50% reaction and no choice between first and second order kinetics could be made. A preliminary study of the effect on the reaction, of several of the common catalysts and inhibitors for vinyl polymerization showed that only cadmium iodide was effective. Thermal initiation appears to be so rapid that the usual free radical catalysts have negligible effect, and the question of free radical initiations can be answered only by examining more active radical-producing substances. Early polymers isolated by precipitation have absorption spectra indicating a conjugated, polyene structure, and give color reactions with strong acids, metallic salts and bromine easily explained on this basis. Cross-linking involves breaking of the conjugation of the chain as indicated by decreased absorption, and the cross-linked polymers readily lose up to 46% of their phenoxyl content on heating. This suggests that the cross-linking may occur by a Diels–Alder reaction and that the hydroaromatic structure so produced is aromatized by loss of phenol. The early polymers are thermosetting and can be separated from later, cross-linked polymers chromatographically. Solvents greatly retard the polymerization and some indication that the primary reaction may involve free radicals was obtained by carrying out the reaction in ether which produced a polymer containing fragments of the ether molecule.

Los Angeles, California Received October 19, 1948

[Chemical Institute, Faculty of Science, Tokyo University]

Raman Frequencies of *n*-Paraffin Molecules

By San-ichiro Mizushima and Takehiko Simanouti

I. Intramolecular Rotation

The experimental results of Raman effect, infrared absorption, dipole moment and electron diffraction made for ethylene dihalides by Mizushima, Morino, Watanabe, Simanouti, and others in our Laboratory[1] has shown that there are three potential minima in one complete rotation about a carbon single bond as axis (Fig. 1). These three potential minima correspond to one *trans* form (T) in which two halogen atoms are at the farthest distance apart and two *gauche* forms (G and G′) obtainable from the *trans* form by internal rotation of ±120° (see Fig. 2). The energy difference between the *trans* and the *gauche* minima amounts to 1 kcal./mole (1.2 kcal. for ethylene dichloride and 1.3 kcal. for ethylene dibromide), from which the equilibrium isomeric ratio in the gaseous state can readily be calculated, but this ratio becomes naturally different in the liquid state owing to the intermolecular effect. In the solid state the intermolecular force (*i. e.*, crystal force) plays such a predominant role as to make only the *trans* form stable, which is most clearly seen from the disappearance of Raman lines assigned to *gauche* form on solidification.[2]

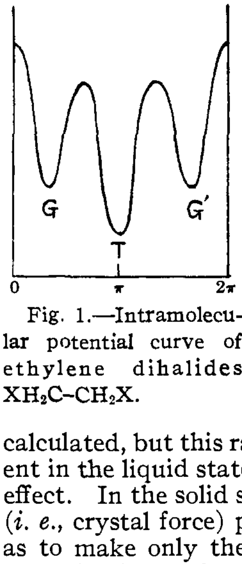

Fig. 1.—Intramolecular potential curve of ethylene dihalides XH_2C-CH_2X.

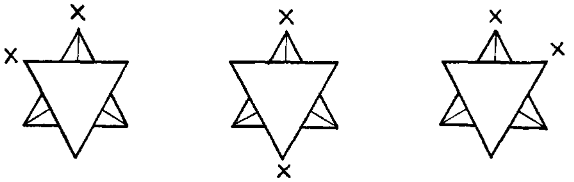

Fig. 2.—Molecular forms corresponding to the three potential minima.

II. Raman Spectra of *n*-Paraffins in the Liquid and Solid States

The change of Raman spectra of *n*-paraffins on solidification observed by Mizushima, Okazaki, Morino, Takeda and Nakamura in our Laboratory (see Table I) can readily be explained, if we assume quite similarly the existence of only one molecular form in the solid state and of several forms in the liquid state. It is seen from the calculation of normal frequency similar to that made for ethylene dihalide that the only one molecular form realized in solid butane is the *trans* form.[3] It is, therefore, quite reasonable to assume that the molecular form of *n*-paraffin in general is the extended zigzag configuration in which four consecutive CH_2-groups form the *trans* configuration. This is also compatible with the results of X-ray investigation made by Müller[4] and Bunn[5] for long chain paraffins. Let us explain in the following the Raman frequencies observed for solid paraffins on the basis of this molecular model.

In Table I we see that in the lower frequency region there was observed only one Raman line for each solid paraffin and its frequency is inversely

---

[1] Mizushima, Morino and others, *Physik. Z.*, **35**, 905 (1934); **38**, 459 (1937); *J. Chem. Phys.*, **9**, 826 (1941); Mizushima, Morino, Watanabe, Simanouti and others, *Sci. Pap. I. P. C. R.* (*Tokyo*), **39**, 396, 401 (1942); **40**, 87, 100, 417, 425 (1942); **42**, *Chem.* 1, 5, 27, 51 (1944).

[2] Mizushima and Morino, *Physik. Z.*, **38**, 459 (1937); Mizushima, Morino and Takeda, *J. Chem. Phys.*, **9**, 826 (1941).

[3] Mizushima, Morino and Simanouti, *Sci. Pap. I. P. C. R.* (*Tokyo*), **40**, 87 (1942).

[4] Müller, *Proc. Roy. Soc.* (*London*), **A120**, 437 (1928); **124**, 317 (1929); **127**, 417 (1930).

[5] Buno, *Trans. Farad. Soc.*, **35**, 482 (1939).

TABLE I

RAMAN SPECTRA OF *n*-PARAFFINS IN THE LIQUID AND SOLID STATES[a]

n-Butane		*n*-Pentane		*n*-Hexane		*n*-Heptane	
Liquid	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid
207 (00)						198 (0)	
223 (0)						222 (0)	
259 (0)							
287 (0)						285 (1)	
				315 (1b)		310 (6)	311 (5)
320 (1)		333 (1)		335 (1)			
						358 (2)	
				370 (4)	373 (3)		
						394 (3)	
		400 (7)	406 (3)	401 (2)		404 (0)	
429 (5)	425 (4)						
		467 (2)		450 (1)		455 (1)	
						506 (2)	
						695 (0)	
						721 (1)	
				746 (0)		742 (1)	
		764 (3)		760 (0)		775 (2b)	
789 (2)				794 (0)			
809 (0)				810 (1)		807 (0)	
827 (6)				826 (3)		829 (2)	
837 (7)	837 (6)	838 (5)				838 (6)	
						851 (3)	
		864 (4)	869 (3)	868 (3)		866 (0)	
				890 (4)		888 (2)	
		904 (1b)		900 (2)	898 (3)	901 (5)	
						909 (3)	905 (5)
						930 (1/2)	
955 (1b)		953 (0)		952 (0)		950 (0)	
				976 (00)		960 (1)	
980 (2)		990 (1)				988 (0)	
				1005 (1)	1005 (0)		
		1025 (3)				1023 (1b)	1028 (1)
		1035 (3)	1031 (0)	1040 (3)		1044 (3)	
1057 (4)	1059 (5)			1065 (1)	1064 (3)	1057 (2)	1056 (3)
1077 (1)		1072 (3b)	1069 (3)			1071 (2)	1072 (2)
				1080 (4)		1086 (4b)	
1150 (2)	1151 (4)	1142 (3)	1145 (3)	1140 (3)	1143 (3)	1139 (4)	1139 (4)
1168 (0)		1165 (0)		1165 (0)		1163 (2)	
						1206 (0)	
				1220 (00)		1237 (1)	
		1264 (1)		1250 (0)		1264 (0)	
1281 (0)						1281 (0)	
1301 (1b)	1300 (4)	1302 (4b)	1303 (3)	1302 (5b)	1300 (4)	1298 (6b)	1296 (4)
						1312 (2)	
				1343 (00)		1342 (1)	
				1366 (0)		1364 (0)	
1444 (5b)	1442 (3)	1437 (5b)	1445 (4)	1436 (5b)	1450 (5)	1432 (7b)	1446 (4b)
	1460 (2)	1458 (6b)	1466 (5)	1459 (7b)	1462 (4)	1460 (7b)	1473 (3)
2666 (1)		2666 (1)	2666 (1)	2672 (1)		2670 (1)	
2702 (1)	2703 (1)	2713 (1)		2703 (0)	2696 (1)	2708 (1)	
2733 (3)	2725 (1)	2733 (2)	2720 (2)	2735 (2)	2723 (2)	2730 (3)	2725 (1)
	2853 (8)	2847 (5)	2848 (2)	2849 (8)	2851 (5)	2848 (10b)	2852 (3)
2860 (8)		2861 (5)	2859 (2)	2862 (5)			2866 (2b)
2877 (10)	2872 (8)	2875 (10)		2875 (10)	2871 (5)	2873 (8)	2878 (7)
			2885 (8)		2885 (8)		
2901 (2)	2896 (10)					2901 (5b)	2904 (2)

[a] These data have been partly published. See Mizushima, Morino and Nakamura, *Sci. Pap. I. P. C. R.* (*Tokyo*), **37**, 205; Mizushima, Morino and Takeda, *ibid.*, **38**, 437 (1941); Okazaki, *J. Chem. Soc.* (*Japan*), **63**, 1500, 1255 (1942). Many of them have, however, been remeasured.

TABLE I (*Continued*)

n-Butane		*n*-Pentane		*n*-Hexane		*n*-Heptane	
Liquid	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid
2914 (5)	2912 (4)	2908 (5b)	2909 (4)	2916 (5)	2907 (5)		
2938 (8b)	2931 (1)	2936 (8b)	2934 (5)	2939 (10)	2934 (5)	2937 (8)	2930 (3)
	2950 (4)		2956 (2)		2953 (3)		2950 (2)
2962 (6b)	2965 (9)	2964 (8b)	2966 (6)	2964 (10b)	2965 (6)	2963 (10b)	2964 (7)

n-Octane		*n*-Nonane		*n*-Decane		*n*-Dodecane		*n*-Cetane	
Liquid	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid
196 (0)		196 (0)				195 (1)	194 (2)	199 (1)	150 (3)
218 (00)		221 (0)		200 (0)		218 (1)		215 (2)	
241 (00)		248 (3)	249 (2)	230 (3)	231 (3)	239 (2b)		231 (1)	
279 (5)	283 (3)	264 (4)		250 (4)				278 (0b)	
295 (1)		283 (1)				308 (0)		330 (0)	
347 (0)		340 (1)		339 (0)		349 (0)		356 (0)	
374 ($^1/_2$)		375 ($^1/_2$)		359 ($^1/_2$)′					
399 (0)		404 (1)		404 (2b)		397 (1)		404 (1)	
427 (1)		417 ($^1/_2$)				421 ($^1/_2$)			
454 (0)		453 ($^1/_2$b)		441 ($^1/_2$)		453 (00)		450 (00)	
		489 (0)		465 ($^1/_2$)		487 (00)			
505 (0b)		510 (0)							
		523 (0)		521 (1)					
		548 (0)		661 (0b)					
696 (00)		697 (0)		697 ($^1/_2$)					
723 ($^1/_2$)		721 ($^1/_2$)		723 (1)		724 (1)		724 (1)	
735 ($^1/_2$)		751 ($^1/_2$)		744 (1)		749 (0)		742 (00)	
765 (1)				772 (2b)		772 (1b)		762 (00)	
		781 (1)						784 (00)	
				810 (2b)		805 (1)		808 (0)	
815 (2b)		820 (3)				817 (1)			
843 (2)		843 (3)		844 (3b)		845 (2b)		839 (2b)	
861 (3)		871 (3)		870 (1)		872 (1)		871 (2)	
878 (3)				886 (3)	886 (2)				
896 (4)	899 (2)	892 (4)	888 (2)	898 (3)		893 (3)	892 (1)	894 (3)	888 (1)
				921 (1)		917 (00)			
		926 (0)				931 (00)			
953 (1)				952 (1)		955 (1)			
970 (2)		970 (1b)		971 (1)		964 (1)		962 (1)	
999 (00)				991 (1)				997 (00)	
				1008 (1)		1002 (00)			
1026 (2)		1019 (1)		1023 (1)		1032 (1b)		1015 (0)	
1045 (2)	1045 ($^1/_2$)	1046 (0)		1047 (2)					
1060 (4)	1062 (2)	1062 (3)	1060 (1)	1062 (4)	1060 (3)	1061 (3)	1061 (2)	1063 (4)	1058 (2)
1083 (4b)		1082 (3b)		1080 (4)		1078 (3)		1082 (5b)	
				1092 (3)		1100 (0)		1108 (0)	
1137 (4)	1138 (2)	1134 (3)	1136 (2)	1133 (4)	1136 (3)	1129 (3)	1136 (3)	1132 (4)	1135 (2)
1162 (1)	1176 (0)	1159 (1)		1161 (2)		1159 (1)		1165 (0)	
1199 (0)		1192 (0)		1189 (0)					
1226 (0)		1217 (0)		1211 (0)					
				1250 (0)					
				1271 (0)					
1299 (5b)	1297 (3)	1299 (4b)	1297 (3)	1301 (6b)	1295 (3)	1300 (6b)	1297 (3)	1304 (7b)	1295 (2)
								1314 (2)	
1342 (0)		1340 (0)		1340 ($^1/_2$)		1341 ($^1/_2$)		1344 (0)	
1366 (0b)	1384 (1)	1365 (0)		1366 (1)		1369 (1)		1368 (1)	
1434 (7b)	1449 (3b)	1433 (8)	1444 (2)	1433 (8b)	1447 (2b)	1433 (7b)	1441 (3b)	1435 (8b)	1442 (2b)
1459 (5b)	1469 (3b)	1460 (8)	1465 (3)	1460 (6b)	1475 (1)	1461 (5b)	1462 (2b)	1460 (6b)	1471 (2b)
			1486 (0)						
2668 (1)		2666 (1)	2660 (1)	2673 (1)	2660 (1)	2670 (0b)		2673 (0b)	
2714 (0)	2699 (0)	2706 (1)				2718 (0)		2713 (2)	
2732 (3)	2727 (0)	2731 (2)	2720 (0)	2732 (3)	2724 (1)	2730 (3b)	2723 (0b)	2730 (3)	
	2765 (0)								
2849 (10)	2853 (3b)	2846 (10)	2847 (2)	2850 (10)	2843 (2)	2849 (10)	2845 (4b)	2847 (10b)	2846 (3)

TABLE I (*Continued*)

n-Octane		*n*-Nonane		*n*-Decane		*n*-Dodecane		*n*-Cetane	
Liquid	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid
2873 (6)	2882 (10)	2873 (2)	2877 (5)		2877 (6)		2879 (10)	2885 (8b)	2878 (5)
2904 (6)		2896 (3)		2897 (6b)		2896 (8b)			
2937 (8)	2937 (2)	2933 (7)	2934 (2)	2936 (7)	2935 (1)	2936 (8)	2933 (1)	2937 (8b)	2934 (1)
2965 (8b)	2965 (5)	2964 (8)	2964 (4)	2966 (8)	2964 (3)	2964 (9b)	2964 (3)	2965 (6b)	2963 (2)

proportional to the number of carbon atoms when it is greater than five. This would be explained simply, if we approximate the extended carbon chain by a continuous rod and assign the said Raman line to its longitudinal motion whose frequency is given by

$$\nu = \frac{1}{2l}\sqrt{\frac{E}{\rho}} \tag{1}$$

where E is Young's modulus, ρ the density, l the length of the rod. This relation means that the frequency is inversely proportional to the length of the chain or to the number of carbon atoms. Putting the observed frequencies into ν of Eq. (1), we obtain a value of E (34×10^{11} dynes/sq. cm.) comparable to that of diamond (55×10^{11} dynes/sq. cm.). This is quite reasonable, since this value of E refers to the carbon chain connected by covalency just as in the case of diamond, but not to the solid paraffins whose molecules are connected by van der Waals forces.

The calculation of skeletal modes of vibration was made by Kirkwood,[6] and by somewhat different method by Thomas, Whitcomb and Nielsen[7] and by Barriol.[8] Kirkwood's formulation will be used here with, however, a modification in the potential function, since the simple valence force formula used by Kirkwood cannot explain the quantitative feature of our problem.

As in the case of our previous calculation[3] for ethylene dihalide we assume the potential function of the form

$$V = K'r_0 \sum_n (\Delta r_n) + \frac{1}{2} K \sum_n (\Delta r_n)^2 + H'r_0 \sum_n (r_0 \Delta\alpha_n) + \frac{1}{2} H \sum_n (r_0\, \Delta\alpha_n)^2 + F' \sum_n q_0\, (\Delta q_n) + \frac{1}{2} F \sum_n (\Delta q_n)^2 \tag{2}$$

where the significance of the force constants K, H, F, etc., and of the increments in atomic distances Δr_n and Δq_n and in bond angles $\Delta\alpha_n$ is clear from Fig. 3. Eliminating q's through the relation $q_n^2 = r_n^2 + r_{n+1}^2 - 2r_n r_{n+1} \cos \alpha_n$, we can set up the equations of motion as

$$\ddot{\xi}_n + \frac{K + 2F'(1 + \cos\alpha_0)}{m}\left[\sin^2\left(\frac{\alpha_0}{2}\right)(2\xi_n - \xi_{n+1} - \xi_{n-1}) + (-1)^n \sin\frac{\alpha_0}{2}\cos\frac{\alpha_0}{2}(\eta_{n+1} - \eta_{n-1})\right] + \frac{H}{m}\left[\cos^2\left(\frac{\alpha_0}{2}\right)(2\xi_n - \xi_{n+2} - \xi_{n-2}) + (-1)^n \sin\frac{\alpha_0}{2}\cos\frac{\alpha_0}{2}(2\eta_{-1} - 2\eta_{n+1} + \eta_{n+2} - \eta_{n-2})\right] + \frac{F}{m}[2\xi_n - \xi_{n+2} - \xi_{n-2}] = 0$$

$$\ddot{\eta}_n + \frac{K + 2F'\,(1 + \cos\alpha_0)}{m}\left[\cos^2\left(\frac{\alpha_0}{2}\right)(2\eta_n - \eta_{n+1} - \eta_{n-1}) + (-1)^n \sin\frac{\alpha_0}{2}\cos\frac{\alpha_0}{2}(\xi_{n+1} - \xi_{n-1})\right] + \frac{H}{m}\left[\sin^2\left(\frac{\alpha_0}{2}\right)(6\eta_n - 4\eta_{n+1} - 4\eta_{-1} + \eta_{n+2} + \eta_{n-2}) - (-1)^n \sin\frac{\alpha_0}{2}\cos\frac{\alpha_0}{2}(2\xi_{n+1} - 2\xi_{n-1} + \xi_{n+2} - \xi_{n-2})\right] - \frac{F'}{m}[6\eta_n - 4\eta_{n+1} - 4\eta_{n-1} + \eta_{n+2} + \eta_{n-2}] = 0$$

where ξ is the displacement from equilibrium along the length of the chain, η the displacement perpendicular to the chain (see Fig. 3), and m the mass of CH_2-group.

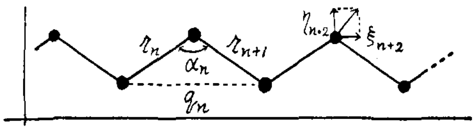

Fig. 3.—Coördinates of the extended chain.

Let N be the number of carbon atoms in the chain. We have then $2N$ such equations of motion, the particular solutions of which are of the form

$$\xi_n = Ae^{i(\omega t + n\lambda)},\ \eta_n = (-1)^n Be^{i(\omega t + n\lambda)}$$

where the amplitudes A and B satisfy the equations.

$$\left.\begin{aligned} (\kappa_{11} - \omega^2)\, A + i\, \kappa_{12}B &= 0 \\ -\, i\kappa_{12}A + (\kappa_{22} - \omega^2)\, B &= 0 \end{aligned}\right\} \tag{3}$$

$$m\kappa_{11} = (1 - \cos\lambda)[\{K + 2F'\,(1 + \cos\alpha_0)\}(1 - \cos\alpha_0) + 2H\,(1 + \cos\alpha_0)(1 + \cos\lambda) + 4F\,(1 + \cos\lambda)]$$

$$m\kappa_{22} = (1 + \cos\lambda)[\{K + 2F'\,(1 + \cos\alpha_0)\}(1 + \cos\alpha_0) + 2H\,(1 - \cos\alpha_0)(1 + \cos\lambda) - 4F'(1 + \cos\lambda)]$$

$$m\kappa_{12} = \sin\lambda\,[-\,\{K + 2F'\,(1 + \cos\alpha_0)\}\sin\alpha_0 + 2H\sin\alpha_0\,(1 + \cos\lambda)]$$

The values of ω^2 corresponding to non-trivial solutions of Eq. (3) satisfy the secular equation

$$\begin{vmatrix} \kappa_{11} - \omega^2 & i\kappa_{12} \\ -i\kappa_{12} & \kappa_{22} - \omega^2 \end{vmatrix} = 0 \tag{4}$$

Since an integral number of half wave length must be completed within the molecule,[9] we have

$$\left.\begin{aligned} \lambda &= \pi l/N \\ l &= 0, 1, 2, \ldots, N - 1 \end{aligned}\right\} \tag{5}$$

---

[6] Kirkwood, *J. Chem. Phys.*, **7**, 506 (1939).

[7] Thomas and Whitcomb, *Phys. Rev.*, **56**, 383 (1939); Whitcomb, Nielsen, and Thomas, *J. Chem. Phys.*, **8**, 143 (1940).

[8] Barriol, *J. phys. rad.*, **10**, 215 (1939).

[9] Instead of Eq. (5) Kirkwood put $\lambda = 2\pi l/N$, which is not correct as pointed out by Pitzer, *J. Chem. Phys.*, **8**, 711 (1940).

By the examination of the character of motion associated with each mode of vibration we see that the two vibrations of $l = 1$ appear in the Raman spectrum as strong lines.[10] One of them corresponds to the symmetric deformation vibration and the other to the symmetric valency vibration. It is evident that the former is assigned to the said Raman line of the lowest frequency and the latter to the line observed at about 900 cm.$^{-1}$. As the values of force constants and equilibrium angle we shall use the following reasonable ones:

$$\left.\begin{aligned} K &= 4.0 \times 10^5 \text{ dynes/cm.} \\ H &= 0.11 \times 10^5 \text{ dynes/cm.} \\ F &= 0.96 \times 10^5 \text{ dynes/cm.} \\ F' &= 0 \\ \alpha_0 &= \text{tetrahedral angle} \end{aligned}\right\} \qquad (6)$$

With these molecular constants we can calculate the two frequencies stated above as shown in Table II. The agreement with the observed and the calculated frequencies is satisfactory.[11]

TABLE II

THE CALCULATED AND OBSERVED SKELETAL FREQUENCIES (IN CM.$^{-1}$) OF *n*-PARAFFIN MOLECULES IN THE EXTENDED FORM[a]

Number of carbon atoms in a molecule	Deformation frequency Calcd.	Obs.	Valency frequency Calcd.	Obs.
4	432	425	835	837
5	402	406	851	869
6	369	373	893	898
7	325	311	890	905
8	289	283	888	899
9	259	249	888	888
10	235	231	887	886
12	198	194	887	892
16	150	150	887	888

[a] The frequencies of *n*-butane and *n*-pentane have been calculated similarly to those of dichloroethane.[3] The values of force constants was put equal to those of the long chain paraffins except that of the end group CH_3-CH_2 for which K was put equal to 3.2×10^5 dynes/cm.

We want to add a few words about the spectra in the liquid state. As already stated they have many more lines than the spectra observed in the solid state (see Table I), which is due to the fact that several rotational isomers co-exist with one another in the liquid state. It is very interesting that the lines observed in the solid state remain very strong in the liquid state for low homologs, while the strong line at 150 cm.$^{-1}$ of solid cetane, $C_{16}H_{34}$, escaped detection in the liquid state. This means that for lower homologs the extended molecular form is abundant in the liquid state, while for cetane this is almost absent in that state. This would have something to do with the idea proposed by Eyring[12] that the long chain molecules act in segments in the liquid state.

III. Intramolecular Rotation of Highly Elastic Substances

We shall take this opportunity to make a short discussion on high elasticity. This property of rubber-like polymers has been considered to be due to the chain structure of their molecules, but all the substances with chain molecules do not show high elasticity. For instance polyisobutylene, $-C(CH_3)_2-CH_2-C(CH_3)_2-CH_2-$, shows highly elastic properties even at considerably lower temperature, while a simpler hydrocarbon polyethylene does not show this property at ordinary temperature.

We consider that such a difference can be explained readily from the result of our study stated in I. A unit structure of these two polymers corresponds, respectively, to 2,2-dimethylbutane, $CH-C(CH_3)_2-CH-CH_3$, (polyisobutylene) and to *n*-butane, $CH_3-CH_2-CH_2-CH_3$, (polyethylene). In the former case the three stable molecular forms are identical and, therefore, have the same energy, while in the latter case the *trans* form has a lower energy than the *gauche* forms. From this fact it immediately follows that the molecular chain of polyisobutylene can be folded more easily than that of polyethylene and hence the former substance shows high elasticity at a lower temperature than the latter.

It seems that high elasticity at lower temperature is observed for a substance whose molecule has at least two potential minima of practically the same energy. In the case of carbon chain such an intramolecular potential will be realized by the existence of side chain, which is quite consistent with our experience. If, however, we consider that the energy difference between the *trans* and the *gauche* forms of *n*-butane amounts only to about 1 kcal./mole, the straight carbon chain will have considerable probability to be folded at a slightly higher temperature. This would be the reason why polyethylene shows elastic property at a temperature higher than about 120°.

Summary

The disappearance of many Raman lines of *n*-paraffins on solidification has been explained by considering only one molecular form in the solid state and several ones in the liquid state. The molecular form in the solid state has been shown to be the extended form for which the calculation of normal vibrations has been made. A short discussion on high elasticity has been added.

BUNKYOKU, TOKYO RECEIVED SEPTEMBER 7, 1948

---

[10] This is consistent with Pitzer's assignment (*J. Chem. Phys.*, **8**, 711 (1940)), but our calculated frequencies are different from those of Pitzer who used the same potential function as Kirkwood.

[11] In Eq. (6) we put $F' = 0$. This means that only the quadratic terms were taken into account in our numerical calculation. Hence the difference of the present calculation from the previous ones results from the last term in potential function (2).

[12] Powell, Clark and Eyring, *J. Chem. Phys.*, **9**, 268 (1941).