

**The Normal Vibrations of Polyatomic Molecules as Calculated by UreyBradley Field. II. Vibrations of Polythene, Ethane, and Their Deuterium Compounds**

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# The Normal Vibrations of Polyatomic Molecules as Calculated by Urey-Bradley Field.

## II. Vibrations of Polythene, Ethane, and Their Deuterium Compounds

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Assuming the Urey-Bradley field as the type of intramolecular potential equations to calculate five optically active frequencies of polythene molecule were derived. If we assume as force constants  $K_{CH}=4.2$ ,  $H_{HCH}=0.15$ ,  $F_{HH}=0.1$ ,  $F_{HC}=0.4$ ,  $F_{HH'}=0$  and  $F_{HC'}=-0.05$  ( $10^6$  dynes/cm), the observed frequencies of  $(CH_2)_n$  and  $(CD_2)_n$  as well as those of  $CH_4$ ,  $CD_4$ ,  $C_2H_6$ ,  $C_2D_6$ , etc., were explained satisfactorily.

### INTRODUCTION

IN the preceding paper<sup>1</sup> which dealt with the calculation of the vibration frequencies of methane and its derivatives, it was concluded that repulsive forces between atoms which are not bonded directly cannot be neglected, as compared with stretching and bending forces of bonds, and that, therefore, the Urey-Bradley field is the most adequate type of potential energy for the normal coordinate treatment of these molecules.

The object of the present work is to determine whether this type of potential field is adequate in the case of polythene,  $(CH_2)_n$ , ethane,  $C_2H_6$ , and fully deuterated polythene,  $(CD_2)_n$ , and ethane,  $C_2D_6$ . Polythene is an interesting molecule because it gives a strikingly simple spectrum and one of its CH deformation frequencies is found to be extraordinarily low.<sup>2</sup> Whitcomb, Nielsen, and Thomas<sup>3</sup> have already developed the normal coordinate treatment of this type of molecule. But either the potential energy resulting from central forces they used or that caused by simple valence forces seems to be incapable of accounting for this frequency.

### THE POTENTIAL ENERGY OF POLYTHENE MOLECULE

The model used for the structures of polythene and deuteropolythene is shown in Fig. 1. Since we assume the Urey-Bradley field, the terms in the potential energy involving the coordinates of the  $h$ th  $CH_2$  group are taken to be

$$V_h = K'_{CH}a(\Delta r_h + \Delta r_h') + \frac{1}{2}K_{CH}\{(\Delta r_h)^2 + (\Delta r_h')^2\} + K'_{CC}b(\Delta R_h) + \frac{1}{2}K_{CC}(\Delta R_h)^2 + H'_{HCH}a^2(\Delta\theta_h) + \frac{1}{2}H_{HCH}a^2(\Delta\theta_h)^2 + H'_{CCC}b^2(\Delta\Theta_h) + \frac{1}{2}H_{CCC}b^2(\Delta\Theta_h)^2 + H'_{HCC}ab(\Delta\varphi_h + \Delta\varphi_h' + \Delta\varphi_h'' + \Delta\varphi_h''') + \frac{1}{2}H_{HCC}ab\{(\Delta\varphi_h)^2 + (\Delta\varphi_h')^2 + (\Delta\varphi_h'')^2 + (\Delta\varphi_h''')^2\} + F'_{HH}(2a \sin\alpha)\Delta q_h + \frac{1}{2}F_{HH}(\Delta q_h)^2 + F'_{CC}(2b \sin\alpha)\Delta Q_h + \frac{1}{2}F_{CC}(\Delta Q_h)^2 + F'_{CH}a(\Delta p_h + \Delta p_h' + \Delta p_h'' + \Delta p_h''') + \frac{1}{2}F_{CH}\{(\Delta p_h)^2 + (\Delta p_h')^2 + (\Delta p_h'')^2 + (\Delta p_h''')^2\}, \quad (1)$$

where internal coordinates  $R_h$ ,  $r_h$ , etc., denote the distances and angles, respectively, with equilibrium values as indicated in parentheses.

$$\begin{aligned} R_h(C_h - C_{h+1} = b), & \quad r_h(C_h - H_h = a), & \quad r_h'(C_h - H_h' = a), \\ \Theta_h(\angle C_{h+1} - C_h - C_{h-1} = 2\beta), & \quad Q_h(C_{h-1} \cdots C_{h+1} = 2b \sin\beta), \\ \theta_h(\angle H_h - C_h - H_h' = 2\alpha), & \quad q_h(H_h \cdots H_h' = 2a \sin\alpha), \\ \varphi_h(\angle H_h - C_h - C_{h+1} = 2\gamma), & \quad p_h(H_h \cdots C_{h+1} = \alpha), \\ \varphi_h'(\angle H_h' - C_h - C_{h+1} = 2\gamma), & \quad p_h'(H_h' \cdots C_{h+1} = \alpha), \\ \varphi_h''(\angle H_h - C_h - C_{h-1} = 2\gamma), & \quad p_h''(H_h \cdots C_{h-1} = \alpha), \\ \varphi_h'''(\angle H_h' - C_h - C_{h-1} = 2\gamma), & \quad p_h'''(H_h' \cdots C_{h-1} = \alpha). \end{aligned} \quad (2)$$

Here

$$\alpha^2 = a^2 + b^2 - 2ab \cos 2\gamma, \quad (3)$$

$$\cos 2\gamma = -\cos\alpha \cos\beta. \quad (4)$$

Since the coordinates  $Q_h$ ,  $q_h$ ,  $p_h$ ,  $p_h'$ ,  $p_h''$ , and  $p_h'''$ , which denote elongations of distances between atoms not bonded directly, are expressed in terms of the other coordinates as shown in the preceding paper,<sup>1</sup> the potential energy is given by

$$\begin{aligned} 2V_h = & K_1\{(\Delta r_h)^2 + (\Delta r_h')^2\} + K_2(\Delta R_h)^2 \\ & + H_1(a\Delta\theta_h)^2 + H_2(b\Delta\Theta_h)^2 \\ & + H_3ab\{(\Delta\varphi_h)^2 + (\Delta\varphi_h')^2 + (\Delta\varphi_h'')^2 + (\Delta\varphi_h''')^2\} \\ & + 2K_{11}(\Delta r_h)(\Delta r_h') + 2K_{22}(\Delta R_h)(\Delta R_{h-1}) \\ & + 2K_{12}\{(\Delta r_h)(\Delta R_h) + (\Delta r_h')(\Delta R_h) \\ & \quad + (\Delta r_h)(\Delta R_{h-1}) + (\Delta r_h')(\Delta R_{h-1})\} \\ & + 2F_{11}(a\Delta\theta_h)(\Delta r_h + \Delta r_h') \\ & \quad + 2F_{22}(b\Delta\Theta_h)(\Delta R_h + \Delta R_{h-1}) \\ & + 2F_{13}(ab)^{\frac{1}{2}}\{(\Delta r_h)(\Delta\varphi_h) + (\Delta r_h')(\Delta\varphi_h') \\ & \quad + (\Delta r_h)(\Delta\varphi_h'') + (\Delta r_h')(\Delta\varphi_h''')\} \\ & + 2F_{23}(ab)^{\frac{1}{2}}\{(\Delta R_h)(\Delta\varphi_h) + (\Delta R_h)(\Delta\varphi_h') \\ & \quad + (\Delta R_{h-1})(\Delta\varphi_h'') + (\Delta R_{h-1})(\Delta\varphi_h''')\} \\ & + 2H_{13}a(ab)^{\frac{1}{2}}\{(\Delta\theta_h)(\Delta\varphi_h) + (\Delta\theta_h)(\Delta\varphi_h') \\ & \quad + (\Delta\theta_h)(\Delta\varphi_h'') + (\Delta\theta_h)(\Delta\varphi_h''')\} \\ & + 2H_{23}b(ab)^{\frac{1}{2}}\{(\Delta\Theta_h)(\Delta\varphi_h) + (\Delta\Theta_h)(\Delta\varphi_h') \\ & \quad + (\Delta\Theta_h)(\Delta\varphi_h'') + (\Delta\Theta_h)(\Delta\varphi_h''')\} \\ & + 2H_{33}ab\{(\Delta\varphi_h)(\Delta\varphi_h') + (\Delta\varphi_h)(\Delta\varphi_h'') \\ & \quad + (\Delta\varphi_h')(\Delta\varphi_h'') + (\Delta\varphi_h'')(\Delta\varphi_h''')\}, \end{aligned} \quad (5)$$

where, with the abbreviations

$$\begin{aligned} s_1 = \sin\alpha, \quad s_2 = \sin\beta, \quad s_3 = (a - b \cos 2\gamma)/\alpha, \\ s_4 = (b - a \cos 2\gamma)/\alpha, \\ t_1 = \cos\alpha, \quad t_2 = \cos\beta, \quad t_3 = b \sin 2\gamma/\alpha, \\ t_4 = a \sin 2\gamma/\alpha, \end{aligned}$$

<sup>1</sup> Takehiko Simanouti, J. Chem. Phys. **17**, 245 (1949).

<sup>2</sup> N. Sheppard and G. B. B. M. Sutherland, Nature **159**, 739 (1947).

<sup>3</sup> S. E. Whitcomb, H. H. Nielsen, and L. H. Thomas, J. Chem. Phys. **8**, 143 (1940).

and intramolecular tension  $\kappa$ , we have

$$\begin{aligned}
 K_1 &= K_{CH} + t_1^2 F'_{HH} + s_1^2 F_{HH} + 2t_3^2 F'_{HC} + 2s_3^2 F_{HC}, \\
 K_2 &= K_{CC} + 2t_2^2 F'_{CC} + 2s_2^2 F_{CC} + 4t_4^2 F'_{HC} + 4s_4^2 F_{HC}, \\
 H_1 &= H_{HCH} - s_1^2 F'_{HH} + t_1^2 F_{HH} + (3\kappa/8^{1/2}a^2), \\
 H_2 &= H_{CCC} - s_2^2 F'_{CC} + t_2^2 F_{CC} + (3\kappa/8^{1/2}b^2), \\
 H_3 &= H_{HCC} - s_3 s_4 F'_{HC} + t_3 t_4 F_{HC} + (3\kappa/8^{1/2}ab), \\
 K_{11} &= -t_1^2 F'_{HH} + s_1^2 F_{HH}, \\
 K_{22} &= -t_2^2 F'_{CC} + s_2^2 F_{CC}, \\
 K_{12} &= -t_3 t_4 F'_{HC} + s_3 s_4 F_{HC}, \\
 F_{11} &= t_1 s_1 (F'_{HH} + F_{HH}), \\
 F_{22} &= t_2 s_2 (F'_{CC} + F_{CC}), \\
 F_{13} &= (b/a)^{1/2} (t_3 s_4 F'_{HC} + s_3 t_4 F_{HC}), \\
 F_{23} &= (a/b)^{1/2} (t_4 s_3 F'_{HC} + s_4 t_3 F_{HC}), \\
 H_{13} &= \kappa/a(2ab)^{1/2}, \\
 H_{23} &= \kappa/b(2ab)^{1/2}, \\
 H_{33} &= \kappa/2^{1/2}ab.
 \end{aligned} \quad (6)$$

### EQUATIONS FOR THE OPTICALLY ACTIVE VIBRATIONS

The same method as developed by Whitcomb, Nielsen, and Thomas<sup>3</sup> is applicable even when we assume Eq. (5) for the potential energy. In this case the following equations are obtained for all the optically active chain vibrations with the designations used by Whitcomb and others.

For  $\nu_2(0\pi)$ , i.e.,  $\text{CH}_2$  bending vibration parallel to chain axis, denoting  $4\pi^2 c^2 \nu^2$  by  $\lambda$ , the reciprocal of the mass of a carbon atom by  $\mu_0$ , and that of a hydrogen atom by  $\mu$ , we have

$$\lambda = 2(2\mu_0 + \mu)(b \sin^2 \beta / a \sin^2 2\gamma) \{H_{HCC} - s_3 s_4 F'_{HC} + t_3 t_4 F_{HC} + (3\kappa/8^{1/2}ab)\}. \quad (7)$$

For  $\nu_3(\pi\sigma)$  and  $\nu_4(\pi\sigma)$ , i.e., symmetric CH stretching and HCH deformation vibrations, respectively, both having the change of dipole moment in the plane of  $\text{CCC} \cdots \text{zigzag}$  chain and perpendicular to the chain axis,

$$\begin{vmatrix} \mu B - \lambda, & \{\mu(2\mu_0 + \mu)\}^{1/2} C \\ \{\mu(2\mu_0 + \mu)\}^{1/2} C, & (2\mu_0 + \mu)A - \lambda \end{vmatrix} = 0, \quad (8)$$

where

$$\begin{aligned}
 A &= s_1^2 K_{CH} + 2s_5^2 H_{HCC} + 2s_1^2 t_1^2 F'_{HH} \\
 &\quad + \{2t_3^2 s_1^2 - 4(b/a)^{1/2} t_3 s_4 s_1 s_5 - 2s_3 s_4 s_5^2\} F'_{HC} \\
 &\quad + 2s_6^2 F_{HC} + (3s_5^2/2^{1/2}ab)\kappa, \\
 B &= t_1^2 K_{CH} + 2t_5^2 H_{HCC} + 2t_1^4 F'_{HH} \\
 &\quad + \{2t_3^2 t_1^2 + 4(b/a)^{1/2} t_3 s_4 t_1 t_5 - 2s_3 s_4 t_5^2\} F'_{HC} \\
 &\quad + 2t_6^2 F_{HC} + (3t_5^2/2^{1/2}ab)\kappa, \\
 C &= s_1 t_1 K_{CH} - 2s_5 t_5 H_{HCC} + 2s_1 t_1^3 F'_{HH} \\
 &\quad + \{2t_3^2 s_1 t_1 + 2(b/a)^{1/2} t_3 s_4 (s_1 t_5 - t_1 s_5) + 2s_3 s_4 s_5 t_5\} F'_{HC} \\
 &\quad + 2s_6 t_6 F_{HC} - (3s_5 t_5/2^{1/2}ab)\kappa,
 \end{aligned}$$

with the abbreviations

$$\begin{aligned}
 s_5(b/a)^{1/2} \sin \alpha \cos \alpha \cos \beta / \sin 2\gamma, & \quad s_6 = a \sin \alpha / d, \\
 t_5(b/a)^{1/2} \sin^2 \alpha \cos \beta / \sin 2\gamma, & \quad t_6 = (a \cos \alpha + b \cos \beta) / d.
 \end{aligned}$$

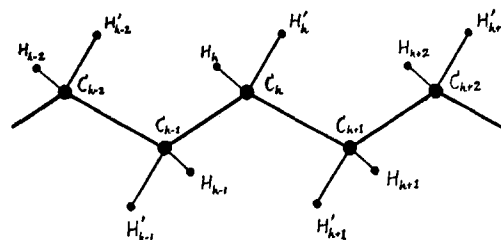


FIG. 1.

For  $\nu_7(\pi\sigma)$  and  $\nu_8(\pi\sigma)$ , i.e., the antisymmetric CH stretching and  $\text{CH}_2$  rocking vibrations, respectively, both having the change of dipole moment perpendicular to the plane of the  $\text{CCC} \cdots \text{zigzag}$  chain,

$$\begin{vmatrix} \mu B' - \lambda, & \{\mu(2\mu_0 + \mu)\}^{1/2} C' \\ \{\mu(2\mu_0 + \mu)\}^{1/2} C', & (2\mu_0 + \mu)A' - \lambda \end{vmatrix} = 0, \quad (9)$$

where

$$\begin{aligned}
 A' &= B + 2s_1^2 H_{HCH} - 2F'_{HH} \\
 &\quad + \{3bs_1^2 - 8(ab)^{1/2} s_1 t_5 + 4at_5^2\} (\kappa/2^{1/2}a^2b), \\
 B' &= A + 2t_1^2 H_{HCH} + 2F_{HH} \\
 &\quad + \{3bt_1^2 - 8(ab)^{1/2} t_1 s_5 + 4as_5^2\} (\kappa/2^{1/2}a^2b), \\
 C' &= C - 2s_1 t_1 H_{HCH} \\
 &\quad - \{3bt_1 s_1 - 8(ab)^{1/2} s_1 s_5 + 4at_5 s_5\} (\kappa/2^{1/2}a^2b).^*
 \end{aligned}$$

### OBSERVED FREQUENCIES OF $(\text{CH}_2)_n$ AND $(\text{CD}_2)_n$

Investigations of the spectrum of polythene were carried out by Fox and Martin,<sup>4</sup> Thompson and Torkington,<sup>5</sup> Glatt and Ellis,<sup>6</sup> and Elliott, Ambrose, and Temple.<sup>7</sup> The writer also measured the spectrum of this substance and the results are in good agreement with those observations. The spectrum of  $(\text{CD}_2)_n$  has recently been investigated by Sheppard and Sutherland.<sup>2</sup> The results of these spectra can be summarized as follows:

$(\text{CH}_2)_n$	$(\text{CD}_2)_n$
728 $\text{cm}^{-1}$	520 $\text{cm}^{-1}$ (perpendicular to the chain axis)
1375	1060 (parallel to the chain axis)
1475	1100 (perpendicular to the chain axis)
2853	—
2926	—

The 1475- and 728- $\text{cm}^{-1}$  vibrations have often been observed to be doublets, but it is most probable that this splitting is due to perturbation of neighboring

\* For  $\nu_9(0\pi)$ , which was expected to be optically active by Whitcomb, Nielsen, and Thomas, we have

$$\lambda = 2\mu(b \sin^2 \beta / a \sin^2 2\gamma) \{H_{HCC} - s_3 s_4 F'_{HC} + t_3 t_4 F_{HC} - (\kappa/8^{1/2}ab)\};$$

but we can understand from Fig. 4 in their paper that this vibration is optically inactive according to the symmetry property of this molecule. In the case of  $(\text{CXY})_n$  molecule instead of  $(\text{CX}_2)_n$  this vibration becomes optically active.

<sup>4</sup> J. J. Fox and A. E. Martin, Proc. Roy. Soc. A157, 961 (1940).

<sup>5</sup> H. W. Thompson and P. Torkington, Proc. Roy. Soc. A184, 3 (1945).

<sup>6</sup> L. Glatt and J. W. Ellis, J. Chem. Phys. 15, 880 (1947).

<sup>7</sup> A. Elliott, E. J. Ambrose, and R. B. Temple, J. Chem. Phys. 16, 877 (1948).

molecules.<sup>7</sup> The weak band at 1375 cm<sup>-1</sup> has been attributed by Thompson and Torkington,<sup>5</sup> and Elliott, Ambrose, and Temple<sup>7</sup> to the presence of methyl groups. Certainly the methyl group gives the symmetrical deformation vibration in this region, but its absorption intensity is ordinarily weaker than degenerate deformation vibration which should be found in the region 800~1000 cm<sup>-1</sup>. We could not find any definite absorption band in this region; hence, it is natural to consider that this 1375-cm<sup>-1</sup> frequency is due to methylene groups.

### ASSIGNMENT AND CALCULATION

When we compare the five observed frequencies with the five optically active vibrations given in Eqs. (7), (8), and (9), it leads at once to the following assignment.

	(CH <sub>2</sub> ) <sub>n</sub>	(CD <sub>2</sub> ) <sub>n</sub>
$\nu_2(0\pi)$	= 1375 cm <sup>-1</sup>	1060 cm <sup>-1</sup>
$\nu_4(\pi\sigma)$	= 1475	1100
$\nu_3(\pi\sigma)$	= 2853	—
$\nu_6(\pi\sigma)$	= 728	520
$\nu_7(\pi\sigma)$	= 2926	—

To calculate these frequencies theoretically from Eqs. (7)–(9), seven force constants,  $K_{CH}$ ,  $H_{HCH}$ ,  $H_{HCC}$ ,  $F_{HH}$ ,  $F_{HC}$ ,  $F'_{HH}$ , and  $F'_{HC}$ , and an intramolecular tension  $\kappa$  are necessary. Four of these constants, however, can be obtained directly from similar bond structures in methane and its derivatives which were treated in the preceding paper.<sup>1</sup>

$$K_{CH}=4.2, \quad H_{HCH}=0.4, \quad F'_{HH}=0, \\ F_{HH}=0.1 \quad (10^5 \text{ dynes/cm}).$$

As the other constants we take the following values so

TABLE I. The fundamental frequencies of ethane in cm<sup>-1</sup>.

	C <sub>2</sub> H <sub>6</sub>			C <sub>2</sub> D <sub>6</sub>		
	Obs. <sup>10</sup>	Calc.*	Diff. %	Obs. <sup>10</sup>	Calc.*	Diff. %
$A_{1g}$	993	1005	1.2	852	821	3.6
	1375	1369	0.4	1158	1171	1.1
	2925	2916	0.3	2115	2086	1.4
$A_{2u}$	1380	1400	1.4	1072	1073	0.1
	2925	2938	0.4	2100	2103	0.1
$E_u$	827	825	0.2	601	596	0.8
	1465	1457	0.5	1102	1053	4.4
	2980	2984	0.1	2237	2215	1.0
$E_g$	1170	997**	14.8	970	789**	18.6
	1460	1438	1.5	1055	1039	1.5
	2960	2973	0.4	2225	2206	0.9

\* The equilibrium distances were assumed to be: C—H, 1.09, C—C, 1.54 Å, with tetrahedral angles.

\*\* This is the only calculated frequency differing by much more than four percent from the observed value. But it was shown by F. Stitt [J. Chem. Phys. 7, 297 (1939)] that inclusion of the interaction terms between the two methyl groups led to higher calculated value for this frequency without destroying the agreement of the other calculated and observed frequencies.

TABLE II. Force constants and intramolecular tensions.

Force constants (10 <sup>5</sup> dynes/cm)			
K	Bond	Value	Molecule calculated
C—H	(CH <sub>4</sub> )	4.8	CH <sub>4</sub> , CH <sub>3</sub> D, CH <sub>2</sub> D <sub>2</sub> , CHD <sub>3</sub> , CD <sub>4</sub>
	(CH <sub>3</sub> —)	4.5	CH <sub>3</sub> Cl, CD <sub>3</sub> Cl, C <sub>2</sub> H <sub>6</sub> , C <sub>2</sub> D <sub>6</sub>
	(CH <sub>2</sub> —)	4.2	CH <sub>2</sub> Cl <sub>2</sub> , (CH <sub>2</sub> ) <sub>n</sub> , (CD <sub>2</sub> ) <sub>n</sub>
	(CH—)	3.9	CHCl <sub>3</sub> , CDCl <sub>3</sub>
C—C		2.8	C <sub>2</sub> H <sub>6</sub> , C <sub>2</sub> D <sub>6</sub>
C—Cl		1.75	CCl <sub>4</sub> , CHCl <sub>3</sub> , CH <sub>2</sub> Cl <sub>2</sub> , CH <sub>3</sub> Cl, CDCl <sub>3</sub> , CD <sub>3</sub> Cl, CCl <sub>3</sub> Br, CCl <sub>2</sub> Br <sub>2</sub> , CClBr <sub>3</sub>
C—Br		1.45	CBr <sub>4</sub> , CClBr <sub>3</sub> , CCl <sub>2</sub> Br <sub>2</sub> , CCl <sub>3</sub> Br
H	Bond Angle	Value	Molecule calculated
H—C—H		0.4	CH <sub>4</sub> ~CD <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , C <sub>2</sub> D <sub>6</sub> , (CH <sub>2</sub> ) <sub>n</sub> , (CD <sub>2</sub> ) <sub>n</sub> , CH <sub>3</sub> Cl, CH <sub>2</sub> Cl <sub>2</sub> , CD <sub>3</sub> Cl
		0.1	CCl <sub>4</sub> , CCl <sub>3</sub> H, CCl <sub>2</sub> H <sub>2</sub> , CDCl <sub>3</sub> , CCl <sub>3</sub> Br, CCl <sub>2</sub> Br <sub>2</sub>
Br—C—Br		0.05	CBr <sub>4</sub> , CClBr <sub>3</sub> , CCl <sub>2</sub> Br <sub>2</sub>
H—C—C		0.15	C <sub>2</sub> H <sub>6</sub> , C <sub>2</sub> D <sub>6</sub> , (CH <sub>2</sub> ) <sub>n</sub> , (CD <sub>2</sub> ) <sub>n</sub>
H—C—Cl		0.05	CHCl <sub>3</sub> , CH <sub>2</sub> Cl <sub>2</sub> , CH <sub>3</sub> Cl, CDCl <sub>3</sub> , CD <sub>3</sub> Cl
Cl—C—Br		0.05	CCl <sub>3</sub> Br, CCl <sub>2</sub> Br <sub>2</sub> , CClBr <sub>3</sub>
F'	Interacting Atoms	Value	Molecule calculated
H...H		0	CH <sub>4</sub> ~CD <sub>4</sub> , CH <sub>3</sub> Cl, CD <sub>3</sub> Cl, CH <sub>2</sub> Cl <sub>2</sub> , C <sub>2</sub> H <sub>6</sub> , C <sub>2</sub> D <sub>6</sub> , (CH <sub>2</sub> ) <sub>n</sub> , (CD <sub>2</sub> ) <sub>n</sub>
		-0.1	CCl <sub>4</sub> , CCl <sub>3</sub> H, CCl <sub>2</sub> H <sub>2</sub> , CCl <sub>3</sub> D, CCl <sub>2</sub> Br <sub>2</sub> , CCl <sub>3</sub> Br
Br...Br		-0.1	CBr <sub>4</sub> , CClBr <sub>3</sub> , CCl <sub>2</sub> Br <sub>2</sub>
H...C		-0.05	C <sub>2</sub> H <sub>6</sub> , C <sub>2</sub> D <sub>6</sub> , (CH <sub>2</sub> ) <sub>n</sub> , (CD <sub>2</sub> ) <sub>n</sub>
H...Cl		-0.05	CCl <sub>3</sub> H, CCl <sub>2</sub> H <sub>2</sub> , CCl <sub>3</sub> D, CClH <sub>3</sub> , CClD <sub>3</sub>
Cl...Br		-0.1	CClBr <sub>3</sub> , CCl <sub>2</sub> Br <sub>2</sub> , CCl <sub>3</sub> Br
F	Interacting Atoms	Value	Molecule calculated
H...H		0.1	CH <sub>4</sub> ~CD <sub>4</sub> , CH <sub>3</sub> Cl, CD <sub>3</sub> Cl, CH <sub>2</sub> Cl <sub>2</sub> , C <sub>2</sub> H <sub>6</sub> , C <sub>2</sub> D <sub>6</sub> , (CH <sub>2</sub> ) <sub>n</sub> , (CD <sub>2</sub> ) <sub>n</sub>
		0.65	CCl <sub>4</sub> , CHCl <sub>3</sub> , CDCl <sub>3</sub> , CCl <sub>2</sub> H <sub>2</sub> , CClBr <sub>3</sub> , CCl <sub>2</sub> Br <sub>2</sub>
Br...Br		0.5	CBr <sub>4</sub> , CClBr <sub>3</sub> , CCl <sub>2</sub> Br <sub>2</sub>
H...C		0.4	C <sub>2</sub> H <sub>6</sub> , C <sub>2</sub> D <sub>6</sub> , (CH <sub>2</sub> ) <sub>n</sub> , (CD <sub>2</sub> ) <sub>n</sub>
H...Cl		0.8	CHCl <sub>3</sub> , CDCl <sub>3</sub> , CCl <sub>2</sub> H <sub>2</sub> , CH <sub>3</sub> Cl, CD <sub>3</sub> Cl
Cl...Br		0.55	CClBr <sub>3</sub> , CCl <sub>2</sub> Br <sub>2</sub> , CCl <sub>3</sub> Br
Intramolecular tensions (10 <sup>-11</sup> dyne·cm)			
Molecule	$\kappa$	Molecule	$\kappa$
CH <sub>4</sub> ~CD <sub>4</sub>	0	CCl <sub>4</sub>	0.3
CH <sub>3</sub> Cl	0.05	CCl <sub>3</sub> Br	0.3
CH <sub>2</sub> Cl <sub>2</sub>	0.1	CCl <sub>2</sub> Br <sub>2</sub>	0.3
CHCl <sub>3</sub>	0.2	CClBr <sub>3</sub>	0.3
		CBr <sub>4</sub>	0.3

as to give the best fit with the observed  $\nu_2$ ,  $\nu_6$ , and  $\nu_7$ .

$$H_{HCC}=0.15, \quad F'_{HC}=-0.05, \quad F_{HC}=0.4 \quad (10^5 \text{ dynes/cm}), \\ \kappa=0.2 \quad (10^{-11} \text{ dyne·cm}).$$

The equilibrium bond distances are assumed to be: C—H 1.09, C—C, 1.54 Å, with tetrahedral angles for carbon atoms. Then from Eqs. (7)–(9) we obtain the calculated frequencies:

	(CH <sub>2</sub> ) <sub>n</sub>	(CD <sub>2</sub> ) <sub>n</sub>
$\nu_2(0\pi)$	= 1349 cm <sup>-1</sup>	1020 cm <sup>-1</sup>
$\nu_4(\pi\sigma)$	= 1474	1083
$\nu_3(\pi\sigma)$	= 2906	2117
$\nu_6(\pi\sigma)$	= 733	530
$\nu_7(\pi\sigma)$	= 2928	2169

The calculated values are in good agreement with the observed ones. The average difference is 1.5 percent and the maximum difference 3.9 percent. The magnitude of the values of force constants and the intramolecular tension arbitrarily chosen in the calculation are also reasonable as compared with those obtained in the case of methane derivatives<sup>1</sup> (see Table II). Accordingly, there is little doubt that the Urey-Bradley field is adequate in the case of these molecules. To confirm this conclusion an attempt was made to calculate the vibration frequencies of ethane and deuterioethane using these force constants.

#### THE CALCULATION OF NORMAL VIBRATIONS OF ETHANE AND DEUTEROETHANE

The normal coordinate treatment was carried out according to the method of Wilson.<sup>8</sup> If we assume that the Urey-Bradley field as the intramolecular potential and interaction between the two methyl groups is neglected, eight force constants,  $K_{CC}$ ,  $K_{CH}$ ,  $H_{HCH}$ ,  $H_{HCC}$ ,  $F_{HH}$ ,  $F_{HC}$ ,  $F'_{HH}$ , and  $F'_{HC}$ , and an intramolecular tension  $\kappa$  are necessary. Seven of these constants have already been obtained as shown in the case of poly-

thene.\*\* As the two remaining constants we take the following values:

$$K_{CC} = 2.8 \times 10^5 \text{ dynes/cm},^{***}$$

$$\kappa = 0.05 \times 10^{-11} \text{ dyne}\cdot\text{cm}.$$

The frequencies calculated in this way are compared with the observed values in Table I. The agreement is good, when it is considered that all were obtained purely from bond structure considerations except two constants. Hence it may be concluded in this case that the Urey-Bradley field is an adequate type of potential energy.

Table II gives the summary of the force constants and the intramolecular tension which have been obtained in this series of research.

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\*\*  $K_{CH}$  is obtained from  $\text{CH}_3\text{Cl}$  (see Table II).

\*\*\* From this value we can calculate the force constant  $K(\text{CH}_2-\text{CH}_2)$ :

$$K(\text{CH}_2-\text{CH}_2) = K_{CC} + 4\kappa^2 F'_{HC} + 4\kappa^2 F_{HC},$$

$$= 4.0 (10^5 \text{ dynes/cm}).$$

This is in agreement with the force constant  $K$  which was obtained when we calculated the skeletal vibrations of normal paraffins. (S. Mizushima and T. Simanouti, accepted for publication for J. Am. Chem. Soc.)

<sup>8</sup> E. B. Wilson, J. Chem. Phys. 7, 1047 (1939); 9, 76 (1941).