THE INFRA-RED AND RAMAN SPECTRA OF HYDROCARBONS.
PART II. PARAFFINS

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IN Part I of this Review,[1] dealing with the acetylenes and the olefins, attention was focused on those features of the spectra which originate from relatively small and rigid parts of, on the whole, much larger molecules. This made the discussion of the spectra a comparatively simple matter and allowed the identification of most of the expected frequencies. To some extent a similar approach is helpful in the interpretation of the spectra of the paraffins, in that many compact groups, such as CH_3, CH_2, $CHMe_2$, and CMe_3, give rise to characteristic frequencies which can be recognised and assigned in the spectra of series of related molecules. However, it is not usually possible to obtain in this way complete interpretations of the spectra of the paraffins, because the vibrations of the different parts of a molecule are so closely coupled as to defy analysis by such a method. This is true, for instance, in the case of the polymethylene chain of the n-paraffins. Further, most of the data available in the infra-red and Raman spectra of the paraffins refer to the liquid or the vapour phase. As will be shown in a later section, under these conditions the substances are usually examined as mixtures of different rotational isomers. This produces other complications, since each isomer of a given paraffin has its own set of characteristic frequencies. It should also be noted that the spectra of even the smallest paraffins, where rotational isomerism is absent (such as propane), are relatively complex, so complete assignments of their frequencies are not available to assist in the interpretation of the spectra of the more complex molecules.

The study and correlation of the spectra of series of related paraffins is clearly of paramount importance and must form the first stage in attempting the assignment of their frequencies. Most of the correlations in the infra-red spectra of paraffins discussed in this Review were noted in the course of a programme of research carried out during the last war on the infra-red spectra of hydrocarbons in aviation fuel at the Universities of Oxford and Cambridge under the direction of Dr. H. W. Thompson and Prof. G. B. B. M. Sutherland. The results have been published in report form [2] and have appeared in a more general review of group frequencies.[3] They were also used in a more detailed discussion of the vibrations of some

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[1] Sheppard and Simpson, *Quart. Reviews*, 1952, **6**, 1.

[2] Fellgett, Harris, Simpson, Sutherland, Thompson, Whiffen, and Willis, Institute of Petroleum, Report XI, 1946.

[3] Thompson, *J.*, 1948, 328.

branched paraffins by Simpson and Sutherland.[4]   D. C. Smith [5] carried out an extensive analysis of the data obtained in Washington, and an article by Barnes and his co-workers [6] lists various paraffin correlations in a general tabulation of group frequencies.   Since the present Review was first written, a paper by McMurry and Thornton [7] has appeared which includes a discussion of the infra-red paraffin correlations between 1500 and 700 cm.$^{-1}$. Their analysis is presented mainly in tabular form and is particularly valuable in that intensities are also listed.   The approach is empirical, with little discussion of the assignment of the various frequencies and none of the analogous Raman data.   Many of the correlations in the Raman spectra of paraffins have already appeared in articles by Stepanov [8, 9] and by Sheppard.[10]   It should also be emphasised that the earlier work of Kohlrausch [11] and Mecke [12] is of considerable importance.

The experimental data on the infra-red spectra used in this Review have as far as possible been taken from curves contributed by the Naval Research Laboratory to the Catalogue of Spectra published by the American Petroleum Institute ; [13] in most cases no observations are available below 450 cm.$^{-1}$.   The Raman data employed are those published in two papers by Fenske and his collaborators.[14, 15]   Together, these cover more than a hundred substances, including observations available on all paraffins up to the dodecanes that have hitherto been investigated.

The Raman data on the paraffins up to 1939 have been reviewed by Hibben,[16] and most of the references up to 1943 as well as tables of frequencies will be found in the most recent book by Kohlrausch ; [17] further references may be obtained from an article by Glockler.[18]   The following papers on the Raman spectra of series of paraffins may be noted : n-paraffins,[19] octanes,[20] hexanes and heptanes ; [21] the work of Bazhulin and his collaborators is also extensive.[22]   The pioneer studies by Lambert and

[4] (a) J. Chem. Phys., 1947, **15**, 153 ; (b) Proc. Roy. Soc., 1949, A, **199**, 169.

[5] D. C. Smith, Report on the infra-red spectra of hydrocarbons, C 3274.   Naval Research Laboratory, Washington, D.C., U.S.A., 1948.

[6] Barnes, Gore, Stafford, and Williams, Analyt. Chem., 1948, **20**, 402.

[7] Ibid., 1952, **24**, 318.   [8] J. Phys. Chem. U.R.S.S., 1946, **20**, 917.

[9] Acta Physicochim. U.R.S.S., 1947, **22**, 238.

[10] J. Chem. Phys., 1948, **16**, 690.

[11] Kohlrausch, " Ramanspektren ", Hand- und Jahrbuch der Chemischen Physik, Becker und Erler, Leipzig, 1943.   [12] Z. phys. Chem., 1937, B, **36**, 347.

[13] American Petroleum Institute, Research Project 44.   Catalogue of infra-red absorption spectral data.   Carnegie Institute of Technology, Pittsburgh, Pa., U.S.A.

[14] Fenske, Braun, Wiegand, Quiggle, McCormick, and Rank, Analyt. Chem., 1947, **19**, 700.   [15] Braun, Spooner, and Fenske, ibid., 1950, **22**, 1074.

[16] " The Raman Effect and its Chemical Applications ", Reinhold, New York, 1939.

[17] Op. cit., 1943, p. 209.   [18] Rev. Mod. Phys., 1943, **15**, 111.

[19] Herz, Kahovec, and Wagner, Monatsh., 1946, **76**, 100.

[20] von Grosse, Rosenbaum, and Jacobson, Analyt. Chem., 1940, **12**, 191.

[21] Cleveland and Porcelli, J. Chem. Phys., 1950, **18**, 1459.

[22] (a) Bazhulin, Plate, Solovova, and Kazanskiĭ, Bull. Acad. Sci. U.R.S.S. (Sér. Chim.), 1941, 13 ; (b) Bazhulin, Bokshteĭn, Liberman, Lukina, Margolis, Solovova, and Kazanskiĭ, ibid., 1943, 198 ; (c) Bazhulin, Ukholin, Bulanova, Kopernina, Plate, and Kazanskiĭ, ibid., 1949, 481.

Lecomte on the infra-red spectra of paraffins should be mentioned,[23, 24] as well as the wartime reports published under the auspices of the British Institute of Petroleum [2, 25, 26] and the investigation of the octanes in the liquid and the vapour state by Oetjen and Randall.[27] Other spectra are to be found in the collection of data published by the American Petroleum Institute,[13] and further references will be given in their appropriate contexts.

1. Introduction

In considering the spectra of the paraffins, it is convenient to divide the vibrations into two main types, those involving mainly the hydrogen atoms and those concerned with the nuclear framework, although in a few cases such a distinction is too drastic. From the earlier discussion [1] it is clear that the skeletal frequencies will differ considerably from one molecule to another, whereas some at least of the hydrogen vibrations may be expected to remain nearly invariant. It is necessary in the first place to describe briefly the various types of hydrogen vibrations associated with the CH_3, CH_2, and CH groups. These fall into two categories : (i) internal vibrations are those that would appear even if the group in question were isolated (for example, the carbon–hydrogen stretching modes) ; (ii) external vibrations (such as many of the carbon–hydrogen deformation modes) are only present if there is some mechanical interaction between the group itself and the rest of the molecule. As might be expected, the former give rise to very constant frequencies, whereas those corresponding to the external vibrations are much more dependent on the structure of the molecule as a whole. These external vibrations may couple extensively with other carbon–hydrogen deformation modes and with the skeletal vibrations.

(a) **Carbon–Hydrogen Stretching Vibrations.**—The carbon–hydrogen stretching vibrations usually appear in the range 3000—2700 cm.$^{-1}$, and are generally intense in both Raman and infra-red spectra. It is possible, as shown by Fox and Martin,[28, 29] to use the infra-red frequencies to distinguish between the different modes of the CH_3, CH_2, and CH groups ; all are internal vibrations. These assignments are listed below :

CH_3	Symmetrical stretching vibration :	2872 cm.$^{-1}$
	Asymmetrical doubly degenerate stretching vibration :	2962 cm.$^{-1}$
CH_2	Symmetrical stretching vibration :	2853 cm.$^{-1}$
	Asymmetrical stretching vibration :	2926 cm.$^{-1}$
CH	Stretching vibration (semi-schematic) :	2890 cm.$^{-1}$

[23] (a) Andant, Lambert, and Lecomte, *Compt. rend.*, 1934, **198**, 1316 ; (b) Lambert and Lecomte, *ibid.*, 1938, **206**, 1174.

[24] Lambert and Lecomte, *Ann. Physique*, 1938, **10**, 503.

[25] Sutherland and Thompson, Petroleum Board, Enemy Oils and Fuels Committee Report, 1943.

[26] *Idem*, Institute of Petroleum, Report X, 1945.

[27] *Rev. Mod. Phys.*, 1944, **16**, 165, and (with Anderson) 260.

[28] *Proc. Roy. Soc.*, 1938, *A*, **167**, 257.

[29] *Ibid.*, 1940, *A*, **175**, 208.

The above are mean values and are to some extent dependent on the number and environment of each type of group present (see also refs. 30—32). Other weaker frequencies are found near 2934 cm.$^{-1}$ (infra-red), 2912 cm.$^{-1}$ (Raman and infra-red), and in the range 2800—2700 cm.$^{-1}$ (Raman). These are interpreted as overtone or combination frequencies of the internal deformation modes of the CH_3 and CH_2 groups, and appear with enhanced intensity through interaction with the neighbouring carbon–hydrogen stretching fundamentals of the same symmetry classes.

(*b*) **Carbon–Hydrogen Deformation Vibrations.**—The deformation modes involving changes in the angles associated with carbon–hydrogen linkages occur in the range 1500—600 cm.$^{-1}$.

(1) *The* CH_3 *Group.*—An isolated CH_3 group attached to a heavy frame-work has three internal deformation vibrations (one symmetrical and two approximately doubly degenerate asymmetrical modes) which are observable as nearly constant frequencies. The two doubly degenerate vibrations appear in the range 1470—1440 cm.$^{-1}$ and are intense in both Raman and infra-red spectra. The symmetrical deformation mode occurs as an intense infra-red band near 1380 cm.$^{-1}$, but the corresponding Raman line is usually missing. As has already been noted,[1] the frequency of this mode shifts to somewhat higher values if the CH_3 group is directly attached to a double or triple bond, and its intensity in the Raman spectrum is then enhanced. In the paraffins, splitting of some of the infra-red bands occurs when a plurality of CH_3 groups is attached to a single carbon atom. The regularities which have been noted are summarised below, and are quoted as average values (in cm.$^{-1}$) : [5, 7]

CH₃—C⟨	isolated :	1380
CH₃, CH₃ \ C / with H	*iso*propyl :	1385, 1370
CH₃, CH₃ \ C / with C₂H₅	3 : 3-dimethyl :	1384, 1367
CH₃, CH₃ \ C / with CH₃	*tert.*-butyl :	1397, 1370

The splitting patterns in more complex paraffins with several of these groups have not yet been fully worked out. Each CH_3 group has also

[30] Sushinskiĭ, *Bull. Acad. Sci. U.R.S.S.* (Sér. Phys.), 1947, **11**, 341.
[31] Saier and Coggeshall, *Analyt. Chem.*, 1948, **20**, 812.
[32] Hastings, Watson, Williams, and Anderson, *ibid.*, 1952, **24**, 612.

three external vibrations, *viz.*, two rocking (or wagging) modes and a torsional motion of the group about the CH_3–C linkage. The frequencies of the CH_3 rocking modes vary considerably in different classes of paraffins and may be coupled strongly with the skeletal vibrations. They appear to be confined to the range 1250—800 cm.$^{-1}$,[33] and may give rise to both prominent Raman lines and intense infra-red bands. The CH_3 torsional mode corresponds in most cases to some sort of restricted rotation, and so may be expected in the low-frequency region < 300 cm.$^{-1}$. This mode seems to be weak in both Raman and infra-red spectra and usually cannot be located directly.

(2) *The* CH_2 *Group.*—An isolated CH_2 group attached to a heavy framework has four deformation modes as shown in Fig. 1.[10, 34] The bending vibration is internal in type and occurs in the narrow range 1470—1440 cm.$^{-1}$ (*i.e.*, it coincides with the asymmetrical CH_3 deformation vibration) ; it is strong in both Raman and infra-red spectra.

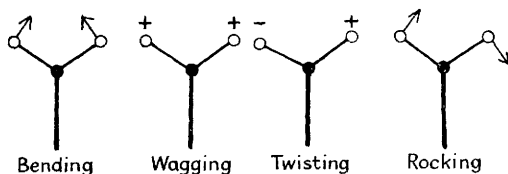Bending   Wagging   Twisting   Rocking

FIG. 1

Approximate diagrams of the deformation modes of an isolated CH_2 *group.*

The three remaining CH_2 modes are all external and so are more variable in frequency. Investigations of the spectra of the long-chain paraffins [35] have suggested that the CH_2 wagging and twisting frequencies are to be found in the range 1350—1150 cm.$^{-1}$; this range is also indicated by calculations for a variety of paraffins.[9, 34, 36-41] Some of these modes give rise to prominent Raman lines near 1300 cm.$^{-1}$; in general the infra-red absorption bands are only of medium or weak intensity. There has been some discussion about the exact interpretation of the various series,[10, 33-35] but no general agreement has been achieved. Further, investigations of the spectra of propane and its deuterated derivatives by McMurry and Thornton [42, 43] (see later) have shown that for these molecules the CH_2 wagging vibration is coupled with other modes of the same symmetry class. It might therefore be thought unrealistic to attempt to assign frequencies to the various external modes of CH_2 groups. However, in the opinion

[33] Torkington, *J. Chem. Phys.*, 1950, **18,** 768.
[34] Rasmussen, *ibid.*, 1948, **16,** 712.
[35] Brown, Sheppard, and Simpson, *Discuss. Faraday Soc.*, 1950, **9,** 261.
[36] Eliashevitch and Stepanov, *Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **32,** 481.
[37] Stepanov, *Bull. Acad. Sci. U.R.S.S.* (Sér. Phys.), 1947, **11,** 357.
[38] Kellner, *Nature*, 1949, **163,** 877.
[39] *Idem, Proc. Phys. Soc.*, 1951, *A*, **64,** 521.
[40] Simanouti, *J. Chem. Phys.*, 1949, **17,** 734.   [41] Barrow, *ibid.*, 1951, **19,** 345.
[42] *Ibid.*, 1950, **18,** 1515.   [43] *Ibid.*, 1951, **19,** 1014.

of the Reviewers such a procedure is still useful as a first approximation, since it is not impossible that the effects of interaction are less drastic in larger molecules.   Such a classification has in fact been used by McMurry and Thornton in their recent analysis.[7]

The CH_2 rocking modes occur in the range 1100—700 cm.$^{-1}$, as suggested by theoretical treatments [37] and investigations of the long-chain paraffins.[35]   These vibrations cannot be identified in the Raman spectra, but give rise to intense infra-red absorption bands, particularly in the region 770—720 cm.$^{-1}$.[44, 45]

(3) *The* CH *Group.*—The two hydrogen deformation modes of a lone CH group appear in symmetrical surroundings as a doubly degenerate pair, as in *isobutane* [46] near 1335 cm.$^{-1}$.   In other circumstances splitting may occur, but one component can usually be recognised as a Raman line between 1360 and 1330 cm.$^{-1}$; [10] owing to the proximity of the intense absorption due to the CH_3 deformation vibration, the corresponding infrared frequencies cannot usually be identified.

(*c*) **Skeletal Vibrations.**—The range of skeletal stretching vibrations in branched paraffins is probably 1300—650 cm.$^{-1}$,[1,4, 47] though it is more restricted for the *n*-paraffins.   It should, however, be noted that some authors [34, 48] still favour an upper limit near 1100 cm.$^{-1}$ as suggested originally by Kohlrausch and Köppl.[49]   The skeletal deformation modes and the torsional vibrations of the nuclear framework occur together below 600 cm.$^{-1}$.

From the above summary it may be concluded that the carbon–hydrogen stretching vibrations and the internal deformation modes of the CH_3 and CH_2 groups are relatively insensitive to changes in structure.   In the following discussion attention will be concentrated on the remaining types of vibration which occur at frequencies below 1350 cm.$^{-1}$, the torsional modes, about which too little is known, being omitted.

2. Rotational Isomerism in the Paraffins

As already noted, the interpretation of the spectra of many paraffins is complicated by the fact that such substances exist as mixtures of two or more rotational isomers in the liquid or vapour state.   Thus, to consider a very simple example, *n*-butane (which may be regarded as symmetrical dimethylethane) can occur in two distinct forms shown in Fig. 2.   The *trans*-form corresponds to the planar zig-zag configuration ; the *gauche* forms (spectroscopically indistinguishable) are derived from this by rotation through approximately 120° of one half of the molecule with respect to the other about the central carbon–carbon linkage.   Although restricted rotation of the CH_3 group can also occur about the terminal C–C linkages,

[44] Sheppard and Sutherland, *Nature*, 1947, **159**, 739.
[45] Vallance Jones and Sutherland, *ibid.*, **160**, 567.
[46] Pitzer and Kilpatrick, *Chem. Reviews*, 1946, **39**, 435.
[47] Ahonen, *J. Chem. Phys.*, 1946, **14**, 625.
[48] Rank, Saksena, and Shull, *Discuss. Faraday Soc.*, 1950, **9**, 187.
[49] *Z. phys. Chem.*, 1934, *B*, **26**, 209.

the high symmetry of this group causes the resulting configurations to be indistinguishable. The existence of such mixtures of rotational isomers in paraffins was first demonstrated spectroscopically by Kohlrausch and Köppl,[49] who investigated Raman spectra in the liquid state and showed that more lines than predicted were present. Since then, considerable evidence, both spectroscopic and thermodynamic, has accumulated to confirm these observations. Of major importance is the fact that the spectroscopic observations indicate that each rotational isomer of a given molecule has its own set of vibrational frequencies.
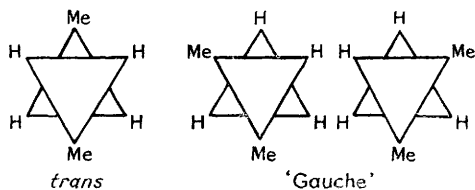

Fig. 2

The configurations of the rotational isomers of n-*butane.*

The number of possible rotational isomers of a particular paraffin may be readily deduced. Systematic discussions have been given by Pitzer,[50] and by Simanouti and Mizushima [51] who have invented a convenient notation for the description of the different forms.

Since all the rotational isomers of a given molecule may theoretically be present in the liquid substance, it is obviously of considerable importance to know their relative stability, since this will determine the proportions of the different forms in the mixture. A direct method of tackling this problem is based on spectroscopic measurements. The spectra (Raman or infra-red) of the crystalline solid and the liquid at different temperatures are compared. The solid material shows the frequencies of one form (often but not always the most stable isomer) ; the extra frequencies in the liquid arise from isomers of different energy content. In favourable circumstances the liquid may contain only one species other than the most stable isomer ; by comparison of the variation with temperature of the intensities of corresponding frequencies of the two forms, the energy difference involved may be determined directly. This method in the hands of Rank and his collaborators has proved very successful for some of the n-paraffins [52-55] (see also ref. 56). Alternatively, it is possible to calculate energy differences from thermodynamic data.[50]

At present, data on the solid-state spectra are available for a rather

[50] *J. Chem. Phys.*, 1940, **8**, 711.
[51] *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1943, **40**, 467.
[52] Szasz, Sheppard, and Rank, *J. Chem. Phys.*, 1948, **16**, 704.
[53] Rank, Sheppard, and Szasz, *ibid.*, 1949, **17**, 83.
[54] Sheppard and Szasz, *ibid.*, p. 86.
[55] (a) Axford and Rank, *ibid.*, p. 430 ; (b) *ibid.*, 1950, **18**, 51.
[56] Mizushima and Okazaki, *J. Amer. Chem. Soc.*, 1949, **71**, 3411.

limited range of molecules.   The isomer present in the crystalline n-paraffins
has the planar zig-zag configuration, as is also known from the X-ray investi-
gation of the solids ; [57] the stability of the other isomers, which are formed
by one or more rotations about the different carbon–carbon bonds away
from the planar configuration, decreases with the number of these rotations.[50]
Thus the *gauche* form of n-butane has a greater energy content than the
trans-isomer.   A few branched paraffins have also been studied, but the
interpretation of the data is still under discussion.[55b, 58–61]

Since each rotational isomer of a particular molecule has its own distinct
set of vibrational frequencies, it might be thought that in order to discuss
the characteristic group frequencies of a series of related paraffins, it would
be essential first of all to distinguish between the frequencies arising from
each type of isomer and then to compare those of each type in turn.   Such
a procedure might be feasible in principle but would in practice be extremely
laborious and time-consuming.   Fortunately, it is found empirically that
characteristic group frequencies may be recognised in various classes of
paraffin even when these substances are investigated in the liquid state.
There are a number of reasons for this ; it might so happen that one or
more vibrations of the different isomers of a given type of molecule all
appear near the same frequency, as for instance for some of the CH_2 wagging
and CH_2 rocking modes of the n-paraffins.   Alternatively, if a symmetrical
unit such as the *tert.*-butyl group forms the common feature of a series of
paraffins, the frequencies of the vibrations characteristic of this group may
remain relatively unaffected by what is happening in the rest of the molecule,
so that they too are nearly the same for different isomers.   Even in less
favourable circumstances it is still possible to pick out frequencies charac-
teristic of particular structures.   Further details of the examples already
discussed and other cases of rotational isomerism will be found in the
appropriate sections.

3. The n-Paraffins

In the discussion of the frequencies characteristic of paraffins, the spectra
of the n-paraffins form an appropriate starting point for a number of reasons.
In the first place most paraffins possess within their structures a carbon–
carbon chain of varying length, so it is necessary to know the characteristic
frequencies of such an arrangement, in order that the frequencies of other
groupings may be identified.   Further, the data on the spectra of the
n-paraffins have provided most of the information on the CH_3 and CH_2
hydrogen vibrations discussed above, and it is desirable at an early stage
to show how this has been derived.   Moreover, as mentioned previously,
only in the case of the n-paraffins are extensive data available for a series

[57] Müller, *Proc. Roy. Soc.*, 1928, *A*, **120**, 437.
[58] Mizushima, Morino, and Takeda, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1941,
38, 437.
[59] Avery and Ellis, *J. Chem. Phys.*, 1942, **10**, 10.
[60] Szasz and Sheppard, *ibid.*, 1949, **17**, 93.
[61] Brown and Sheppard, *ibid.*, 1951, **19**, 976.

of rotational isomers of a particular type (in this case with the *trans*-planar zig-zag configuration), and the data on the liquid substances are also much more complete than those for any other class of paraffin. Comparison of the spectra of the *trans*-isomers with those of mixtures of the isomers as found in the liquids is very instructive (Fig. 3). Finally, much attention
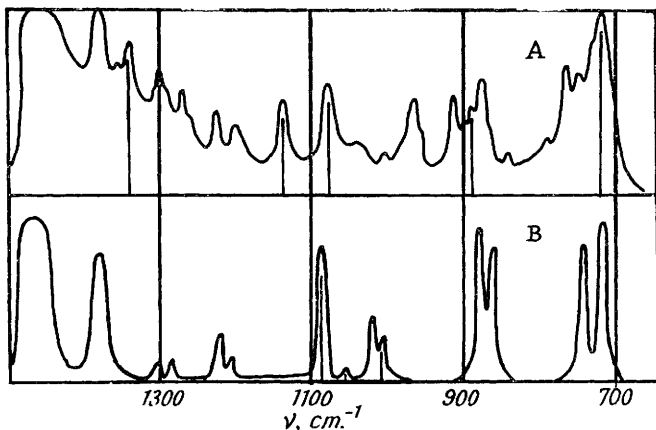

FIG. 3

Infra-red spectra between 1500 *and* 700 *cm.$^{-1}$ of n-octane in the liquid* (A) *and the crystalline solid* (B) *phase.[87]* (*Vertical lines indicate characteristic absorption frequencies, listed below.*)

has been given to the theoretical treatment of the skeletal vibrations of chains of repeating units of which the *trans*-isomers of the *n*-paraffins form examples. Comparison of the theoretical expectations with the experimental results for these molecules gives some indication as to how far such treatments are likely to be helpful guides in the interpretation of spectra.

(*a*) **Methane and Ethane.**—The smallest paraffin, methane, is in a class by itself since it has only one carbon atom and therefore no skeletal vibrations. The frequencies of the four hydrogen modes are well-known ; those listed by Herzberg [62] have been confirmed by more recent work.[63, 64] Extensive investigations and assignments have also been made for the various deuterated derivatives.[62]

The structure of ethane has been the subject of some discussion ; free rotation about the carbon–carbon linkage is definitely absent and on the whole the staggered configuration with a centre of symmetry is preferred.[65, 66] The frequencies as given by Herzberg [65] have been slightly revised by the recent work of L. G. Smith.[66] The CH stretching modes and the internal CH_3 deformation vibrations give frequencies corresponding to those listed on pp. 21, 22. The single skeletal mode appears as a polarised Raman line

[62] " Infra-red and Raman Spectra of Polyatomic Molecules ", Van Nostrand, New York, 1945, p. 306.
[63] Holden, Taylor, and Johnston, *J. Chem. Phys.*, 1949, **17**, 1356.
[64] Rank, Shull, and Axford, *ibid.*, 1950, **18**, 116.
[65] *Op. cit.*, 1945, p. 342.　　　　　　　[66] *J. Chem. Phys.*, 1949, **17**, 139.

at 993 cm.$^{-1}$. The two doubly degenerate CH_3 rocking vibrations appear at 1190 cm.$^{-1}$ (infra-red active) and 822 cm.$^{-1}$ (Raman active, depolarised). The frequency of the torsional mode has been located at 290 cm.$^{-1}$; this is in good agreement with the thermodynamic data. The molecule C_2D_6 has also been investigated; references, and the generally accepted assignments of the frequencies, may be found in Herzberg's book.[65]

(b) **Propane.**—Although propane and several of its deuterated derivatives have been extensively studied,[17, 25, 42, 43, 67-70] the assignment of its frequencies below 1350 cm.$^{-1}$ has proved unexpectedly troublesome.[34, 36, 42, 43, 67-72] The main reason for this difficulty is that, although it is formally possible to draw up a scheme classifying the vibrations in this region as CH_3 torsion, CH_3 rocking, CH_2 deformation, and skeletal modes, yet in this molecule (because of the small number of atoms) vibrations of the same symmetry type become more or less mixed so that such clear-cut distinctions become unrealistic.[42, 43]

For the present purpose it is not necessary to discuss in detail the eight CH stretching modes and the six internal deformation vibrations of the CH_3 groups. These occur in the expected frequency regions as set out on pp. 21, 22. With regard to the remaining vibrations, the following seems to be the most plausible assignment on the data available (ν in cm.$^{-1}$). It should be emphasised, however, that more experimental work is necessary before it can be considered established. In particular, the polarisations of the Raman lines of propane itself are required, as well as further investigations on the deuterated derivatives.

B_1 C–C stretching (asymmetrical): 1053
A_1 C–C stretching (symmetrical):   870

A_1 CH_3 rocking (in-plane, symmetrical):   1155
B_1 CH_3 rocking (in-plane, asymmetrical):   923
B_2 CH_3 rocking (out-of-plane, symmetrical):
A_2 CH_3 rocking (out-of-plane, asymmetrical):   940?

A_1	CH_2 bending: 1460	A_2	CH_2 twisting: 1278
B_1	CH_2 wagging: 1336	B_2	CH_2 rocking: 748

A_1 C–C–C deformation: 372

The above assignment is essentially that of Pitzer,[72] as modified by Rasmussen,[34] and is based on the earlier infra-red and Raman studies of the molecule.[17, 67] The two CH_3 torsional modes have been put at 283 and 202 cm.$^{-1}$ by Pitzer,[72] using indirect methods. More recent investigations have not modified this interpretation, though some difficulties remain. The infra-red band corresponding to the A_1 CH_3 rocking mode

[67] Wu and Barker, *J. Chem. Phys.*, 1941, **9**, 487.
[68] A.P.I. Infra-red Spectrograms Nos. 60, 99, 529, 791, 792, 793, 1141.
[69] McMurry, Thornton, and Condon, *J. Chem. Phys.*, 1949, **17**, 918.
[70] Friedman and Turkevitch, *ibid.*, p. 1012.
[71] Wagner, *Z. phys. Chem.*, 1939—1940, *B*, **45**, 69.
[72] Pitzer, *J. Chem. Phys.*, 1944, **12**, 310.

has a somewhat anomalous contour under low resolution, the reality of the weak Raman line corresponding to the A_2 CH_3 rocking mode needs confirmation, and the position of the B_2 CH_3 rocking mode has yet to be established.

Infra-red data are available for a number of deuterated derivatives of propane. The results for the unsymmetrical molecules are not easy to interpret.[69, 70] From the investigations of the molecules $CH_3 \cdot CD_2 \cdot CH_3$,[42] $CD_3 \cdot CH_2 \cdot CD_3$, and C_3D_8,[43] it has been established that the external carbon–hydrogen deformation vibrations and the skeletal modes of the same symmetry classes interact significantly, so that in propane the A_1 frequencies at 1155 and 870 cm.$^{-1}$ and the B_1 frequencies at 1336, 1053, and 923 cm.$^{-1}$ are respectively coupled together. Although the Reviewers agree with the conclusion that it is not strictly correct to attribute a given frequency solely to one particular type of group vibration, yet they feel that such a classification is valuable as a first approximation, even for propane. It should also be noted that for the undeuterated molecule the separation of some of the interacting frequencies of the same symmetry class is quite large. Further, it appears not impossible that owing to the large shifts in the carbon–hydrogen deformation frequencies that occur on deuteration, the degree of coupling of vibrations of the same symmetry type may alter significantly and is possibly more important, the more deuterated the molecule.[43]

(c) **The *trans*-Isomers of the *n*-Paraffins.**—As has already been noted. in the crystalline solids the *n*-paraffins C_nH_{2n+2} assume a planar zigzag *trans*-configuration. This implies that molecules with an even number of carbon atoms have a centre of symmetry so that vibrations are allowed in either Raman or infra-red spectra ; on the other hand, many of the vibrations in molecules with an odd number of carbon atoms may appear in both types of spectra. These differing selection rules have proved most valuable in assigning the various series of frequencies that are observed.

Further guidance for this purpose is provided by the theoretical discussions (of varying degrees of complexity) of the skeletal vibrations of a regular chain of repeating units, such as that represented by the *trans*-isomers of the *n*-paraffins.[12, 33, 35–41, 47, 49, 50, 73–86] The results of these investigations indicate that the $(n - 1)$ skeletal stretching modes of a *n*-paraffin C_nH_{2n+2} are confined to a definite range of frequencies depending mainly on the magnitude of the carbon–carbon stretching force constant.

[73] Bartholomé and Teller, *Z. phys. Chem.*, 1932, *B*, **19**, 366.
[74] Bauermeister and Weizel, *Physikal. Z.*, 1936, **37**, 169.
[75] Barriol, *J. Phys. Radium*, 1939, **10**, 215.
[76] Barriol and Chappelle, *ibid.*, 1947, **8**, 8.   [77] Parodi, *ibid.*, 1941, **2**, 58.
[78] Stepanov, *J. Phys. Chem. U.R.S.S.*, 1940, **14**, 474.
[79] Eliashevitsch and Stepanov, *ibid.*, 1943, **17**, 145.
[80] Kellner, *Trans. Faraday Soc.*, 1945, **41**, 217.
[81] Kassel, *J. Chem. Phys.*, 1935, **3**, 326.   [82] Kirkwood, *ibid.*, 1939, **7**, 506.
[83] Whitcomb, Nielsen, and Thomas, *ibid.*, 1940, **8**, 143.
[84] Mizushima and Simanouti, *J. Amer. Chem. Soc.*, 1949, **71**, 1320.
[85] Simanouti and Mizushima, *J. Chem. Phys.*, 1949, **17**, 1102.
[86] Gates, *ibid.*, p. 393.

The widest possible range may be put as 1200—700 cm.$^{-1}$. Further, as the value of n increases, the highest and lowest frequencies approach definite limiting values ; the lower limit, corresponding to the most symmetrical modes, should appear as highly polarised Raman lines, whatever the value of n. The $(2n - 5)$ skeletal deformation modes are probably restricted to the region below 500 cm.$^{-1}$. The most symmetrical of these are expected to give rise to prominent polarised Raman lines, which do not, however, correspond to the upper limit.

Each *trans-n-*paraffin has two pairs of CH_3 rocking vibrations corresponding to in-plane and out-of-plane motions. The data on ethane and propane (p. 28) suggest that their frequencies should lie between 1190 and 820 cm.$^{-1}$, *i.e.*, they fall in the same frequency range as the skeletal stretching modes. Interaction between the CH_3 rocking modes and the skeletal stretching vibrations of the same symmetry type may therefore be expected.

It should be emphasised that the value of these theoretical treatments lies in the guidance they have provided in the interpretation of the spectra. The simple methods do not give good agreement between the calculated and the observed frequencies. More ambitious discussions can overcome this difficulty, but the effort involved is considerable. Complete treatments of both skeletal and hydrogen vibrations, such as those given by Stepanov for n-butane and n-pentane,[9, 36] could in principle be carried out for higher members of the series, but it is doubtful whether such laborious calculations would add a proportionate amount to the understanding of the spectra.

Experimental data for the *trans*-isomers of the n-paraffins are available for all molecules up to n-decane and for some higher members of the series. The Raman spectra were obtained by Mizushima and his co-workers.[84, 85] Raman and infra-red spectra have been published for the lower members by Rank and his collaborators,[52-55] and further work on the infra-red spectra has been carried out in Cambridge.[35, 87] A fairly complete assignment of the frequencies of *trans-n-*butane has been given [35] and sufficient data are also available to permit adequate discussion of the *gauche* isomer.

Table 1 gives the characteristic frequencies that can be picked out in the spectra of the n-paraffins in the solid state ; infra-red data are not available below 700 cm.$^{-1}$. The series of prominent Raman lines near 1300 cm.$^{-1}$ (col. 3), which have rather weak infra-red counterparts, corresponds to CH_2 wagging or twisting modes as already indicated in the introduction. Molecules with an even number of carbon atoms should, on account of their centre of symmetry, give rise to frequencies that appear only in the Raman or the infra-red spectra. Since the series near 1300 cm.$^{-1}$ shows up consistently in both types of spectra, it must correspond to at least two modes with different selection rules but coincident frequencies. Four series (cols. 4—7) occur in the region 1200—800 cm.$^{-1}$ appropriate to the skeletal stretching and CH_3 rocking frequencies. Like the 1300 cm.$^{-1}$ series, that near 1060 cm.$^{-1}$ (col. 6) must correspond to at least two modes of vibration, for it is observed in both types of spectra. Specific assign-

[87] Brown and Sheppard, unpublished data.

TABLE 1.* Characteristic frequencies (in cm.⁻¹) of the n-paraffins in the crystalline state

Paraffin		CH_2, w/t	ν_{C-C} or CH_3 rocking			ν_{C-C}	CH_2, r	δ_{C-C}	Ref.
n-Butane .	IR	1350	f	965	984	f	732	f	55a
	R	1300	1151	f	1059	837	—	425	84
n Pentane	IR	1308	1138	1025	1065⎱ 1025⎰	868	728	NI	55b
	R	1303	1145	1031	1069⎱ 1031⎰	869	—	406	84
n-Hexane .	IR	1307	f	1057	1066	f	726	f	55b
	R	1300	1143	f	1064	898	—	373	84
n-Heptane	IR	1305	1140	1075	[1057]	910	723	NI	87
	R	1296	1139	—	[1056]	905	—	311	84
n-Octane .	IR	1303	f	1088	1058	f	722	f	35
	R	1297	1138	f	1062	899	—	283	84
n-Nonane .	IR	1298	1138	1094	[1063]	889	721	NI	35
	R	1297	1136	—	[1060]	888	—	249	84
n-Decane .	IR	1303	f	1103	1062	f	720	f	35
	R	1295	1136	f	1060	886	—	231	84
n-Undecane	IR	1299	1137	1106	[1064]	889	720	NI	87
	R	←————————— No observations —————————→							—
n-Dodecane	IR	1303	f	1112	1062	f	722	f	35
	R	1297	1136 ·	f	1061	892	—	194	84
n-Tridecane	IR	1304	1138	1110	[1064]	893	723	NI	87
	R	←————————— No observations —————————→							—
n-Tetra-decane	IR	1305	f	1114	1060	f	722	f	35
	R	←————————— No observations —————————→							—
n-Hexa-decane	IR	←————————— No observations —————————→							—
	R	1295	1135	f	1058	888	—	150	84
n-Nona-decane	IR	1300	1134	1121	[1056]	890	720	NI	87
	R	←————————— No observations —————————→							—
Infra-red intensity		w	m	st	w	m	st	NI	
Raman intensity		st	st	v.w	m	st	abs	st	
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)

[ ] indicates two modes with coincident frequencies

ments for each of these series have been suggested,[35] but only in the case of the highly polarised Raman lines near 890 cm.$^{-1}$ (col. 7) is there general agreement—they correspond to the lower limiting skeletal stretching modes.[10, 35, 84, 85] Prominent infra-red absorption bands which have no observable Raman counterparts are found in the region 1100—700 cm.$^{-1}$; these correspond to the CH_2 rocking modes. All molecules for $n \geqslant 5$ show the intense bands near 720 cm.$^{-1}$ (col. 8) which are characteristic of this type of vibration; these can almost certainly be assigned to the lower limiting vibrations. In addition, bands which spread to higher frequencies (up to 1050 cm.$^{-1}$) split off as the chain length increases; [35] they seem to be approaching an upper limit, as is also suggested by the theoretical treatments.[41] The series of polarised Raman lines below 500 cm.$^{-1}$ (col. 9) corresponds to the most symmetrical skeletal deformation vibrations.[10, 35, 84, 85]

Polythene must be mentioned here, since it represents an infinite paraffin chain with the [—$CH_2 \cdot CH_2$—] repeating unit. For detailed discussions reference must be made to the original papers; [35, 38-41, 45, 85, 88, 89] it is sufficient to note that the assignments of the polythene frequencies can be correlated in a satisfactory way with those given above for the *trans*-isomers of the *n*-paraffins.

(*d*) **Spectra of the *n*-Paraffins in the Liquid State.**—Experimental data on the Raman and infra-red spectra for the *n*-paraffins in the liquid state are available for all molecules up to and including *n*-tetradecane and for some higher members. The prominent regularities already noted in the spectra of the *trans*-*n*-paraffins are also apparent in the spectra of the liquids, which consist of mixtures of rotational isomers. Some modifications in intensity and activity are observed because in many cases the non-planar isomers may have identical frequencies but different selection rules, as, *e.g.*, in the 1140 cm.$^{-1}$ series. Other series may be recognised which must be due only to non-planar isomers.[49] Since all these are of some practical importance for the identification of unbranched chains they are given in Table 2, together with brief comments on their behaviour. Most of these series have effectively constant frequencies. Others, in which progressive shifts are observed, have been noted among the weaker bands in the range 1320—1220 cm.$^{-1}$; these must correspond to additional CH_2 wagging and twisting modes.[7] In the spectra of the liquids, the region 800—700 cm.$^{-1}$ is somewhat complex. The intense band at 720 cm.$^{-1}$ is accompanied by subsidiary bands at higher frequencies, which can also be arranged in shifting sequences. It may be noted in this connection that paraffins with an unbranched chain of four carbon atoms show an intense band near 740 cm.$^{-1}$ (compare *n*-butane, 747 and 731 cm.$^{-1}$), and those with a chain of three carbon atoms, *i.e.*, an ethyl group, one usually near 770 cm.$^{-1}$; [2] these are to be attributed to CH_2 rocking modes of the shorter chains (see also ref. 23*b*).

From the above discussion it may be concluded that the spectra of the liquid *n*-paraffins are closely related if there are five or more carbon atoms

[88] Thompson and Torkington, *Proc. Roy. Soc.*, 1945, *A*, **184**, 3.
[89] Elliott, Ambrose, and Temple, *J. Chem. Phys.*, 1948, **16**, 877.

present. In the Raman spectra there is some alternation of frequency for n even and n odd, but this is not distinguishable among the infra-red bands.[5] The most prominent frequencies in the infra-red spectra are those associated with the hydrogen deformation modes. It follows that the features that

TABLE 2. *Characteristic frequencies (in cm.$^{-1}$) of the* n-*paraffins in the liquid state*

ν, approx.*	Infra-red spectra	Raman spectra	Assignments and comments
1370⎫ 1355⎬ 1340⎭ · ·	Moderately prominent	Absent	Hydrogen deformation modes of non-planar isomers ; nearly constant $n \geqslant 5$
1305 · · ·	Moderate	Prominent	CH_2 wagging or twisting modes ; nearly constant $n \geqslant 5$; intensities of the bands increase as n increases
1140 · · ·	Moderate	Prominent	Nearly constant $n \geqslant 4$
1120—965 ·	Moderate	Weak	Intensities and frequencies of the bands increase as n increases ; gives indication of the chain length
1070 · · ·	Difficult to distinguish	Prominent	Nearly constant $n \geqslant 4$
890 · · ·	Weak ; difficult to distinguish	Prominent ; polarised	Lower limiting skeletal stretching modes ; nearly constant $n \geqslant 5$
870–840⎫ 840–810⎭ ·	Weak ; difficult to distinguish	Prominent ; polarised	Lower limiting skeletal stretching modes of non-planar isomers ; alternating frequencies n even $< n$ odd
720 · · ·	Intense	Absent	CH_2 rocking modes ; nearly constant $n \geqslant 5$
425–150 · ·	No data	Prominent ; polarised	Symmetrical skeletal deformation modes ; decrease regularly as n increases

* Characteristics frequencies found also in spectra of the *trans*-isomers are in italics.

are valuable for recognising the n-paraffins or the presence of an extended unbranched carbon chain are limited in number, the most reliable being the group of Raman lines between 900 and 800 cm.$^{-1}$, and the infra-red absorption bands in the region 730—700 cm.$^{-1}$.

4. The *tert.*-Butyl Group

(a) *neo*Pentane.—*neo*Pentane (2 : 2-dimethylpropane) may be considered as the first member of the series of paraffins having the general formula CMe_3R, where R is an alkyl radical. This symmetrical molecule has, apart from the CH_3 torsional modes, seven distinct vibrations which should occur in the region below 1350 cm.$^{-1}$, two of which are inactive in both the Raman and the infra-red spectra. The substance has been extensively investigated [12, 25, 34, 48, 49, 90–93] and attempts to assign the frequencies have been

[90] A.P.I. Infra-red Spectrograms, Nos. 104, 442, 514, 784.
[91] Young, Koehler, and McKinney, *J. Amer. Chem. Soc.*, 1947, **69**, 1410.
[92] Rank and Bordner, *J. Chem. Phys.*, 1935, **3**, 248.
[93] Kohlrausch, *Z. phys. Chem.*, 1935, *B*, **28**, 340.

made by many authors, but as yet complete agreement has not been achieved. The following are those assignments (v in cm.$^{-1}$) about which there is no controversy (see also Table 3):

n_1, Symmetrical skeletal stretching vibration: 733
n_2, Doubly degenerate skeletal deformation vibration: 335
n_4, Triply degenerate skeletal deformation vibration: 415

Ambiguity arises over the interpretation of the 1249 and 921 cm.$^{-1}$ frequencies, both of which appear as depolarised Raman lines and intense infra-red bands. The assignment proposed originally by Kohlrausch and Köppl [49] has since been favoured by a number of authors.[34, 48, 91, 92, 94] This puts the 1249 cm.$^{-1}$ frequency as the triply degenerate CH_3 rocking mode, and the 921 cm.$^{-1}$ frequency as the triply degenerate skeletal stretching vibration, n_3; the reverse interpretation has been preferred by other investigators.[4, 10, 46, 95, 96] Most of these authors have attempted some

TABLE 3. *Relationships between the skeletal modes of* neo*pentane and those of paraffins with one* tert.*-butyl group*

neoPentane, CH_3—$\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}$—$CH_3$ Paraffins with one tert.-butyl group, CH_3—$\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}$—R

Numbering	Degeneracy	Selection rules		Numbering	Degeneracy	Selection rules :	
		Raman	infra-red			Raman	infra-red
n_1 . .	1	p	ia	v_1 . .	1	p	a
n_2 . .	2	dp	ia	v_4 . .	2	dp	a
n_3 . .	3	dp	a	v_3 . .	1	p	a
				v_2 . .	2	dp	a
n_4 . .	3	dp	a	v_5 . .	1	p	a
				v_6 . .	2	dp	a

p = polarised; dp = depolarised; a = active; ia = inactive

kind of theoretical treatment. Pitzer and Kilpatrick [46] have suggested schematically that the two inactive CH_3 rocking modes are at about 1150 cm.$^{-1}$ for the doubly and 950 cm.$^{-1}$ for the triply degenerate vibrations, while Rasmussen [34] prefers 1200 and 900 cm.$^{-1}$ respectively.

Unfortunately, it does not seem possible to come to any final decision on the data at present available for *neo*pentane, and investigations of the deuterated derivative $(CH_3)_3C \cdot CH_2D$ have not been conclusive.[48] (See the discussion between Rank [97] and Sheppard, Simpson, and Sutherland.[98]) For the purpose of considering the characteristic frequencies of the *tert.*-butyl group this is not a serious difficulty.

[94] Wagner, *Z. phys. Chem.*, 1939, *B*, **45**, 341.
[95] Wall and Eddy, *J. Chem. Phys.*, 1938, **6**, 107.
[96] Silver, *ibid.*, 1940, **8**, 919.
[97] *Discuss. Faraday Soc.*, 1950, **9**, 219.   [98] *Ibid.*, p. 216.

TABLE 4.   *Characteristic frequencies (in cm.⁻¹) of paraffins with
tert.-butyl groups in the liquid state* *

A.   Paraffins with one *tert.*-butyl group.

Paraffin		ν_{C-C} or CH₃ rocking			ν_{C-C}	δ_{C-C}	Refs.	API Nos.
2 : 2-Dimethylbutane . .	IR	1252	1217	929	711	NI	13	655, 670
	R	1258	1221	929	714	361	14	
2 : 2-Dimethylpentane . .	IR	1250	1209	926	741	NI	13	571, 588
	R	1254	1210	928	746	340	14	
2 : 2-Dimethylhexane . .	IR	1250	1202	932	—	NI	25	
	R	1251	1204	928	746	303	14	
2 : 2-Dimethylheptane . .	IR	1250	1203	932	—	NI	2	
	R	1251	1202	930	750	283	14	
2 : 2 : 3-Trimethylbutane .	IR	1252	1212	927	686	NI	13	573, 587
	R	1255	1220	920	686	364	14	
2 : 2 : 3-Trimethylpentane .	IR	1244	1218	928	716	NI	13	576, 590
	R	1245	1220	927	717	319	14	
2 : 2 : 3-Trimethylhexane .	IR	←———	No observations	——→			—	
	R	1239	1223	924	720	310	15	
2 : 2 : 4-Trimethylpentane .	IR	1247	1206	928	745	NI	13	577, 589
	R	1254	1212	931	749	301	14	
2 : 2 : 4-Trimethylhexane .	IR	1247	1205	926	744	NI	13	667, 676
	R	1250	1210	927	744	305	14	
2 : 2 : 4-Trimethylheptane .	IR	←———	No observations	——→			—	
	R	1252	1202	926	750	293	15	
2 : 2 : 4-Trimethyloctane .	IR	←———	No observations	——→			—	
	R	1252	1204	926	744	—	15	
2 : 2 : 5-Trimethylhexane .	IR	1248	1205	920	—	NI	13	579, 592
	R	1257	1206	929	746	302	14	
2 : 2 : 6-Trimethylheptane .	IR	1255	1204	920	—	NI	25	
	R	1249	1201	923	745	—	14	
2 : 2-Dimethyl-3-ethylpentane	IR	1236	1218	919	729	NI	13	683, 685
	R	1236	1226	925	727	308	14	
2 : 2-Dimethyl-4-ethylhexane	IR	←———	No observations	——→			—	
	R	1245	1205	926	739	307	15	
(1)	(2)	(3)	(4)	(5)	(6)	(7)		(8)

B.   Paraffins with two *tert.*-butyl groups.

Paraffin		ν_{C-C} or CH_3 rocking			ν_{C-C}	δ_{C-C}	Refs	API Nos.
2 : 2 : 4 : 4-Tetramethyl-pentane	IR	1244	—	916	730		13	583, 594
	R	1249	—	920	731		14	
2 : 2 : 5 : 5-Tetramethyl-hexane	IR	1247	—	910	755		13	690, 691
	R	←	No observations		→		—	
2 : 2 : 3 : 4 : 4-Penta-methylpentane	IR	1238	1214	930	748		13	693, 694
	R	←	No observations		→		—	
2 : 2 : 3 : 5 : 5-Penta-methylhexane	IR	←	No observations		→		—	
	R	1255	1211	924	753		15	
2 : 2 : 4 : 6 : 6-Penta-methylheptane	IR	1244	1208	927	—		5	
	R	1248	1209	924	758		14	
Infra-red intensity . . .		st	st	m	w	NI		
Raman intensity		m	m	m	st	m		
(1)	(2)	(3)	(4)	(5)	(6)	(7)		(8)

* For the meaning of symbols and abbreviations see the foot of Table 1.

(*b*) **Paraffins with one** *tert.*-**Butyl Group.**—Before discussing the frequencies characteristic of the *tert.*-butyl group, it is helpful to consider briefly how the skeletal vibrations of *neo*pentane are likely to alter when the symmetry of the molecule is reduced by the substitution of an alkyl radical R for one CH_3 group.   Table 3 shows the relationships between the modes of the parent and the derived molecules, together with the degeneracies and the selection rules;   these relationships are well known.[99]   In order to get some idea of the magnitude of the splitting of the frequencies of n_3 and n_4, and the variation with the nature of R of the frequencies ν_1 to ν_6 for the molecules CMe_3R, it is necessary to assume a suitable model and to make calculations using force constants chosen from the values available in the literature.   Two such investigations have been made. Kohlrausch and his co-workers [100] were interested primarily in those molecules in which R is a halogen atom;   Simpson and Sutherland [4] were concerned with the 2 : 2-dimethyl paraffins.   The conclusions reached in both treatments are similar.

The vibrations ν_1, ν_4, and ν_5 shift steadily to lower frequencies as the mass of R increases; ν_3 after an initial decrease changes more slowly and appears to approach a limiting value, while the modes ν_2 and ν_6 remain effectively invariant.   Further, it seems probable that the maximum splitting of n_3 for the 2 : 2-dimethyl paraffins is unlikely to be greater than 50 cm.$^{-1}$, though that of n_4 is probably considerably larger.[4]

[99] Kohlrausch, *op. cit.*, 1943, p. 158.
[100] *Idem, ibid.*, p. 188.

Tables 4A and 4B summarise the characteristic frequencies in the Raman and infra-red spectra of the liquids for most of the paraffins having one or two *tert.*-butyl groups hitherto investigated (some very complicated molecules are not included). Figs. 4A and 4B show typical spectra for a paraffin of this class. The *tert.*-butyl group provides a particularly favourable configuration for the discussion of the characteristic frequencies of such a unit, because it forms a rigid group which cannot, because of its threefold symmetry axis, itself give rise to rotational isomerism, *i.e.*, the existence of rotational isomers in any molecule in which it occurs must be dependent on changes in the radical R. It seems plausible to suppose that such changes are unlikely to influence the vibrations of the *tert.*-butyl group, though direct experimental evidence on this point is not available.

The various characteristic frequencies of molecules having a single *tert.*-butyl group will now be discussed in turn. As already noted (p. 22), there is a splitting of the band due to the CH_3 symmetrical deformation modes to give a doublet at 1397 and 1370 cm.$^{-1}$. The other series, as given in Table 4, can all be related to frequencies in *neo*pentane by using the theoretical conclusions outlined above. Col. 6 lists the frequencies of the symmetrical stretching vibration ν_1 of the C_5 unit associated with the *tert.*-butyl group (750—710 cm.$^{-1}$). These frequencies are easily recognised in the Raman spectrum on account of their strength and high degree of polarisation ; [10] the corresponding infra-red bands are not prominent and are in many cases overlapped by strong absorption due to the CH_2 rocking modes. This series is related to the Raman line at 733 cm.$^{-1}$ in the spectrum of *neo*pentane. From the figures given it is apparent that the actual frequency of this mode is dependent on the nature of the radical R ; thus if R is branched next to the *tert.*-butyl group (as in 2 : 2 : 3-trimethylbutane) a marked lowering occurs. The second general trend is that, as the mass of R increases for a given type of R, the frequency of this vibration also increases. This is contrary to the theoretical predictions, but as they were based on drastically simplified models it is perhaps not surprising.

Col. 7 gives the frequencies of the symmetrical skeletal deformation vibration ν_5 as observed in the Raman spectra below 400 cm.$^{-1}$. This mode can be picked out with fair confidence on account of its polarisation, but is by no means easy to identify in the more complex molecules. The actual frequencies decrease with increasing mass of R, and seem to be dependent to some extent on its structure. This vibration, on account of its considerable variation, is less valuable as a means of identifying the *tert.*-butyl group. The skeletal deformation modes ν_4 and ν_6, which should occur as depolarised Raman lines below 500 cm.$^{-1}$, cannot be recognised with certainty, though tentative series have been proposed for these vibrations in the simple 2 : 2-dimethyl paraffins.[4]

The two frequencies near 1250 and 1210 cm.$^{-1}$ (cols. 3 and 4) are of the greatest practical importance in the identification of the *tert.*-butyl group, as they almost invariably appear as fairly prominent Raman lines [8, 10] and as very strong infra-red bands.[4, 5] They undoubtedly arise by the splitting of the 1249 cm.$^{-1}$ frequency in *neo*pentane. According to the

Fig. 4A
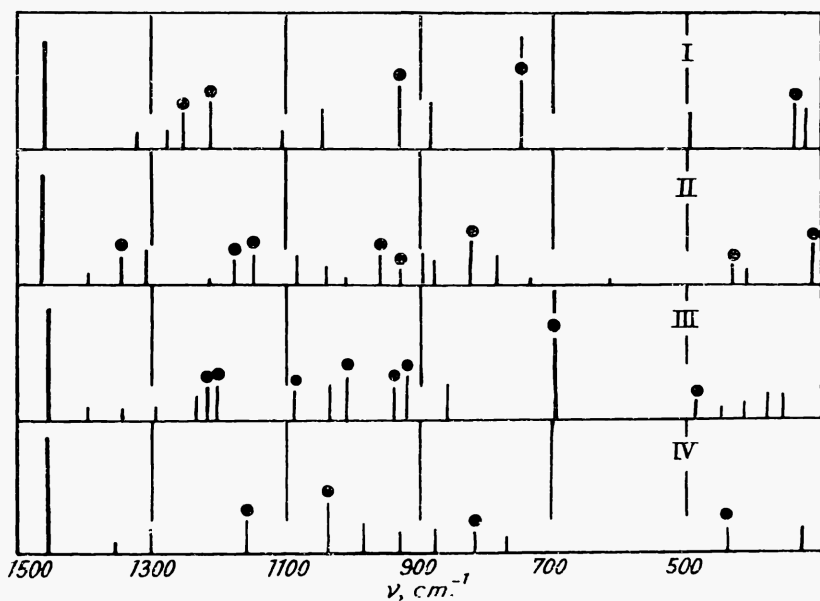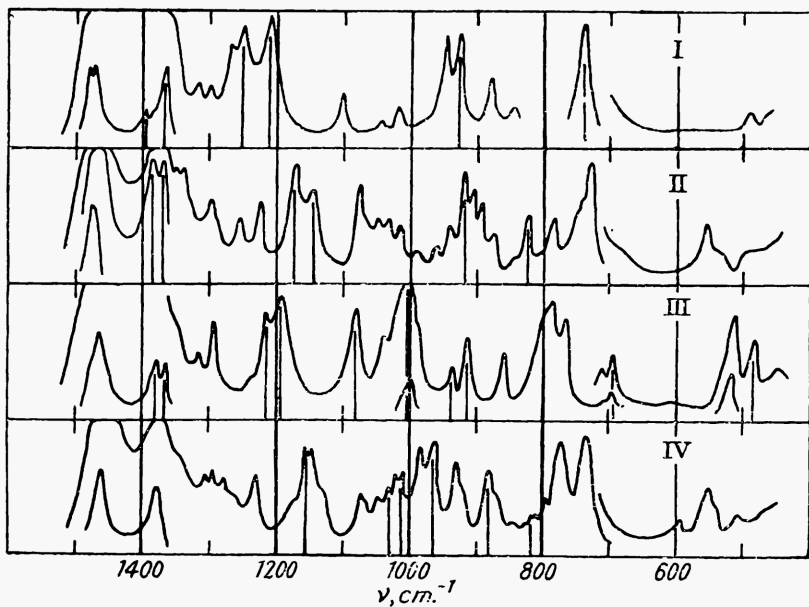
Fig. 4B

A. *Infra-red spectra between 1500 and 500 cm.⁻¹ of some typical branched paraffins in the liquid state.* (*After American Petroleum Institute Infra-red Spectrograms Nos. 571, 588 ; 552, 554 ; 572, 588 ; 602, 611.*) (*Vertical lines indicate characteristic absorption frequencies mentioned in the text.*)

B. *Raman spectra between 1500 and 300 cm.⁻¹ of the same paraffins in the liquid state.* (*After Fenske* et al.[14]) (*Characteristic frequencies mentioned in the text are indicated by ●.*)

I, 2 : 2-*Dimethylpentane.*   III, 3 : 3-*Dimethylpentane.*
II, 2-*Methylhexane.*   IV, 3-*Methylhexane.*

interpretation given for the symmetrical molecule (p. 33), they may be assigned either as CH_3 rocking modes of the *tert.*-butyl group or as the two skeletal vibrations ν_2 and ν_3. As may be seen from col. 3, the 1250 cm.$^{-1}$ frequency remains remarkably constant whatever the nature of the radical R. The other series near 1210 cm.$^{-1}$ (col. 4) shows more variation ; there is a general lowering as the mass of R increases, though the lowering is less pronounced if R is branched near the *tert.*-butyl group. The behaviour of the 1250 and 1210 cm.$^{-1}$ series is in general agreement with the theoretical predictions for ν_2 and ν_3, though this is not conclusive evidence in favour of these assignments. The relative intensities of the infra-red bands near 1250 and 1210 cm.$^{-1}$ are interesting ; in general, the former are stronger unless R is branched near the *tert.*-butyl group, in which case the lower frequency becomes more prominent.[2]

Col. 5 gives figures for the remaining frequency (near 930 cm.$^{-1}$) that can be definitely associated with the *tert.*-butyl group. This appears as a prominent Raman line, and a recognisable but not very strong infra-red band. Like the 1250 cm.$^{-1}$ frequency, it remains nearly invariant whatever the nature of R, but is less valuable for the identification of the *tert.*-butyl group, because many other paraffins have frequencies in this region. The 930 cm.$^{-1}$ series in molecules with a *tert.*-butyl group is undoubtedly associated with the 921 cm.$^{-1}$ frequency in *neo*pentane, and so may be assigned either to the invariant skeletal modes ν_2 or to CH_3 rocking vibrations of the *tert.*-butyl group. It should be noted, however, that if the former interpretation is preferred, it is not possible to pick out any series which could be attributed to the other skeletal vibrations ν_3.

Of the substances listed in Table 4A, only 2 : 2-dimethylbutane has been the subject of detailed consideration, probably because rotational isomerism is absent in this molecule. The conclusions of Kilpatrick and Pitzer [101] and Sheppard [102] are in fair agreement. Table 4A does not include the data for some ten more complicated paraffins with one *tert.*-butyl group. All the characteristic frequencies noted above appear consistently, except that the 1210 cm.$^{-1}$ frequency is missing for the two molecules with a 2 : 2 : 3 : 3-tetramethyl grouping. It is also interesting to find that these same frequencies may readily be recognised in the spectra of *tert.*-butylethylene and *tert.*-butylacetylene (3 : 3-dimethylbut-1-ene and -1-yne).[102] Two somewhat weaker frequencies near 1025 and 880 cm.$^{-1}$ which appear to be associated with the *tert.*-butyl group in these molecules cannot be recognised with certainty in the spectra of the relevant paraffins.

(c) **Paraffins with two** *tert.*-**Butyl Groups.**—The molecule 2 : 2 : 3 : 3-tetramethylbutane might be considered as the first member of the series of paraffins with two *tert.*-butyl groups. However, both the electron-diffraction data [103] and the spectroscopic evidence [104] suggest that it has a staggered configuration analogous to that of ethane. Because of the

[101] Kilpatrick and Pitzer, *J. Amer. Chem. Soc.*, 1946, **68**, 1066.
[102] *J. Chem. Phys.*, 1949, **17**, 455.
[103] Bauer and Beach, *J. Amer. Chem. Soc.*, 1942, **64**, 1142.
[104] Cleveland, Lamport, and Mitchell, *J. Chem. Phys.*, 1950, **18**, 1320.

resulting centre of symmetry the skeletal vibrations of such a molecule cannot be completely related to those of other substances with a *tert.*-butyl group. The spectra of this paraffin have been investigated by a number of authors [25, 27b, 47, 104, 105] and an assignment of its frequencies, which seems satisfactory, has recently been given.[106]

The data on other molecules with two *tert.*-butyl groups are somewhat scanty ; they are collected in Table 4B. Most of the frequencies characteristic of a single *tert.*-butyl group (except the skeletal deformation mode) may be recognised without difficulty in the spectra of these more complex paraffins.

5. The *iso*Propyl Group

(a) *iso*Butane.—*iso*Butane may be considered as the first member of the series of paraffins having the general formula $CHMe_2R$, where R is an alkyl group ; it has nine distinct vibrations (other than the CH_3 torsional modes) that should occur in the region below 1350 cm.$^{-1}$, all but one of which are active in both Raman and infra-red spectra ; the remaining mode is forbidden. This molecule has been the subject of many investigations [17, 24, 25, 34, 107, 108] but no definite assignment of the frequencies is generally accepted. Apart from the doubly degenerate CH deformation mode observed as a Raman line near 1335 cm.$^{-1}$, the only vibration about which there is no controversy is the non-degenerate skeletal stretching mode n_1 at 795 cm.$^{-1}$ (see also Table 5).

The two skeletal deformation frequencies occur at 435 and 370 cm.$^{-1}$. Most authors allot these respectively to the symmetrical non-degenerate (n_2) and unsymmetrical doubly degenerate (n_4) vibrations on the basis of Ananthakrishnan's polarisation measurements.[108] Simpson and Sutherland [4] have given reasons for preferring the opposite interpretation, but further work will be needed before a final conclusion can be reached.

There has been considerable discussion about the assignment of the unsymmetrical doubly degenerate skeletal stretching vibration n_3, which has been variously located at 925,[46] 965, [34, 94] and 1170 cm.$^{-1}$.[4, 10] The infra-red spectrum of the molecule $(CH_3)_3 \cdot CD$ has been published but not analysed.[109] It is clear that some of its modes of vibration are coupled together (compare discussion on propane, p. 28) ; the observations do not, however, allow the identification of n_3. The inactive CH_3 rocking mode has been schematically put at 1200 cm.$^{-1}$ by Pitzer and Kilpatrick,[46] and at 900 cm.$^{-1}$ by Rasmussen.[34] The active singly degenerate CH_3 rocking vibration probably occurs at 1095 cm.$^{-1}$.[46] The two active doubly degenerate CH_3 rocking modes correspond to the two frequencies of those listed above which are not attributed to the unsymmetrical skeletal stretching vibration.

[105] A.P.I. Infra-red Spectrogram, No. 444.

[106] Scott, Douslin, Gross, Oliver, and Huffmann, *J. Amer. Chem. Soc.*, 1952, **74**, 883.

[107] A.P.I. Infra-red Spectrograms, Nos. 62, 374, 439, 1142.

[108] *Proc. Indian Acad. Sci.*, 1936, A, **3**, 527.

[109] Condon, McMurry, and Thornton, *J. Chem. Phys.*, 1951, **19**, 1010.

It is unfortunate that the assignment of frequencies of this key molecule is so uncertain ; however, it is possible to discuss the frequencies characteristic of the *iso*propyl group without difficulty although their exact interpretation is ambiguous.

(b) **Paraffins with one *iso*Propyl Group.**—It is clear from the foregoing discussion that it is profitable to consider the relationships between the skeletal vibrations of the most symmetrical and the other members of a related series. Thus in the present instance it is desirable to know how the skeletal modes of *iso*butane are related to those of other molecules of the type $CHMe_2R$. The general arguments are analogous to those already given for the *tert.*-butyl group and the relevant calculations have been carried out on similar lines by the same authors.[4, 100] Their conclusions are summarised in Table 5.

TABLE 5. *Relationships between the skeletal modes of* isobutane *and those of paraffins with one* isopropyl *group*

*iso*Butane, CH₃—C(H)—CH₃ with CH₃		Selection rules		Paraffins with one *iso*propyl group CH₃—C(H)—R with CH₃	Selection rules		Effect on frequency of increase of mass of R
Numbering	Degeneracy	Raman	infra-red	Numbering	Raman	infra-red	
n_1	1	p	a	ν_1	p	a	Decreases fairly slowly
n_2	1	p	a	ν_2	p	a	Decreases steadily
n_3	2	dp	a	$-\nu_3$	dp	a	Effectively constant
				$-\nu_5$	p	a	Decreases fairly slowly
				ν_4	p	a	Effectively constant
n_4	2	dp	a	$-\nu_6$	dp	a	Decreases steadily

Tables 6A and 6B list the characteristic frequencies in the Raman and infra-red spectra for a selection of paraffins having one or two *iso*propyl groups respectively ; all substances were investigated in the liquid state. Figs. 4A and 4B show typical spectra for a paraffin of this class.

Unlike the *tert.*-butyl group, the *iso*propyl unit is not symmetrical, so that even the simplest molecules (such as 2-methylbutane)[61] can exist as mixtures of rotational isomers in the liquid state. Moreover, in all the molecules listed (except 2 : 2 : 3-trimethylbutane where such isomerism is absent) the *iso*propyl group itself is actively concerned in the variations in configuration. Since it is probable, from the work on molecules where one form has been isolated, that certain frequencies of the various isomers of a given molecule may differ considerably, it follows that those given in Table 6 may in fact correspond to different forms of the molecules. However, it is possible to make quite reasonable assignments on the assumption that they all correspond to one particular type of isomer, although

TABLE 6. *Characteristic frequencies (in cm.$^{-1}$) of paraffins with* iso*propyl groups in the liquid state* *

A. Paraffins with one *iso*propyl group.

Paraffins		δ_{C-H}	ν_{C-C} or CH$_3$ rocking					ν_{C-C}	δ_{C-C}	δ_{C-C}	Refs	API Nos.
2-Methylbutane	IR		1176	1149		—	920	794	463	NI	13	550, 555
	R	1343	1175	1154		953	—	794	459	368	14	
2-Methylpentane	IR		1172	1147		959	920	816	NI	NI	13	551, 554
	R	1344	1176	1154		954	—	815	442	325	14	
2-Methylhexane	IR		1171	1145		—	918	822	NI	NI	13	552, 554
	R	1345	1179	1148		957	928	822	430	311	14	
2-Methylheptane	IR		1171	1144		961	919	813	NI	NI	13	553, 555
	R	1344	1177	1149		958	—	814	434	289	14	
2-Methyloctane	IR		1167	1143		951	919	824	NI	NI	13	605, 614
	R	1345	1175	1148		961	—	826	—	256	14	
2-Methylnonane	IR		1167	1142		957	918	833	NI	NI	13	608, 614
	R		← —————— No observations —————— →								—	
4-*iso*Propylheptane	IR		1177	1150		950	920	—	NI	NI	2	
	R		← —————— No observations —————— →								—	
2 : 2 : 3-Trimethylbutane	IR		1161	—		957	927	832	NI		13	573, 587
	R	1331	—	—		—	920	830	449		14	
2 : 2 : 4-Trimethylpentane	IR		1168	—		956	928	826	NI		13	577, 589
	R	—	1176	—		957	931	829	423		14	
2 : 2 : 5-Trimethylhexane	IR		1170		1121	950	920	826	NI		13	579, 592
	R	1345	—		1125	958	917	828	407		14	
2 : 2 : 6-Trimethylheptane	IR		1170		1125	949	920	835	NI		25	
	R	—	—		1125	—	923	833	—		14	

B. Paraffins with two *iso*propyl groups.

Paraffins		δ_{C-H}	ν_{C-C} or CH$_3$ rocking					ν_{C-C}	δ_{C-C}	δ_{C-C}	Refs	API Nos.
2 : 3-Dimethylbutane	IR		—	1153		—	921	—	NI	NI	13	656, 670
	R	1348	1165	—		939	—	754	—	—	14	
2 : 4-Dimethylpentane	IR		1170	—		956	919	809	NI	NI	13	659, 672
	R	1348	1164	—		956	924	810	414	306	14	
2 : 5-Dimethylhexane	IR		1171	—		949	920	839	NI	NI	13	663, 674
	R	1341	1175	1154		963	911	840	440	263	14	
2 : 6-Dimethylheptane	IR		1170	1150		950	920	835	NI	NI	2	
	R	1341	1171	1149		953	—	840	423	255	15	
Infra-red intensity . .				st	st	m	m.st	m	NI	NI		
Raman intensity . .		m	m		m	m	m	st	m	m		
(1)		(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	

* For the meaning of symbols and abbreviations see foot of Table I.

the resulting conclusions must be considered as tentative until confirmatory experimental evidence becomes available. The various characteristic frequencies of molecules having a single *iso*propyl group will now be discussed in turn. As already noted (p. 22) there is a splitting of the band due to the CH_3 symmetrical deformation modes of the group to give a doublet at 1385 and 1370 cm.$^{-1}$. The CH deformation vibrations give rise to a series of Raman lines near 1345 cm.$^{-1}$,[10] which are shown in Table 6A, col. 3. Col. 8 gives the series (835—749 cm.$^{-1}$) that can certainly be attributed to the symmetrical stretching vibrations ν_1 of the *iso*propyl group. This is easily recognised in the Raman spectrum on account of the strength and polarisation of the lines ; the corresponding infra-red bands are usually weak.[10] These frequencies correspond to the vibration observed at 795 cm.$^{-1}$ in the spectra of *iso*butane. From the figures given, it is apparent that the actual frequency of this mode is not strongly dependent on the nature of R, though a slight shift to higher frequencies may be noted as the mass of R increases. This variation is not in agreement with the predictions of the simple theory.

Col. 9 gives the series of polarised Raman lines (465—430 cm.$^{-1}$) that may be assigned to the constant skeletal deformation vibrations ν_4. These may be recognised without much difficulty [10] and could be used to detect the presence of an *iso*propyl group, although in such paraffins there are usually a number of lines in this spectral region. Col. 10 lists another series of polarised Raman lines below 400 cm.$^{-1}$. These lines may be assigned to the skeletal deformation modes ν_2, and diminish in frequency as the mass of R increases, in accordance with the theoretical predictions. They may be identified with fair certainty in the simpler molecules, but would be of little value for recognising the presence of the *iso*propyl group. The series of depolarised lines below 500 cm.$^{-1}$ corresponding to the skeletal deformation modes ν_6 cannot be definitely identified ; a tentative interpretation has been proposed for the 2-methyl paraffins.[4] Smith [5] has noted a series of weak infra-red bands between 550 and 530 cm.$^{-1}$ appearing regularly in the spectra of paraffins with an *iso*propyl group, which can possibly be assigned as combination bands. The spectra in this region are, however, rather complex, so this series is not very helpful for structural analysis.

The frequencies near 1170 cm.$^{-1}$ listed in col. 4 are those which are of the greatest importance in the identification of the *iso*propyl group ; this series is always prominent as strong bands in the infra-red spectrum [4, 5] that usually have corresponding Raman lines.[8, 10] The frequencies are very insensitive to changes in the nature of R, and are undoubtedly associated with the 1170 cm.$^{-1}$ frequency in *iso*butane. Col. 5 lists a fairly constant frequency near 1150 cm.$^{-1}$ which appears regularly in the spectra of the 2-methyl paraffins, though not generally in the more complex molecules.[2] This series also appears to be associated with the 1170 cm.$^{-1}$ frequency of *iso*butane. These two series may be interpreted either as CH_3 rocking modes of the *iso*propyl group or as the skeletal stretching vibrations ν_3 and ν_5.
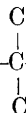
The series listed in col. 6 appears as prominent Raman lines and as infra-red bands of variable intensity near 955 cm.$^{-1}$; the frequencies remain almost unaffected by alteration in the structure of the radical R, and may be correlated with the vibration appearing at 965 cm.$^{-1}$ in the Raman spectrum of *iso*butane. Col. 7 shows a series near 920 cm.$^{-1}$ which appears as prominent infra-red bands that sometimes have corresponding Raman lines. These frequencies show very little variation; they would seem to be correlated with the 925 cm.$^{-1}$ absorption in *iso*butane. Paraffins with a *tert.*-butyl group also have frequencies in this region (Section 4). It should be noted that there is no real evidence for any consistent splitting of either the 955 or the 920 cm.$^{-1}$ series in *iso*propyl compounds, *i.e.*, if either of these is assigned to the skeletal modes ν_3, there are no characteristic frequencies recognisable in this region that could correspond to skeletal vibrations ν_5.

Data are available for some 25 more highly branched paraffins with *iso*propyl groups. Of the characteristic frequencies listed in Table 6A, the Raman lines near 1345 cm.$^{-1}$ are usually present. The 1170 and 955 cm.$^{-1}$ frequencies are nearly always found in both infra-red and Raman spectra and those near 920 cm.$^{-1}$ as infra-red bands. A frequency corresponding to the symmetrical stretching mode ν_1 and another that may be attributed to the constant skeletal deformation vibration ν_4 may be identified in the Raman spectra of about half the molecules. The behaviour of the 540 cm.$^{-1}$ infra-red series is somewhat erratic; the 1150 cm.$^{-1}$ frequency is usually absent and the deformation vibration ν_2 cannot be distinguished with certainty.

(c) **Paraffins with two** *iso***Propyl Groups.**—The data on the simpler paraffins with two *iso*propyl groups are summarised in Table 6B, which shows that most of the characteristic frequencies of the *iso*propyl group may be easily recognised in these more complex molecules. The frequencies of 2 : 3-dimethylbutane seem a little anomalous. In the liquid this molecule is known to consist of a mixture of two rotational isomers, one of which has a symmetrical structure with a centre of symmetry.[61] This may possibly account for the discrepancies observed. Further, the two *iso*propyl groups must be closely coupled together, so that deviations due to their interaction may be expected.

6. Paraffins with an Internal Quaternary Carbon Atom

The molecules of this class possess a C_5 structural unit $C-\overset{\displaystyle C}{\underset{\displaystyle C}{|}}-C$ in common with those with the *tert.*-butyl group previously discussed (Section 4). Consequently, analogies may be sought in the spectra of these two classes of paraffin. Further, it might be expected that the assignments made for *neo*pentane would prove helpful in the interpretation of the spectra; this method of approach has already been used by both Sheppard [10] and Smith.[5] A number of paraffins with an internal quaternary carbon atom have been

TABLE 7.   *Characteristic frequencies (in cm.$^{-1}$) of paraffins with an internal quaternary carbon atom in the liquid state* *

Paraffin		ν_{C-C} or CH$_3$ rocking			ν_{C-C}	δ_{C-I}	Refs	API Nos
3 : 3-Dimethyl-pentane	IR	1217	1192	1000	695	482	13	572, 588
	R	1217	1200	1007	695	482	14	
3 : 3-Dimethyl hexane	IR	1212	1189	1006	725	482	13	574, 589
	R	1208	—	—	722	492	14	
3 : 3-Dimethyl-heptane	IR	1215	1187	1010	727	NI	2	
	R	—	—	—	724	478	14	
2 : 3 : 3-Trimethyl pentane	IR	1211	1188	1005	672	472	13	578, 590
	R	1218	—	—	676	470	14	
2 : 3 : 3-Trimethyl hexane	IR	1206	1186	*	689	490	13	668, 676
	R	1210	1191	*	691	483	14	
2 : 3 : 3 : 4-Tetra-methylpentane	IR	1221	1183	*	672	471	13	585, 593
	R	1227	1186	*	671	467	14	
3 : 3 : 4-Trimethyl-hexane	IR	1205	1182	1006	701	482	13	681, 682
	R	1211	1192	—	704	484	14	
3 : 3 : 5-Trimethyl-heptane	IR	1211	1186	1011	721	—	13	686, 688
	R	←——— No observations ——————→				—	—	
3 : 3 : 4 : 4-Tetra-methylhexane	IR	←——— No observations ——————→				—	—	
	R	1216	—	1017	658	—	14	
4 : 4-Dimethyl-heptane	IR	1210	1193	*	—	NI	2	
	R	1211	1195	*	753	493	14	
2 : 4 : 4-Trimethyl-hexane	IR	1230	1188	1010	723	481	13	580, 592
	R	1229	—	1018	721	478	14	
3-Ethyl-3-methylpentane	IR	1232	1179	1016	686	468	13	575, 591
	R	—	1192	—	681	475	14	
3-Ethyl-3-methylhexane	IR	1235	1183	1000	NI	NI	2	
	R	1229	1191	999	706	485	14	
3 : 3-Diethyl-pentane	IR	1225	1190	1012	—	455	13	581, 591
	R	—	—	1015	684	—	15	
3 : 3-Diethyl-hexane	IR	1220	1175	1015	733	NI	2	
	R	←——— No observations ——————→				—		
Infra-red intensity . .		st	st	st	w	w		
Raman intensity		m	w	m	st	w		
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	

* For the meaning of symbols and abbreviations see foot of Table 1.

investigated ; Table 7 includes the relevant experimental data on the Raman and infra-red spectra of the liquids for all these except for the four which also possess a *tert.*-butyl group. Fig. 4A and 4B show typical spectra for a paraffin of this class.

As noted on p. 22, there is a characteristic splitting of the band due to the CH_3 deformation modes of the 3 : 3-dimethyl paraffins to give a doublet at 1384 and 1367 cm.$^{-1}$. Table 7 shows that, corresponding to the 1250, 1210 cm.$^{-1}$ frequencies of the *tert.*-butyl group, two series are found consistently in the infra-red spectra of paraffins with an internal quaternary carbon atom ; the corresponding Raman lines are not always present. One series near 1190 cm.$^{-1}$ remains nearly constant in frequency (col. 4) and in the infra-red spectra is more intense than the other, near 1210 cm.$^{-1}$ (col. 3), which is more variable in its behaviour. The former provides the most reliable method of distinguishing the presence of an internal quaternary carbon atom.

The region 1100—1000 cm.$^{-1}$, which is not very helpful for structural analysis, gives rise to a number of characteristic frequencies in molecules with an internal quaternary carbon atom that seem to have no counterparts in paraffins with a *tert.*-butyl group. The bands in this range are somewhat complex with much splitting, but regions of prominent absorption are apparent near 1100, 1040, and in most cases near 1010 cm.$^{-1}$, and many molecules also show corresponding Raman lines. The frequencies of the first two series behave in a somewhat erratic fashion, there being no obvious relationship to the structures. Tentatively they may be assigned to CH_3 rocking modes not involving the C_5 structural unit, since this is the only type of vibration in the appropriate range common to all the molecules listed, and similar frequencies are found in some other classes of paraffins (compare Table 10). The absorption bands near 1010 cm.$^{-1}$ (col. 5) are always prominent in paraffins with an internal quaternary carbon atom if they also have at least one ethyl group ; the Raman counterparts are usually absent. It seems plausible to suggest that these bands are to be assigned to the carbon–carbon stretching vibrations within the ethyl group, analogous to the mode that appears as a Raman line at 993 cm.$^{-1}$ in the spectrum of ethane. Such molecules also have intense bands near 770 cm.$^{-1}$ which were noticed by Smith ;[5] these are attributable to the CH_2 rocking modes of the ethyl groups.

Characteristic frequencies analogous to those near 930 cm.$^{-1}$ in the spectra of the *tert.*-butyl compounds might be expected to appear, for paraffins with an internal quaternary atom, in the range 950—900 cm.$^{-1}$. The infra-red bands in this region are usually complicated and on the whole not very intense ; Raman lines are found for some molecules near 930 cm.$^{-1}$ and in the range 920—910 cm.$^{-1}$. It is difficult to distinguish any plausible series that is consistently observed for all these molecules and could be used to characterise them, especially as the other groups present also have frequencies in this region.

As may be seen from col. 6, all paraffins with an internal quaternary carbon atom possess a strong polarised Raman line that may be assigned

to the symmetrical stretching mode of the C_5 unit (750—685 cm.$^{-1}$) ; the corresponding infra-red bands, if they can be picked out from among those of the CH_2 rocking vibrations, are weak. These frequencies are analogous to those already described for the *tert.*-butyl compounds and correspond to the 733 cm.$^{-1}$ Raman line in *neo*pentane. Moreover, their variation is similar ; in particular, substitution near the C_5 unit produces a marked lowering in frequency. This variation reduces the usefulness of these lines as a means of identifying the presence of an internal quaternary carbon atom.

Below 500 cm.$^{-1}$ two series of Raman lines can be picked out that may be assigned to skeletal deformation modes of the C_5 unit, though the exact relationship to the corresponding vibrations of the *tert.*-butyl group is not very clear. One series (col. 7) has a fairly constant frequency ; the other, between 350 and 305 cm.$^{-1}$ (not listed), is polarised, and the frequencies decrease as the molecule becomes larger. Neither would be very valuable as a method of identification, as paraffins with an internal quaternary carbon atom possess a number of Raman lines in this region.

The above discussion has not specifically taken into account the probability that paraffins with an internal quaternary carbon atom exist in the liquid state as mixtures of rotational isomers. It is significant that the symmetrical stretching vibration of the C_5 structural unit does not appear to show any tendency to split. This suggests that the vibrations of this unit are little affected by the configuration of the rest of the molecule (just as in the analogous *tert.*-butyl paraffins), and provides support for the assignment of the pair of frequencies near 1200 cm.$^{-1}$ and the Raman lines near 485 cm.$^{-1}$ to such modes.

7. Paraffins with other Structural Units

(a) **Paraffins with One Internal Tertiary Carbon Atom.**—The molecules of this class possess a C_4 structural unit C—C—C in common with those, with an H above the central C and a C below, with the *iso*propyl group previously discussed (Section 5). The most hopeful method of approach, already used by Sheppard [10] and Smith,[5] is to seek analogies between the spectra of these two classes of paraffin. As will be apparent from the following discussion, the interpretation of the spectra of molecules with an internal tertiary carbon atom is not easy. Serious difficulties are encountered, probably because the different rotational isomers have differing frequencies even for those vibrations that can be associated with the C_4 unit.

Experimental data for a large number of molecules are available. Table 8 lists the relevant Raman and infra-red frequencies of the liquids for those paraffins which have a single C_4 unit and no other branched grouping. Figs. 4A and 4B show typical spectra for a paraffin of this class.

TABLE 8. *Characteristic frequencies (in cm.$^{-1}$) of paraffins with one internal tertiary carbon atom in the liquid state* *

Paraffin		r_{C-C} or CH$_3$ rocking			ν_{C-C}	δ_{C-C}	Refs.	API Nos.
3-Methylpentane	IR	1155	1043	1015	—	443	13	601, 611
	R	1162	1046	—	819	445	14	
3-Methylhexane	IR	1155	1032	1002	817	NI	13	602, 611
	R	1158	1036	—	816	436	14	
3-Methylheptane	IR	1155	—	1011	819	NI	13	603, 612
	R	1156	1044	—	820	—	14	
3-Methyloctane	IR	1155	1049	1012	—	NI	13	606, 612
	R	1155	1041	—	—	422	14	
3-Methylnonane	IR	1155	—	1012	819	NI	13	609, 615
	R	← No observations →					—	
3-Methylundecane	IR	1156	—	1015	—	NI	5	
	R	← No observations →					—	
4-Methylheptane	IR	1156	1047	*	826	NI	13	604, 613
	R	1156	1042	*	824	418	14	
4-Methyloctane	IR	1156	1044	•	834	NI	13	607, 613
	R	1155	1044	*	830	414	14	
4-Methylnonane	IR	1157	1045	*	842	NI	13	610, 615
	R	← No observations →					—	
3-Ethylpentane	IR	1167	1042	1004	832	457	13	657, 671
	R	1164	1039	1007	832	447	14	
3-Ethylhexane	IR	1155	1043	1011	821	NI	13	660, 671
	R	1156	1042	—	823	434	14	
3-Ethylheptane	IR	1155	1050	1005	835	NI	2	
	R	1161	1047	—	836	457	14	
4-Ethylheptane	IR	1145	1045	1005	850	NI	2	
	R	1154	1047	—	848	433	14	
Infra-red intensity		m.st	w	m	w	w		
Raman intensity		m	m	v.w	m	m		
(1)	(2)	(3)	(4)	(5)	(6)	(7)		(8)

* For the meaning of symbols and abbreviations see foot of Table 1.

In the Raman spectra of paraffins with an internal tertiary carbon atom, lines are observed for most molecules near 1360 cm.$^{-1}$ (not listed); these can be assigned to the CH deformation modes. Table 8 shows that a nearly constant frequency (1155 cm.$^{-1}$) appears consistently in the Raman and infra-red spectra of these molecules (col. 3). This series may be readily

identified, and forms the most useful means of recognising the presence of an internal tertiary carbon atom. The infra-red bands are prominent (though they show some evidence of splitting), and the corresponding Raman lines are the only ones that occur in this region. There is little doubt that this series is analogous to that occurring near 1170 cm.$^{-1}$ in the *iso*propyl paraffins. The assignment is thus dependent on the final interpretation of the 1170 cm.$^{-1}$ frequency in the *iso*butane spectra. It should be noted, however, that the persistence of this series, even when no CH_3 groups are directly attached to the tertiary carbon atom, does seem to suggest that the relevant vibration must be predominantly skeletal in character.

The frequencies shown in col. 4 near 1040 cm.$^{-1}$ are found in the Raman and infra-red spectra of most of the molecules listed, and are only slightly affected by changes in structure. This series seems analogous to that already discussed for the paraffins having an internal quaternary carbon atom (Section 6), and presumably may also be attributed to CH_3 rocking modes not involving the C_4 structural unit. The infra-red bands near 1010 cm.$^{-1}$ (col. 5) are found in all molecules having an ethyl group, in agreement with the interpretation previously given.
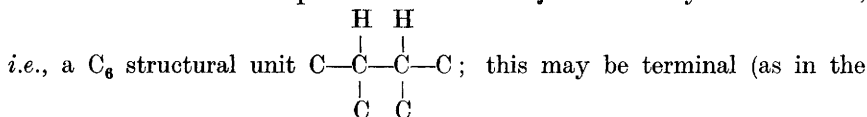
Examination of the 850—700 cm.$^{-1}$ region of the Raman spectra shows that paraffins with a single internal tertiary carbon atom have at least one nearly constant frequency (col. 6) that can be assigned to the symmetrical stretching vibration of the C_4 structural unit, analogous to those already described for the *iso*propyl compounds. The corresponding infra-red bands are insignificant. There is evidence, especially in the 3-ethyl paraffins, of a second Raman series at a somewhat lower frequency (770—750 cm.$^{-1}$) which can be attributed to the same vibration in a second type of isomer. Analysis in the range 770—740 cm.$^{-1}$ is, however, complicated by the presence of the CH_2 rocking modes of the ethyl and n-propyl groups which are also present. Col. 7 shows that a series (450—415 cm.$^{-1}$) attributable to skeletal deformation modes can be distinguished in the Raman spectra ; it is presumably analogous to the series already noted in the *iso*propyl paraffins near 435 cm.$^{-1}$. The actual frequencies depend on whether the molecules are 3-methyl, 4-methyl, or 3-ethyl paraffins, but are fairly constant for a particular class of molecules. Neither of these Raman series is very helpful for identifying the presence of an internal tertiary carbon atom, because in both cases a number of other lines are present in the same frequency region.

Besides the series shown in Table 8, which are common to all these molecules, other regularities have been separately noted in the spectra of the 3-methyl, 4-methyl, and 3-ethyl paraffins ; these are given in Table 10. It must, however, be emphasised that correlations based on a limited number of molecules are sometimes misleading and are found to be invalid when more experimental data become available. The frequencies near 1130 cm.$^{-1}$ of the 3-ethyl paraffins are remarkably constant. The 1080 cm.$^{-1}$ infra-red frequencies of the 4-methyl paraffins are presumably analogous to those already discussed for molecules with an internal quaternary carbon atom

(Section 6). The various series observed in the region 970—870 cm.$^{-1}$ can be correlated with those found near 955 cm.$^{-1}$ in the Raman spectra and 920 cm.$^{-1}$ in the infra-red spectra of paraffins with an *iso*propyl group. The weak bands near 550 cm.$^{-1}$ in the spectra of the 3- and 4-methyl paraffins can probably be correlated with similar series found at slightly lower frequencies for paraffins with an *iso*propyl group.[5]

Data are also available for some twelve molecules having an internal tertiary carbon atom together with a *tert.*-butyl group or an internal quaternary carbon atom. The prominent features which can be attributed to the internal tertiary carbon atom can also be recognised in the spectra of these more complex molecules.

(*b*) **Paraffins with Two Adjacent Tertiary Carbon Atoms.**—Data are available for a fair number of paraffins with two adjacent tertiary carbon atoms,

$$i.e., \text{ a } C_6 \text{ structural unit } \underset{\underset{C}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{C}{|}}{\overset{\overset{H}{|}}{C}}-C\ ;$$

i.e., a C_6 structural unit C—C—C—C ; this may be terminal (as in the

2 : 3-dimethyl paraffins) or, in a more limited number of cases, internal.[5] It is desirable to discuss whether any of the characteristic frequencies already noted for molecules with a single tertiary carbon atom persist in these more complex paraffins. Accordingly, Table 9 lists the relevant data on the liquid spectra of some molecules with this C_6 structural unit, but does not include any of the more complicated examples. With regard to the interpretation of the frequencies dealt with in the following discussion, it should be emphasised that in these rather complex paraffins significant disturbing effects due to the presence of mixtures of rotational isomers are to be expected, as in the case of 2 : 3-dimethylbutane already noted.[61]

Col. 3 gives a series of Raman lines near 1160 cm.$^{-1}$ which usually have no infra-red counterparts ; in paraffins with an *iso*propyl group the corresponding frequencies always appear in both types of spectra. Col. 4, on the other hand, shows a series of prominent infra-red bands of nearly constant frequency (near 1125 cm.$^{-1}$) ; no corresponding Raman lines can be recognised ; these bands are absent in other paraffins having a tertiary carbon atom. These two series taken together provide the most reliable guide for the identification of this C_6 structural unit.

The spectra of paraffins with this C_6 structural unit are difficult to analyse in the range 1100—900 cm.$^{-1}$. Three or four Raman lines occur sporadically and the infra-red spectra show a large number of small bands. On the whole, absorption is weaker if the C_6 unit is terminal. Most molecules show a band near 1070 cm.$^{-1}$ (col. 5) ; but this feature is not usually prominent (compare Table 10). Some molecules also have somewhat variable frequencies near 1040 cm.$^{-1}$ in both Raman and infra-red spectra. These series are evidently analogous to those discussed for other paraffins with a tertiary carbon atom, and can probably also be assigned to CH_3 rocking modes. The absorption band near 1010 cm.$^{-1}$ shows up regularly for molecules with an ethyl group. Below this frequency there are indications of a variable series near 960 cm.$^{-1}$ and a more constant series of

infra-red bands near 915 cm.$^{-1}$ (col. 6). Possibly they are analogous to those found near 955 and 920 cm.$^{-1}$ for paraffins with an *iso*propyl group. None of the series in the range 1100—900 cm.$^{-1}$ is very helpful in identifying this C_6 structural unit.

Col. 7 shows that it is possible to distinguish prominent polarised Raman lines (770—740 cm.$^{-1}$) which, by analogy with the paraffins previously discussed, may be assigned to symmetrical skeletal vibrations. The fre-

TABLE 9. *Characteristic frequencies (in cm.$^{-1}$) of paraffins with two adjacent tertiary carbon atoms in the liquid state* *

Paraffin		ν_{C-C} or CH$_3$ rocking				ν_{C-C}	δ_{C-C}	Refs	API Nos
2 : 3-Dimethylbutane	IR	—	1129	1066	921	—	480	13	656, 670
	R	1165	—	—	—	754	477	14	
2 : 3-Dimethylpentane	IR	1166	1122	1075	918	740	464	13	658, 672
	R	1166	—	—	915	747	459	14	
2 : 3-Dimethylhexane	IR	—	1127	1075	919	756	—	13	661, 673
	R	1163	—	—	—	765	457	14	
2 : 3-Dimethylheptane	IR	—	1126	1080	918	760	NI	2	
	R	1159	—	—	926	760	469	15	
2 : 3-Dimethyloctane	IR	—	1128	1080	915	770	NI	2	
	R	← No observations →						—	
3 : 4-Dimethylhexane	IR	1160	1122	1071	—	736	467	13	664, 673
	R	1166	—	—	—	738	471	14	
3 : 4-Dimethylheptane	IR	—	1122	1063	920	765	NI	2	
	R	1166	—	—	—	751	—	14	
4 : 5-Dimethyloctane	IR	—	1124	1077	910	—	NI	2	
	R	← No observations →						—	
Infra-red intensity .		w	st	m	m	w	w		
Raman intensity . .		m	abs.	abs.	usually abs.	m	w		
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)		(9)

* For the meaning of symbols and abbreviations see foot of Table 1.

quencies are moderately constant ; the corresponding infra-red bands are weak. This series gives a valuable indication of the presence of the C_6 structural unit. It is also possible to pick out a fairly reliable series of Raman lines (col. 8) which lie in the region of the spectrum in which the skeletal deformation modes are found (480—460 cm.$^{-1}$). Smith [5] has found evidence for a series of weak bands near 550 cm.$^{-1}$ similar to those mentioned for other molecules with a single tertiary carbon atom (pp. 41, 47).

Some eight other paraffins with adjacent tertiary carbon atoms have been examined. It is satisfactory to find that all the frequencies listed

in Table 9 may be found in their spectra ; those near 1125 and 755 cm.$^{-1}$ remain prominent, and so seem to provide a reliable method of identifying this C_6 structural unit.

(c) **The Ethyl Group.**—Many of the paraffins discussed in the preceding sections possess one or more ethyl groups, and two characteristic frequencies have already been noted that can definitely be attributed to this radical, *viz.*, an infra-red band near 1010 cm.$^{-1}$, which may possibly be assigned to a carbon–carbon stretching vibration, and one near 770 cm.$^{-1}$ attributable to a CH_2 rocking mode. In this connection it is noteworthy that Kohlrausch,[110] working some years ago on the Raman spectra of other types of molecule, was able to recognise a Raman line near 1000 cm.$^{-1}$ as characteristic of the ethyl group. No definite evidence is available to suggest that the other CH_2 deformation modes appear at frequencies differing from those discussed on p. 23 ; nor can any series (other than the 1010 cm.$^{-1}$ bands) be found which might be assigned to the two CH_3 rocking modes of the ethyl group. Presumably they occur in the complicated range 1150—850 cm.$^{-1}$; either they are not sufficiently prominent to be recognised, or they coincide with the frequencies of other radicals. The deformation skeletal mode of the $CH_3 \cdot CH_2 \cdot C$ group must occur below 500 cm.$^{-1}$, but cannot be identified among the many Raman lines that most paraffins show in this region.

8. Conclusion

We conclude with some general remarks on the preceding sections. First, it must be emphasised that the larger the number of molecules of a particular class the more reliable are the characteristic frequencies. Secondly, where there is evidence for disturbing effects due to the presence of mixtures of rotational isomers, the interpretation of the characteristic frequencies must be considered tentative. In this connection there is no doubt that investigations of the solid-state spectra would prove as illuminating for other molecules as they have been for the *n*-paraffins.

Thirdly, examination of the spectra of paraffins which have two or more structural units of the types described in the earlier sections suggests that in many cases each unit retains at least some of its characteristic frequencies. This is particularly apparent for the *tert.*-butyl group, but in other cases some exceptions have been noted,[5] and accidental coincidences in frequencies become more probable the more complex the molecule. Fourthly, it must be admitted that the use of characteristic frequencies to recognise certain groupings is to some extent a matter of experience. This is particularly true of the region below 500 cm.$^{-1}$ in the Raman spectra and for infra-red bands generally. The absorption spectra of the larger paraffins between 1350 and 800 cm.$^{-1}$ tend to degenerate into a somewhat puzzling area of bands of moderate intensity with complicated splitting patterns, and only after comparison with those of smaller molecules of the same type do the regularities become apparent.

Finally, it is desirable to indicate those regions of the spectra which

[110] *Op. cit.*, 1943, p. 228.

TABLE 10.   *Characteristic frequencies (in cm.$^{-1}$) of paraffins in the liquid state*

(The frequencies of less well established series are shown in parentheses.   Frequencies marked with an asterisk are particularly prominent.)

Frequency range, cm.$^{-1}$	Infra-red intensity	Raman intensity	Classes of paraffin and comments	Table
* 1470—1440 .	strong	strong	CH_3 asymm. δ, CH_2 bending	
* 1397, 1370 .	strong	absent ⎫		
* 1385, 1370 .	strong	absent ⎪	CH_3 symm. δ ⎰ tert.-butyl	
* 1384, 1365 .	strong	absent ⎬	⎰ isopropyl	
* 1380 . . .	strong	absent ⎭	⎱ 3 : 3-dimethyl	
			⎱ CH_3 isolated	
* 1360—1330 .	obscured	prominent	CH deformation	
1370 . . .	medium	absent ⎫		2
1355 . . .	medium	absent ⎬	n-paraffins, hydrogen deformation	2
1340 . . .	medium	absent ⎭		2
* 1310—1300 .	medium	prominent	CH_2 wagging or twisting	
* 1260—1250 .	strong	medium ⎫	tert.-butyl	4
* 1220—1200 .	strong	medium ⎭		4
* 1215—1210 .	strong	medium ⎫	internal quaternary carbon atom	7
* 1200—1190 .	strong	weak ⎭		7
* 1175—1165 .	strong	medium	isopropyl	6
* 1165—1150 .	weak	medium	adjacent tertiary carbon atoms	9
* 1160—1150 .	m. strong	medium	internal tertiary carbon atom	8
* 1150—1140 .	strong	medium	isopropyl	6
* ∼ 1140 . .	medium	prominent	n-paraffins	2
* 1130—1120 .	strong	absent	adjacent tertiary carbon atoms	9
(1130) . .	active	·absent	3-ethyl	
1120—965 .	medium	weak	n-paraffins	2
(1100—1080)	active	active	internal quaternary carbon atom	
1080—1065 .	medium	absent	adjacent tertiary carbon atoms	9
(∼ 1080) . .	active	absent	4-methyl	
* ∼ 1070 . .	not promin.	prominent	n-paraffins	2
1045—1035 .	weak	medium	internal tertiary carbon atom	8
(∼ 1040) . .	active	active	internal quaternary and adjacent tertiary carbon atoms	
* 1020—1000 .	strong	medium	ethyl	⎰ 7 ⎱ 8
(∼ 960) . .	active	active	3-methyl and adjacent tertiary carbon atoms	
* 960—950 . .	medium	medium	isopropyl	6
(950) . . .	active	absent	4-methyl	

TABLE 10 (*cont.*)

Frequency range, cm.$^{-1}$	Infra-red intensity	Raman intensity	Classes of paraffin and comments	Table
($\sim$ 930) . .	active	active	internal quaternary carbon atom	
* 930—925 .	medium	medium	*tert.*-butyl	4
* $\sim$ 920 . .	m. strong	medium	*iso*propyl	6
920—915 . .	medium	absent	adjacent tertiary carbon atoms	9
(920—910) .	active	active	internal quaternary carbon atom	
(900—890) .	active	active	4-methyl	
($\sim$ 890) . .	active	active	3-ethyl	
($\sim$ 880) . .	active	active	3-methyl	
* $\sim$ 890 ⎫		prominent		2
* 870—840 ⎬ .	weak	polarised	*n*-paraffins, ν_{C-C}	2
* 840—810 ⎭				2
850—815 . .	weak	medium	internal tertiary carbon atom, ν_{C-C}	8
* 835—795 . .	medium	prominent	*iso*propyl, ν_{C-C}	6
(770—750) .	obscured	prominent	3-ethyl, ν_{C-C}	
770—740 . .	weak	medium	adjacent tertiary carbon atoms, ν_{C-C}	9
* $\sim$ 770 . .	strong	absent	CH_2 rocking, ethyl	
* 750—710 . .	weak	prominent polarised	*tert.*-butyl, ν_{C-C}	4
* 750—685 . .	weak	prominent polarised	internal quaternary carbon atom, ν_{C-C}	7
* $\sim$ 740 . .	strong	absent	CH_2 rocking, *n*-propyl	
* $\sim$ 720 . .	strong	absent	CH_2 rocking, 5 carbon chain	
($\sim$ 550) . .	weak		3-methyl, 4-methyl, adjacent tertiary carbon atoms	
(550—530) .	weak		*iso*propyl	
490—480 . .	weak	weak	internal quaternary carbon atom, δ_{C-C}	7
480—460 . .	weak	weak	adjacent tertiary carbon atoms, δ_{C-C}	9
465—430 . .	NI	medium	*iso*propyl, δ_{C-C}	6
450—415 . .	NI	medium	internal tertiary carbon atom, δ_{C-C}	8
* 425—150 . .	NI	prominent polarised	*n*-paraffins, δ_{C-C}	2
370—255 . .	NI	medium polarised	*iso*propyl, δ_{C-C}	6
360—280 . .	NI	medium polarised	*tert.*-butyl, δ_{C-C}	4
(350—305) .	NI	weak polarised	internal quaternary carbon atom, δ_{C-C}	

are most profitable for the purposes of structural identification.   Table 10 gathers together all the characteristic frequencies for the liquid paraffins which have been listed or discussed in the preceding sections, and includes also the hydrogen deformation frequencies common to all types of molecule. Examination of this table suggests that the infra-red bands in the range 1260—1100 cm.$^{-1}$ and the polarised Raman lines between 900 and 650 cm.$^{-1}$ are the features likely to be most valuable for this purpose, since they are prominent and on the whole show little variation in frequency.   In the intermediate region the series are less satisfactory since they often lack one or both of these desirable characteristics and some are common to several classes of paraffin.   These series and other weaker frequencies are not in themselves sufficient to characterise the various structural groupings.