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A Theoretical Evaluation of Normal Frequencies of Vibration of the Isomeric Octanes¹

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A theoretical evaluation of some of the normal frequencies of vibration of the isomeric octanes has been made. This report gives the skeletal frequencies for those of the eighteen isomeric octanes which lead to representations having 7 or fewer frequencies. The forces are assumed to be valence forces. The force constants used are 4.12×10^8 dynes per cm for the C—C bond stretching, and 0.37×10^8 dynes per cm for the bending between two C—C bonds, the values being based on computations by the author for *n*-propane, using the experimental data of E. F. Barker and Violet L. Wu. The angle between two C—C bonds was taken as 107° whenever possible. The results of this investigation are summarized by means of charts, showing the location of bands calculated. For the molecules reported all normal skeletal frequencies for a valence force model were evaluated, and attempts at correlation between experimental and theoretical bands have been made.

INTRODUCTION

IT has been shown² that for small oscillations which are assumed to be simple harmonic the frequencies obtained on the basis of classical mechanics are identical with those obtained by quantum mechanics. For this reason, it is still customary to use classical theory of small oscillations to obtain the normal frequencies of vibration of molecules.

In obtaining the frequencies belonging to normal modes of vibration, it is assumed that the potential energy is a function of the displacement coordinates, and, in order to express this function explicitly, it is necessary to make use of a definite force model. The earliest model used was the central force model, in which the potential energy depends only on the changes in the distances which separate the atoms of the molecule. It was found, however, that such a model is not adequate to represent the force field, as far as the study of vibration spectra is concerned. In the valence force model the atoms are connected by valence bonds, and it is assumed that a change in angle between two bonds, as well as a change in the length of a bond, results in an increase in potential energy. The valence force model has been more successful in the treatment of vibration spectra, though it is still, at best, an approx-

imation, and the results obtained with it cannot be expected to be identical with experimental values. It is found, for example, that in many cases zero frequencies arise, caused by the fact that, for the force field chosen, the displacements of the atoms from the equilibrium positions give rise only to terms of third or higher order in the potential function. If additional forces, such as those restricting free rotation about bonds, were introduced these zero frequencies might be removed. The actual frequencies, though not exactly zero, should, if the valence force model is any good at all, be very small. The frequencies obtained are to be regarded as approximations, the force model being too crude to obtain exact results.

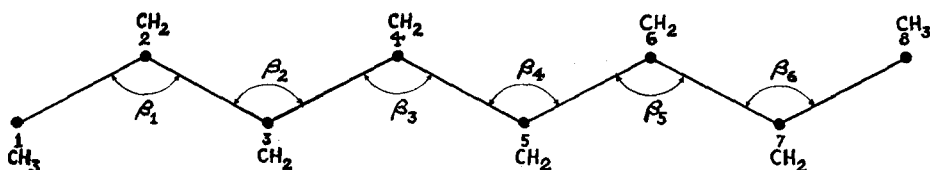
In the following discussion, a molecule is assumed to consist of n atoms bound to equilibrium positions by valence forces. The atoms are bound together in such a way that a change in length of a valence bond by an amount ΔL gives rise to an increase in potential energy of $\frac{1}{2}K_{cc}|\Delta L|^2$, and a change $\Delta\theta$ in the angle between two valence bonds meeting at a single atom results in an increase in potential energy of $\frac{1}{2}K_\theta(\Delta\theta)^2$. Hence, the total increase in potential energy, because of an arbitrary change, is

$$V = \frac{1}{2} \sum K_{cc} |\Delta L|^2 + \frac{1}{2} \sum K_\theta (\Delta\theta)^2,$$

where the summation extends over all valence bonds in the first term and over all valence angles in the second term.

¹ This research was completed at the Harrison M. Randall Laboratory of Physics, University of Michigan, Ann Arbor, Michigan, 1945.

² D. M. Dennison, "Infrared spectra of polyatomic molecules," *Rev. Mod. Phys.* **3**, No. 2 (April, 1931).

FIG. 1. Skeletal form of *n*-octane. $\beta_1^\circ = \beta_2^\circ = \beta_3^\circ = \beta_4^\circ = \beta_5^\circ = \beta_6^\circ = 107^\circ$.

The isomeric octanes constitute a group of saturated hydrocarbons, each possessing 8 carbon and 18 hydrogen atoms. The direct application of the above theory to a molecule of that type would lead to a secular determinant of order 72, and, even with the aid of group theory, a complete determination of the frequencies would present a task too formidable to be attempted. It has been found, however, that the skeletal frequencies obtained by considering the hydrogen atoms frozen to the carbon atoms are not much changed. In the present discussion, all hydrogen atoms are considered frozen to the carbon atoms, thus reducing the original system in each case to a system of 8 mass points, made up of the combined masses of 1 carbon and 3 or fewer hydrogen atoms. The present paper gives the skeletal frequencies of those isomeric octanes which belong to point groups of higher symmetry than the C_s . For the C_s group, the frequencies belonging to the lower ordered representations have also been worked out, but will not be reported here.

In general, the atoms constituting a hydrocarbon tend to stretch out and form a rather symmetric pattern, as has been indicated by measurement on oil films. The molecules are assumed to consist of zigzag chains arranged as symmetrically as possible, and since the effect of the C—H bonds is eliminated, the distinction between optical isomers is ignored. No systematic experimental spectra are available which distinguish the optical isomers, and it is felt that significant information is obtained about the skeletal frequencies with the forms chosen. The angles in the main chains of the molecules are taken as 107° in the equilibrium position, though in some cases this had to be altered because of symmetry considerations. Values for the angles between valence bonds ranging from 99° to 116° have been used by other investigators for various molecules involving CH_3 groups.³ Although the

angle would vary with position, 107° was chosen, somewhat arbitrarily, as representative, this value having been used with some success as the tetrahedral angle for certain hydrocarbons. Four types of masses occur, representing the masses of C, CH, CH_2 , and CH_3 groups, respectively. The values for these masses were determined from the masses of the hydrogen and carbon atoms given by R. T. Birge.⁴ The values used are

$$\begin{aligned} \text{C} &= 19.93 \times 10^{-24} \text{ g}, \\ \text{CH} &= (19.93 + 1.673) \times 10^{-24} \text{ g} = 21.6 \times 10^{-24} \text{ g}, \\ \text{CH}_2 &= (19.93 + 2 \times 1.673) \times 10^{-24} \text{ g} \\ &= 23.3 \times 10^{-24} \text{ g}, \\ \text{CH}_3 &= (19.93 + 3 \times 1.673) \times 10^{-24} \text{ g} \\ &= 24.9 \times 10^{-24} \text{ g}. \end{aligned}$$

The force constants used are based on computations by the author on *n*-propane, using the experimental data of E. F. Barker and Violet L. Wu.⁵ The values chosen as best suited for the octanes are

For C—C stretching, $K_{cc} = 4.12 \times 10^5$ dynes/cm.

For $\begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \end{array}$ bending, $K_\theta = .37 \times 10^5$ dynes/cm.

TABLE I. Table of characters.

C_{2h}	E	C_2	σ_h	i	Raman	Infra-red	No.
$\Gamma^{(1)} \sim A_g$	1	1	1	1	<i>P</i>	<i>IA</i>	7
$\Gamma^{(2)} \sim B_g$	1	-1	-1	1	<i>DP</i>	<i>IA</i>	2
$\Gamma^{(3)} \sim A_u$	1	1	-1	-1	<i>F</i>	<i>A</i>	3
$\Gamma^{(4)} \sim B_u$	1	-1	1	-1	<i>F</i>	<i>A</i>	6
ϕ_R	0	π	0	π			
U_R	8	0	8	0			
$\pm 1 + 2 \cos \phi_R$	3	-1	1	-3			
$\chi^{(R)}$	24	0	8	0			
Ξ	18	2	8	0			

⁴ Raymond T. Birge, "A new table of values of the general physical constants," *Rev. Mod. Phys.* **13**, 233 (1941).

⁵ E. F. Barker and Violet L. Wu, "The infra-red absorption spectrum of propane," *J. Chem. Phys.* **9**, No. 7, 490 (July, 1941).

³ K. W. F. Kohlrausch, *Der Smekal-Raman Effekt* (Verlagsbuchhandlung, Julius Springer, Berlin, 1938).

MOLECULES BELONGING TO THE
POINT GROUP C_{2h}

 N-Octane⁶ (Table I, Fig. 1)

Representation $\Gamma^{(1)}$: The values obtained for the 7 bands belonging to this representation are

$$\frac{1}{\lambda_1} = 200.0 \text{ cm}^{-1}, \quad \frac{1}{\lambda_4} = 955.7 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_2} = 224.3 \text{ cm}^{-1}, \quad \frac{1}{\lambda_5} = 1053 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_3} = 443.4 \text{ cm}^{-1}, \quad \frac{1}{\lambda_6} = 1054 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_7} = 1127 \text{ cm}^{-1}.$$

Representation $\Gamma^{(2)}$: Because of the choice of potential function, the values obtained for the 2 bands belonging to this representation are

$$\frac{1}{\lambda_1} = 0 \text{ cm}^{-1}, \quad \frac{1}{\lambda_2} = 0 \text{ cm}^{-1}.$$

Representation $\Gamma^{(3)}$: Because of the choice of potential function, the values obtained for the 3 bands belonging to this representation are

$$\frac{1}{\lambda_1} = 0 \text{ cm}^{-1}, \quad \frac{1}{\lambda_2} = 0 \text{ cm}^{-1}, \quad \frac{1}{\lambda_3} = 0 \text{ cm}^{-1}.$$

Representation $\Gamma^{(4)}$: The values obtained for the 6 bands belonging to this representation

TABLE II. Table of characters.

C_{2h}	E	C_2	σ_h	i	Raman	Infra- red	No.
$\Gamma^{(1)} \sim A_g$	1	1	1	1	P	IA	6
$\Gamma^{(2)} \sim B_g$	1	-1	-1	1	DP	IA	3
$\Gamma^{(3)} \sim A_u$	1	1	-1	-1	F	A	4
$\Gamma^{(4)} \sim B_u$	1	-1	1	-1	F	A	5
ϕ_R	0	π	0	π			
U_R	8	0	4	0			
$\pm 1 + 2 \cos \phi_R$	3	-1	1	-3			
$\chi(R)$	24	0	4	0			
\bar{E}	18	2	4	0			

⁶ Details of the calculation for this, as well as for the other molecules are given in a thesis submitted by the author to the Horace H. Rackham School of Graduate Studies, University of Michigan, 1945.

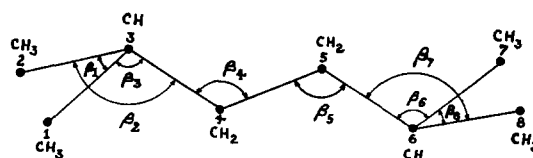


FIG. 2. Skeletal form of 2-5-dimethylhexane. $\beta_1^\circ = \beta_2^\circ = \beta_3^\circ = \beta_4^\circ = \beta_5^\circ = \beta_6^\circ = \beta_7^\circ = \beta_8^\circ = 107^\circ$.

are

$$\frac{1}{\lambda_1} = 86.16 \text{ cm}^{-1}, \quad \frac{1}{\lambda_4} = 986.3 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_2} = 344.0 \text{ cm}^{-1}, \quad \frac{1}{\lambda_5} = 996.7 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_3} = 396.6 \text{ cm}^{-1}, \quad \frac{1}{\lambda_6} = 1104 \text{ cm}^{-1}.$$

2-5-Dimethylhexane (Table II, Fig. 2)

Representation $\Gamma^{(1)}$: The values obtained for the 6 bands belonging to this representation are

$$\frac{1}{\lambda_1} = 0 \text{ cm}^{-1}, \quad \frac{1}{\lambda_4} = 851.3 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_2} = 217.9 \text{ cm}^{-1}, \quad \frac{1}{\lambda_5} = 1032 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_3} = 367.1 \text{ cm}^{-1}, \quad \frac{1}{\lambda_6} = 1146 \text{ cm}^{-1}.$$

Representation $\Gamma^{(2)}$: The values obtained for the 3 bands belonging to this representation are

$$\frac{1}{\lambda_1} = 0 \text{ cm}^{-1}, \quad \frac{1}{\lambda_2} = 376.0 \text{ cm}^{-1}, \quad \frac{1}{\lambda_3} = 1113 \text{ cm}^{-1}.$$

Representation $\Gamma^{(3)}$: The values obtained for the 4 bands belonging to this representation are

$$\frac{1}{\lambda_1} = 0 \text{ cm}^{-1}, \quad \frac{1}{\lambda_4} = 257.9 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_2} = 0 \text{ cm}^{-1}, \quad \frac{1}{\lambda_5} = 1061 \text{ cm}^{-1}.$$

Representation $\Gamma^{(4)}$: The values obtained for the 5 bands belonging to this representation

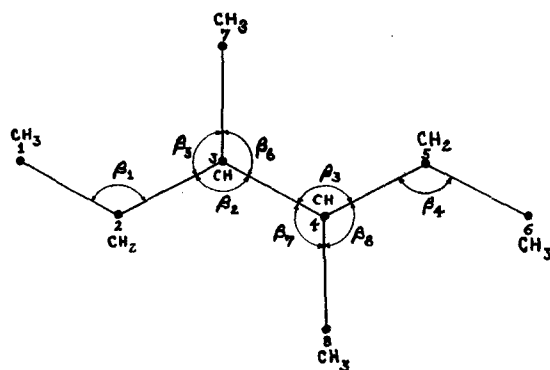


FIG. 3. Skeletal form of 3,4-dimethylhexane. $\beta_1^\circ = \beta_2^\circ = \beta_3^\circ = \beta_4^\circ = 107^\circ$. $\beta_5^\circ = \beta_6^\circ = \beta_7^\circ = \beta_8^\circ = 126.5^\circ$

are

$$\frac{1}{\lambda_1} = 152.6 \text{ cm}^{-1}, \quad \frac{1}{\lambda_4} = 883.7 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_2} = 372.6 \text{ cm}^{-1}, \quad \frac{1}{\lambda_5} = 1124 \text{ cm}^{-1}.$$

$$\frac{1}{\lambda_3} = 426.8 \text{ cm}^{-1},$$

3,4-Dimethylhexane (Table III, Fig. 3)

Representation $\Gamma^{(1)}$: The values obtained for the 7 bands belonging to this representation are

$$\frac{1}{\lambda_1} = 222.2 \text{ cm}^{-1}, \quad \frac{1}{\lambda_4} = 670.9 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_2} = 276.4 \text{ cm}^{-1}, \quad \frac{1}{\lambda_5} = 1005 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_3} = 429.7 \text{ cm}^{-1}, \quad \frac{1}{\lambda_6} = 1274 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_7} = 1369 \text{ cm}^{-1}.$$

Representation $\Gamma^{(2)}$: Because of the choice of potential function, the values obtained for the 2 bands belonging to this representation are

$$\frac{1}{\lambda_1} = 0 \text{ cm}^{-1}, \quad \frac{1}{\lambda_2} = 0 \text{ cm}^{-1}.$$

Representation $\Gamma^{(3)}$: Because of the choice of potential function, the values obtained for the

3 bands belonging to this representation are

$$\frac{1}{\lambda_1} = 0 \text{ cm}^{-1}, \quad \frac{1}{\lambda_2} = 0 \text{ cm}^{-1}, \quad \frac{1}{\lambda_3} = 0 \text{ cm}^{-1}.$$

Representation $\Gamma^{(4)}$: The values obtained for the 6 bands belonging to this representation are

$$\frac{1}{\lambda_1} = 146.1 \text{ cm}^{-1}, \quad \frac{1}{\lambda_4} = 856.5 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_2} = 255.9 \text{ cm}^{-1}, \quad \frac{1}{\lambda_5} = 1031 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_3} = 554.9 \text{ cm}^{-1}, \quad \frac{1}{\lambda_6} = 1208 \text{ cm}^{-1}.$$

MOLECULES BELONGING TO THE POINT GROUP C_{2v}

4-Methylheptane (Table IV, Fig. 4)

Representation $\Gamma^{(1)}$: The values obtained for the 7 bands belonging to this representation are

$$\frac{1}{\lambda_1} = 109.6 \text{ cm}^{-1}, \quad \frac{1}{\lambda_4} = 743.6 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_2} = 239.2 \text{ cm}^{-1}, \quad \frac{1}{\lambda_5} = 984.2 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_3} = 410.5 \text{ cm}^{-1}, \quad \frac{1}{\lambda_6} = 1089 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_7} = 1288 \text{ cm}^{-1}.$$

Representation $\Gamma^{(2)}$: The values obtained for the 6 bands belonging to this representation

TABLE III. Table of characters.

C_{2h}	E	C_2	σ_h	i	Raman	Infra-red	No.
$\Gamma^{(1)} \sim A_g$	1	1	1	1	P	IA	7
$\Gamma^{(2)} \sim B_g$	1	-1	-1	1	DP	IA	2
$\Gamma^{(3)} \sim A_u$	1	1	-1	-1	F	A	3
$\Gamma^{(4)} \sim B_u$	1	-1	1	-1	F	A	6
ϕ_R	0	π	0	π			
U_R	8	0	8	0			
$\pm 1 + 2 \cos \phi_R$	3	-1	1	-3			
$\chi(R)$	24	0	8	0			
Ξ	18	2	8	0			

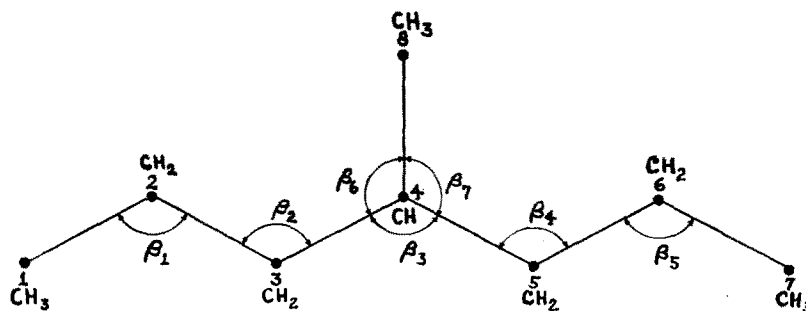


FIG. 4. Skeletal form of 4-methylheptane. $\beta_1^\circ = \beta_2^\circ = \beta_3^\circ = \beta_4^\circ = \beta_5^\circ = 107^\circ$.
 $\beta_6^\circ = \beta_7^\circ = 126.5^\circ$.

are

$$\frac{1}{\lambda_1} = 245.5 \text{ cm}^{-1}, \quad \frac{1}{\lambda_4} = 898.6 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_2} = 288.5 \text{ cm}^{-1}, \quad \frac{1}{\lambda_5} = 1034 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_3} = 475.3 \text{ cm}^{-1}, \quad \frac{1}{\lambda_6} = 1280 \text{ cm}^{-1}.$$

Representation $\Gamma^{(3)}$: Because of the choice of potential function, the values obtained for the 2 bands belonging to this representation are

$$\frac{1}{\lambda_1} = 0 \text{ cm}^{-1}, \quad \frac{1}{\lambda_2} = 0 \text{ cm}^{-1}.$$

Representation $\Gamma^{(4)}$: Because of the choice of potential function, the values obtained for the 3 bands belonging to this representation are

$$\frac{1}{\lambda_1} = 0 \text{ cm}^{-1}, \quad \frac{1}{\lambda_2} = 0 \text{ cm}^{-1}, \quad \frac{1}{\lambda_3} = 0 \text{ cm}^{-1}.$$

TABLE IV. Table of characters.

C_{2v}	E	C_2	σ_z	σ_y	Raman	Infra-red	No.
$\Gamma^{(1)} \sim A_1$	1	1	1	1	P	A	7
$\Gamma^{(2)} \sim B_1$	1	-1	-1	1	DP	A	6
$\Gamma^{(3)} \sim A_2$	1	1	-1	-1	DP	IA	2
$\Gamma^{(4)} \sim B_2$	1	-1	1	-1	DP	A	3
ϕ_R	0	π	0	0			
U_R	8	2	2	8			
$\pm 1 + 2 \cos \phi_R$	3	-1	1	1			
$\chi(R)$	24	-2	2	8			
Ξ	18	0	2	8			

2-3-4-Trimethylpentane (Table V, Fig. 5)

Representation $\Gamma^{(1)}$: The values obtained for the 6 bands belonging to this representation are

$$\frac{1}{\lambda_1} = 202.0 \text{ cm}^{-1}, \quad \frac{1}{\lambda_4} = 722.4 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_2} = 251.3 \text{ cm}^{-1}, \quad \frac{1}{\lambda_5} = 1027 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_3} = 427.3 \text{ cm}^{-1}, \quad \frac{1}{\lambda_6} = 1288 \text{ cm}^{-1}.$$

Representation $\Gamma^{(2)}$: The values obtained for the 5 bands belonging to this representation are

$$\frac{1}{\lambda_1} = 231.3 \text{ cm}^{-1}, \quad \frac{1}{\lambda_4} = 889.3 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_2} = 374.3 \text{ cm}^{-1}, \quad \frac{1}{\lambda_6} = 1238 \text{ cm}^{-1}.$$

$$\frac{1}{\lambda_3} = 587.9 \text{ cm}^{-1},$$

Representation $\Gamma^{(3)}$: The values obtained for the 3 bands belonging to this representation are

$$\frac{1}{\lambda_1} = 0 \text{ cm}^{-1}, \quad \frac{1}{\lambda_3} = 1111 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_2} = 286.9 \text{ cm}^{-1},$$

Representation $\Gamma^{(4)}$: The values obtained for the 4 bands belonging to this representation

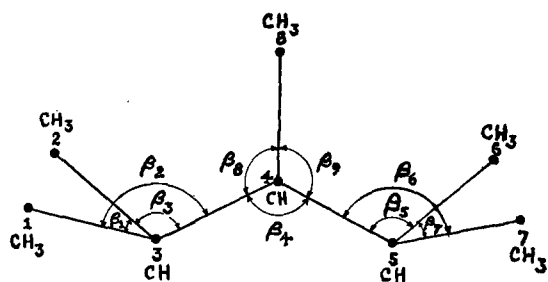


FIG. 5. Skeletal form of 2-3-4-trimethylpentane. $\beta_1^\circ = \beta_2^\circ = \beta_3^\circ = \beta_4^\circ = \beta_5^\circ = \beta_6^\circ = \beta_7^\circ = 107^\circ$. $\beta_8^\circ = \beta_9^\circ = 126.5^\circ$.

are

$$\frac{1}{\lambda_1} = 0 \text{ cm}^{-1}, \quad \frac{1}{\lambda_3} = 457.2 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_2} = 0 \text{ cm}^{-1}, \quad \frac{1}{\lambda_4} = 1115 \text{ cm}^{-1}.$$

2-Methyl-3-Ethylpentane (Table VI, Fig. 6)

Representation $\Gamma^{(1)}$: The values obtained for the 7 bands belonging to this representation are

$$\frac{1}{\lambda_1} = 175.8 \text{ cm}^{-1}, \quad \frac{1}{\lambda_4} = 584.1 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_2} = 311.2 \text{ cm}^{-1}, \quad \frac{1}{\lambda_5} = 1017 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_3} = 410.2 \text{ cm}^{-1}, \quad \frac{1}{\lambda_6} = 1043 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_7} = 1364 \text{ cm}^{-1}.$$

Representation $\Gamma^{(2)}$: The values obtained for the 5 bands belonging to this representation are

$$\frac{1}{\lambda_1} = 0 \text{ cm}^{-1}, \quad \frac{1}{\lambda_4} = 957.1 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_2} = 252.4 \text{ cm}^{-1}, \quad \frac{1}{\lambda_5} = 1206 \text{ cm}^{-1}.$$

$$\frac{1}{\lambda_3} = 549.5 \text{ cm}^{-1},$$

Representation $\Gamma^{(3)}$: Because of the choice of potential function, the values obtained for the

2 bands belonging to this representation are

$$\frac{1}{\lambda_1} = 0 \text{ cm}^{-1}, \quad \frac{1}{\lambda_2} = 0 \text{ cm}^{-1}.$$

Representation $\Gamma^{(4)}$: The values obtained for the 4 bands belonging to this representation are

$$\frac{1}{\lambda_1} = 0 \text{ cm}^{-1}, \quad \frac{1}{\lambda_3} = 450.5 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_2} = 0 \text{ cm}^{-1}, \quad \frac{1}{\lambda_4} = 1103 \text{ cm}^{-1}.$$

MOLECULES BELONGING TO THE POINT GROUP D_{3h}

2-2-3-3-Tetramethylbutane (Table VII, Fig. 7)

Representation $\Gamma^{(1)}$: The values obtained for the 3 bands belonging to this representation are

$$\frac{1}{\lambda_1} = 247.4 \text{ cm}^{-1}, \quad \frac{1}{\lambda_3} = 1284 \text{ cm}^{-1}.$$

$$\frac{1}{\lambda_2} = 639.4 \text{ cm}^{-1},$$

Representation $\Gamma^{(3)}$: Because of the choice of potential function, the value obtained for the 1 band belonging to this representation is

$$\frac{1}{\lambda_1} = 0 \text{ cm}^{-1}.$$

Representation $\Gamma^{(4)}$: The values obtained for the 2 bands belonging to this representation are

$$\frac{1}{\lambda_1} = 484.1 \text{ cm}^{-1}, \quad \frac{1}{\lambda_2} = 847.0 \text{ cm}^{-1}.$$

TABLE V. Table of characters.

C_{2v}	E	C_2	σ_z	σ_y	Raman	Infra-red	No.
$\Gamma^{(1)} \sim A_1$	1	1	1	1	P	A	6
$\Gamma^{(2)} \sim B_1$	1	-1	-1	1	DP	A	5
$\Gamma^{(3)} \sim A_2$	1	1	-1	-1	DP	IA	3
$\Gamma^{(4)} \sim B_2$	1	-1	1	-1	DP	A	4
ϕ_R	0	π	0	0			
U_R	8	2	2	4			
$\pm 1 + 2 \cos \phi_R$	3	-1	1	1			
$\chi(R)$	24	-2	2	4			
Ξ	18	0	2	4			

Representation $\Gamma^{(5)}$ (doubly degenerate): The values obtained for the 3 bands belonging to this representation are

$$\frac{1}{\lambda_1} = 353.6 \text{ cm}^{-1}, \quad \frac{1}{\lambda_3} = 1270 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_2} = 570.7 \text{ cm}^{-1},$$

Representation $\Gamma^{(6)}$ (doubly degenerate): The values obtained for the 3 bands belonging to this representation are

$$\frac{1}{\lambda_1} = 209.5 \text{ cm}^{-1}, \quad \frac{1}{\lambda_3} = 1123 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_2} = 657.4 \text{ cm}^{-1},$$

SUPPLEMENTARY EVALUATIONS

The frequencies for *n*-butane and *n*-hexane were evaluated by the method described for the octanes for the purpose of determining how these bands merge with those of *n*-octane.

N-Butane (Table VIII, Fig. 8)

Representation $\Gamma^{(1)}$: The values obtained for the 3 bands belonging to this representation are

$$\frac{1}{\lambda_1} = 359.6 \text{ cm}^{-1}, \quad \frac{1}{\lambda_3} = 1092 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_2} = 979.7 \text{ cm}^{-1},$$

TABLE VI. Table of characters.

C_{2v}	E	C_2	σ_z	σ_y	Raman	Infra-red	No.
$\Gamma^{(1)} \sim A_1$	1	1	1	1	<i>P</i>	<i>A</i>	7
$\Gamma^{(2)} \sim B_1$	1	-1	-1	1	<i>DP</i>	<i>A</i>	5
$\Gamma^{(3)} \sim A_2$	1	1	-1	-1	<i>DP</i>	<i>IA</i>	2
$\Gamma^{(4)} \sim B_2$	1	-1	1	-1	<i>DP</i>	<i>A</i>	4
ϕ_R	0	π	0	0			
U_R	8	2	4	6			
$\pm 1 + 2 \cos \phi_R$	3	-1	1	1			
$\chi(R)$	24	-2	4	6			
Ξ	18	0	4	6			

Representation $\Gamma^{(3)}$: Because of the choice of potential function, the value obtained for the 1

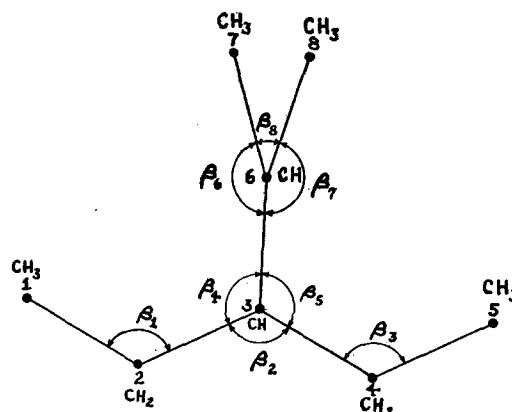


FIG. 6. Skeletal form of 2-methyl-3-ethylpentane. $\beta_1^\circ = \beta_2^\circ = \beta_3^\circ = \beta_4^\circ = 107^\circ$. $\beta_5^\circ = \beta_6^\circ = 126.5^\circ$.

band belonging to this representation is

$$\frac{1}{\lambda_1} = 0 \text{ cm}^{-1}.$$

Representation $\Gamma^{(4)}$: The values obtained for the 2 bands belonging to this representation are

$$\frac{1}{\lambda_1} = 294.3 \text{ cm}^{-1}, \quad \frac{1}{\lambda_2} = 982.1 \text{ cm}^{-1}.$$

N-Hexane (Table IX, Fig. 9)

Representation $\Gamma^{(1)}$: The values obtained for the 5 bands belonging to this representation are

$$\frac{1}{\lambda_1} = 261.6 \text{ cm}^{-1}, \quad \frac{1}{\lambda_4} = 1034 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_2} = 348.0 \text{ cm}^{-1}, \quad \frac{1}{\lambda_5} = 1119 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_3} = 987.4 \text{ cm}^{-1},$$

Representation $\Gamma^{(2)}$: Because of the choice of potential function, the value obtained for the 1 band belonging to this representation is

$$\frac{1}{\lambda_1} = 0 \text{ cm}^{-1}.$$

Representation $\Gamma^{(3)}$: Because of the choice of potential function, the values obtained for the 2

bands belonging to this representation are

$$\frac{1}{\lambda_1} = 0 \text{ cm}^{-1}, \quad \frac{1}{\lambda_2} = 0 \text{ cm}^{-1}.$$

Representation $\Gamma^{(4)}$: The values obtained for the 4 bands belonging to this representation are

$$\begin{aligned} \frac{1}{\lambda_1} &= 149.1 \text{ cm}^{-1}, & \frac{1}{\lambda_3} &= 972.4 \text{ cm}^{-1}, \\ \frac{1}{\lambda_2} &= 427.0 \text{ cm}^{-1}, & \frac{1}{\lambda_4} &= 1092 \text{ cm}^{-1}. \end{aligned}$$

SUMMARY AND ANALYSIS OF RESULTS

Internal Consistency of the Theoretical Spectra

The calculated bands for all the molecules fall, roughly, into two main regions, one below 500 cm^{-1} and the other between 800 cm^{-1} and 1300 cm^{-1} , although there is some intermixture as well. The bands in the higher region may be assigned to modes in which the motions of the masses are mainly along the valence bonds, resulting in changes in the lengths of these bonds, while the bands in the lower region may be assigned to modes in which the motions of the masses are mainly perpendicular to the valence bonds, resulting in changes in the valence angles. This is borne out by the evaluation by the discussed method of the skeletal frequencies of the ethane and *n*-propane molecules. In the case of ethane, the motion for the frequency is a pure stretching of the valence bond, and gives rise to a band at 965 cm^{-1} , and, for *n*-propane the motion in which the angle between the valence bonds is changed gives rise to a band at 375 cm^{-1} . On the whole, the calculated spectra show no very distinct systematic displacement of the bands. (See Chart I.)

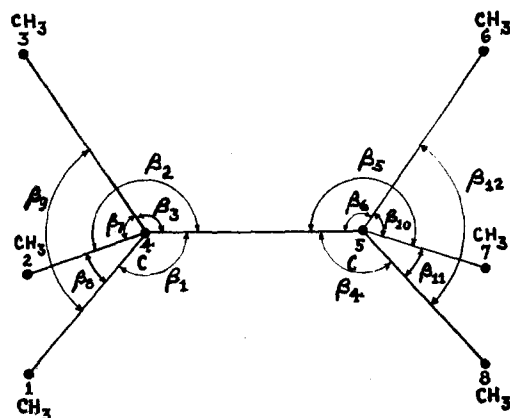


FIG. 7. Skeletal form of 2-2-3-3-tetramethylbutane. $\beta_1^\circ = \beta_2^\circ = \beta_3^\circ = \beta_4^\circ = \beta_5^\circ = \beta_6^\circ = 107^\circ$. $\beta_7^\circ = \beta_8^\circ = \beta_9^\circ = \beta_{10}^\circ = \beta_{11}^\circ = \beta_{12}^\circ = 111^\circ 50'$.

From the spectra of the plane zigzag chain molecules, *n*-butane, *n*-hexane, and *n*-octane, may be seen the types of shift that result when new members are added to the chain of carbons. The single band at 965 cm^{-1} in the spectrum of ethane, corresponding to a stretching motion of the valence bond, becomes multiple in the others in a somewhat irregular fashion, and, starting with *n*-butane, bending vibrations appear at lower frequencies, which again spread out into several more bands in the spectra of the longer chains. These results are to be expected from general considerations, the additional bands resulting from the addition of more elements to the chain.

The main conclusion to be drawn is that small changes in form, and possibly also small changes in the potential function constants, result in large variations in the positions of the bands. Theory would lead us to expect no very systematic pattern for the bands in the spectra of the

TABLE VII. Table of characters.

D_{sh}	E	σ_h	$2C_2$	$2S_2$	$3C_2$	$3\sigma_v$	Raman	Infra-red	No.
$\Gamma^{(1)} \sim A_1'$	1	1	1	1	1	1	<i>P</i>	<i>IA</i>	3
$\Gamma^{(2)} \sim A_2'$	1	1	1	1	-1	-1	<i>F</i>	<i>IA</i>	0
$\Gamma^{(3)} \sim A_1''$	1	-1	1	-1	1	-1	<i>F</i>	<i>IA</i>	1
$\Gamma^{(4)} \sim A_2''$	1	-1	1	-1	-1	1	<i>F</i>	<i>A</i>	2
$\Gamma^{(5)} \sim E'$	2	2	-1	-1	0	0	<i>DP</i>	<i>A</i>	3
$\Gamma^{(6)} \sim E''$	2	-2	-1	1	0	0	<i>DP</i>	<i>IA</i>	3
ϕ_R	0	0	$2\pi/3$	$2\pi/3$	π	0			
U_R	8	0	2	0	0	4			
$\pm 1 + 2 \cos \phi_R$	3	1	0	-1	-1	1			
$\chi(R)$	24	0	0	0	0	4			
$\bar{\chi}$	18	0	0	0	2	4			

TABLE VIII. Table of characters.

C_{2h}	E	C_2	σ_h	i	Raman	Infra-red	No.
$\Gamma^{(1)} \sim A_G$	1	1	1	1	P	IA	3
$\Gamma^{(2)} \sim B_G$	1	-1	-1	1	DP	IA	0
$\Gamma^{(3)} \sim A_u$	1	1	-1	-1	F	A	1
$\Gamma^{(4)} \sim B_u$	1	-1	1	-1	F	A	2
ϕ_R	0	π	0	π			
U_R	4	0	4	0			
$\pm 1 + 2 \cos \phi_R$	3	-1	1	-3			
$\chi(R)$	12	0	4	0			
Ξ	6	2	4	0			

octanes. It becomes evident that comparison of experimental with theoretical spectra will be difficult, and that for the most part only qualitative correspondence may be expected. An exact agreement with experiment would, of course, be extremely unlikely, since the exact forms of the molecules are not known, the forms used having been somewhat arbitrarily chosen to give the most symmetry possible consistent with chemical evidence. Also, the valence force model is itself an approximation.

Correlation with Experimental Spectra⁷

Any attempt to establish correlation of the theoretical spectra with spectra found experimentally meets with certain difficulties. The observed Raman and infra-red spectra are far from complete. The infra-red spectra do not include frequencies much below 700 cm^{-1} , and the Raman spectra, although somewhat more complete as to range covered, are available only for a few molecules. The purity of the experimental material is often questionable, especially in the case of the Raman spectra, so that extraneous bands due to impurities may be present. Both the Raman and the infra-red spectra show, besides the fundamental vibrations, many harmonics and overtones, as well as combination bands. Usually the fundamental bands should be stronger than the overtones or harmonics, but exceptions have been known. Acetylene is an example of a case in which the harmonic is very

pronounced, being stronger than the fundamental. In addition, the observed spectra show not only the skeletal frequencies (i.e., frequencies arising from carbon vibrations), but also those resulting from the hydrogen vibrations. In most cases the hydrogen bands are readily identified, because of their position, and because of the fact that they repeat from molecule to molecule in the same pattern. For example, in the region covered by the charts, there are two infra-red bands at about 1380 cm^{-1} and 1470 cm^{-1} , and three Raman bands at about 1280 cm^{-1} , 1340 cm^{-1} , and 1460 cm^{-1} , which clearly repeat in all the spectra, and so may be classed as very likely caused by hydrogen vibrations, and excluded from further discussion. (See Chart II.)

On the whole, the observed skeletal frequencies show the same type of irregularity as is found for the calculated frequencies, and the general groupings are qualitatively alike. The lack of pattern in the experimental bands may be regarded as a definite correlation between experiment and theory, even though of a negative character. The absence of trends in the experimental spectra of the octanes might have seemed somewhat surprising, since in certain classes of spectra a particular atom and bond are known to give rise to a characteristic frequency, which persists even when terms are added to the molecules. This is observable in the case of the C—H vibrations, as well as in cases where a double bond occurs, such as C=C, the so-called ethylenic linkage, for example, the frequency for which persists throughout a series of compounds.

Possible correlation of bands in the theoretical and experimental spectra of the isomeric octanes for which all normal skeletal frequencies were evaluated is indicated in Chart II. The identification of lines is merely tentative. The following observations may be of interest.

N-octane.—The experimentally observed skeletal vibrations appear to fall into two main

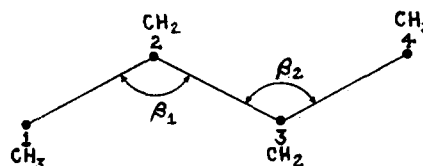


FIG. 8. Skeletal form of *n*-butane. $\beta_1^\circ = \beta_2^\circ = 107^\circ$.

⁷ The infra-red spectra for all molecules are given by R. A. Oetjen, "The infrared spectra of the isomeric octanes," Thesis (University of Michigan, 1941). The Raman spectra for 2-5-dimethylhexane and 3-4-dimethylhexane are given by J. W. Murray, J. Chem. Phys. 2, 618 (1934). The Raman spectrum for *n*-octane is given by K. W. F. Kohlrausch, *Der Smekal-Raman-Effekt* (Verlagsbuchhandlung, Julius Springer, Berlin, 1938), p. 154.

TABLE IX. Table of characters.

C_{2h}	E	C_2	σ_h	i	Raman	Infra-red	No.
$\Gamma^{(1)} \sim A_g$	1	1	1	1	P	IA	5
$\Gamma^{(2)} \sim B_g$	1	-1	-1	1	DP	IA	1
$\Gamma^{(3)} \sim A_u$	1	1	-1	-1	F	A	2
$\Gamma^{(4)} \sim B_u$	1	-1	1	-1	F	A	4
ϕ_R	0	π	0	π			
U_R	6	0	6	0			
$\pm 1 + 2 \cos \phi_R$	3	-1	1	-3			
$\chi(R)$	18	0	6	0			
Ξ	12	2	6	0			

groups, corresponding to stretching and bending motions, as predicted. There seems to be some correlation of fundamental lines in the two spectra, as well as a possibility of establishing a correlation for the overtones in the infra-red. The two lines at 344.0 cm^{-1} and 396.6 cm^{-1} in the theoretical spectrum are repeated at 723 cm^{-1} and 768 cm^{-1} in the experimental spectrum, with decreased intensity. Whether this is an actual case of correlation or not is uncertain.

Infra-red	Calculated	Observed
	86.16	} Not measured
	344.0	
	396.6	
	2(344.0)	723
	2(396.6)	768
		882
		915
	986.3	970
	996.7	
	1104	1081
		1140
Raman	Calculated	Observed
	200.0	250
	224.3	
	443.4	420
		500
		810
		870
		890
	955.7	950
		1030
	1053	1060
	1054	1070
	1127	1130

2-5-dimethylhexane.—The same type of grouping of bands is observable in the theoretical and experimental spectra, in the regions covered by both, and there is a comparatively good possibility for correlation of lines.

Infra-red	Calculated	Observed
	152.6	} Not measured
	257.9	
	372.6	
	426.8	
		750
	883.7	922
		955
	1061	1046
		1091
	1124	1173
		1229

Raman	Calculated	Observed
	217.9	265
		313
	367.1	444
	376.0	
		778
	851.3	836
	1032	962
		1048
	1113	1150
	1146	1176
		1302

2-2-3-3-tetramethylbutane.—Possible correlation of lines in the theoretical and experimental spectra is given in the table below, including overtone bands, as indicated.

Infra-red	Calculated	Observed
	209.5	} Not measured
	484.1	
	657.4	
		788
	847.0	796
		803
	2(484.1)	931
		999
	1123	1184

4-methylheptane, 3-4-dimethylhexane, 2-3-4-trimethylpentane, and 2-methyl-3-ethylpentane.—The frequencies fall into two main groups, corresponding to stretching and bending motions, as before. Identification of lines is extremely uncertain, but the correlation indicated in Chart II is regarded as possible.

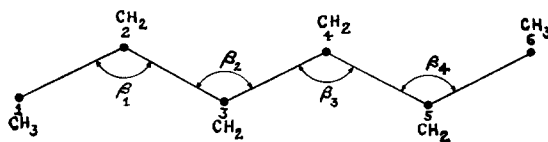


FIG. 9. Skeletal form of *n*-hexane.
 $\beta_1^\circ = \beta_2^\circ = \beta_3^\circ = \beta_4^\circ = 107^\circ$.

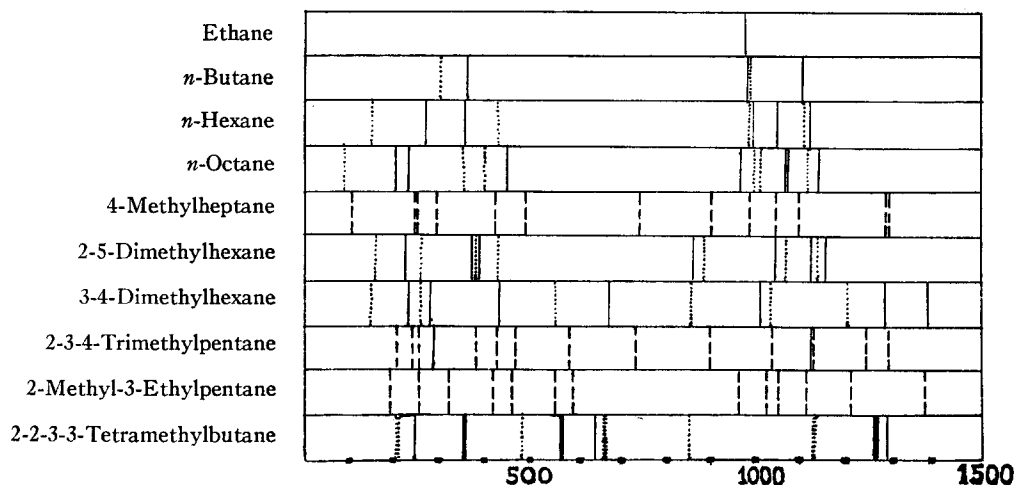


CHART I. Shows theoretical values of $1/\lambda$ in cm^{-1} . Infra-red active \cdots , Raman active $-$, Active in both $- \cdot -$.

The agreement between theory and experiment is not very good, but in view of the fact that small changes in form, and possibly also small changes in the potential function constants, result in considerable shifts in the location of the bands, it is, perhaps, what might be expected. The lack of pattern in both the theoretical and experimental bands is a definite correlation.

The tentative correlation established by this research is valuable, since it can give the type of motion belonging to the observed spectral bands, and this knowledge may be of considerable value in interpreting the spectra of the derivatives of the octanes. For example, if it is known that a certain band corresponds to a given motion of the atoms of an octane, the disappearance of

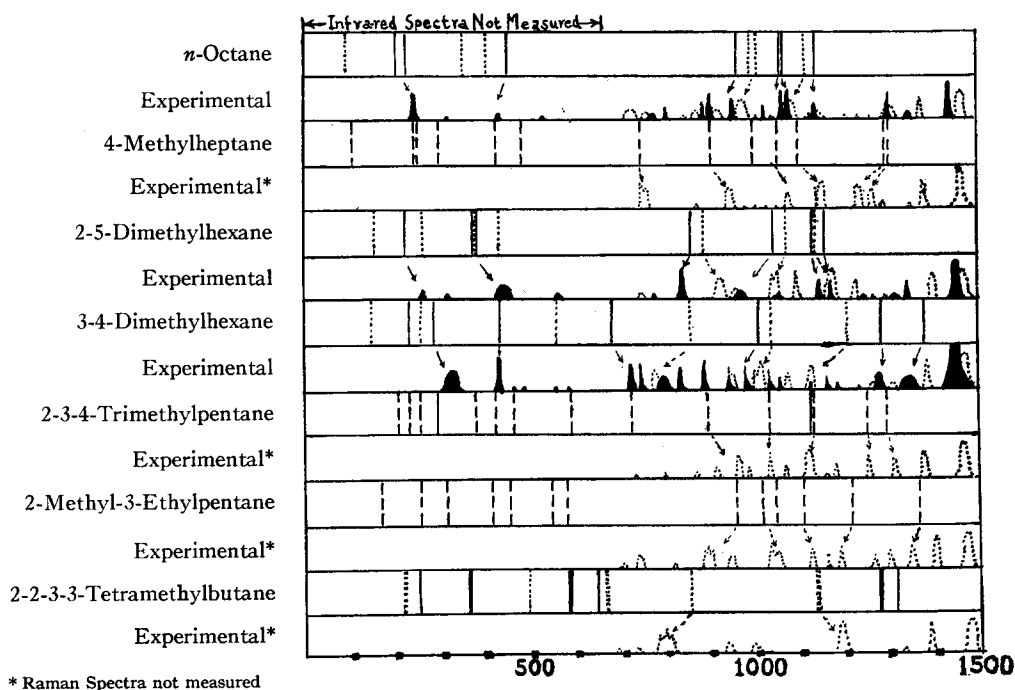


CHART II. Shows theoretical and experimental values of $1/\lambda$ in cm^{-1} . Infra-red active \cdots , Raman active $-$, Active in both $- \cdot -$.

this band in a derivative of this octane would indicate that the atomic group whose motion is responsible for the band has been changed by the added terms, while the persistence of the band would indicate that the added terms are not connected to that group in such a way as to interfere with its motion.

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The Intrinsic Viscosity of Polymer Solutions

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1. INTRODUCTION

RECENTLY some articles have been published dealing with the behavior of polymers of the coiling type suspended in a flowing liquid.¹ One of the issues is to establish a physical reason for Staudinger's rule according to which the intrinsic viscosity of polymer solutions should be proportional to the molecular weight of the polymer. I would like to present here a detailed picture of the motion of the polymer molecule and its parts, which makes it easy to see why the rule should hold for the very simplified model currently substituted for the actual molecule.

2. MOTION OF THE POLYMER MOLECULE

The model is as usual a number of identical atomic groups connected to each other by rigid links, the consecutive ones making a definite angle with each other and able to turn freely around each other. It is also assumed that each of these groups is acted upon by a frictional force $f\mathbf{v}$ if in a solvent flowing along with the velocity \mathbf{v} and that neither the links suffer friction from the medium nor any interaction between the different groups exists, due to their individual disturbance of the general flow.

The velocity of the liquid in a rectangular x, y, z system of coordinates may be represented

by the vector \mathbf{V} with the components

$$\mathbf{V} = \begin{cases} \alpha z = v_x \\ 0 = v_y \\ 0 = v_z \end{cases} \quad (1)$$

as it would result for instance from the motion of a plate in the x, y -plane moving with a constant velocity in the x -direction at a constant distance above another parallel plate at rest. The velocity gradient in the z -direction is α .

A polymer molecule suspended in this liquid will be set in motion by the frictional forces acting upon each atomic group of the chain. If now we confine our attention to the center of gravity of the molecule, it can easily be seen that this center of gravity (apart from its irregular Brownian motion) will move with the velocity of the liquid as it is at the position where this center is momentarily situated. In this way we have taken care of the condition that the sum of all the forces acting on the whole molecule, averaged over all the configurations the chain can acquire is zero.

Let us now take the center of gravity as the origin of our system of coordinates. Equation (1) will then represent the relative velocity of the liquid with respect to this center and will appear as represented in Fig. 1. It is evident from Fig. 1 that the still remaining frictional forces will now tend to rotate the molecule as a whole around the y -axis. Call the angular velocity of such a

¹ John G. Kirkwood, *J. Chem. Phys.* **14**, 180, 347 (1946); H. A. Kramers, *J. Chem. Phys.* **14**, 415 (1946), a sequence to an article by J. J. Hermans, *Physica* **10**, 777 (1943).