Vibrational Frequency Assignments for Paraffin Hydrocarbons; InfraRed Absorption Spectra of the Butanes and Pentanes

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The infra-red absorption spectra from 2 to 15μ are given for *n*-butane, isobutane, *n*-pentane, isopentane, and neopentane. Vibrational assignments for these molecules and for propane are deduced. The band positions correlatable with particular types of vibration of various hydrocarbon groupings are discussed.

COMPLETE or almost complete vibrational frequency assignments are known for the hydrocarbons methane, ethane, ethylene, acetylene, methylacetylene, and dimethylacetylene.[1,1a] Pitzer[2a] has discussed the assignment for propane, isobutane and neopentane have been discussed by Pitzer and Kilpatrick[2b] and neopentane by Young, Koehler, and McKinney.[2c] In this paper, the assignments for propane, the butanes, and the pentanes are considered, with some modifications of the previous assignments, and an attempt is made to generalize these results toward the understanding of more complex paraffin spectra.

I. GENERAL CONSIDERATIONS

The general problem is to correlate observed infra-red and Raman frequencies with specific vibrations of groups. Strictly speaking, a given normal mode of vibration involves motion of all the atoms in a molecule. However, to a certain approximation, the normal modes may be assigned to particular vibrations of small groups of atoms, the motions of these atoms being only weakly coupled with other atoms in the molecule.[3]

From the vibrational assignments of the simpler molecules referred to in the introduction and from a comparative examination of the spectra of a much larger number of other organic molecules, certain general frequency regions have come to be recognized. Thus, the vibrations involving principally the stretching of CH bonds give rise to the numerous infra-red bands and Raman shifts in the interval 2900 to 3100 cm^{-1}. Similarly, vibrations due mainly to changes in HCH angle give rise to frequencies near 1400 cm^{-1}. These frequencies appear as the well marked infra-red bands near 6.8μ and 7.2μ present in the spectra of all paraffin hydrocarbons[4] and as the strong shift near 1460 cm^{-1} present in their Raman spectra.[5] Specifically, the three HCH bending vibrations of a methyl group combine to give a "symmetric" methyl bending vibration (symmetry representation A_1 of the C_{3v} point group about the carbon atom) which appears near 1380 cm^{-1} and is strong in the infra-red but weak or missing in the Raman; and a doubly degenerate "antisymmetric" pair of vibrations (symmetry representation E) appearing near 1460 cm^{-1} and strong in both the Raman and infra-red.[6] The methylene group of

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[1] References for and discussions of these cases are given by G. Herzberg, *Infra-Red and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), Ch. III.

[1a] Recently Pitzer and co-workers have given assignments based on careful consideration of recent spectra, of propylene and certain butenes [J. Res. Nat. Bur. Standards 38, 191 (1947)], of cyclopentane [J. Am. Chem. Soc. 69, 2483 (1948)], and of cyclohexane and some substituted cyclohexanes [J. Am. Chem. Soc. 69, 2488 (1948)].

[2a] K. S. Pitzer, J. Chem. Phys. 12, 310 (1944).

[2b] K. S. Pitzer and J. E. Kilpatrick, Chem. Rev. 39, 435 (1946).

[2c] C. W. Young, J. S. Koehler, and D. S. McKinney, J. Am. Chem. Soc. 69, 1410 (1947).

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[3] G. Herzberg, *Infra-Red and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), pp. 192–201.

[4] See references to spectra of paraffins given by R. S. Rasmussen and R. R. Brattain, J. Chem. Phys. 15, 120 (1947); also American Petroleum Institute Research Project 44, Infra-Red Absorption Spectrograms.

[5] K. W. F. Kohlrausch and F. Köppl, reference 12b.

[6] These symmetry designations apply to the local symmetry of the methyl group and are used here merely as descriptive devices. The over-all molecular symmetry may cause the degeneracy to disappear or may create new degeneracies involving more than one methyl group.

the system $C-CH_2-C$ gives rise to a single HCH bending vibration of frequency near 1460 cm^{-1}, as judged from cycloparaffins.

The region from 1350 cm^{-1} to 650 cm^{-1} includes two further types of vibration, *viz.*, CC stretching vibrations and motions involving changes of HCC angles, while the low frequency region (<700 cm^{-1}) includes the CCC bending vibrations. It will be desirable to consider separately the skeletal vibrations (CC stretching and CCC bending) and the HCC bending vibrations. The former will, in general, be more highly dependent on the geometry of the molecule, with normal vibrations not being localized in particular bonds but involving motion of the whole skeleton. This follows from the near equality of force constants and masses of the vibrating groups, leading to a large amount of coupling between motions of adjacent bonds and bond angles.

In contrast, the HCC bending vibrations might be expected to exhibit a certain amount of regularity irrespective of the particular carbon skeleton involved. This follows from the fact that the motions are essentially those of light hydrogen nuclei attached to the heavy carbon skeleton and presumably would not couple strongly with or through the skeleton. As has been already the practice of the Harvard group in normal frequency calculations of simpler molecules, the HCC bending motions will be described as shown in Fig. 1. The methyl rocking vibrations are essentially equivalent motions at right angles to each other, as are the two tertiary CH wagging vibrations. These motions correspond to the correct orthogonal combinations of the angle displacement coordinates $\Delta\beta$, consistent with the local symmetry about the carbon atom of interest. In the notation of Fig. 1, these combinations are (exclusive of normalization factors):

methyl group rocking:
$$\Delta\beta_1-\Delta\beta_2, \quad \Delta\beta_1+\Delta\beta_2-2\Delta\beta_3;$$
methylene group rocking:
$$\Delta\beta_{11}-\Delta\beta_{12}+\Delta\beta_{21}-\Delta\beta_{22};$$
methylene group twisting:
$$\Delta\beta_{11}-\Delta\beta_{12}-\Delta\beta_{21}+\Delta\beta_{22};$$
methylene group wagging:
$$\Delta\beta_{11}+\Delta\beta_{12}-\Delta\beta_{21}-\Delta\beta_{22};$$
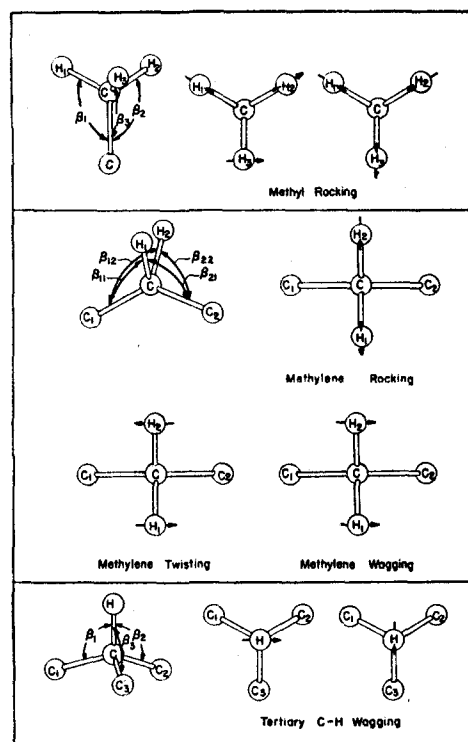
FIG. 1. Types of HCC vibrations.

tertiary CH wagging:
$$\Delta\beta_1-\Delta\beta_2, \quad \Delta\beta_1+\Delta\beta_2-2\Delta\beta_3.$$

The apparent degeneracy in the two methyl rocking and the two tertiary CH wagging vibrations may, of course, be removed when the remainder of the molecule is taken into account. Particularly for the methyl rocking frequencies, the two motions shown may occur with quite different frequencies because of different interactions with other groups of the molecule (e.g., see propane below).

The remainder of this paper is concerned with the assignment for these frequencies in the range less than 1350 cm^{-1}, i.e., the skeletal frequencies and HCC bending frequencies.

II. METHOD AND EXPERIMENTAL DATA

The molecules whose frequency assignments are considered here in detail are propane, *n*-butane, isobutane, *n*-pentane, isopentane, and neopentane.

The general method used is to make as complete an assignment as possible for the simpler molecules, where infra-red and Raman selection
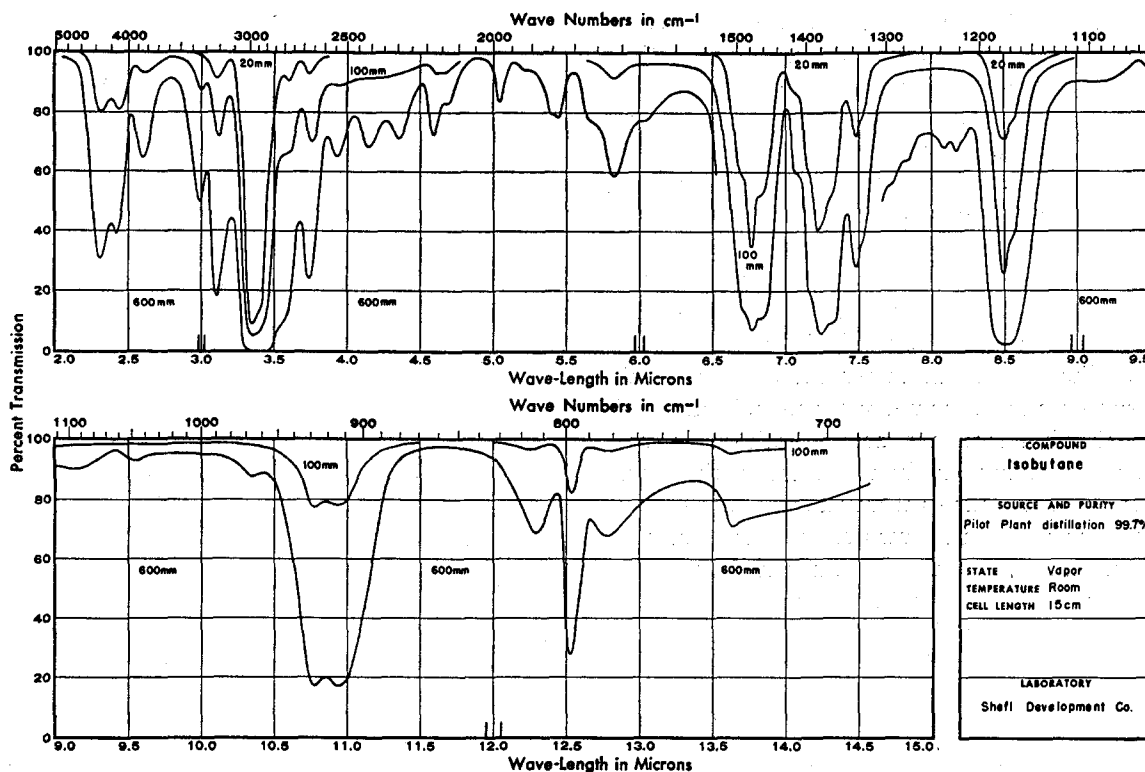
FIG. 2. Isobutane.

rules can be used to advantage. Simplified force constant treatments have been made on certain models. It was not expected that these calculations would give close agreement with experiment, but they were used merely to give indications of the general regions in which given types of vibrations were to be expected. The results on these simpler molecules are then compared with spectra of higher molecules of the same type and thus afford some guide as to the interpretation of groups of frequencies even where specific assignments of individual infra-red bands or Raman lines are impossible.

No attempt has been made to carry out complete force-constant treatments. Improved methods of setting up and solving the secular determinants[7, 8] and the demonstrated validity of the transfer of physically similar force constants from one molecule to another[9] have brought such calculations within reason for

molecules of the complexity of those considered here. However, lack of *a priori* knowledge of the correct cross term interactions to include in the potential function and of the effect of anharmonicity made it seem more worth-while to follow a more empirical approach for the present. However, further elucidation of some of the unknown or doubtful frequencies will ultimately require force constant calculations.

Experimental infra-red data used are, for propane, the high resolution grating absorption spectrum given by Wu and Barker,[10] and, for the butanes and pentanes, the vapor spectra shown in Figs. 2 to 6, obtained by means of the rocksalt prism spectrograph of this laboratory.[11] Wave-lengths, frequencies, and intensities are given in Tables I to V.

[7] E. B. Wilson, Jr., J. Chem. Phys. 7, 1047 (1939); 9, 76 (1941).

[8] B. L. Hicks, J. Chem. Phys. 8, 569 (1940).

[9] B. L. Crawford, Jr., and S. R. Brinkley, Jr., J. Chem. Phys. 9, 69 (1941).

[10] V. L. Wu and E. F. Barker, J. Chem. Phys. 9, 487 (1941). Since it is difficult to estimate intensities from the grating curves, those shown in Fig. 7 have been taken from salt-prism spectra from this laboratory.

[11] This instrument, the methods used in obtaining curves, and the accuracy achieved are described by R. S. Rasmussen and R. R. Brattain, J. Chem. Phys. 15, 120 (1947).
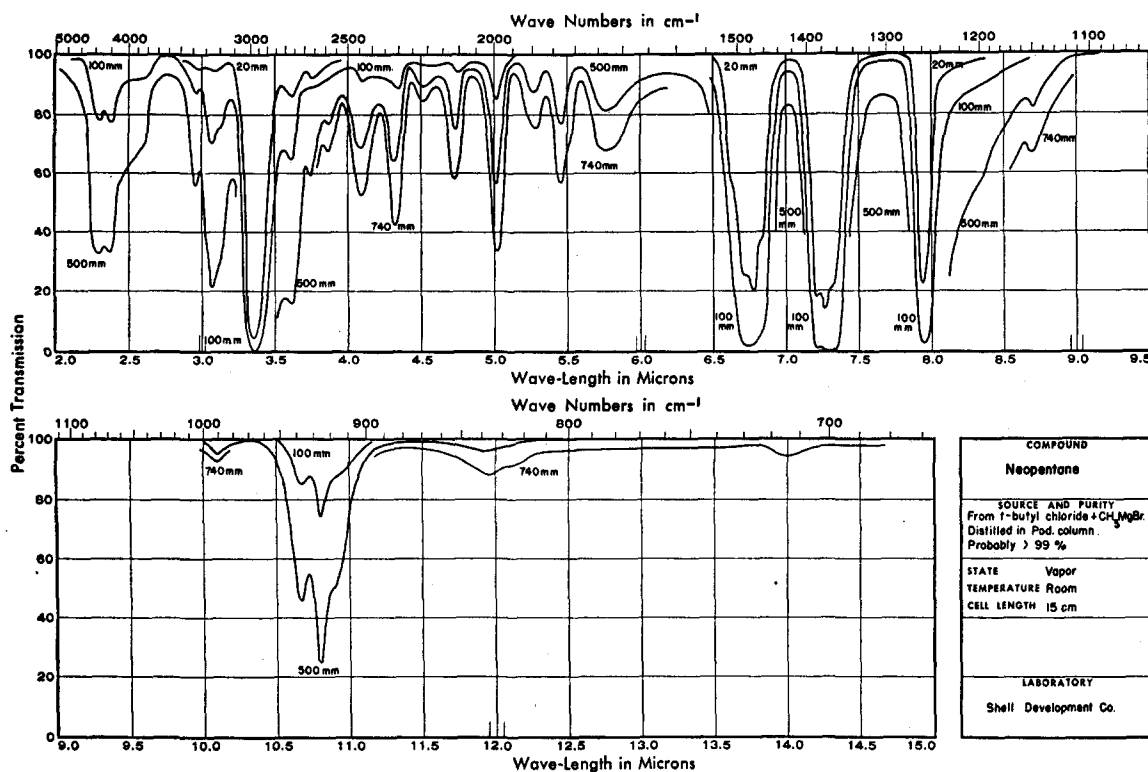
FIG. 3. Neopentane.

Raman data were taken from various literature sources,[12] average values being used. All Raman data refer to the liquid state. Infra-red and Raman data are plotted together for easy comparison in Fig. 7. Since the resolution was not sufficient to deduce the centers of infra-red bands with certainty in all cases, the band positions shown are reasonable estimates, taking into account probable envelope shapes.

III. PROPANE

Pitzer[2] has discussed the frequency assignment for propane, with which that advanced here

agrees in the main. However, the present assignment differs in a significant point, so that further discussion is required. As indicated in Fig. 7, there are nine infra-red bands in the region of interest (700 to 1350 cm^{-1}). Except for the extremely weak band at 1250 cm^{-1}, observed in high pressure spectra and certainly an overtone, the symmetry types of these bands are unambiguously determined from the spectrum given by Wu and Barker.[10] The symmetry designations shown in Fig. 7 have the following meanings:

| | Symmetry to reflection through: | | |
	CCC plane	Central CH$_2$ plane	Activity
A_1	+	+	IR, R
A_2	−	−	R
B_1	+	−	IR, R
B_2	−	+	IR, R

In accord with Kohlrausch and Köppl[12b] and Pitzer, the 870-cm^{-1} and 1053-cm^{-1} bands may be assigned as the symmetric and antisymmetric CC stretching frequencies. This follows from their intensities in the Raman spectrum, their symmetries from the infra-red, and simple valence-type force constant considerations. The

[12a] S. Bhagavantam, Ind. J. Phys. 6, 595 (1931): propane, n-butane, isobutane.

[b] K. W. F. Kohlrausch and F. Köppl, Zeits. f. physik. Chemie 26B, 209 (1934): propane, n-butane, isobutane, n-pentane, neopentane.

[c] J. W. Murray and D. H. Andrews, J. Chem. Phys. 1, 406 (1933): n-butane.

[d] R. Ananthakrishnan, Proc. Ind. Acad. Sci. 5A, 285 (1937): n-butane; ibid. 3A, 527 (1936): isobutane.

[e] P. A. Bazhulin, A. F. Platé, O. P. Solovova, and B. A. Kazanskii, Bull. Acad. Sci. U.R.S.S., Classe de sci. chim. 1941 (1), 13; Survey For. Pet. Literature, Sept. 5, 1941: n-pentane, isopentane.
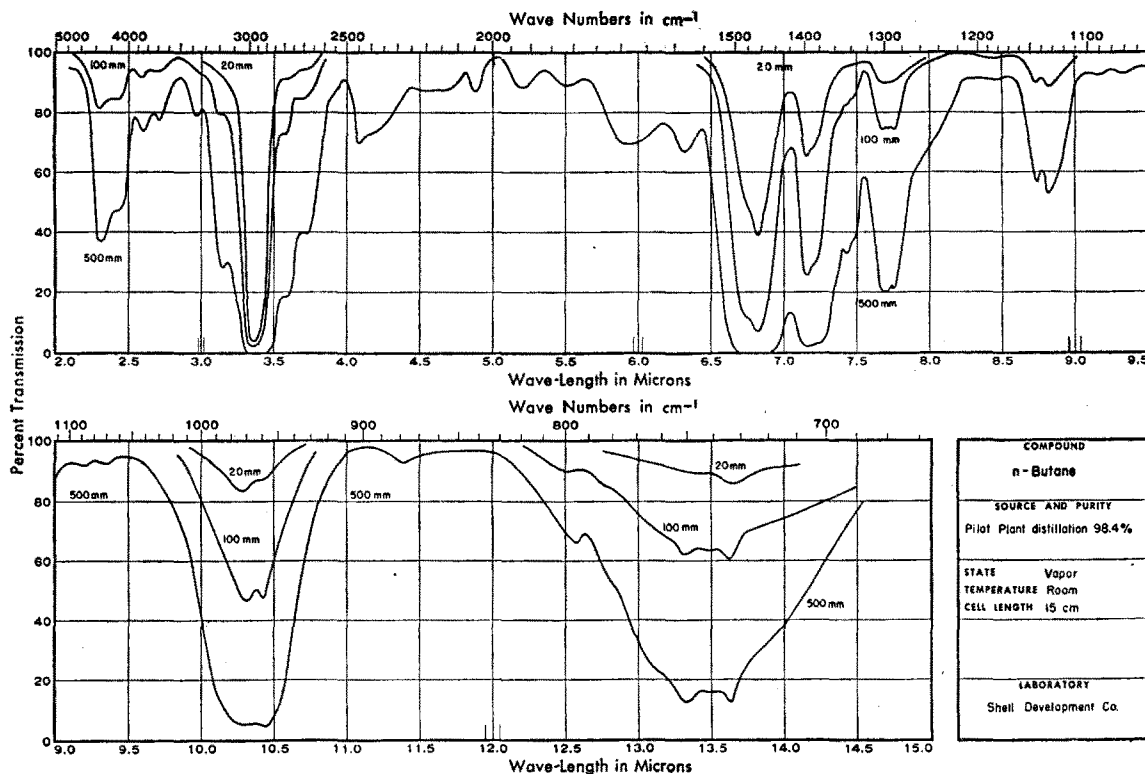
[f] H. Kopper, R. Seka, and K. W. F. Kohlrausch, Monats. 61, 397 (1932): isopentane.

[g] D. H. Rank and E. R. Bordner, J. Chem. Phys. 3, 248 (1935): neopentane.

FIG. 4. n-Butane.

CCC bending frequency lies at 374 cm⁻¹, from Raman work.[12] Wu and Barker[10] failed to find an analogous band in the infra-red, presumably because of its unexpectedly low intensity. As discussed by Pitzer, the weak 720-cm⁻¹ band is taken to be a difference band from an excited methyl torsion level.

There remain the four methyl rocking frequencies (A_1, A_2, B_1, B_2) and the three methylene frequencies (A_2, B_1, B_2) to be assigned. Empirical evidence indicates that the 748-cm⁻¹ infra-red band and the 1278-cm⁻¹ Raman line are associated with the CH₂ group. This follows from the fact that all aliphatic hydrocarbons containing CH₂ groups show infra-red bands at 700 to 800 cm⁻¹, which appear stronger the more CH₂ groups are present,[4] and similarly for the Raman spectral lines near 1300 cm⁻¹, of which the propane 1278 cm⁻¹ is the prototype.[12b] A force constant calculation for the CH₂X₂-type molecule, where X=methyl, using force constants from independent sources, yields the following values for the CH₂ frequencies: rocking (B_2), 761 cm⁻¹; twisting (A_2), 1175 cm⁻¹;

wagging (B_1), 1205 cm⁻¹ (see Appendix B for details of calculation). By using these approximate values as a guide, the observed 748 cm⁻¹, 1278 cm⁻¹, and 1338 cm⁻¹ frequencies are to be assigned to these vibrations, in keeping with the symmetry types of the observed 748-cm⁻¹ and 1338-cm⁻¹ bands, and with the fact that the A_2 frequency at 1278-cm⁻¹ should appear in the Raman but not the infra-red. Any other assignment consistent with the symmetries of the infra-red bands would lead to disagreements with the calculated results of the order of 400 cm⁻¹, which is unlikely.

The remaining unassigned bands at 922 cm⁻¹ (B_1), 1160 cm⁻¹ (A_1), and 1179 cm⁻¹ (B_2) must be assigned as the methyl rocking frequencies of the indicated symmetries. The fourth methyl rocking frequency, of type A_2 and hence infra-red inactive, has not been observed. It is noteworthy that the two methyl rocking vibrations which involve the close approach of the methyl groups are the A_1 (in the carbon plane) and B_2 (out of the carbon plane) and that these two exhibit the higher frequency values, near 1170 cm⁻¹. The
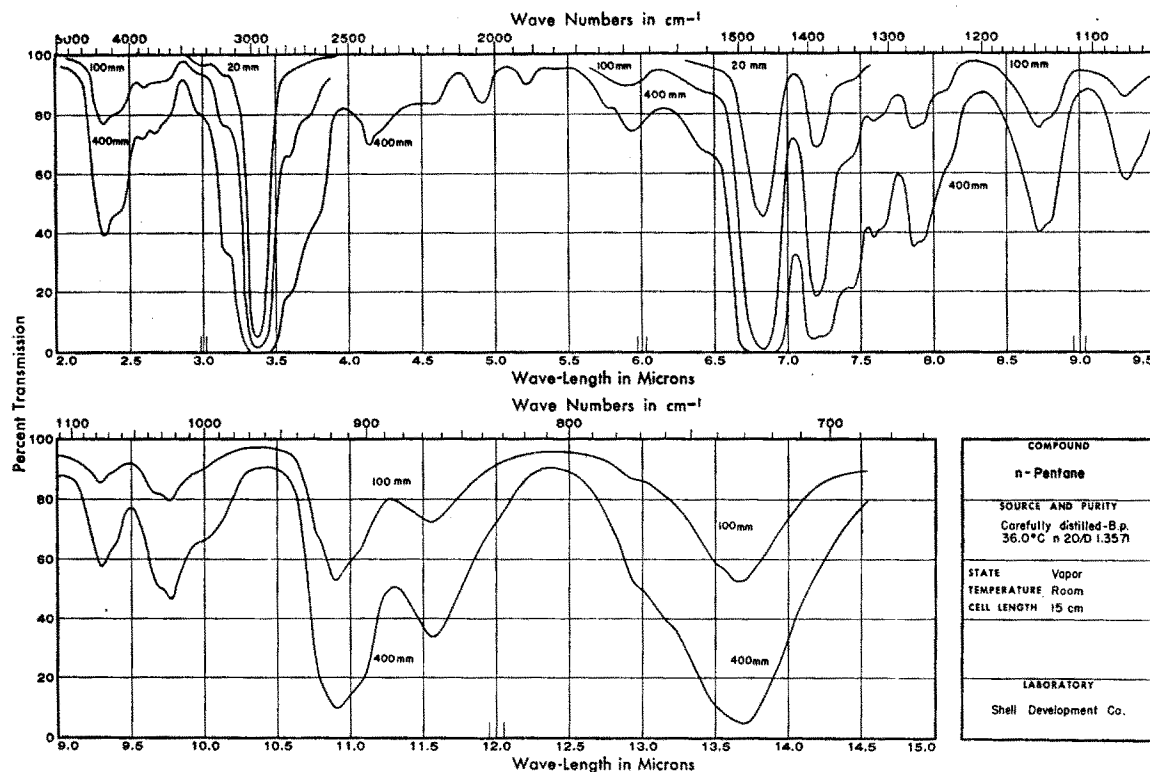
FIG. 5. *n*-Pentane.

B_1 vibration, in which one methyl group moves away from and the other toward the twofold axis, has the lower value of 922 cm^{-1}. If the higher values of the A_1 and B_2 frequencies are attributed to steric repulsion of the methyl groups, it would be anticipated that the A_2 frequency would be in the 900-cm^{-1} region; like the B_2, it is a vibration in which the methyl groups do not approach each other closely, one moving out of the carbon plane on one side while the other moves out on the other.

The important point in the above conclusions is the assignment of the low 748-cm^{-1} frequency to the methylene rocking vibration. Previously, this band had been considered as a carbon-stretching frequency or a methyl-rocking frequency. The former possibility, besides being implausible on other grounds, has been rather definitely contraindicated by recent work by Sheppard and Sutherland[13] on completely deuterated hydrocarbons. It was shown that the ~720-cm^{-1} band of long chain paraffins, which

is the analog of the propane 748-cm^{-1} band, arose from a CH and not a C—C type of vibration. Pitzer[2] considered the two B_2 vibrations (CH$_2$ wagging and CH$_3$ out-of-plane wagging) to interact strongly, so that the two B_2 frequencies (748 cm^{-1} and 1179 cm^{-1}) each corresponded to a mixed vibration involving both motions.**

** At the suggestion of Dr. Pitzer, the present point of view is further elucidated here. To a certain extent, the names given to these frequencies are merely a matter of convenient labeling, since certainly there is interaction of some extent between them, neither corresponding to a pure vibration of the one sort or other. In order accurately to assess the participation of each motion in each of the true normal coordinates corresponding to the observed frequencies, a normal coordinate analysis of reasonable accuracy would have to be made. However, it is felt by the author that there is good ground for the proposed assignment, and that actually the 748-cm^{-1} band corresponds to a vibration essentially only of the CH$_2$ group, and the 1179-cm^{-1} band similarly for the CH$_3$ groups. The reasons follow: (1) The frequency calculation made on the simplified model CH$_2$X$_2$ (X=CH$_3$; see Appendix B) indicated the CH$_2$ wagging frequency to be in the 750-cm^{-1} region, so it is not necessary to adduce any large amount of interaction with CH$_3$ vibrations to explain the observed position at 748 cm^{-1}. (2) As described later, and as also suggested by Sutherland,[13] the strong bands of higher paraffins at 720–780 cm^{-1} are attributable to vibrations of CH$_2$ chains. The 748-cm^{-1} band of propane seems clearly the prototype of these, and its occurrence in the same region

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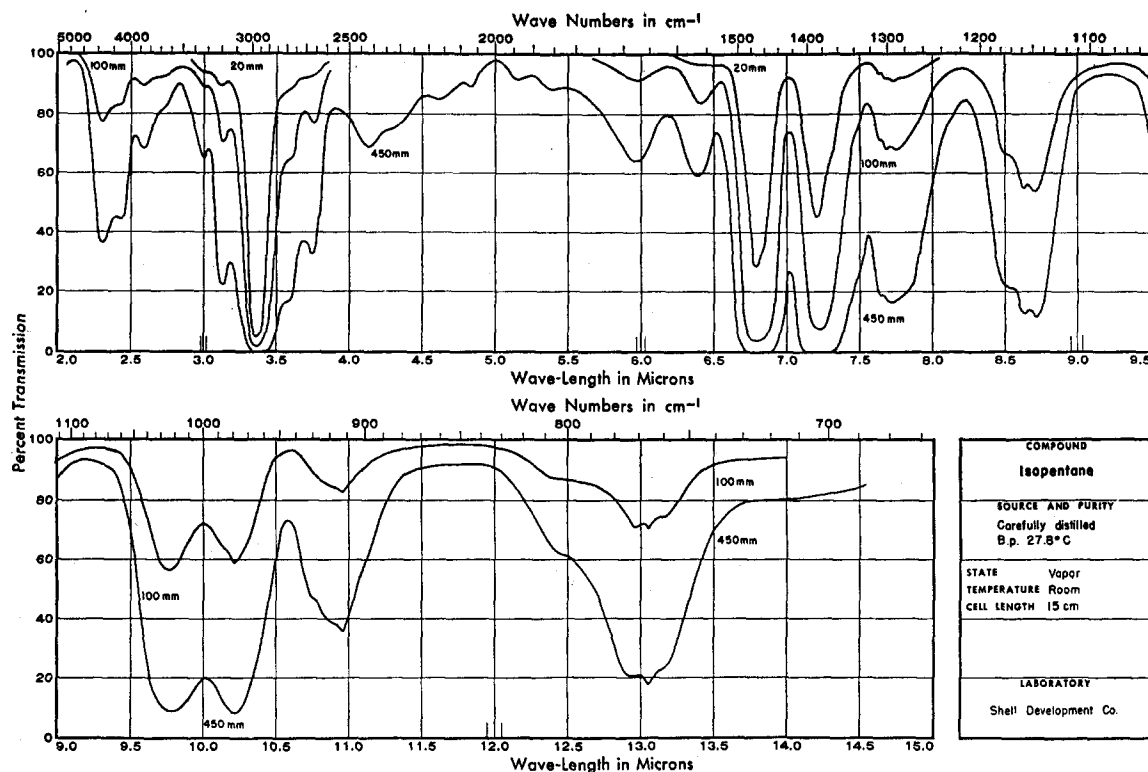[13] N. Sheppard and G. B. B. M. Sutherland, Nature 159, 739 (1947).

FIG. 6. Isopentane.

IV. ISOBUTANE AND NEOPENTANE

Isobutane and neopentane will be considered next, since there is no ambiguity in their structures and since with ethane and propane they form a related series obtained by successive substitution of methyl groups on methane.

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would indicate only a small interaction with the CH$_3$ vibrations. (3) Further, the exact position of these CH$_2$ chain bands are a function of the CH$_2$ chain length, irrespective of the groups (methyl or otherwise) that terminate the chain; whereas, an 1179-cm^{-1} band is observed with great constancy for all molecules of the type (CH$_3$)$_2$CHR(R=H or primary radical). (4) We have recently obtained spectra of 1-deutero- and 2-deutero-propane, and find for the 2-d compound a disappearance of the 748 cm^{-1}, a new band at 667 cm^{-1} appearing ascribable to the C—D wagging; whereas, for the 1-d compound a band is found with two Q branches at 743 and 702 cm^{-1}. While this splitting is not understood, it is clear that the deuterium substitution which has the profoundest effect on the 748-cm^{-1} band is that on the 2 position, not the 1.

The reason for Pitzer's assignment of the 748-cm^{-1} band as involving, at least partly, a CH$_3$ vibration follows mainly from a consideration of the ethane spectrum. It is definitely known that one of the CH$_3$ rocking motions of ethane is rather low (827 cm^{-1}), so it seems reasonable to expect analogous motions of the methyl groups of propane to be in this region. That this is seemingly not the case to any large extent must be ascribed simply to unforeseeable differences in kinetic interactions, and possibly also potential interactions, between the vibrations in the two cases.

Isobutane (symmetry C_{3v}) has vibrations of three symmetry types, A_1, A_2, and E, of which all three are Raman active and the A_1 and E infra-red active. Aside from the CH stretching and HCH bending vibrations and the methyl torsional oscillations, the following vibrations have to be assigned:

Skeletal:	CC stretching	$A_1, E,$
	CCC bending	$A_1, E.$

HCC bending: CH$_3$ rocking (in planes through axis) $A_1, E,$
CH$_3$ rocking (perpendicular to planes through axis) $A_2, E,$
Tertiary CH wagging $E.$

The observed frequencies are 371 (4) D, 437 (1) P (Raman[12]), and those given in Fig. 7. The Raman polarization data shown are from Ananthakrishnan.[12d] The infra-red band envelopes are unfortunately of little use in fixing the symmetry types of the absorption bands, since the molecule is sufficiently close to a spherical rotator that no

TABLE I. Wave-length, frequencies, and intensities of absorption maxima of isobutane vapor. Intensities estimated in units of 10 percent absorption; s = shoulder.

$\lambda(\mu)$	ω(cm^{-1})	I	$\lambda(\mu)$	ω(cm^{-1})	I
2.31	4330	2	7.05	1418	1s
2.43	4115	1	7.16	1397	}
2.61	3830	0	7.22·	1385·	}9
3.00	3335	0	7.32	1361	}
3.11	3215	1	7.475	1338	}5
3.35	2985	}	7.53	1328	}
3.40	2940	}9	7.72	1295	0s
3.59	2785	1s	7.83	1277	0s
3.74	2675	1	8.08	1238	0
3.93	2545	0	8.16	1225	0
4.15	2410	0	8.21	1218	0s
4.36	2295	0	8.48	1179	}
4.59	2180	0	8.56	1168	}7
4.69	2130	0s	ca. 9.18	ca. 1090	0
5.04	1984	0	9.55	1047	0
5.21	1919	0	10.34	967	0
5.39	1855	}	10.77	929	}
5.44	1838	}1	10.94	914	}2
5.67	1764	0s	12.29	814	
5.82	1718	1	12.52	799	}
6.04	1656	0s	12.77	783	}1
6.69	1495	}	13.62	734	}
6.76	1479	}9	ca. 14.1	ca. 710	}1
6.83	1464	}			

TABLE II. Wave-length, frequencies, and intensities of absorption maxima of neopentane vapor. Intensities estimated in units of 10 percent absorption; s = shoulder.

$\lambda(\mu)$	ω(cm^{-1})	I	$\lambda(\mu)$	ω(cm^{-1})	I
2.31	4330	2	5.75	1739	}
2.38	4200	2	5.85	1709	}0
2.58	3875	0s	6.63	1508	
2.96	3380	1s	6.72	1488	}
3.085	3240	2	6.78	1475	}10
3.14	3185	0s	6.85	1460	
3.37	2965	10	7.22	1385	}
3.63	2755	2s	7.27	1376	}10
3.76	2660	0s	7.33	1364	}
3.88	2575	0s	7.955	1257	9
4.10	2440	0	ca. 8.35	ca. 1200	1s
4.335	2305	1	8.71	1148	0
4.52	2210	0	10.105	990	0
4.74	2110	0	10.675	937	}
5.025	1990	1	10.80	926	}2
5.28	1894	0	10.91	917	}
5.46	1832	1	11.98	835	}
5.53	1808	0s	12.16	822	}0
			14.03	713	0

significant difference is to be expected between parallel (A_1) and perpendicular (E) bands on the basis of Gerhard and Dennison's work[14] (moments of inertia: $A = B = 83$, $C = 110$ at wt. units $\times A^2$).

A skeletal vibrational assignment which is thought by the present author to be correct has been given by Ananthakrishnan.[12d] The polarization characters of the low frequency Raman lines indicate that the A_1 bending vibration is of frequency 437 cm^{-1} and the E of frequency 371 cm^{-1}. From its high Raman intensity and polarization character, the 799-cm^{-1} frequency corresponds to the symmetrical (A_1) CC stretching vibration. The antisymmetrical (E) CC stretching vibration was assigned to the moderately strong, depolarized 965-cm^{-1} Raman line on the basis of a central force calculation by Kohlrausch and Köppl.[12b] Since Bonner[15] had assigned the 1169-cm^{-1} line to this vibration, a more detailed force constant calculation was made here, using constants from ethane and propane and using the isobutane skeletal bending frequencies (see Appendix A for details). As illustrated in Fig. 8, the trend of calculated

skeletal frequencies in the sequence ethane-propane-isobutane-neopentane offers a strong indication that the isobutane E vibration is to be assigned to the 965-cm^{-1} frequency and not the 1169-cm^{-1} one, despite the lack of close agreement between calculation and observation. A further point of interest is the extreme weakness of the CC stretching band in the infra-red at 965 cm^{-1}. In contradistinction to the Raman spectrum, where skeletal vibrations generally give rise to the strongest lines in the spectrum below 1350 cm^{-1}, these vibrations often give fairly weak infra-red bands. The HCC bending types, which are usually weak or missing in the Raman, are relatively strong in the infra-red.

Of the four methyl rocking frequencies, the 1169-cm^{-1} Raman line may be assigned, in view of its high Raman intensity, to the A_1 methyl rocking vibration. This is not contradictory to the fact that the line is depolarized, since El'yashevich and Vol'kenshtein[16] have indicated that totally symmetric bending vibrations may be highly depolarized. If the same explanation be applied here as was used for propane (i.e., that the higher methyl rocking frequencies are those in which the methyl groups approach each other most closely), then the A_1 vibration should be found, as suggested by the propane assignment, in the 1170 cm^{-1} region, since all methyl groups

[14] S. L. Gerhard and D. M. Dennison, Phys. Rev. **43**, 197 (1933).
[15] L. G. Bonner, J. Chem. Phys. **5**, 293 (1937).

[16] M. A. El'yashevich and V. V. Vol'kenshtein, Comptes rendus Acad. Sci. U.R.S.S. **41**, 366 (1943).

TABLE III. Wave-lengths, frequencies, and intensities of absorption maxima of n-butane vapor. Intensities estimated in units of 10 percent absorption; s = shoulder.

$\lambda(\mu)$	$\omega(cm^{-1})$	I	$\lambda(\mu)$	$\omega(cm^{-1})$	I
2.31	4330	2	7.43	1346	}
2.42	4130	1s	7.49	1335	}1
2.60	3845	0	7.67	1304	}
2.71	3690	0	7.71	1297	}2
2.96	3380	0s	7.76	1289	}
3.14	3185	1s	ca. 8.04	ca. 1244	0
3.25	3075	0s	8.43	1186	0
3.37	2965	10	8.74	1144	}
3.59	2785	1s	8.82	1134	}1
3.73	2680	1s	8.89	1125	}
3.93	2545	0	9.18	1089	0
4.09	2445	1	9.33	1072	0
ca. 4.26	ca. 2350	0s	ca. 10.1	ca. 990	}
ca. 4.54	ca. 2200	0	10.31	970	}5
4.70	2130	0	10.43	959	}
4.89	2045	0	11.38	879	0
5.21	1919	0	12.58	795	0
5.52	1812	0	ca. 12.78	ca. 782	0s
ca. 5.95	ca. 1680	1	ca. 13.12	ca. 762	}
6.33	1580	0	13.32	751	}
6.74	1484	}	13.50	741	}4
6.82	1466	}9	13.63	734	}
6.89	1451	}	ca. 13.98	ca. 715	}
7.16	1397	}			
7.23	1383	}7			

TABLE IV. Wave-lengths, frequencies, and intensities of absorption maxima of n-pentane vapor. Intensities estimated in units of 10 percent absorption; s = shoulder.

$\lambda(\mu)$	$\omega(cm^{-1})$	I	$\lambda(\mu)$	$\omega(cm^{-1})$	I
2.32	4310	2	7.19	1391	7
2.44	4100	1s	7.38	1355	}
2.58 •	3875	0	7.44	1344	}1s
2.68	3730	0	7.58	1319	}
2.76	3625	0s	7.65	1307	}2
2.96	3380	0s	7.85	1274	}
3.14	3185	1s	7.92	1263	}2
3.365	2970	10	8.07	1239	0s
3.59	2785	1s	8.71	1148	}
3.75	2665	1s	8.79	1138	}2
4.04	2475	0	9.30	1075	}
4.13	2420	1	9.40	1064	}1
4.23	2365	0s	9.67	1034	}
4.60	2175	0	9.78	1022	}2
4.91	2035	0	10.01	999	0s
5.21	1919	0	10.78	928	}
5.41	1848	0	10.915	916	}4
5.77	1733	0	11.09	902	}
5.93	1686	1	11.58	864	2
6.42	1558	1s	12.94	773	0s
6.78	1475	}	13.52	740	}
6.83	1464	}10	13.69	730	}4

approach each other simultaneously. The E vibrations involve approach of some groups but avoidance by others, so that their positions cannot be predicted. One of these must be the moderately intense 920-cm⁻¹ infra-red band. The other is probably the strong 1179-cm⁻¹ band. However, there is the possibility that this band represents the A_1 frequency, the difference from the Raman position being due to liquid-vapor shift. In this event, the other E frequency would probably be represented by one of the very weak bands in the 1000- to 1100-cm⁻¹ region. The A_2 methyl rocking vibration, which is infra-red inactive and does not appear in the Raman spectrum although allowed, is of the type where methyl group hydrogens do not approach closely to one another and hence is probably of a frequency near 900 cm⁻¹.

The final vibration to be considered is the tertiary CH wagging. Since the propane CH₂ wagging vibration is found at 1338 cm⁻¹, the frequency represented by the Raman line at 1324 cm⁻¹ and the infra-red band at 1335 cm⁻¹ may logically be taken for this vibration. The fact that the Raman line is depolarized is consistent with this assignment. A force constant calculation similar to that for the methylene

group of propane shows that this frequency is indeed expected to be high although, because of the approximations in the calculation, no significance can be given to the calculated value, 1113 cm⁻¹ (details of the calculation are given in Appendix B).

The above assignment is presented in Table VI. The remainder of the weak infra-red bands shown in Figs. 2 and 7 are presumably overtones or different bands. No attempt has been made to assign these, since the existence of the two methyl torsional vibrations of very low and uncertain frequency makes this pointless.

For neopentane (symmetry T_d) the following vibrations are to be assigned:

Skeletal: CC stretching	$A_1, T_2,$
CCC bending	$E, T_2,$
HCC bending: CH₃ rocking	$E, T_1, T_2,$
Infra-red active:	$T_2,$
Raman active:	$A_1, E, T_2,$
Inactive:	$T_1.$

From central force field calculations and analogy with carbon tetrachloride, Kohlrausch[12b] and Rank and Bordner[12a] have assigned the four skeletal frequencies from Raman work as: stretching, 731 (A_1), 924 (T_2); bending, 332 (E),

415 (T_2). The infra-red spectrum is consistent with this (Figs. 3 and 7) in that the 731-cm^{-1} frequency does not appear, whereas the 924-cm^{-1} one does. Also an extension of the skeletal force constant calculations made for isobutane confirms the assignment, the calculated frequencies showing a trend in agreement with the above assignment (Fig. 8; see Appendix A for details of calculation).

Of the methyl rocking frequencies, the T_2 is clearly present as the strong infra-red band at 1257 cm^{-1} (Fig. 7). If it is assumed that the strong Raman line at 1250 cm^{-1} represents the same frequency, the other Raman-active rocking frequency (E) is unobserved, as is the inactive T_1. From the propane and isobutane assignments, one of these might be expected in the 900-cm^{-1} region and the other probably in the 1200-cm^{-1} region.

The assignment is recapitulated in Table VI. The remainder of weak infra-red bands are to be attributed to overtone or difference bands.

V. NORMAL BUTANE AND NORMAL PENTANE

These compounds introduce an additional possibility of uncertainty in that the carbon skeleton may be capable of existence in more than one configuration due to rotation about CC bonds. The question has not been settled as to whether, in n-butane for example, there are truly three potential minima (stable trans-form and two equivalent metastable skew-cis-forms) or whether due to the repulsion of the end methyl groups there is only one minimum (trans-form). The former assumption has been used by Pitzer[17] and by Aston and co-workers[18] in statistical calculations of thermodynamic functions. However, more recent attempts by Aston and co-workers to deduce the true form of the barrier to internal rotation indicate the possibility that there is only a single very shallow minimum corresponding to the trans-form.[19]

It is clear from the Raman work on liquid n-butane (e.g., see Fig. 7) that no single configuration will fit the spectrum, since many more lines are observed than are to be expected on the

centrosymmetric trans-structure. Kohlrausch and Köppl[12b] and Pitzer[17] have assigned the observed lines on the basis of a mixture of the two stereoisomeric forms. However, it must be pointed out that conclusions from the Raman spectrum may be vitiated because of liquid-state interactions. Even if one assumes with Aston a single minimum potential curve in which the valley is very broad and shallow, it is to be expected that the molecule in the liquid will not oscillate freely in this valley but will be constrained by neighboring molecules to certain portions of the valley. Since the internal rotations do not separate in the kinetic energy from the other skeletal vibrations, this will result in a complex and ill defined liquid spectrum such as is actually observed in hydrocarbons with skeletal torsion.

The infra-red spectra of the vapors present a contrastingly simpler picture. In the region in which the skeletal stretching vibrations of normal paraffins are expected (roughly 800 to 1100 cm^{-1}),[20] n-butane has only a single band of appreciable intensity, at 962 cm^{-1} (Figs. 4 and 7). This is to be expected if the trans-structure is assumed as the only one present, since the sym-

TABLE V. Wave-lengths, frequencies, and intensities of absorption maxima of isopentane vapor. Intensities estimated in units of 10 percent absorption; s = shoulder.

$\lambda(\mu)$	ω(cm^{-1})	I	$\lambda(\mu)$	ω(cm^{-1})	I
2.27	4405	0s	7.21	1387	}9
2.31	4330	2	7.32	1366	
2.43	4115	1s	7.49	1335	0s
2.59	3860	0	7.635	1310	
2.73	3665	0	7.68	1302	}3
3.00	3335	0s	7.74	1292	
3.13	3195	1s	7.84	1276	
3.24	3085	0s	8.50	1176	
3.36	2975	10	8.63	1159	}4
3.59	2785	1s	8.71	1148	
3.75	2665	1s	9.78	1022	
4.14	2415	1	10.13	987	}4
4.35	2300	0s	10.225	978	
4.62	2165	0	10.77	929	
4.83	2070	0	10.87	920	}2
5.15	1942	0	10.97	912	
5.89	1698	0	12.42	805	1s
5.97	1675	1	12.97	771	
6.40	1563	1	13.065	765	}3
6.795	1472	}10	13.18	759	
6.84	1462				

[17] E.g., K. S. Pitzer, J. Chem. Phys. **8**, 711 (1940).
[18] E.g., J. G. Aston and G. H. Messerly, J. Am. Chem. Soc. **62**, 1917 (1940).
[19] J. G. Aston, S. Isserow, G. J. Szasz, and R. M. Kennedy, J. Chem. Phys. **12**, 336 (1944).
[20] The limits of these vibrations for normal paraffins have been calculated, using various simplifying assumptions, by Pitzer (reference 17) and L. Kellner, Trans. Faraday Soc. **41**, 217 (1945), among others. Inspection of the Raman spectra given by Kohlrausch and Köppl (reference 12b) leads to the limits quoted, with which the calculations are in approximate agreement.
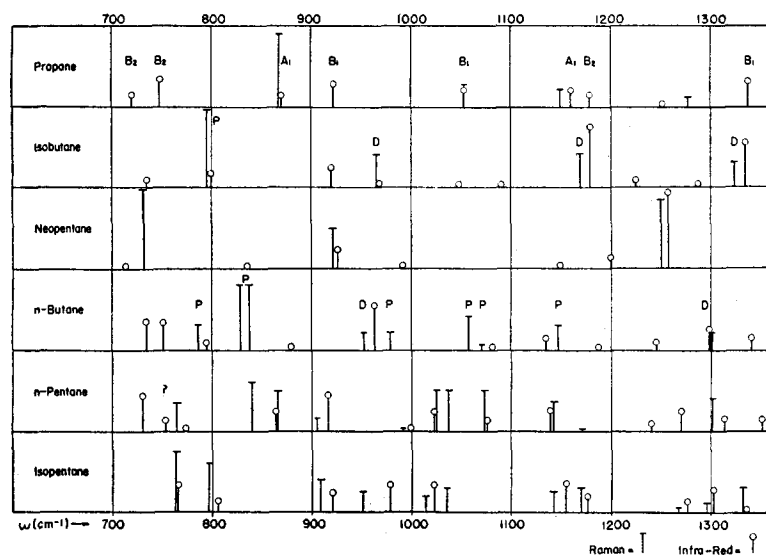
FIG. 7. Observed infra-red and Raman frequencies.

metry (C_{2h}) allows only the B_u CC stretching frequency to appear in the infra-red, the other two (A_g) frequencies being forbidden. Similarly, n-pentane, which—like n-butane—exhibits more Raman lines in the liquid than can be accounted for by any single structure, has the correct number of infra-red bands in the vapor if the all-*trans*-planar structure is assumed; all four CC stretching frequencies should be infra-red active, and four bands are found (864, 916, 1022, and 1075 cm^{-1}; Figs. 5 and 7). However, assignment of these four bands as the four skeletal frequencies is highly uncertain, since one or more may be overtone or difference bands, or methyl rocking fundamentals. Interpolation between these n-pentane frequencies and the propane skeletal frequencies leads to probable values of 865 cm^{-1} and 1070 cm^{-1} for the vapor-phase frequencies of the two infra-red inactive n-butane skeletal vibrations.

The HCC bending frequencies in both n-butane and n-pentane fit rather well with the pattern indicated by the propane assignment. On the basis of the *trans*-forms for these two molecules in the vapor state, frequencies of the following symmetries are expected:

	n-butane (C_{2h})	n-pentane (C_{2v})
CH$_2$ rocking	A_u, B_g	$A_2, 2B_2$
CH$_2$ twisting	A_u, B_g	$2A_2, B_2$
CH$_2$ wagging	A_g, B_u	$A_1, 2B_1$
CH$_3$ rocking (in-plane)	A_g, B_u	A_1, B_1
CH$_3$ rocking (out-of-plane)	A_u, A_g	A_2, B_2
IR active	A_u, B_u	A_1, B_1, B_2
Raman active	A_g, B_g	A_1, A_2, B_1, B_2

Symmetry designations for n-butane:

	Reflection	Inversion
A_g	+	+
A_u	−	−
B_g	−	+
B_u	+	−

Symmetry designations for n-pentane: same as for propane (see Section III).

For n-butane, one CH$_2$ rocking frequency is expected in the infra-red, in the 750 cm^{-1} region. The band observed here is of a peculiar shape, exhibiting two Q branch-like maxima and seeming to be a superposition of two close bands of A_u symmetry.[21] It is possible that one of these is the true fundamental and the other a band of the $(\nu + \nu_t) - \nu_t$ type, where ν_t is, say, the thermally excited methyl torsion frequency of A_u symmetry, which might interact strongly with the A_u CH$_2$ rocking vibration. For n-pentane, two infra-red bands are to be expected in this region. The observed absorption shows a single strong maximum, but some asymmetrical broadening on the short wave-length side indicates a possible weaker band here (Fig. 5). For both n-butane and n-pentane, the Raman lines shown at 760 to 800 cm^{-1} in Fig. 7 are believed to be caused by skeletal vibrations of non-planar forms and not to CH$_2$ rocking vibrations. This

[21] Like the B_1 bands of propane, the A_u bands of *trans*-n-butane should exhibit weak, stubby Q branches, and P and R branches with ill defined shoulders. The B_u bands, on the other hand, should have well defined P and R branches, but the resolution of the spectrograph is not adequate to demonstrate this on the bands shown in Fig. 4.

follows from the fact that the 786-cm⁻¹ line in n-butane is polarized and hence cannot be the B_g CH$_2$ rocking fundamental, and also that higher n-paraffins do not exhibit strong Raman lines in the 600 to 800-cm⁻¹ region. As has been noted with propane, Raman lines associated with many HCC bending vibrations are not observed because of weakness.

The CH$_2$ twisting frequencies (propane: 1278 cm⁻¹) would be expected to be weak in the infra-red even though the over-all symmetry allows their appearance, since to a first approximation these motions involve no dipole changes. As mentioned above, the characteristic Raman shifts at 1300 cm⁻¹ in n-paraffins[12b] may be ascribed to this type of vibration. In n-butane, the 1297-cm⁻¹ band may be assigned to the infra-red active A_u twisting vibration, but in n-pentane (Fig. 7) and higher hydrocarbons[4] there are no obvious infra-red analogs of the 1300 cm⁻¹ Raman lines, probably because of the weakness of the infra-red counterparts and because of the overlapping of the stronger CH$_2$ wagging types.

The CH$_2$ wagging frequencies (propane: 1338 cm⁻¹) should yield one infra-red band for n-butane and three for n-pentane. The observed spectra fit this expectation adequately; n-butane shows a band at 1340 cm⁻¹, and n-pentane shows three at 1350 cm⁻¹, 1313 cm⁻¹, and 1269 cm⁻¹. If this interpretation is accepted, it is clear that a reasonable spreading apart of the wagging frequencies has occurred, due to both kinetic and potential interactions.

Regarding the methyl rocking frequencies, two considerations are to be noted initially. Firstly, in n-butane and higher n-paraffins the end methyl groups are sufficiently separated that very little interaction between them is to be expected. Hence, the symmetric and antisymmetric combinations of which one would usually speak become indistinguishable, and very little separation in their frequencies will occur. Secondly, the assignment in propane indicates that the difference to be expected between methyl rocking frequencies for in-plane and out-of-plane rocking motions is small, of the order of only 20 cm⁻¹ (the plane referred to is the carbon plane).

The only bands so far lacking assignment in the n-butane and n-pentane spectra are those in the 1140-cm⁻¹ region (Fig. 7), and in view of the fact that some of the propane methyl-rocking frequencies occur near here, it becomes plausible to assign all the methyl rocking vibrations to this frequency region. Owing to lack of resolution, it is not possible to observe whether there are the correct number of infra-red bands in this region. The possibility cannot be excluded, however, that the 1140-cm⁻¹ frequencies represent only one set of methyl rocking bands (in-plane or out-of-plane) and that the other occurs at lower frequencies, in among the skeletal stretching frequencies.

The n-butane and n-pentane assignments discussed above are recapitulated in Table VI.

VI. ISOPENTANE

The spectrum of this molecule can be interpreted in a satisfactory fashion in light of the considerations given above. Internal skeletal torsion is present here also, so that the same difficulties arise in interpreting the Raman spectrum of the liquid in the CC stretching vibration region as were noted for n-butane and n-pentane. Hence, no further attempt will be made to discuss these except to note that both Raman and infra-red spectra indicate a skeletal frequency near 800 cm⁻¹, close to the symmetrical (A_1) isobutane skeletal frequency and hence presumably representing an analogous motion in isopentane.

The CH$_2$ rocking vibration appears as a moderately strong infra-red band at 765 cm⁻¹. The Raman line occurring at this position (Fig.
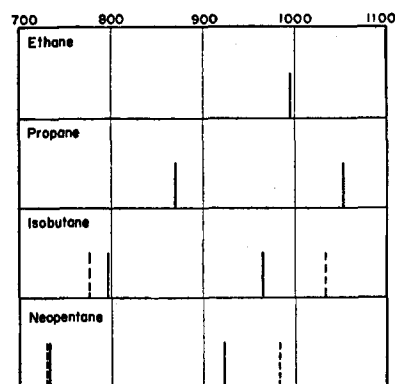

FIG. 8. Calculated (full line) and observed (broken line) skeletal stretching frequencies.

TABLE VI. Frequency assignments for paraffin hydrocarbons. Frequencies in cm^{-1} ( ) signifies estimated value.

Type vibration	Propane	Isobutane	Neopentane	n-Butane (trans)	n-Pentane (trans)	Isopentane	Higher paraffins
CC stretching	870 (A_1) 1053 (B_1)	799 (A_1) 965 (E)	731 (A_1) 924 (T_2)	(~865) (A_g) 962 (B_u) (~1070) (A_g)	864 (A_1) 916 (B_1) 1022 (A_1) 1075 (B_1)	800 3 at 850– 1050	n-Paraffins and n-alkyl chains: one frequency per CC bond, filling the range 800–1100 cm^{-1}; branched structures, one or more ≤800 cm^{-1}
CH$_2$ rocking	748 (B_2)			740 (A_u) (~770) (B_g)	730 (B_2) (~760) (B_2) (~800) (A_2)	765	One per CH$_2$, 720–790 cm^{-1}
CH$_2$ twisting	1278 (A_2)			1297 (A_u) 1300 (B_g)	3 at 1300 (2 A_2+B_2)	1300	One per CH$_2$, ~1300 cm^{-1}
CH$_2$ wagging	1338 (B_1)			1340 (B_u) (~1300) (A_g)	1350 1313 $\}$(A_2+2B_1) 1269	1270	One per CH$_2$, 1200–1350 cm^{-1}
CH wagging		1335 (E)				1334	Two per CH, 1300–1350 cm^{-1}
CH$_3$ rocking	922 (B_1) (~900) (A_2) 1160 (A_1) 1179 (B_2)	920 (E) (~900) (A_2) 1170 (A_1) 1179 (E)	(~900)$\}$(E+T_1) (~1200) 1257 (T_2)	1134$\}$(A_u+B_u) (~1140) 1146$\}$(A_g+B_g) (~1140)	4 at ~1140 (A_1+A_2+B_1 +B_2)	(~900) 920 2 at ~1140 1164 1176	Terminal on ethyl or longer alkyl chain: two per CH$_3$, ~1150 cm^{-1}; methyl on tertiary carbon: two per CH$_3$, ~900 and ~1170 cm^{-1}; methyl on quaternary carbon: two per CH$_3$, CH$_3$, 900–1250 cm^{-1}

7) is believed to represent one of the skeletal vibrations, since higher isoparaffins show no strong Raman lines in this region (600 to 800 cm^{-1}), whereas the strong infra-red bands, attributable to CH$_2$ rocking vibrations, persist. The CH$_2$ twisting and wagging vibrations may be reasonably assigned to the infra-red bands and Raman lines near 1270 cm^{-1} and 1300 cm^{-1}. By analogy with isobutane, the tertiary CH wagging vibration may be taken to be represented by the 1134-cm^{-1} frequency.

As to the methyl rock frequencies, the methyl of the ethyl group would be expected to be not greatly different from that of n-butane and to exhibit its rocking frequencies near 1150 cm^{-1}. The two methyl groups on the branched end of the molecule bear the same relation to each other as the methyl groups of propane and by analogy should exhibit two of the rocking frequencies in the 1150- to 1180-cm^{-1} region and two in the 900-cm^{-1} region, of which one should be unobservably weak. That such bands, attributable to the isopropyl group, are present is evident from the fact that all isoparaffins (i.e., 2-methylalkanes) exhibit bands near 920 cm^{-1} and 1175 cm^{-1}, which may be taken as the analogs of the propane B_1 and B_2 methyl rocking bands. The 920-cm^{-1} and 1176-cm^{-1} isopentane bands may then be ascribed to the same origin.

This frequency assignment is recapitulated in Table VI.

VII. EXTENSION TO HIGHER PARAFFINS

As noted in various places above, several of the conclusions receive confirmation when the spectra of higher paraffins are examined.

In view of the ambiguities of structure of most higher paraffins due to possibilities of internal rotation of the carbon skeleton, little can be said regarding the skeletal vibrations. However, it is apparent from the richness of the Raman spectra in the region 800 to 1100 cm^{-1},[22] that most of the skeletal vibrations lie in this range. Infra-red spectra also (generally of the liquid state, as with the Raman work) show great complexity and lack of regularity in this region. Branched structures show one or more strong Raman lines near 800 cm^{-1} or lower, ascribable to low frequency skeletal vibrations analogous to those observed in the branched molecules isobutane (799 cm^{-1}) and neopentane (731 cm^{-1}).

In line with the interpretations given above for HCC bending vibrations, the strong infra-red bands in the 720- to 790-cm^{-1} range, which are an obvious feature of most paraffin spectra, are

[22] E.g., see reference 12b, and E. J. Rosenbaum, A. V. Grosse, and H. F. Jacobson, J. Am. Chem. Soc. 61, 689 (1939).

TABLE VII. Force constants for skeletal frequency calculations of isobutane and neopentane.

Constant		Calculated value, 10^5 dynes/cm	Source of calculated value
K_c	C—C stretching	4.36[a]	Ethane C—C stretching frequency at 993 cm^{-1}
k_1	C—C stretching: C—C stretching interaction for adjacent bonds	0.20	From propane skeletal frequencies at 374, 870, and 1053 cm^{-1} (see Section III)
H_c	C—C—C bending	0.35[b]	
g_1	C—C stretching: C—C—C bending interaction for a C—C—C angle and an included C—C bond	0.35[b]	
h_1	C—C—C bending: C—C—C bending interaction for angles with a C—C bond in common	0.10[b]	Isobutane skeletal bending frequency at 434 cm^{-1}

[a] In order to allow for the known lowering in C—C bond strength in propane, isobutane, and neopentane over ethane, this value was decreased for these molecules proportionately to the decrease in total bond energy as determined from electron impact measurements. The values so obtained are: propane, 4.24·10^5; isobutane, 4.15·10^5; and neopentane, 4.10·10^5 dynes/cm. The decrease in force constants for this sequence of molecules was noted by Kohlrausch and Köppl (see reference 12b). The electron impact data from which the above adjustment was calculated are from D. P. Stevenson and J. A. Hipple, J. Am. Chem. Soc. 64, 1588 (1942).

[b] These constants refer to bending coordinates which are angular displacements multiplied by the equilibrium C—C distance, and hence carry the same units as linear displacement coordinates.

ascribed to CH$_2$ rocking vibrations, and, in fact, positions of the strongest bands in this region can be nicely correlated with the lengths of CH$_2$ chains present. The group of bands of moderate intensity found in the range 1200 to 1300 cm^{-1} is ascribable to CH$_2$ wagging and twisting and to tertiary CH wagging vibrations. In general, the simpler compounds show only a few bands in these regions (as with the assignments discussed in detail above), but as more complex compounds are considered (containing more CH$_2$ or CH groups) bands become more numerous and fill up the intervals.

Methyl rocking vibrations of higher paraffins are to be found, in accordance with the discussion given previously, in the region near 1150 cm^{-1}. This accords with the observed spectra[4] in that bands are found in this region which are, in general, stronger and more numerous for compounds with more methyl groups and whose positions can be correlated with various arrangements of methyl groups.[23] For those arrangements where methyl groups are adjacent, as two methyl groups on a tertiary carbon, some of the methyl rocking frequencies may be expected to occur also in the lower frequency region near 900 cm^{-1}, as typified by propane and isobutane.

An exception to the above methyl rocking positions occurs when two or more methyl groups are attached to a quaternary carbon. These compounds exhibit strong bands in the 1200- to 1250-cm^{-1} region, which from the assignment in neopentane are to be attributed to methyl rocking vibrations of the quaternary methyl groups. A qualitative explanation of this shift to higher frequencies is at hand in the fact that methyl groups attached to secondary or tertiary carbons can, by expansion of CCC angles, push themselves away from the remainder of the molecule. Quaternary methyl groups, on the other hand, are constrained to closer contact with adjacent groups and hence suffer increased repulsion, which results in increased methyl rocking frequencies. Two lines of evidence support this concept: the CCC angle in propane and isobutane is shown by electron diffraction studies to be greater than tetrahedral,[24] presumably due to methyl group repulsion, and the barrier to methyl torsion is greater in neopentane than in either propane or isobutane, arising from the increased interaction due to closer neighbors.[25]

VIII. CONCLUDING REMARKS

Table VI shows, along with the specific frequency assignments discussed earlier, the general

[23] A. Y. Mottlau, Serial No. 26, American Petroleum Institute Hydrocarbon Research Project, Ohio State University Research Foundation, Columbus, Ohio; the same correlations have been independently noted by Dr. G. B. B. M. Sutherland and Dr. H. W. Thompson in Great Britain (private communication) and by ourselves.

[24] L. Pauling and L. O. Brockway, J. Am. Chem. Soc. 59, 1223 (1937); J. G. Beach and J. Walter, J. Chem. Phys. 8, 303 (1940).

[25] E.g., see discussion given by F. A. French and R. S. Rasmussen, J. Chem. Phys. 14, 389 (1946).

TABLE VIII. Force constants for HCC bending frequency calculations.

Constant	Type	Calculated value, 10^5 dynes/cm	Source of calculated value
K_c	Same as Table VII	4.45[b]	See reference a
k_1	Same as Table VII	0.20	See Table VII
H_c	Same as Table VII	0.35[c]	See Table VII
h_1	Same as Table VII	0.10[c]	See Table VII
g_1	Same as Table VII	0.35[c]	See Table VII
H_H	H−C−H bending	0.42[c]	From methane 1306 and 1500 cm^{-1} frequencies[d]
h_2	H−C−H bending: H−C−H bending interaction for angles with a C−H bond in common	−0.01[c]	
H_{CH}	H−C−C bending	0.43[c]	
h_3	H−C−H bending: H−C−C bending interaction for angles with a C−H bond in common	−0.05[c]	
h_4	H−C−C bending: H−C−C bending interaction for angles at the same end of a common C−C bond	−0.05[c]	From ethane frequencies at 821, 993, 1374, 1379, and 1480 cm^{-1} [d]
g_2	C−C stretching: H−C−C bending interaction for an H−C−C angle and included C−C bond	0.18[c]	
h_5	H−C−C bending: H−C−C bending interaction for angles with a C−H bond in common	−0.05[c]	
h_6	C−C−C bending: H−C−C bending interaction for angles with a C−C bond in common	−0.05[c]	Assumed equal to h_3 and h_4

[a] Taken as the average between the constant calculated from the full ethane treatment and that from the diatomic-molecule approximation. In the propane and isobutane models to which these constants are applied, one end of a C−C bond follows the diatomic approximation (i.e., the methyl is considered a point mass) while the other end follows the full treatment.

[b] For use in propane and isobutane, this value was modified in the fashion described in Table VII, footnote a.

[c] The constants refer to bending coordinates which are angular displacements multiplied by the equilibrium C−H distance (in the case of H−C−H and H−C−H angles) or by the equilibrium C−C−C distance (in the case of C−C−C angles). This procedure gives the coordinates and constants the same units as with linear displacement coordinates.

[d] Essentially the same values as given by Herzberg (reference 1).

regions in which various types of vibrations may be expected in more complicated molecules. These have been found of use in thermodynamic calculations, since they give a much more accurate distribution of vibrational levels than has hitherto been available. For this purpose they are also applicable, with sufficient accuracy for the purpose, to the hydrocarbon portions of non-hydrocarbon compounds. Further use has been made of the assignments in gaining some knowledge of the structures of complex molecules, or compositions of complex hydrocarbon mixtures, particularly by making use of the correlations mentioned in the preceding section.

It is realized that the considerations employed here represent to some extent a fitting of facts into an oversimplified scheme, particularly as regards the assignment of observed frequencies to single vibration types. The justification for this procedure is that a certain degree of order can be attained and useful correlations made. Further work is contemplated toward verifying the assignments given, mainly by examination of deuterated compounds, and toward extension of the same type of treatment to other classes of organic compounds.

APPENDIX A

Skeletal Force Constant Calculations on Ethane Propane, Isobutane, and Neopentane

These calculations were made under the usual assumption that CH_3, CH_2, and CH groups could be treated as point masses, hydrogen vibrations being ignored. Tetrahedral carbon angles were assumed, the small error introduced in the cases of propane and isobutane being considered negligible.

The method of Wilson[7] was used for setting up the inverse kinetic energy matrices (G matrices) in terms of suitable symmetry coordinates. The matrix terms were evaluated numerically, and subsequent operations (ob-

taining, expanding, and solving the secular determinants) were carried out numerically.

The force constants given in Table VII were evaluated from known frequencies of ethane, propane, as shown in the table. The frequencies calculated from these force constants, which are discussed in Sections III and IV are:

Isobutane:	A_1	776 cm^{-1}
		(434)
	E	1034
		369
Neopentane:	A_1	729 cm^{-1}
	E	230
	T_2	983
		422

APPENDIX B

HCC Bending Force Constant Calculations on Propane and Isobutane

In the models used, the CH_3 groups were considered as point masses, but the secondary and tertiary hydrogens were included in the calculations. The methods used were the same as those described in Appendix A, with the additional simplification that the CH stretching force constants were set equal to infinity and the CH stretching vibrations were separated from the others and subsequently ignored, according to the procedure given by Wilson.[7]

In order to obtain suitable force constants for use with these models, calculations were made under similar assumptions on methane and ethane. The force constants used, and their sources, are given in Table VIII. The calculated frequencies, which are discussed in Sections III and IV, are:

Propane:	A_1	898 cm^{-1} (C−C stretching)
		1467 (HCH bending)
		427 (C−C−C bending)
	A_2	1175 (CH$_2$ twisting)
	B_1	998 (C−C stretching)
		1205 (CH$_2$ wagging)
	B_2	761 (CH$_2$ rocking)
Isobutane:	A_1	821 cm^{-1} (C−C stretching)
		571 (C−C−C bending)
	E	994 (C−C stretching)
		319 (C−C−C bending)
		1113 (CH wagging)

The Nature of Bond Orbitals in Quadricovalent Complexes of Transition Elements*

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In quadricovalent complexes of transition elements (Ni^{II}, Pd^{II}, Pt^{II}, Au^{III}, Ag^{II}, Cu^{II}) the central atom uses four s or d orbitals of its outer shell for unshared electron pairs and two s or d and two p orbitals for bond formation. The problem here is to find the strongest possible four hybrid bond orbitals obtained by combining the two $s-d$ and the two p orbitals available for bond formation. The strongest bond orbitals thus obtained are directed from the middle towards the four corners of a square, as it is expected from experimental evidence; they are composed of 4/9 s, 14/9 d, and two p orbitals, the strength being 2.943. These strongest possible orbitals are presumably used in complex of Ni^{II}, Pt^{II}, Au^{III}, and Cu^{II}, but probably not in complexes of Pd^{II} and Ag^{II}; in the latter two cases there must be assumed square bond orbitals of composition $s^n d^{2-n} p^2$ with n somewhere between 1 and 4/9, i.e., orbitals of character between that of the strongest square bond orbitals of composition $s^{4/9} d^{14/9} p^2$ mentioned above and that of sdp^2 square orbitals discovered by Pauling.

1. INTRODUCTION

THE problem of directed valence was first developed by Pauling[1] and Slater.[2] Pauling

formulated a very simple method of discussing the bond-forming power of an atomic bond orbital. The fundamental assumption of this method is that in the case of bond orbitals with the same or nearly the same radial part of the wave function the magnitude of the angular part of a bond along the bond axis (that is, in the direction of the ligand) is a measure of its relative bond-forming power.

[1] L. Pauling, J. Am. Chem. Soc. 53, 1367 (1931); The Nature of the Chemical Bond (Cornell University Press, Ithaca, New York, 1945), second edition.
[2] J. C. Slater, Phys. Rev. 37, 481 (1931).