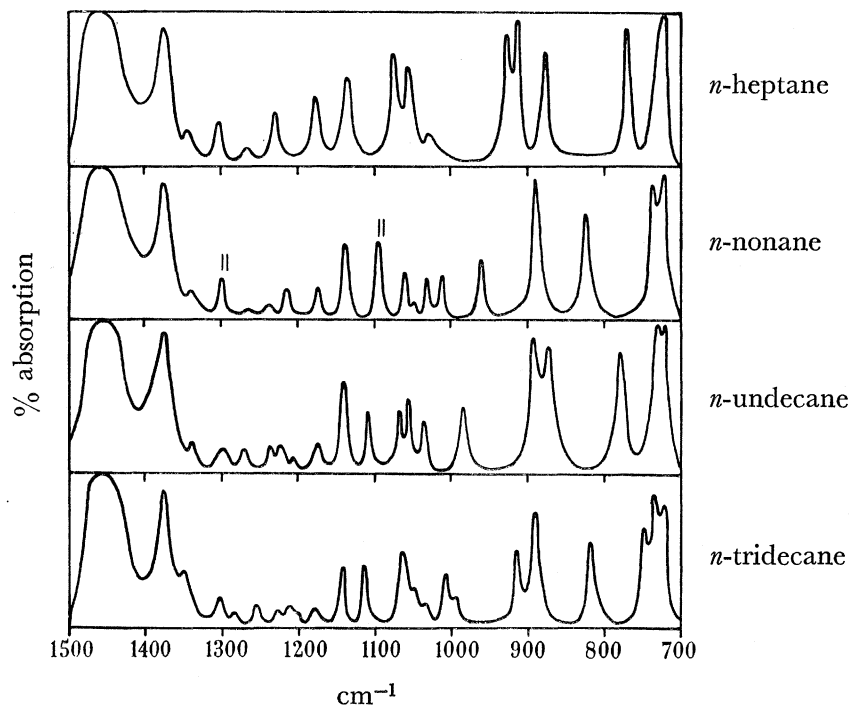


FIGURE 1. The infra-red spectra between 1500 and 700 cm^{-1} of the odd-numbered *n*-paraffins from *n*-heptane to *n*-tridecane in the crystalline solid state. ||, absorption band arising from a vibration parallel to the chain axis.

are observed; some of these have been correlated with particular types of vibration. Many more frequencies appear in the infra-red spectra of the crystalline *n*-paraffins (Axford & Rank 1949, 1950; Brown, Sheppard & Simpson 1950) and the information obtainable is therefore more detailed.

In an earlier paper (Brown *et al.* 1950) an attempt was made to analyze the infra-red spectra of those *n*-paraffins which have an even number of carbon atoms in the chain. As these molecules are centrosymmetric in the solid state, the selection rules are of particular value in the interpretation of their spectra. Since then, a corresponding study of the less symmetrical odd-numbered molecules has been undertaken; the results of this work are presented in figure 1. It has been found that many series of absorption bands picked out in the spectra of the even-numbered molecules also occur in those of the odd-numbered members, so that the whole set of *n*-paraffins can profitably be discussed together. The alternating symmetries and selection rules encountered on passing from odd- to even-

numbered compounds have proved to be of great value in the interpretation of the spectra. The more complete analysis presented as a result of the present work confirms many, but not all, of the conclusions reached previously from the study of the even-numbered n -paraffins.

THEORETICAL CONSIDERATIONS

The detailed investigation of the infra-red spectra of the n -paraffins has again been confined to the region 1500 to 700 cm^{-1} . At frequencies higher than 1500 cm^{-1} the fundamental C—H stretching vibrational frequencies of the CH_2 and CH_3 groups are found; as they represent internal vibrations of these groups they have very constant and well-known frequencies (Fox & Martin 1940). The angle deformation and torsional frequencies associated with the carbon skeleton and the torsional frequencies of the methyl groups lie below 700 cm^{-1} ; these are beyond the accessible range of the apparatus available.

In the region 1500 to 700 cm^{-1} , a n -paraffin of formula $\text{C}_n\text{H}_{2n+2}$ should show frequencies corresponding to the following symmetry co-ordinates: $(n-1)$ C—C stretching modes; $(n-2)$ of each of the CH_2 bending (internal), wagging, twisting and rocking vibrations (Sheppard & Simpson 1953); four asymmetrical and two symmetrical CH_3 deformation modes (both internal in type) and four CH_3 rocking (wagging) modes. Some interaction may be expected between the various types of motion which are not internal in character, provided that they are of the same symmetry classes.

The overall symmetry of the n -paraffins in the planar zigzag form is C_{2h} for n even and C_{2v} for n odd. This is correct provided that interaction with other molecules in the crystallographic unit cell can be neglected. The available evidence suggests that this is a reasonable assumption which is adequate for most purposes, although the possibility of such interaction cannot be entirely ignored for these molecules (see, for example, Stein & Sutherland 1953). The various types of symmetry co-ordinates are assigned to their symmetry classes in table 1, which also includes the selection rules.

TABLE 1. THE SYMMETRY TYPES, SELECTION RULES AND APPROXIMATE FREQUENCY RANGES FOR THE FUNDAMENTAL VIBRATIONS OF THE n -PARAFFINS $\text{C}_n\text{H}_{2n+2}$ BETWEEN 1500 AND 700 cm^{-1}

types of symmetry co-ordinates	approximate frequency range (cm^{-1}) (Brown <i>et al.</i> 1950)	n even (C_{2h})				n odd (C_{2v})			
		A_g	B_g	B_u	A_u	A_1	A_2	B_1	B_2
CH_3 asymmetrical deformation	<i>ca.</i> 1460	1	1	1	1	1	1	1	1
CH_3 symmetrical deformation	<i>ca.</i> 1380	—	—	—	—	1	—	1	—
CH_2 bending	<i>ca.</i> 1460	$\frac{1}{2}(n-2)$	—	$\frac{1}{2}(n-2)$	—	$\frac{1}{2}(n-1)$	—	$\frac{1}{2}(n-3)$	—
CH_2 wagging	1200 to 1350	$\frac{1}{2}(n-2)$	—	$\frac{1}{2}(n-2)$	—	$\frac{1}{2}(n-3)$	—	$\frac{1}{2}(n-1)$	—
CH_2 twisting	1100 to 1350	—	$\frac{1}{2}(n-2)$	—	$\frac{1}{2}(n-2)$	—	$\frac{1}{2}(n-1)$	—	$\frac{1}{2}(n-3)$
CH_3 rocking	800 to 1200	1	1	1	1	1	1	1	1
C—C stretching	800 to 1200	$\frac{1}{2}(n)$	—	$\frac{1}{2}(n-2)$	—	$\frac{1}{2}(n-1)$	—	$\frac{1}{2}(n-1)$	—
CH_2 rocking	700 to 1050	—	$\frac{1}{2}(n-2)$	—	$\frac{1}{2}(n-2)$	—	$\frac{1}{2}(n-3)$	—	$\frac{1}{2}(n-1)$
selection rules		R., p.	R., dp.	i.r.	.r.	R., p., i.r.	R., dp.	R., dp., i.r.	R., dp., i.r.

R. = Raman active; i.r. = infra-red active; p. = polarized; dp. = depolarized.

For later comparison with the results on oriented crystal layers it should also be noted that each of the infra-red active symmetry classes for n odd corresponds to a particular direction of dipole moment change during the vibration, as follows:

A_1 , perpendicular to the chain length, but in the skeletal plane of the molecule;

B_1 , parallel to the chain length;

B_2 , perpendicular to the chain length, and to the skeletal plane.

The choice of orientation of B_1 and B_2 is that generally adopted in the discussion of the spectrum of propane (Herzberg 1945, p. 359).

The complete experimental infra-red and Raman data for the n -paraffins in the crystalline state (i.e. in the planar zigzag form) are summarized diagrammatically in figures 2 and 3. They are taken from the present work and the previous studies cited; the data for ethane and propane (which have rigid skeletons) are taken from other sources (Herzberg 1945, pp. 342, 359; Smith 1949; McMurry & Thornton 1951). As mentioned above, the Raman spectra (figure 3) consist only of a few series of lines, but the infra-red spectra are much

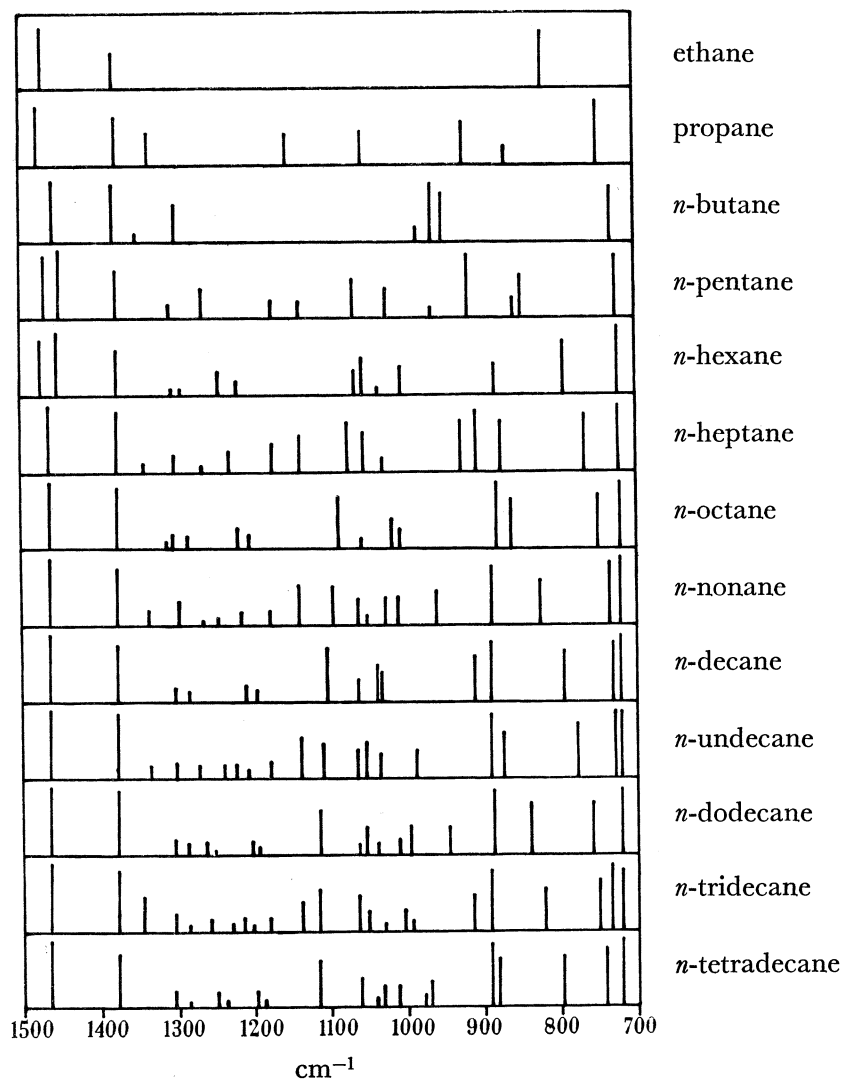


FIGURE 2. The collected infra-red absorption data for the n -paraffins in the crystalline solid state.

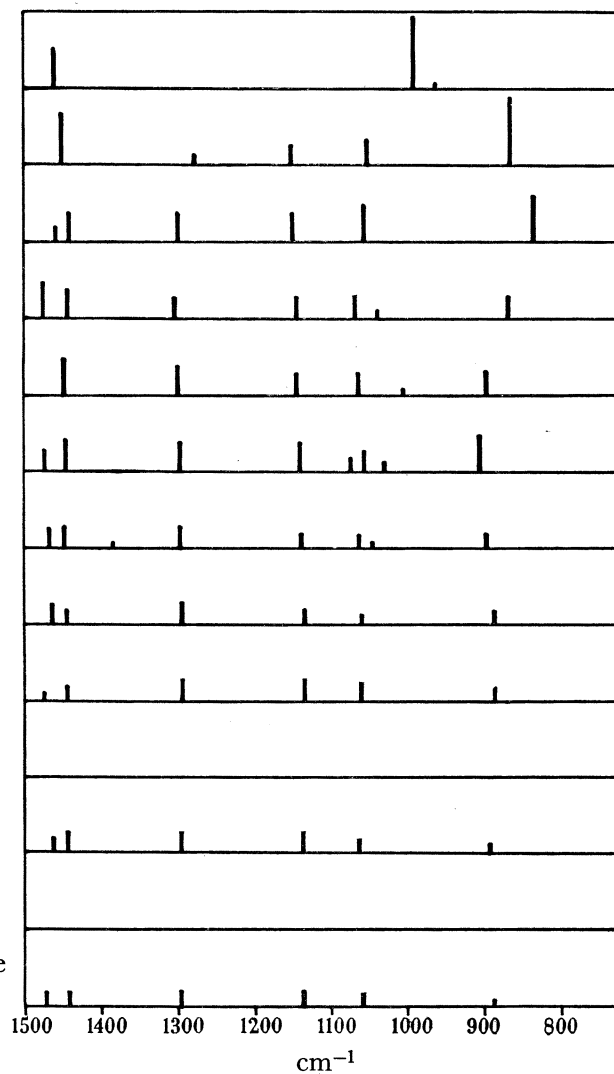


FIGURE 3. The collected Raman data for the n -paraffins in the crystalline solid state.

more complex. In the latter case, however, several well-marked series of absorption bands can readily be recognized.

In order to analyze the spectra the frequency range will be considered to a first approximation as being divided into regions characteristic of CH₂ wagging, twisting, rocking and C—C stretching frequencies. These are assumed to split out with increasing chain length from the known frequencies of the first member of each set as determined from the detailed assignments of the spectra of propane (CH₂ modes) and ethane (C—C stretching). It is generally agreed that the CH₂ twisting and rocking fundamentals in propane have the frequencies 1278 and 748 cm⁻¹ respectively (Rasmussen 1948; McMurry & Thornton 1951) and the C—C stretching mode in ethane gives rise to a Raman line at 993 cm⁻¹ (Bhagavantam 1931–2). The assignment of the B₁ CH₂ wagging mode in propane is complicated by the fact that it is to some extent coupled with other vibrations of the same

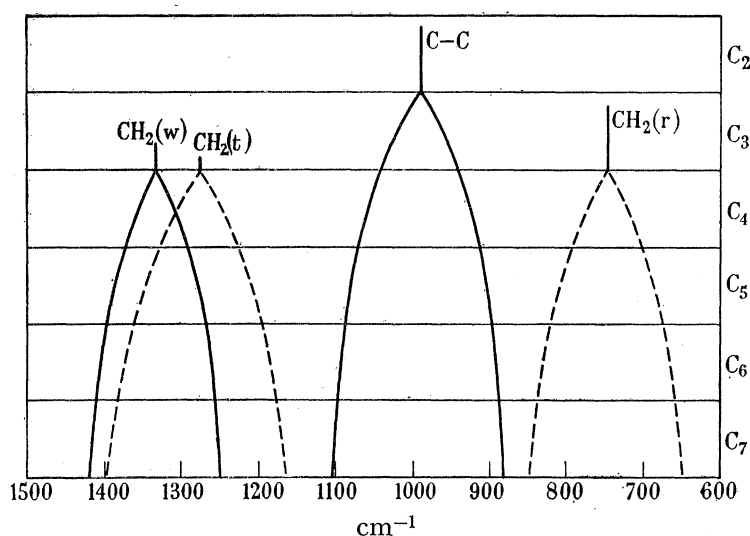


FIGURE 4. A schematic representation of the vibrational spectra of the *n*-paraffins divided into regions characteristic of the various CH₂ and skeletal vibrations. CH₂(t) = CH₂ twisting; CH₂(w) = CH₂ wagging; CH₂(r) = CH₂ rocking; C—C = skeletal stretching.

symmetry class (McMurry & Thornton 1951). However, there appears to be good reason for suggesting that the absorption band at 1336 cm⁻¹, which is of the correct contour, arises principally from this type of motion (Pitzer 1944), as it forms the origin of a series of CH₂ bands (see later discussion).

Figure 4 shows schematically how the various sets of frequencies might split out from their origins in ethane and propane. The CH₂ wagging and C—C stretching modes (solid outline) have been distinguished from the CH₂ twisting and rocking modes (dashed outline) as they involve motion either in or parallel to the skeletal plane, while the latter involve movement perpendicular to this plane. Vibrational interaction can occur between the two in-plane or the two out-of-plane sets of frequencies, but as their origins are well separated it might reasonably be expected that the above picture would be valid for small values of *n*. The constant frequencies observed near 1460 cm⁻¹ (CH₂ and CH₃ internal deformation modes) and 1380 cm⁻¹ (symmetrical CH₃ internal deformation modes), which are prominent in the infra-red spectra of all the *n*-paraffins (figure 2), are not shown in figure 4, nor are the four methyl rocking frequencies. To a first approximation

these latter should give rise to four series of frequencies in the general region of the skeletal modes (table 1). The in-plane methyl rocking modes can couple to some extent with the skeletal vibrations.

The spectroscopic behaviour of each of the sets of frequencies shown in figure 4 can be described in more detail after the symmetry properties and selection rules associated with each individual vibration have been considered. For simplicity it will be assumed that the actual frequencies split out in a regular fashion from the origin in each case. The approximate forms of vibration of a chain consisting of a number of identical vibrating units can be deduced, ignoring end-effects, from an application of the Born-Kármán conditions (1912). These imply that standing waves are set up in the chain with up to x half-wave-lengths, where x is the number of identical vibrating units. This concept has been applied

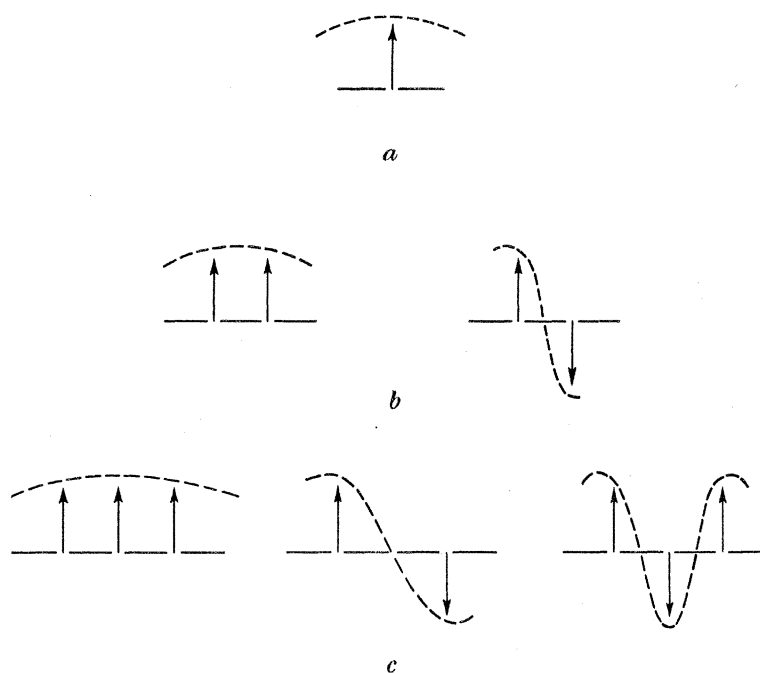


FIGURE 5. 'Wave diagrams' representing schematically the CH_2 rocking modes of (a) propane, (b) n -butane and (c) n -pentane.

with success in discussing the vibrations of zigzag n -paraffin or polymethylene chains (Bartholomé & Teller 1932; Whitcomb, Nielsen & Thomas 1940; Pitzer 1940; Simanouti & Mizushima 1949; Barrow 1951; Deeds 1951; for other references see Brown *et al.* 1950). Although the form of a particular vibration deduced in this manner is only approximate, it has the correct symmetry properties and can therefore be used to predict the infra-red or Raman activity of the mode.

The CH_2 rocking modes of the planar zigzag n -paraffins may be used as an illustration of this method. A single CH_2 group (e.g. in propane) gives rise to a change in dipole moment when it rocks against the carbon skeleton; in this case the direction of the dipole change is perpendicular to the plane of the three carbon atoms. In figure 5a the carbon chain of propane is viewed edge-on, so that the carbon atoms, when projected in the plane of the paper, appear to be collinear. The dipole change perpendicular to the skeletal plane associated with the CH_2 rocking vibration is then represented by an arrow directed from

the central carbon atom. The coupled in- and out-of-phase CH_2 rocking vibrations of n -butane are likewise represented in figure 5*b*, and those of n -pentane in figure 5*c*. For x CH_2 groups the number of nodes in the waves varies from 0 to $(x-1)$, i.e. there are x wave diagrams. The infra-red activity or otherwise of these chain vibrations can now be deduced, remembering that there must be an overall change in dipole moment for a vibration to be active. This is the case when the number of nodes is zero or even, but not when it is odd. Similar considerations can be used to deduce the Raman activity of the various vibrations. The total numbers of infra-red and Raman-active modes of each type predicted in this fashion are in complete agreement with those given in table 1.

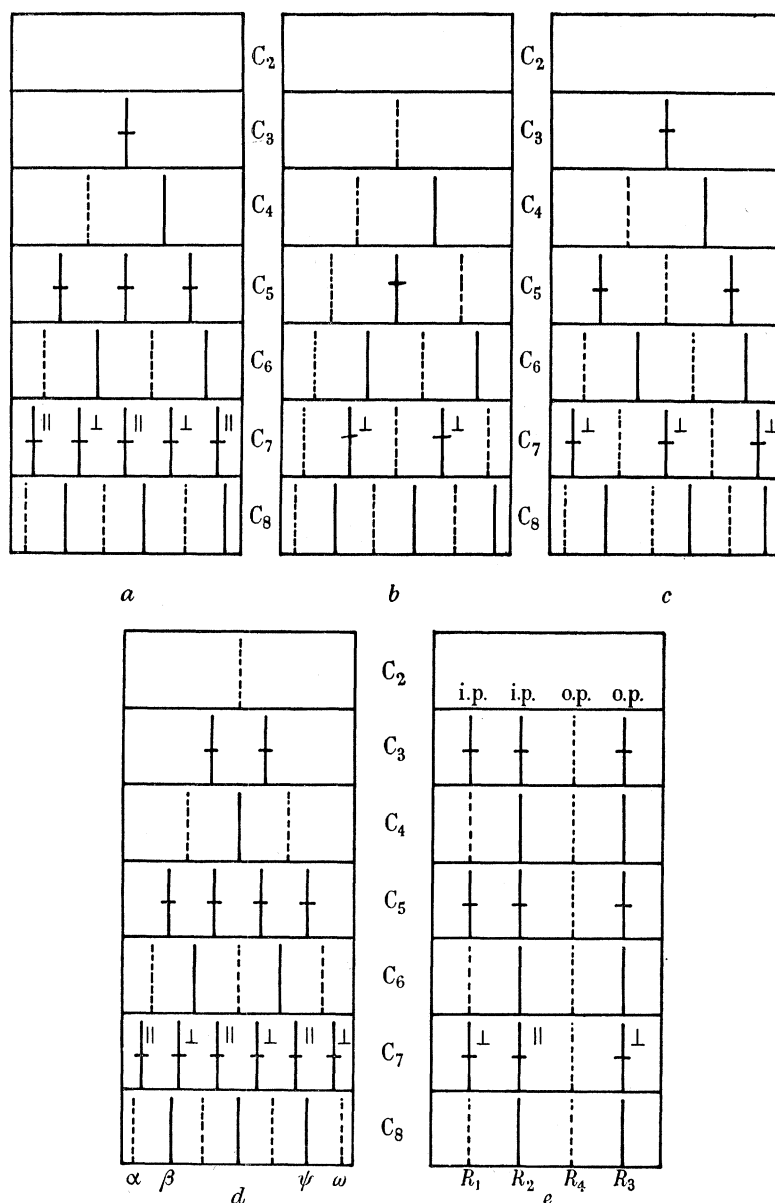


FIGURE 6. Simple theoretical frequency distributions corresponding to (a) CH_2 wagging modes, (b) CH_2 twisting modes, (c) CH_2 rocking modes, (d) skeletal stretching modes and (e) CH_3 rocking modes. i-p = in-plane; o-p = out-of-plane; | = infra-red-active; \ddagger = Raman-active; + = infra-red- and Raman-active; || = dipole moment change parallel to chain length; \perp = dipole moment change perpendicular to chain length.

Figure 6 shows the simplified schematic frequency distributions and their selection rules for each of the CH_2 wagging, twisting, rocking and C—C stretching modes. The infra-red-active vibrations which give rise to dipole changes parallel and perpendicular to the chain length are also indicated for later correlation with the spectra of oriented crystallites. The corresponding selection rules for the four methyl rocking modes are also shown. The selection rule distribution for each of the simple theoretical patterns corresponding to the CH_2 and C—C vibrations is asymmetrical about its central axis; the orientation of the pattern and the magnitude of the splitting remain to be determined from the experimental data. The model adopted is undoubtedly an over-simplified one, as interaction between vibrations of the same symmetry class has been ignored. Nevertheless, as will be appreciated in the later discussion, the approximate pictures provide a useful guide in analyzing the spectra.

EXPERIMENTAL

The experimental technique employed was the same as that described previously (Brown *et al.* 1950). The rock-salt cell had a thickness of about 0.2 mm and a Hilger D 209 double-beam spectrometer with a 30° rock-salt prism was used to record the spectra in the region 1500 to 700 cm^{-1} . A list of the frequencies observed for the crystalline *n*-paraffins well below their freezing-points is given at the end of this section; the earlier experimental work on several of the molecules has been repeated using a greater cell thickness and a few weak absorption bands not previously listed have been located. In addition, the crystalline solid-state spectrum of *n*-heptane has been examined and found to be in general agreement with the published data (Axford & Rank 1950), although a few weak absorption bands have been observed which were not included in this earlier work. The splitting of the 726 cm^{-1} absorption band on crystallization has not been confirmed, but the lower resolution of the spectrometer used in this work may account for this.

It was noticed that the intensity of several absorption bands in the crystalline solid-state spectrum of *n*-nonane varied considerably after melting and refreezing of the liquid; the absorption bands at 1298 and 1094 cm^{-1} showed the most marked change. These variations were ascribed to orientation effects involving different directions of the *n*-paraffin chains with respect to the incident radiation. It was decided to examine another *n*-paraffin in more detail under controlled conditions of crystal orientation, so that the maximum use could be made of this effect in the assignment of the vibrational frequencies. *n*-Nonadecane, $\text{C}_{19}\text{H}_{40}$, was selected for this purpose, as it has a known crystal structure (Müller 1930) and is solid at room temperature.

Two orientations of the paraffin chains were required, one in which their long axes were pointing in the direction of the incident radiation and one in which the molecular axes had no preferred orientation. In the first case the frequencies of all vibrations involving a change in dipole moment parallel to the chain should be absent from the infra-red spectrum. Several attempts to grow a suitable crystal of *n*-nonadecane, both by slow cooling from the melt and by crystallization from a number of solvents, were unsuccessful. Only very small single crystals were obtained. The chief difficulty was to obtain a thickness (at least 0.3 to 0.4 mm) sufficient to observe a good spectrum. However, oriented polycrystalline material was produced by slow cooling from the melt, and thin specimens

obtained in this way, mounted on rock salt, were examined under a polarizing microscope. They were found to consist almost entirely of plate-like crystallites. These plates showed low-order interference colours and fairly sharp extinctions. In convergent light a well-defined interference figure was observed of the type shown by biaxial crystals, with the acute bisectrix perpendicular to the plates. In the case of the *n*-paraffin crystal, however, the acute optic axial angle was small, and the figure was of the pseudo-uniaxial type. It is well known that the paraffin chains are oriented parallel to each other and in the direction of the pseudo-hexagonal axis; it follows, therefore, that they lie perpendicular to the

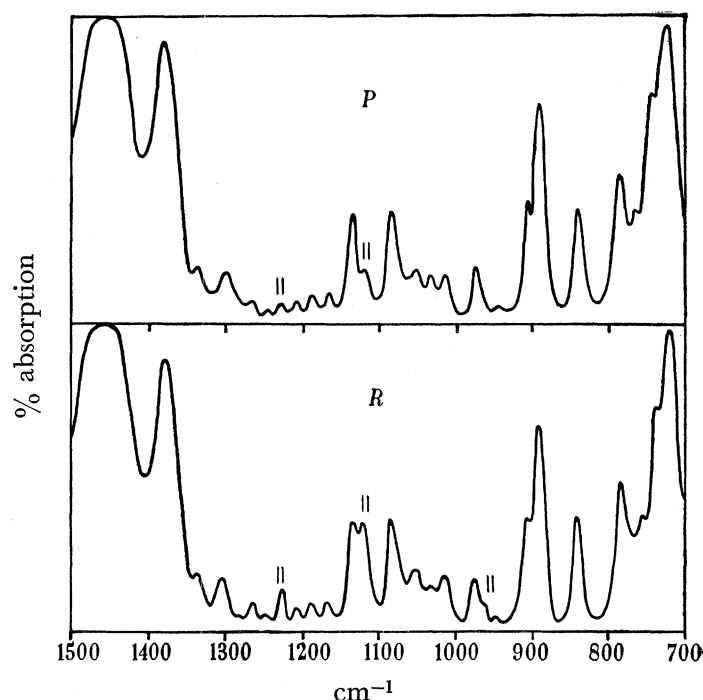


FIGURE 7. The infra-red spectrum of *n*-nonadecane in the crystalline solid state with (*R*) crystallites (rods) oriented randomly in the plane of illumination, (*P*) crystallites (plates) having the paraffin chains perpendicular to the plane of illumination. ||, absorption band arising from a vibration parallel to the chain axis.

plates. Tests with a sensitive tint and mica plate showed the crystals to have positive birefringence, i.e. the greatest refractive index was in the direction of the acute bisectrix (or pseudo-hexagonal axis). Thus, as expected, the greatest refractive index is in the direction of the chain length. Thick specimens were grown in exactly the same way, and thin portions near the edges tested with the polarizing microscope. A large porportion of plate-like crystallites was observed for these preparations, and all showed the same properties.

Variously oriented crystals were obtained by rapid cooling from the melt, and examination of these under the polarizing microscope showed them to be almost entirely rod-like structures. These rods gave very sharp extinctions both parallel and perpendicular to their length. In this case the direction of greater refractive index was found to be perpendicular to the rod length. Convergent light gave no well-defined interference figure. It was concluded from this observation that the rods contain in general carbon chains perpendicular

to their long axes. These chains lay either in the plane of observation or somewhat inclined to it.

The infra-red spectrum of each type (rods and plates) is shown in figure 7. The curve marked *R* (rods) was obtained with randomly oriented *n*-paraffin chains, while in *P* (plates) they were pointing in the direction of propagation of the infra-red radiation. It is immediately obvious that the two spectra differ. In spectrum *P* several absorption bands are much weaker than their analogues in *R*, and these must be of the parallel type; others are perpendicular. It is not expected that all absorption bands arising from vibrations parallel to the chains will be entirely absent from spectrum *P*, as the crystallites were not perfectly oriented and there was some convergence of the incident beam. The parallel bands are emphasized in figure 7 for *n*-nonadecane and in figure 1 for *n*-nonane.

n-Heptane

Source: American Petroleum Institute, Research Project 44.

Purity: b.p. 98.4° C, 760 mm Hg; n_D^{20} 1.3876.

Infra-red frequencies: ca. 726(s); 769(s); 876(m); 910(s); 927(m); 1030(w); 1056(m); 1072(m); 1139(m); 1176(m); 1230(m); 1268(w); 1302(m); 1338(w); 1376(s); ca. 1470(s).

n-Undecane

Source: Anglo-Iranian Oil Co.

Purity: 99.99 mole %.

Infra-red frequencies: 720(s); 728(s); 776(s); 876(s); 889(s); 988(m); 1035(m); 1052(m); 1064(m); 1106(m); 1137(m); 1175(w); 1204(w); 1222(w); 1239(w); 1270(w); 1299(w); 1335(w); 1376(s); ca. 1465(s).

n-Tridecane

Source: Anglo-Iranian Oil Co.

Purity: ca. 95 mole %.

Infra-red frequencies: 723(s); 734(s); 750(m); 819(m); 892(s); 914(m); 993(w); 1006(m); ca. 1030(w); ca. 1050(m); 1064(m); 1112(m); 1138(m); 1178(w); 1212(w); 1227(w); 1255(w); ca. 1282(w); 1304(w); ca. 1345(m); 1376(s); ca. 1465(s).

n-Nonadecane

Source: Dr Stenhagen.

Purity: m.p. 31.8 to 32.0° C; s.p. 31.7° C (lit. m.p. 32° C).

Infra-red frequencies: Type *R* spectrum: 720(s); 740(s); 765(m); 783(m); 840(m); 890(s); 906(m); ca. 945(w); 958(w); 972(m); 1013(m); 1034(m); 1056(m); 1089(m); 1121(m); 1134(m); 1170(w); 1189(w); 1208(w); 1226(w); ca. 1246(w); ca. 1262(w); ca. 1300(m); ca. 1337(m); 1378(s); ca. 1465(s).

INTERPRETATION OF THE SPECTRA

The general appearance of the infra-red spectra of the *n*-paraffins shown in figure 1 and in the earlier work (Brown *et al.* 1950) suggests a rough subdivision of the frequency region 1500 to 700 cm⁻¹ into three sections. From 1500 to 1370 cm⁻¹ a few strong absorption

bands are observed; these arise from the well-known internal deformation vibrations of the CH_2 and CH_3 groups. Between 1370 and 1150 cm^{-1} there are a number of weak absorption bands which, from the general considerations cited above, are probably associated with the CH_2 wagging and twisting vibrations. Considerably stronger absorption bands are observed between 1150 and 700 cm^{-1} ; these are mainly attributed to the skeletal stretching and CH_2 rocking modes. The interpretation of this last region was first undertaken, since the CH_2 rocking modes should give rise to easily recognizable series of strong absorption bands.

(a) *The CH_2 rocking modes*

The earlier work (Brown *et al.* 1950) on the even-numbered *n*-paraffins showed several series of absorption bands lying between 1000 and 700 cm^{-1} , which were attributed to CH_2 rocking modes. The new data on the odd-numbered molecules show that their analogous absorption bands can be readily fitted in with the earlier results to give a consistent pattern of the type predicted in figure 6*c* for these modes.

The band contour of the 748 cm^{-1} absorption band in the propane spectrum has the shape (type *C*) expected for a CH_2 rocking fundamental (B_2), and the analogous contour of the 732 cm^{-1} absorption band of *n*-butane (Gates, 1949) leaves no doubt that it also arises from vibration of the correct symmetry class (A_u) (Brown *et al.* 1950). These two absorption bands form the beginning of a series (figure 2) which can be traced in the spectra to a limit of 720 cm^{-1} in the long-chain molecules. If this series corresponds to CH_2 rocking modes it determines the orientation of the theoretical pattern (figure 6*c*); other series, which are infra-red-active throughout, should then be observable starting at *n*-pentane, *n*-heptane, *n*-nonane, *n*-undecane and *n*-tridecane and moving towards lower frequencies. Each of these series can readily be selected from the observed spectra. In a few cases some difficulty was at first experienced in the identification of the highest frequency members of some of the series, but this was readily resolved when the whole pattern of absorption bands became discernible. It is apparent that the CH_2 rocking modes account for all the observed bands in the region 750 to 850 cm^{-1} and extend as high as 1050 cm^{-1} in the longer-chain molecules.

The extreme regularity of the whole observed pattern, and the agreement with the simplified theoretical predictions of figure 6*c* can leave no doubt that these frequencies are correctly assigned as rocking modes. The set of absorption bands arising from these modes has been isolated from the infra-red spectra and drawn out in figure 8. The only deviation from the simple theoretical picture is a crowding together of the set of frequencies towards the lower limit at 720 cm^{-1} .

Approximately half the CH_2 rocking modes are infra-red-inactive, but should appear in the Raman spectrum. Although no Raman lines have been observed in this region (figure 3) it is probable that the frequencies of Raman active series are interleaved between the infra-red series. Furthermore, the intensities of the infra-red-active CH_2 rocking modes of a given molecule decrease in a regular fashion with increasing frequency. This is also to be expected since the 720 cm^{-1} absorption bands are associated with the in-phase motion of all the groups, and therefore arise from the greatest dipole moment change; only this frequency would be active for an infinite zigzag chain. Finally, as can be seen from

the spectrum of *n*-nonadecane shown in figure 7, the analogous absorption bands from this long-chain molecule exhibit the correct perpendicular polarization properties for assignment to CH_2 rocking modes.

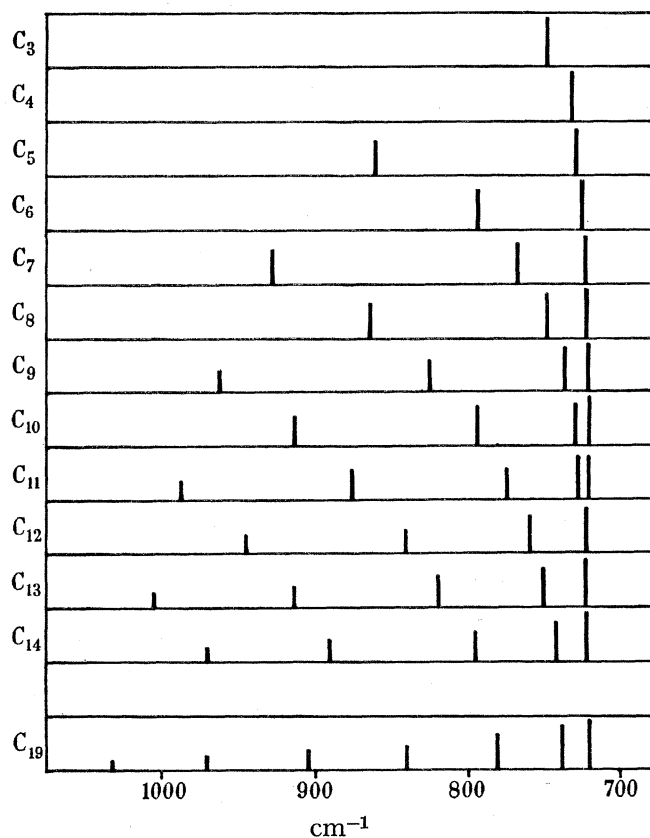


FIGURE 8. Distribution of CH_2 rocking frequencies observed in the infra-red spectra of the crystalline *n*-paraffins.

(b) *The C—C stretching and CH_3 rocking modes*

(i) *The assignment of symmetry classes*

The skeletal C—C stretching and the CH_3 rocking modes are discussed together because they have overlapping frequency ranges so that interaction may be expected between those vibrations which belong to the same symmetry classes. These two types of vibration probably account for the remaining absorption bands in the range 1150 to 850 cm^{-1} . Moreover, in the spectra of the longer chain *n*-paraffins the majority of the observed frequencies must correspond principally to skeletal stretching vibrations. It is apparent at the outset that the observable regularities are not comparable with those found for the CH_2 rocking modes. Nevertheless, a number of series of infra-red and Raman frequencies can readily be picked out on passing from low to high values of *n*. The first step in the analysis is to select those series which originate in the spectrum of propane and to assign them to their appropriate symmetry classes. Propane rather than ethane was chosen for this purpose, as ethane has a higher symmetry than any of the other *n*-paraffins. Examination of figures 2 and 3 shows that in the spectra of the crystalline *n*-paraffins four regular series originating in the spectrum of propane can readily be distinguished. Three

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of these, near 1140, 1060 and 890 cm^{-1} , are Raman-active throughout; the other (923 cm^{-1} in propane to 1121 cm^{-1} in n -nonadecane) is infra-red-active for all values of n . It is also profitable to consider (as will be explained later) a fifth series, starting at 951 cm^{-1} in the spectrum of n -butane and reaching 890 cm^{-1} in that of n -nonadecane; this is also infra-red-active throughout.

As has already been noted, in the crystalline state the n -paraffins almost certainly assume planar zigzag configurations with overall symmetry C_{2v} for n odd and C_{2h} for n even. Further, the frequencies of any one series must correspond to related vibrations which involve motion either in or out of the plane of the molecule. No other information is needed to deduce all the possible symmetry class combinations to which the observed series could be assigned. Table 2 summarizes these combinations, and includes the selection rules for n odd and n even, the infra-red band contours, the expected Raman polarizations and the infra-red polarization properties for n odd. Since the relevant experimental data are available (at least for some molecules), all these types of evidence can be used to assign the observed series to their symmetry classes.

TABLE 2. POSSIBLE SYMMETRY CLASS COMBINATIONS FOR SERIES OF RELATED VIBRATIONS OF THE PLANAR ZIGZAG CONFIGURATIONS OF THE n -PARAFFINS

symmetry class combinations		infra-red activity		Raman activity		infra-red band contour		Raman polarization		infra-red polarization
n odd	n even	n odd	n even	n odd	n even	n odd	n even	n odd	n even	n odd
in-plane										
A_1	A_g	+	-	+	+	B	-	p.	p.	\perp
A_1	B_u	+	+	+	-	B	A/B	p.	-	\perp
B_1	A_g	+	-	+	+	A	-	dp.	p.	
B_1	B_u	+	+	+	-	A	A/B	dp.	-	
out-of-plane										
A_2	B_g	-	-	+	+	-	-	dp.	dp.	-
A_2	A_u	-	+	+	-	-	C	dp.	-	-
B_2	B_g	+	-	+	+	C	-	dp.	dp.	\perp
B_2	A_u	+	+	+	-	C	C	dp.	-	\perp

+ = active; - = inactive; p. = polarized; dp. = depolarized; \perp = mode of vibration perpendicular to chain length; || = mode of vibration parallel to chain length; A , B and C are the expected types of band contour (Herzberg 1945).

(ii) *The 890 cm^{-1} Raman series*

This series (figure 3), which is Raman-active for all values of n , originates at 867 cm^{-1} in the Raman spectrum of propane and has a constant value near 890 cm^{-1} for $n > 8$. The corresponding infra-red absorption bands are observed only for odd values of n as far as n -heptane (figure 2); they are overlapped by another series for $n > 7$. Table 2 shows that the possible symmetry class combinations consistent with this behaviour are (A_1, A_g) , (B_1, A_g) or (B_2, B_g) . The band contour of the infra-red absorption at 870 cm^{-1} in the spectrum of propane is of type B (Wu & Barker, 1941), and the Raman lines at 868 and 905 cm^{-1} in the spectra of n -pentane and n -heptane respectively are both polarized (Herz, Kahovec & Wagner 1946). All these observations indicate that the symmetry class is A_1 for n odd. For n even the symmetry class must therefore be A_g , and the polarization of the Raman lines at 835 and 898 cm^{-1} in the spectra of n -butane and n -hexane confirms this conclusion.

Although these polarization data are taken from measurements of the spectra in the liquid state, there appears to be little overlapping of Raman frequencies in this region, so that these deductions can be safely applied to the spectra in the solid state. For the longer-chain n -paraffins ($n > 8$) both infra-red and Raman frequencies are observed near 890 cm^{-1} , whatever the value of n . Since for n even the molecules have a centre of symmetry, it is impossible for a single series to be both Raman and infra-red-active throughout. Hence, as will be discussed below, the absorption bands near 890 cm^{-1} for n even must arise from a second series which overlaps the Raman-active series, and those for n odd presumably arise from both series.

(iii) *The 1060 cm^{-1} series*

Figures 2 and 3 show that this series is Raman-active throughout, and that, for molecules with $n \leq 5$, infra-red absorption bands are observed for n odd. Thus the symmetry class combinations must be (A_1, A_g) , (B_1, A_g) or (B_2, B_g) . For $n \geq 6$ there is always an infra-red absorption band near 1060 cm^{-1} for all values of n ; this must correspond (as in the previous case) to a second overlapping series. The absorption band at 1053 cm^{-1} in the spectrum of propane has a type A contour corresponding to symmetry B_1 for odd values of n (Wu & Barker 1941). Hence the symmetry class combination for this series must be (B_1, A_g) . Unfortunately the infra-red measurements on oriented crystals of n -nonadecane cannot be used to confirm the symmetry class in this case, because of the overlapping of the two series for high values of n . The Raman line at 1058 cm^{-1} in the spectrum of liquid n -butane is polarized, which is consistent with symmetry A_g , and that of liquid n -pentane at 1067 cm^{-1} is depolarized in good agreement with symmetry B_1 (Herz *et al.* 1946); however, in this region there may be overlapping of frequencies from more than one rotational isomer.

(iv) *The 1120 cm^{-1} series*

As already noted this series originates at 923 cm^{-1} in the infra-red spectrum of propane and moves to higher frequencies, reaching 1121 cm^{-1} in the spectrum of n -nonadecane. The first few members are also observed to be Raman-active for n odd. Possible symmetry class combinations are thus (A_1, B_u) , (B_1, B_u) or (B_2, A_u) . In propane the 923 cm^{-1} absorption band has a type A contour (Wu & Barker 1941), showing that the symmetry class is B_1 for n odd. The parallel polarization of the 1121 cm^{-1} band of n -nonadecane confirms this assignment. It follows that the symmetry class for n even must be B_u , as is also suggested by the infra-red contour of the 965 cm^{-1} band of n -butane (Gates 1949; Brown *et al.* 1950).

(v) *The 1140 cm^{-1} series*

This series originates at 1155 cm^{-1} in the infra-red and Raman spectrum of propane and reaches 1134 cm^{-1} in the infra-red spectrum of n -nonadecane. The frequencies are Raman-active throughout, but infra-red-active only for odd values of n . Possible symmetry class combinations are thus (A_1, A_g) , (B_1, A_g) or (B_2, B_g) . The infra-red band contour of the 1155 cm^{-1} frequency in propane is of an indefinite shape and so cannot be used to decide between the symmetry classes for n odd. However, the polarization measurements on n -nonadecane leave no doubt that the corresponding member of this series arises from

a vibration perpendicular to the chain axis, i.e. its symmetry class is A_1 or B_2 . The observation that the Raman lines at 1148 cm^{-1} in liquid n -butane and 1138 cm^{-1} in liquid n -pentane are polarized (Herz *et al.* 1946) suggests that the symmetry class combination is (A_1, A_g) , though the same reservations apply to this evidence as those discussed for the 1060 cm^{-1} series. This interpretation implies that the symmetry class of the 1155 cm^{-1} frequency in propane is A_1 . A similar conclusion has been reached from investigations of the spectra of symmetrically deuterated propanes and the application of the product rule (McMurry & Thornton 1951).

(vi) *The 890 cm^{-1} infra-red series*

As has already been noted, a fifth series can be picked out in the infra-red spectra which has frequencies active for all n ; this occurs near 890 cm^{-1} for large values of n and can be traced back to a strong absorption band at 951 cm^{-1} in the spectrum of n -butane (figure 2). The fact that this series cannot be associated with any band in the spectrum of propane would at first suggest that it should not be considered here. However, one of the expected infra-red frequencies of propane of symmetry B_2 has not been observed, presumably because of overlapping with the frequency of another mode (Sheppard & Simpson 1953). Earlier work has shown that the 951 cm^{-1} absorption band of n -butane has a type C contour corresponding to symmetry A_u (Gates, 1949; Brown *et al.* 1950) and the infra-red polarization data on n -nonadecane show that the corresponding frequency (at 890 cm^{-1}) arises from a perpendicular vibration, i.e. A_1 or B_2 . The only possible symmetry class combination for this series consistent with all these data is thus (B_2, A_u) (see table 2).

(vii) *General discussion*

The experimental evidence cited in the previous section shows that the symmetry class combinations of the five prominent series in this region of the spectrum can be determined. The next stage in the analysis is to attempt to assign these series to their appropriate types of vibration, giving due consideration to the possible coupling of the vibrational modes of the same symmetry class. If as a first approximation such interaction is ignored, then eight related series originating in the spectrum of propane should be recognizable. Four of these correspond to methyl rocking modes, two in-plane R_1 (A_1, A_g) and R_2 (B_1, B_u), and two out-of-plane R_3 (B_2, A_u) and R_4 (A_2, B_g); each would give rise to a separate frequency in the spectrum of propane (figure 6*e*). The remaining four series labelled α (B_1, A_g), β (A_1, B_u), ψ (B_1, B_u) and ω (A_1, A_g) in figure 6*d* correspond to skeletal vibrations. Propane has two frequencies due to such modes one of which splits to give the α and ψ series and the other to give the β and ω series. In n -butane the β and ψ series correspond to a single frequency. Although this schematic picture is very probably too simple, as interaction can occur, the type or types of vibration which may be associated with any observed series of a given symmetry class combination can be deduced as shown below:

observed series	symmetry class	approximate assignment
890 cm^{-1} (Raman)	(A_1, A_g)	R_1, ω
1060 cm^{-1}	(B_1, A_g)	α
1120 cm^{-1}	(B_1, B_u)	R_2, ψ
1140 cm^{-1}	(A_1, A_g)	R_1, ω
890 cm^{-1} (infra-red)	(B_2, A_u)	R_3

It should be emphasized that these assignments can only be made *because of the observed regularities in the spectra*. The presence of very strong interaction between all the vibrations of the same symmetry class for each molecule might well have resulted in spectra from which no related series could have been picked out; in this case no further analysis of the data would have been possible. The above comparison gives the approximate assignments of the 1060 and 890 cm^{-1} (infra-red) series directly. For the other series empirical evidence

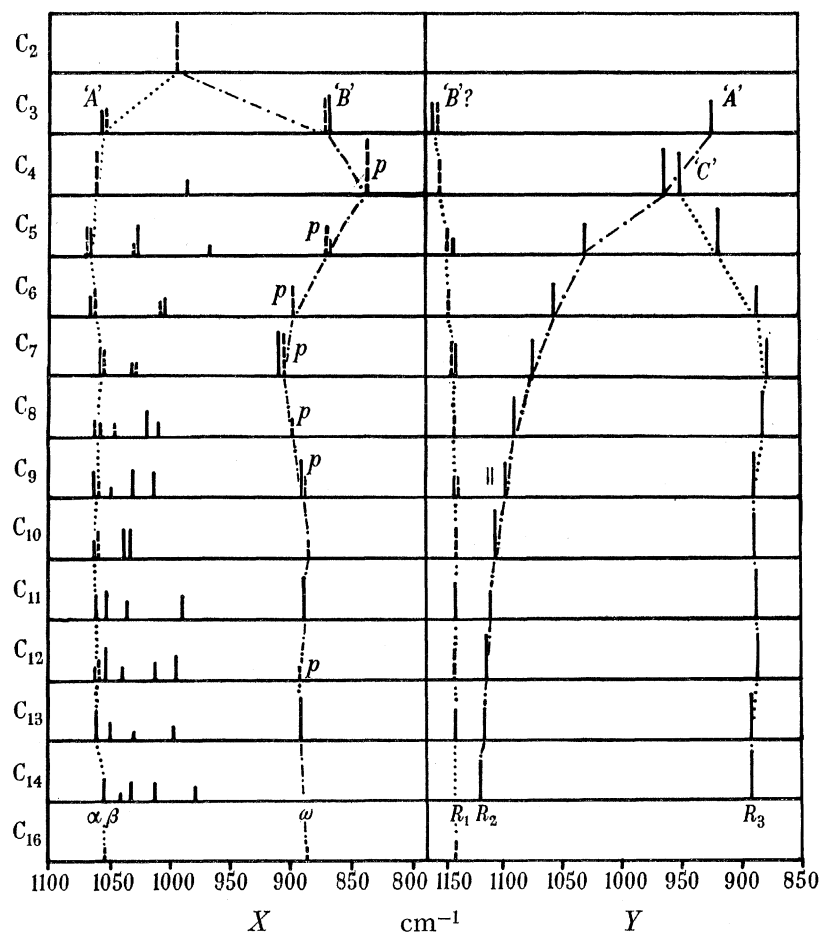


FIGURE 9. Assigned distributions of (*X*) skeletal stretching frequencies and (*Y*) methyl rocking frequencies observed in the infra-red and Raman spectra of the crystalline *n*-paraffins. | = infra-red absorption band; ∷ = Raman line; *p* = polarized; 'A', 'B' and 'C' indicate observed types of infra-red band contour.

must be used to decide which type of vibration is the more appropriate. The observed series near 1140 and 890 cm^{-1} have the same symmetry class combination—that appropriate to the ω skeletal series or the R_1 methyl rocking modes. Both these series might correspond to a mixture of the two types of vibration, but the following evidence suggests that the 890 cm^{-1} series may be assigned principally to the ω skeletal modes. According to the simplified theoretical distribution (figure 6*d*) the α and ω series form the limits of the skeletal stretching modes and have a common origin in the 993 cm^{-1} frequency of ethane; the other skeletal stretching modes are found between these limits. In the observed distribution both the 1060 cm^{-1} series (already identified as α) and particularly

the 890 cm^{-1} series tend towards the 993 cm^{-1} frequency in ethane as n decreases. As the paraffin chain lengthens, weak absorption bands are found in the range 1060 to 890 cm^{-1} , their number increasing with increasing n ; these can readily be interpreted as arising from the other skeletal stretching modes. Normal co-ordinate calculations with reasonable force constants (for example, Stepanov 1947) have consistently indicated that the ω series lies at lower frequencies than the α series (although this order could be reversed if less plausible force constants were chosen). The 1140 cm^{-1} series, on the other hand, shows none of the characteristics predicted for the ω skeletal series and for this reason is considered to arise principally from the in-plane methyl rocking modes R_1 . The 1120 cm^{-1} series has a symmetry class combination appropriate to the ψ skeletal or the R_2 methyl rocking modes. If this series were interpreted as the ψ skeletal series then it should move towards the ω series near 890 cm^{-1} with increasing n ; in fact, it is observed to move away from this value and converges towards the 1140 cm^{-1} series as the chain lengthens. Further, if it is the ψ skeletal series it should converge to the α skeletal frequency in propane, i.e. 1053 cm^{-1} . However, it moves away from this value as the chain length decreases and can be traced back smoothly to an origin at 923 cm^{-1} in propane. This evidence suggests that it is more satisfactory to attribute the 1120 cm^{-1} series to the in-plane methyl rocking modes, R_2 . Such an assignment has already been made for the 923 cm^{-1} band of propane on deuteration evidence (McMurry & Thornton 1951).

The foregoing assignments of the observed series shown in figures 9 X and 9 Y are based on the simplest theoretical predictions; nevertheless, they present an interpretation of the spectra of the crystalline n -paraffins which is straightforward and self-consistent; moreover, this interpretation fits in convincingly with the accepted assignments of the fundamental frequencies of propane (Sheppard & Simpson 1953). It should be noted that an earlier suggestion (Brown *et al.* 1950) that the 1140 and 1120 cm^{-1} series represent the α and β skeletal modes is incorrect. Although consistent with the results for the even-numbered molecules, the new data available, particularly the information derived from infra-red studies of oriented crystals, have shown this earlier assignment to be untenable.

The simple theoretical treatment suggests that in addition to the five series already discussed, three others should originate in the spectrum of propane. Of these one corresponds to the out-of-plane methyl rocking modes R_4 , and is only allowed in the Raman spectra. This series cannot be generally recognized, but in the Raman spectra of liquid n -butane and n -pentane weak lines showing the correct temperature dependence are found (Sheppard & Szasz 1949), which (as shown in the detailed assignments) can be tentatively attributed to the first members. The two remaining series correspond to the β and ψ skeletal vibrations. The weak infra-red bands between the limiting series α at 1060 cm^{-1} and ω at 890 cm^{-1} show little obvious regularity; they are crowded together towards the upper end of the range. However, a few of the intermediate series can be tentatively recognized, in particular the α and β frequencies overlap near 1060 cm^{-1} for large values of n . The irregularities observed in this region may be due in part to coupling with the in-plane methyl rocking modes R_1 and R_2 , to interaction between members of the different series and possibly to coupling with the low frequency skeletal bending modes.

Convincing confirmatory evidence for the assignment of all these frequencies comes from the study of other long-chain molecules which have similar planar zigzag structures

of their paraffin chains in the crystalline state. Thus in the spectra of the straight-chain alcohols, the skeletal modes are enhanced in intensity by the presence of the polar C—O bond. The majority of these vibrations occur between 1075 and 950 cm^{-1} , in a frequency range similar to that observed for the *n*-paraffins (Brown & Sheppard 1950). Furthermore, decamethylene dibromide gives a solid-state spectrum in which the absorption bands assigned to methyl rocking modes in the *n*-paraffins, namely, near 1140, 1120 and 890 cm^{-1} , are missing, whereas skeletal absorption bands of medium strength between 1070 and 980 cm^{-1} persist (Brown & Sheppard, unpublished work). The long-chain *n*-alkyl bromides on the other hand once again show absorption near 1120 and 890 cm^{-1} associated with a single methyl group (Brown & Sheppard, unpublished work).

In conclusion, a few comments on the relative intensities of the infra-red absorption bands are not inappropriate. It has been suggested (Person & Pimentel 1953) that as the chain length increases the strength of the bands due to methyl modes should decrease in relation to those arising from skeletal or CH_2 vibrations. Figure 2 shows that the three infra-red series attributed to methyl rocking modes (at 1140, 1120 and 890 cm^{-1}) are prominent compared to the skeletal frequencies but less intense than the CH_2 rocking frequencies. Their relative intensities do not alter markedly as the chain length varies. However, it should be emphasized that each infra-red active skeletal vibration or CH_2 rocking mode gives rise to a separate absorption band, so that the integrated intensities of all of these should be compared with the methyl rocking band arising from a single vibration. When this is taken into account there appears to be no discrepancy with the theoretical predictions.

(c) *The CH_2 twisting and wagging modes*

The region between 1370 and 1150 cm^{-1} contains a number of weak absorption bands which may be considered as splitting out from the 1336 and 1278 cm^{-1} frequencies in the vibrational spectra of propane. That is to say, they arise from CH_2 wagging and twisting modes. The fact that these absorption bands are weak and overlap considerably in the spectra of the long-chain *n*-paraffins means that the task of separating them into series is much more difficult. This is particularly true for the region 1370 to 1320 cm^{-1} , where water-vapour absorption bands interfere with the experimental study of the spectra. Nevertheless, some progress is possible with the aid of the schematic frequency distributions shown in figures 6*a* and 6*b*. The first point to notice is that the limiting series of each distribution have different selection rules. Thus, the limiting series of the CH_2 wagging modes are either infra-red-active for odd and even values of *n*, or active only in the odd-numbered molecules. On the other hand, the limiting series of CH_2 twisting modes are either infra-red-inactive throughout or active in the even-numbered members. The second point is that the direction of dipole change for the infra-red-active CH_2 twisting modes is always perpendicular to the long axis of the carbon chain, while for both the upper and lower limiting series of the CH_2 wagging mode distribution it is parallel to the long axis for odd values of *n*.

The first step in analyzing the observed frequencies is to select series which originate in the propane spectrum and which are active for all the molecules in either the infra-red or Raman spectra. If the correlations are correct, then each series will define a limit

of one or other of the distributions, and also fix their orientations. One such series is well marked in the infra-red spectra starting at 1336 cm^{-1} in propane and moving to a limit near 1200 cm^{-1} in the longer-chain molecules. The selection of this series therefore fixes the lower limit of the CH_2 wagging modes, and orients the schematic distribution. Another series, which is Raman-active throughout, may be traced from 1278 cm^{-1} in

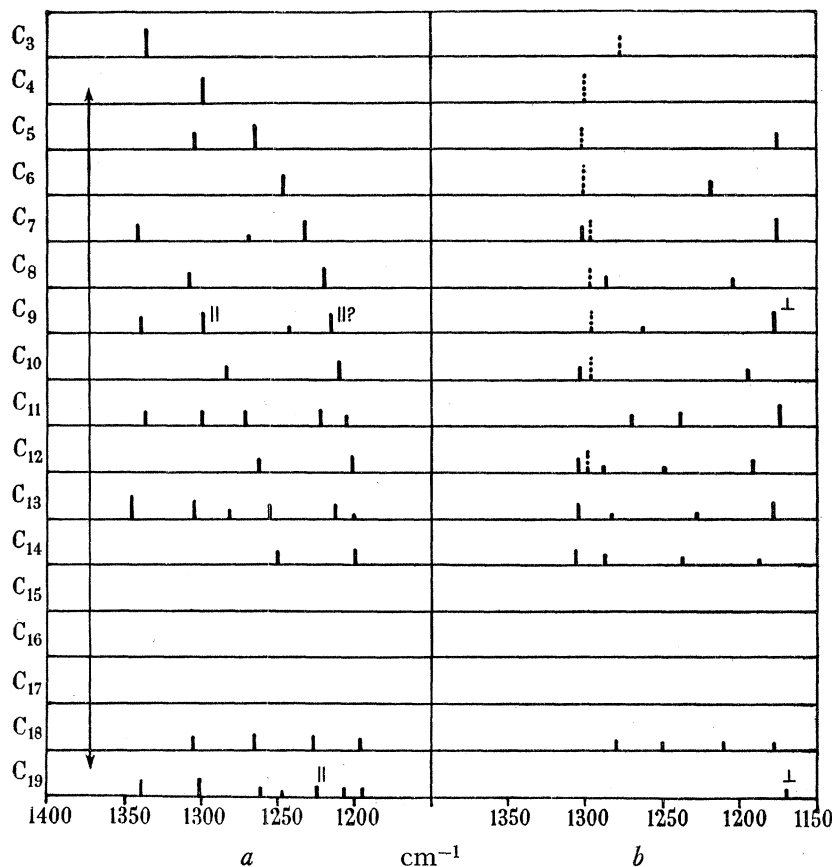


FIGURE 10. Distributions of (a) CH_2 wagging frequencies and (b) CH_2 twisting frequencies observed in the infra-red and Raman spectra of the crystalline n -paraffins. | = infra-red absorption band; \cdot = Raman line; || and \perp dipole moment change parallel and perpendicular to chain length. The arrow indicates the region obscured by methyl group absorption.

propane to a limit of approximately 1300 cm^{-1} in the larger molecules. This has been selected as the upper limit of the distribution of CH_2 twisting modes. Other series have been fitted in, both for the CH_2 wagging and twisting modes, which conform to the selection rules and polarization data for n -nonane and n -nonadecane. The infra-red spectrum of a film of n -octadecane in the region 1150 to 1370 cm^{-1} (Jones, McKay & Sinclair 1952) has been used, and several of the series found for the simpler molecules extrapolated satisfactorily both to this compound and to n -nonadecane. Jones *et al.* (1952) have assigned frequencies in the above region in general terms to CH_2 wagging and twisting modes in a number of substituted n -paraffins. The sets of frequencies selected in the n -paraffins are shown in figures 10a and 10b. It is seen that the CH_2 wagging modes in particular show marked regularities and provide a convincing distribution. A number of the higher frequencies in the distribution of CH_2 wagging modes are obscured by the strong methyl

absorption band near 1380 cm^{-1} ; this has been treated, rather arbitrarily, as an upper limit. The range of CH_2 wagging modes thus extends between 1200 and at least 1375 cm^{-1} in the long-chain n -paraffins. This range is in good agreement with that observed both for the decamethylene and n -alkyl bromides (Brown & Sheppard 1953, unpublished work), where the CH_2 wagging modes give rise to outstandingly strong absorption bands between 1190 and 1380 cm^{-1} .

Unfortunately, the experimental data allow the identification of only a few of the twisting modes. One limit has already been identified for the CH_2 twisting modes, namely at 1300 cm^{-1} . The lower limit has not been observed. According to the selection rules it should have infra-red-active frequencies only in the even-numbered molecules. The next series to this, which has infra-red-active frequencies only in the odd-numbered n -paraffins, has been assigned to a nearly constant frequency near 1175 cm^{-1} . The polarization data for n -nonane and n -nonadecane show that these absorption bands arise from perpendicular vibrations, as expected for CH_2 twisting modes. In general, the CH_2 twisting modes give rise to weaker bands than the wagging modes, a fact also corroborated by observations of the n -alkyl and polymethylene halides (Brown & Sheppard 1953, unpublished work).

It should be noted that the limits chosen earlier in this section rely on the correct identification of the series in the early members of the n -paraffins, and that, if these correlations are not accepted, other schemes are possible. A number of such schemes have been tried, but they all gave patterns which were either irregular or did not conform with the infra-red measurements on oriented crystals. The least certain assignment is that of the second lowest CH_2 twisting series to the 1175 cm^{-1} frequencies. The most plausible alternative interpretation would be to assign this series as the lower limit of the CH_2 wagging modes, with the 1200 cm^{-1} frequencies as the second series. In this case it must be assumed that the possibility of extrapolating the 1200 cm^{-1} series back to propane is fortuitous. A reorientation of the distribution of the CH_2 wagging modes would then allow this interpretation to be in agreement with the selection rules. However, the polarization data rule out this alternative, for the absorption bands near 1175 cm^{-1} arise from perpendicular vibrations, and the parallel absorption bands of n -nonane and n -nonadecane do not fit correctly into this scheme.

It has been found necessary to disregard very weak absorption bands at 1350 cm^{-1} in n -butane and at 1307 and 1293 cm^{-1} in n -hexane in order to obtain a regular scheme (Axford & Rank 1949, 1950). Further infra-red work to check the solid-state spectra of the smaller molecules in this region would probably provide the best test of the validity of the distributions proposed, and might also locate the lower limit of the CH_2 twisting modes.

PROPANE, n -BUTANE AND n -PENTANE

The fact that the series selected for the skeletal, methyl rocking and CH_2 modes fit smoothly into the spectra of the earlier members of the set of n -paraffins allows us to review, and where necessary to amend, the existing assignments for these molecules with confidence. Further, it is possible to extend the detailed interpretation of the solid-state spectra as far as n -pentane for which there has been no previous assignment.

(a) *Propane*

The assignment of the fundamental vibrational frequencies of propane has recently been reviewed (Sheppard & Simpson 1953). It is particularly satisfactory that all the frequencies considered to be correctly assigned at that time are consistent with the present analysis of the longer-chain paraffins. However, as mentioned earlier, an infra-red absorption band which arises from the out-of-plane methyl rocking mode of symmetry B_2 has not been observed in the spectrum of propane. It is probable that this frequency lies considerably above 1000 cm^{-1} and may overlap the 1155 cm^{-1} A_1 fundamental. In view of the abnormal contour of the absorption band at this frequency (Wu & Barker 1941) it would be of interest to reinvestigate this under high resolution.

The assignment of the 1336 cm^{-1} infra-red absorption band of propane has been the subject of considerable discussion (McMurry & Thornton 1950, 1951). It is significant to note that this frequency forms the natural origin of the series of CH_2 wagging modes in the larger molecules, and therefore is principally a CH_2 wagging mode.

(b) *n-Butane*

Several alterations are necessary in the previous assignment of the fundamentals of *trans n-butane* (Brown *et al.* 1950). These consist mainly of the interchange of in-plane methyl rocking and C—C stretching frequencies required by the polarization data for the longer-chain molecules. In addition, the weak absorption band at 1350 cm^{-1} is no longer considered to arise from a CH_2 twisting mode and, for consistency with the spectrum of propane, the B_u CH_2 wagging mode is now placed at 1299 cm^{-1} . The revised assignment is listed below; the earlier numbering of the fundamentals (Brown *et al.* 1950) has been retained:

$$\begin{array}{lllll} \nu_4 = 1455; & \nu_5 = (1455); & \nu_6 = 1370; & \nu_7 = ?; & \nu_8 = 1058; \\ \nu_9 = 835; & \nu_{10} = 1148; & \nu_{11} = 432; & \nu_{14} = (1461); & \nu_{15} = ?; \\ \nu_{16} = 951; & \nu_{17} = 732; & \nu_{18} = ?; & \nu_{19} = ?; & \nu_{22} = (1455); \\ \nu_{23} = 1304; & \nu_{24} = 956; & \nu_{25} = ca. 820; * & \nu_{26} = ?; & \nu_{30} = 1461; \\ \nu_{31} = (1461); & \nu_{32} = 1382; & \nu_{33} = 1299; & \nu_{34} = 984; & \nu_{35} = 965; \\ \nu_{36} = ? & & & & \end{array}$$

* Frequency estimated from CH_2 rocking mode distribution. Frequencies in brackets are assumed values.

(c) *n-Pentane*

A detailed assignment of the fundamental vibrational frequencies of *n-pentane* (C_{2v} form) is given in table 3. The numbering of the fundamentals follows Herzberg's conventions (1945); the C—H stretching and the CH_2 and CH_3 internal deformation modes are assumed to have their usual frequencies (Sheppard & Simpson 1953).

CONCLUSION

The analysis of the vibrational spectra of the *n*-paraffins in the crystalline state presented above is consistent with the selection rules and polarization data for the whole set of molecules, as well as with the band contours and Raman polarization for the smaller members. Although some changes have been made in the earlier assignments of the

even-numbered paraffins, it should be emphasized that these changes have in every case been dictated by the new experimental results. The presence of numerous prominent series of Raman lines and absorption bands in the spectra and the regularity of all these series suggests that each may be assigned principally to one type of vibration, although this may be coupled to some extent with other vibrations of the same symmetry class. The simplified schematic frequency distributions shown in figure 6 have proved most valuable, and have enabled the vibrations appropriate to each of these series to be identified. Some progress has also been achieved in the analysis and assignment of the remaining less regular observed frequencies, but the conclusions are necessarily more tentative and have not been discussed in detail. Only a few weak absorption bands cannot be fitted into the complete scheme; these have all been noted in the previous discussions.

TABLE 3. AN ASSIGNMENT OF THE FUNDAMENTAL VIBRATIONS OF *n*-PENTANE BETWEEN 1370 AND 400 cm^{-1}

description	A_1 (R., p.; i.r.) (cm^{-1})	A_2 (R., dp.) (cm^{-1})	B_1 (R., dp.; i.r.) (cm^{-1})	B_2 (R., dp.; i.r.) (cm^{-1})
CH_2 wagging	$\nu_9 = 1308$	—	$\begin{cases} \nu_{30} = \text{ca. } 1370 \\ \nu_{31} = 1265 \end{cases}$	—
CH_2 twisting	—	$\begin{cases} \nu_{18} = 1303 \\ \nu_{19} = ? \end{cases}$	—	$\nu_{40} = 1176$
CH_3 rocking	$\nu_{10} = 1138$	$\nu_{20} = 900^*$	$\nu_{32} = 1025$	$\nu_{41} = 919$
C—C stretching	$\begin{cases} \nu_{11} = 1067 \\ \nu_{12} = 868 \end{cases}$	—	$\begin{cases} \nu_{33} = 1025 \\ \nu_{34} = 965 \end{cases}$	—
CH_2 rocking	—	$\nu_{21} = \text{ca. } 765^\dagger$	—	$\begin{cases} \nu_{42} = 861 \\ \nu_{43} = 728^\ddagger \end{cases}$
skeletal bending	$\begin{cases} \nu_{13} = 406 \\ \nu_{14} = ? \end{cases}$	—	$\nu_{35} = ?$	—

* Frequency observed in the liquid state.

† Frequency estimated from the CH_2 rocking mode distribution.

‡ The infra-red solid-state spectrum is reported as showing a doublet 721, 728 cm^{-1} (Axford & Rank 1950). Only one member of the doublet is required for a rocking mode; the splitting may arise from vibrational coupling in the crystal.

To summarize: of the CH_2 frequencies, the assignment of the CH_2 bending modes to *ca.* 1460 cm^{-1} has long been accepted. The present work has established the position of the CH_2 rocking vibrations with the lower limiting series at 720 cm^{-1} beyond doubt. The assignment of the CH_2 wagging and twisting modes is less certain. Nevertheless, the first few low-frequency series of the CH_2 wagging modes have probably been correctly identified; the upper limiting CH_2 wagging series is less certainly located at 1375 cm^{-1} . The proposals for the CH_2 twisting series are more tentative but the upper limiting series probably lies near 1300 cm^{-1} . The analysis of the 1150 to 850 cm^{-1} region is incomplete, but each of the more important series has been assigned to its symmetry class combination. Using empirical evidence it has been shown that the three most prominent infra-red series probably correspond mainly to methyl rocking vibrations; and the Raman series near 1060 and 890 cm^{-1} to the limits of the skeletal stretching distribution. The irregular pattern of weak infra-red absorption bands between these frequency limits (which correspond to the C—C stretching frequencies) precludes any detailed analysis of the whole set. The paucity of Raman data throughout the spectra necessarily limits the completeness of the analysis.

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[*Note added in proof*, 30 April 1954]. Primas & Günthard (1953) have very recently published extensive calculations of the vibration frequencies below 1600 cm^{-1} of zigzag polymethylene chains. These detailed results confirm our assumption that the spectra may be divided into regions characteristic of the C—C and the various CH_2 vibrations. The frequency ranges calculated for the different types of vibration are in fair agreement with our analysis of the experimental data for the *n*-paraffins although, as would be expected, the detailed frequencies differ considerably from the observed values. One point of particular interest is that the pattern predicted for the CH_2 rocking modes shows the asymmetrical distribution actually observed.

It has also been brought to our notice that a brief account of an attempt to analyze the available experimental data on the *n*-paraffins has been published (Tschamler 1952, and private communication) based on somewhat similar premises to those used in this paper.

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