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## Potential Functions of Molecular Groups and the Vibrations of the Halogen Derivatives of Methane

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On the assumption of the invariance of the molecular groups  $YZ_3$  and  $YX$  formulas are given connecting the potential energy constants of the molecules  $YZ_4$ ,  $XYZ_3$ ,  $ZYX_3$ , and  $ZX_4$ . The validity of the assumption is tested for the series  $CH_4$ ,  $ClCH_3$ ,  $HCCl_3$ , and  $CCl_4$ ; the consistency of the results definitely shows it to be a very good approximation. The application leads to a determination of the general potential functions of all four molecules. Frequencies of  $HCCl_3$  and  $DCCl_3$  are calculated from those of  $CH_4$ ,  $ClCH_3$ , and  $CCl_4$ , and are found to be in excellent agreement with the observed data. Predictions are made for the frequencies of  $ClCD_3$ . A certain ambiguity exists

for the constants for the perpendicular frequencies of both  $HCCl_3$  and  $ClCH_3$ , since two different chemically acceptable sets will account for the observed frequencies. A discussion of the methane constants shows that, while individual constants are quite sensitive to various methods of determination, certain linear combinations of them, to which a definite physical meaning can be attached, are practically invariant. The methane constants are used to redetermine the constants computed by Sutherland and Dennison for ethane; they yield an entirely different set, which, however, is equally suited to an explanation of the frequencies.

A CORRELATION of the vibrations of polyatomic molecules with intramolecular forces has been attempted many times on the basis of various simplified models, and some of these—notably the valence force assumption and its various modifications such as the Urey-Bradley field—have met with a certain amount of success. With reference to these simplified models, it has been possible to speak of force constants characteristic of certain bonds. However, a molecule can only be completely described in terms of a general potential function, and it is only the corresponding generalization of the bond constants that can have any definite meaning.

Spectroscopic observations on deuterium derivatives have enabled determination of the most general quadratic potential functions for certain simple hydrides; but in molecules where the hydrogens are of minor importance or completely absent, isotope shifts are too small to be of much help. An enticing alternative method of determining general potential functions is the assumption proposed by Sutherland and Dennison,<sup>1</sup> and others, that the forces remain constant within certain molecular groups in passing from one

molecule to another. The validity of this assumption is a question of considerable physical interest, and, if substantiated, should enable calculation of the frequencies of molecules for which experimental data are not available.

In the present paper it is proposed to apply this method to the series  $YZ_4$ ,  $XYZ_3$ ,  $ZYX_3$ ,  $YX_4$ , and to make a specific numerical test of the assumption for the special case  $CH_4$ ,  $ClCH_3$ ,  $HCCl_3$ ,  $CCl_4$ . Stated more explicitly, our assumption means that the potential energy for the  $YZ_3$  group is the same whether it is attached to an X or to another Z atom; and furthermore, that the force between Y and X is not changed by the nature of the other atoms in the molecule.<sup>2</sup> While there is no reason for supposing that the methyl group in methyl chloride is identical with that in methane, or that the  $CCl_3$  radical remains entirely unchanged in passing from carbon tetrachloride to chloroform, it is believed that such an assumption is not far from the truth. Modern valence theory supports this idea, and experimental data appear to verify it. Thus the recent electron diffraction experiments of Sutton and Brockway,<sup>3</sup> in contradistinction to earlier observations, indicate that

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<sup>1</sup> G. B. B. M. Sutherland and D. M. Dennison, *Proc. Roy. Soc. A* **864**, 250 (1935).

<sup>2</sup> This does not imply that the force between Y and X is the same as in the diatomic molecule YX. However such an extension of the assumption is not too unreasonable, and it might be worth while to check it by comparison with experimental data.

<sup>3</sup> L. E. Sutton and L. O. Brockway, *J. Am. Chem. Soc.* **57**, 473 (1935).

the Cl—C—Cl angle in  $\text{HCCl}_3$  is very near the tetrahedral value, and Johnston and Dennison<sup>4</sup> conclude, from the moments of inertia, that the  $\text{CH}_3$  group has the same dimensions in methane and in the methyl halides. Because there is no obvious connection between potential functions and dipole moments, the difference between the dipole moments of chloroform and methyl chloride does not seriously indict the assumption.

#### CONNECTIONS BETWEEN $\text{XYZ}_3$ AND $\text{YZ}_4$ CONSTANTS

An analytic formulation of the assumption leads to a functional relationship between the constants<sup>5</sup>  $A$ ,  $B$ ,  $C$ ,  $D$  and  $E$  of  $\text{YZ}_4$ , the con-

stants<sup>6</sup>  $G_{11}$ ,  $G_{12}$ ,  $\dots$   $G_{66}$  of  $\text{XYZ}_3$ , the constants  $\bar{G}_{11}$ ,  $\dots$   $\bar{G}_{66}$  of  $\text{ZYX}_3$ , and the constants  $\bar{A}$ ,  $\bar{B}$ ,  $\bar{C}$ ,  $\bar{D}$  and  $\bar{E}$  of  $\text{YX}_4$ .

We start by separating the quadratic potential function of  $\text{YZ}_4$  into three parts  $V_1$ ,  $V_2$ ,  $V_3$  corresponding to forces within the  $\text{YZ}_3$  group, the  $\text{YZ}$  group, and the interactions between the two. Thus

$$V = V_1(\delta r_1, \delta r_2, \delta r_3, \delta q_{12}, \delta q_{13}, \delta q_{23}) \\ + V_2(\delta r_4^2) + V_3, \quad (1)$$

where  $V_3$  is a function of displacements of the type  $\delta q_{14}$ , and also contains terms linear in  $\delta r_4$ . For the notation, see I. In terms of the variables  $s_1 \dots s_6$ , the potential energy of  $\text{YZ}_4$  becomes<sup>7</sup>

$$2V = (9A/16 + 4B + 4E - 3D)s_1^2 + (2/3)(A/4 + 4B - 2D)s_3^2 + 2(2/3)^{1/2}(5D/2 - 3A/8 - 4B)s_1s_3 \\ + (3A/8)s_4^2 + (A/16 + B + C - D/2)s_6^2 + 2(3/8)^{1/2}(D - A/4)s_4s_6, \\ 2V_2 = (A/16 + 4B + 4E + D)s_2^2, \\ 2V_3 = (A/16 + B + C - D/2)s_5^2 + 2[(4B + 4E - 3A/16 - D)s_1s_2 + (2/3)^{1/2}(A/8 - 4B + D/2)s_2s_3 \\ + (3/8)^{1/2}(D - A/4)s_4s_5 + (A/16 + B - C - D/2)s_5s_6]. \quad (2)$$

By comparing Eqs. (2) with Eq. (2) of I, it is seen that the assumption stated above, which also postulates invariance of the tetrahedral angle in the group  $\text{YZ}_3$ , leads to the following relations:

$$G_{11} = 9A/16 + 4B + 4E - 3D, \\ G_{13} = (-3A/8 - 4B + 5D/2)(2/3)^{1/2}, \\ G_{33} = (2/3)(A/4 + 4B - 2D), \\ G_{44} = 3A/8, \\ G_{46} = (D - A/4)(3/8)^{1/2}, \\ G_{66} = A/16 + B + C - D/2, \\ G_{22} = \bar{A}/16 + 4\bar{B} + 4\bar{E} + \bar{D}. \quad (3)$$

Similar relations for the quantities  $\bar{G}_{ij}$  may be obtained by interchanging  $A$  and  $\bar{A}$  etc. No connection is expected between the constants  $G_{12}$ ,  $G_{23}$ ,  $G_{45}$ ,  $G_{55}$ , and  $G_{56}$  and the coefficients in the expression for  $V_3$  for  $\text{YZ}_4$ , since, obviously, the

forces between an X atom and a  $\text{YZ}_3$  group are different from the forces between the same group and a Z atom. The expression for  $V_3$  has, however, been given explicitly to permit a comparison of the magnitude of the interaction terms in  $\text{YZ}_4$  and  $\text{XYZ}_3$ . It may be stated in this connection that the applicability of the formulas (3) (with the exception of the expression for  $G_{22}$ ) is not limited to the  $\text{XYZ}_3$  molecule but extends to other molecules containing the  $\text{YZ}_3$  group.

Substitution of relations (3) into the expressions for the parallel and perpendicular frequencies (Eqs. (4) and (11) of I), where  $\theta$  has been set equal to its value for a regular tetrahedron leads to Eqs. (4) and (5) given below. For the parallel frequencies

$$m^3\lambda^3 - m^2\lambda^2R_1 + m\lambda R_2 - R_3 = 0,$$

with

<sup>6</sup> Cf. the preceding paper on the vibrations of the  $\text{XYZ}_3$  molecule. This will henceforth be referred to as I.

<sup>7</sup> It should be pointed out that the variables  $s$  are not geometrical symmetry coordinates for the molecule  $\text{YZ}_4$ , since they only satisfy the symmetry requirements of the group  $C_{3v}$ , and not those of the group  $T_d$ .

<sup>4</sup> M. Johnston and D. M. Dennison, Phys. Rev. **48**, 868 (1935).

<sup>5</sup> Cf. J. E. Rosenthal, Phys. Rev. **45**, 538 (1934).

$$\begin{aligned}
R_1 &= m(1/M + 1/n)(\bar{A}/16 + 4\bar{B} + 4\bar{E} + \bar{D}) + (1 + 3m/M)(3A/16 - D) + 4(1 + m/M)B \\
&\quad + 4(3 + m/M)E - 2(m/M)G_{12}, \\
R_2 &= -4m(1/M + 1/n)[9G_{23}^2/4 + 2G_{12}G_{23}(3/2)^{\frac{1}{2}}] + (1 + 3m/M)(AB/2 - D^2/2 + 2AE \\
&\quad + 32EB - 16ED) - 4(m/M)[4G_{12}B - G_{12}D - G_{23}(8E - 4B + 3D/2)(3/2)^{\frac{1}{2}}] \\
&\quad - m(3/M + 3/n + m/Mn)G_{12}^2 + (m/Mn)(\bar{A}/16 + 4\bar{B} + 4\bar{E} + \bar{D})[(M + n + 3m)(3A/16 - D) \\
&\quad + 4(M + m + n)B + 4(3M + 3n + m)E], \\
R_3 &= m(1/M + 1/n + 3m/Mn)[(\bar{A}/16 + 4\bar{B} + 4\bar{E} + \bar{D})(AB/2 - D^2/2 + 2AE + 32EB - 16ED) \\
&\quad - 3G_{23}^2(9A/16 + 4B + 4E - 3D) - (G_{12}^2/2)(A + 16B - 8D) - (3A/2 + 16B - 10D)G_{12}G_{23}(3/2)^{\frac{1}{2}}].
\end{aligned} \tag{4}$$

The corresponding expression for the perpendicular frequencies is

$$m^3\lambda^3 - m^2\lambda^2P_1 + m\lambda P_2 - P_3 = 0,$$

where

$$\begin{aligned}
P_1 &= (3m \sin^2 \varphi/n + 2)G_{55} + (4/3)(2\sqrt{2} \sin \varphi + \cos \varphi)G_{45} + 2(3)^{\frac{1}{2}} \sin \varphi G_{56} \\
&\quad + (7/16 + m/M)A + 3B + 3C + D/2, \\
P_2 &= (5/4 + 3m/M)[A(B + C) - D^2] + 3(3m \sin^2 \varphi/n + 1 + \cos^2 \varphi)[(B + C)G_{55} - G_{56}^2] \\
&\quad + \sin \varphi[(\sqrt{2}/3 + \sqrt{2}m/M - \cot \varphi/12)A + 4(\cot \varphi + \sqrt{2})(B + C) - (7\sqrt{2}/3 + 4\sqrt{2}m/M \\
&\quad + 2 \cot \varphi/3)D]G_{45} + (3)^{\frac{1}{2}} \sin \varphi[(2m/M + 2/3 - \sqrt{2} \cot \varphi/12)A - (\sqrt{2} \cot \varphi + 2)D]G_{56} \\
&\quad - 8 \sin^2 \varphi[(2 \cot \varphi - \sqrt{2}/2)^2/9 + m^2/Mn + 3m/4n + 2m(1 + \cot^2 \varphi)/3M]G_{45}^2 \\
&\quad + 4(3)^{\frac{1}{2}} \sin^2 \varphi[(1/3) \cot \varphi - (2/3)\sqrt{2} \cot^2 \varphi - \sqrt{2}m/n]G_{45}G_{56} \\
&\quad + 3 \sin^2 \varphi[(17 \cot^2 \varphi/72 - 5\sqrt{2} \cot \varphi/36 + 17/144 + 2m/3M + 2m \cot^2 \varphi/3M + 7m/16n \\
&\quad + m^2/Mn)A + \frac{1}{3} \cot^2 \varphi - \frac{1}{3}\sqrt{2} \cot \varphi + m/2n - 1/2)D]G_{55}, \\
P_3 &= \sin^2 \varphi[(2\sqrt{2} \cot \varphi - 1)^2/3 + 9m/n + 8m/M + 4m(3m - M - n)/Mn + 8m \cot^2 \varphi/M] \\
&\quad \times [\frac{3}{4}(AB + AC - D^2)G_{55} + (D - A/4)G_{45}G_{56}(6)^{\frac{1}{2}} - (A/8 + 2B + 2C - D)G_{45}^2 - 3AG_{56}^2/4].
\end{aligned} \tag{5}$$

#### DISCUSSION OF THE METHANE CONSTANTS

All the theoretical expressions given above refer to the  $\omega$ 's, the frequencies with infinitesimal amplitudes. Since a sufficient number of combination bands is not known for any of the molecules treated to enable us to derive the  $\omega$ 's from the experimentally observed frequencies  $\nu_i$ , the only way to proceed is to set  $\nu_i = \omega_i$ , thus introducing into the calculations an error of the order of magnitude of the anharmonicity corrections. However, since the anharmonicity is usually of the same sign, we may expect at least a partial cancelation of the errors, with a final result correct to about five percent. The constants discussed below are so adjusted as to give the best

possible fit for the  $\nu$ 's. With these reservations we pass to the discussion of the methane constants.

The general formulas for the fundamental vibrations of methane<sup>5</sup> involve five force constants; and, with only four frequencies, an additional relationship is necessary for evaluation of the constants. This was obtained from the interaction between vibration and rotation by Dennison and Johnston,<sup>8</sup> who determined the constants and used them in the formulas of Rosenthal<sup>5</sup> to calculate the frequencies of the deuterium derivatives of methane. They obtained two alternate sets of constants and gave two sets of fre-

<sup>8</sup> D. M. Dennison and M. Johnston, Phys. Rev. **47**, 93 (1935).

quencies. The infrared absorption frequencies of  $\text{CH}_3\text{D}$  observed by Ginsburg and Barker<sup>9</sup> were found to agree well with one of the alternate sets calculated.<sup>10</sup> The observed frequencies may be used to recompute the five methane constants.<sup>11</sup> However, in the following the constants derived by Dennison and Johnston have been used, since they reproduce the  $\text{CH}_3\text{D}$  frequencies as well as the set calculated from the best individual observed frequency (2205). These constants are

$$A = 7.67 \times 10^5 \text{ dynes/cm}, B = 0.4760, C = 0.3409, D = 1.2779, E = 0.1336.$$

They are based on the methane frequencies

$$\begin{array}{ll} \nu_1 = 2915, & \nu_2 = 1520, \\ \nu_3 = 3014 & \nu_4 = 1304, \end{array}$$

for which the assignments are quite certain.

As a matter of fact the two sets of constants are not, for our purposes, as widely divergent as they at first appear to be. While the individual constants calculated by the two methods may differ by as much as 13 percent, certain linear combinations of them which appear prominently in our potential functions are found to be practically invariant. Thus  $A/16 + 4B + 4E + D$  is equal respectively to  $4.88 \times 10^5$  dynes/cm and 4.92, a difference of less than one percent. This particular quantity on our assumption corresponds to the constant of the C-H bond.

With the values of the methane constants known, it is possible to calculate the three constants  $a, b, d$  used by Sutherland and Dennison<sup>1</sup> to characterize the parallel vibrations of the  $\text{CH}_3$  group. The analytic relationships may be found directly, or by way of Eqs. (12) I and Eqs. (3) of

this paper. They are

$$\begin{aligned} a &= 9A/16 + 4B + 4E - 3D, & b &= 8B + 32E, \\ d &= (\sqrt{2})(8E + 3D/2 - 4B). \end{aligned}$$

On substitution of the methane constants the values  $a = 3.67 \times 10^5$  dynes/cm,  $b = 13.95$ ,  $d = 3.59$  are obtained. These are to be compared to the values  $a = 8.24$ ,  $b = 8.01$ ,  $d = \pm 5.07$  which were chosen to fit ethane by Sutherland and Dennison; or  $a = 8.47$ ,  $b = 0.83$ ,  $d = \pm 5.39$  chosen to fit methyl chloride. In spite of the marked differences, the two sets of constants, when used in the formulas of reference 1, fit the observed parallel frequencies of ethane and methyl chloride equally well, and lead to the same values of the X- $\text{CH}_3$  bond constant  $c$ . This is another example of the situation mentioned above—only certain combinations of the constants (here  $ab - d^2$  for instance) are important in the formulas for the frequencies. The sensitivity of the individual constants is due largely to the manner in which the potential function is defined. However it should be pointed out that the  $\text{CH}_3$  constants  $a, b, d$  derived from the methane constants are more reasonable physically, since they indicate larger stretching and smaller bending forces than do the constants derived by Sutherland and Dennison.

#### EXPERIMENTAL DATA

The frequencies employed are listed in Table I. Those for  $\text{ClCH}_3$  are from infrared absorption of the gas.<sup>12, 13, 14</sup>  $731.5 \text{ cm}^{-1}$  is the weighed mean of the two isotopic lines for this vibration. 2924 is the average of the two observed lines 2880 and 2967, taken under the plausible assumption of Adel and Barker<sup>12</sup> that the pair is produced by resonance between  $\nu_1$  and  $2\nu_4 = 2920$ . There are few data for chloroform or carbon tetrachloride in the gaseous state, but since the frequencies of methane and methyl chloride are those for the free molecules, it has been thought advisable to correct the observed Raman spectra for the liquids  $\text{HCCl}_2$  and  $\text{CCl}_4$  in order to secure fre-

<sup>9</sup> N. Ginsburg and E. F. Barker, J. Chem. Phys. **3**, 668 (1935).

<sup>10</sup> Recently MacWood and Urey (J. Chem. Phys. **3**, 650 (1935)) have given the Raman spectrum of  $\text{CH}_3\text{D}$ . Their results agree moderately well with the infrared absorption spectrum except for an intense line at  $2315 \text{ cm}^{-1}$ , which they interpret as an overtone. The appearance of a strong overtone in the Raman effect is most unusual, but the force constants derived on the assumption that it is a fundamental are incompatible with the other  $\text{CH}_3\text{D}$  frequencies and the parallel frequencies of ethane. Resonance with the 2200 fundamental may help in explaining the intensity of this overtone.

<sup>11</sup> There is an error in the constants calculated by Ginsburg and Barker. For instance the values derived from  $\text{CH}_3\text{D}$  2205 should be  $A = 8.69 \times 10^5$  dynes/cm,  $B = 0.437$ ,  $D = 1.33$  instead of  $A = 7.30$ ,  $B = 0.430$ ,  $D = 1.33$ . Whenever their constants are referred to, it is the corrected values that are implied.

<sup>12</sup> A. Adel and E. F. Barker, J. Chem. Phys. **2**, 627 (1934).

<sup>13</sup> A. H. Nielsen and E. F. Barker, Phys. Rev. **46**, 970 (1934).

<sup>14</sup> E. F. Barker and E. K. Plyler, J. Chem. Phys. **3**, 367 (1935).

TABLE I. *Vibration frequencies in cm<sup>-1</sup>, assignments, and corrections which have been added to secure gaseous frequencies.*

	ClCH <sub>3</sub>	HCCL <sub>3</sub>	DCCl <sub>3</sub>	CCl <sub>4</sub>
$\nu_1$	2924	3033 15	2267 (11)	$\nu_1$ 467 (8) $A_1$
$\nu_3$	1355	683 (16)	666 (16)	$\nu_2$ 222 (5) $E$
$\nu_5$	731.5	376 (10)	376 (10)	
$\nu_2$	3047	1225 (10)	916 (8)	
$\nu_4$	1460	776 (16)	753 (16)	$\nu_3$ 318 (5) $T_2$
$\nu_6$	1020	271 (10)	271 (9)	$\nu_4$ 782 7

quencies for the gases throughout. The alteration in passing from liquid to gas is usually a shift toward greater frequency,<sup>15</sup> and that has been the uniform assumption in applying corrections. On the basis of the known displacements for certain CH<sub>4</sub> and ClCH<sub>3</sub> lines, as well as for 782 of CCl<sub>4</sub> and 3033 of HCCL<sub>3</sub>,<sup>16</sup> small corrections to the Raman spectra of the liquids<sup>17</sup> have been made. In doing this, the approximate modes of vibration for these molecules described by Kohlrausch<sup>18</sup> have been employed to characterize lines, and the dipole moments of molecular groups have been accepted as the chief cause of the displacements. The corrections, which have been added to the observed spectra for the liquids to give the values listed, are also shown in Table I. Those not in parentheses are based upon direct experimental knowledge. Actually these corrections do not affect the calculations or conclusions to any extent, and their inclusion is a matter of minor importance. The frequency 782 for CCl<sub>4</sub> is the mean of the two resonating components<sup>19</sup> 768 and 797, observed in infrared absorption by Schaefer and Kern.<sup>20</sup> The assignments of frequencies are rendered quite certain by the observed character of the bands in the case of infrared absorption,<sup>13, 14</sup> and by polarization meas-

urements<sup>21</sup> for the Raman lines. For CCl<sub>4</sub> the assignments are indicated in the table by the representation of  $T_d$  to which the vibration corresponds.

The perpendicular frequencies depend upon the molecular geometry, and it is necessary to know the relative bond distances before computations can be carried out. The values C—Cl = 1.77,<sup>22</sup> C—H = 1.08<sup>23</sup> have been used.

#### THE PARALLEL FREQUENCIES

We are now ready to apply the formulas derived above. In doing this, it is sometimes found that several alternate solutions for the constants are possible. The criterion for choosing between these, in addition to that of general self-consistency, is that the constants shall be physically reasonable. Thus large negative values, and those with large imaginary parts are considered suspect. Small imaginary parts are not sufficient cause for the rejection of constants, for they may be due to the uncertainties arising from anharmonicity, etc. Only small values of  $G_{12}$  and  $G_{23}$  are to be expected, for physical reasons.

The first application is to methyl chloride. When the methane constants are substituted in formulas (4), it is possible to solve for the three remaining constants  $G_{22}$ ,  $G_{12}$  and  $G_{23}$ , by using the values of the three parallel frequencies of methyl chloride as given in Table I. Throughout unbarred constants refer to methane and methyl chloride, while barred constants refer to carbon tetrachloride and chloroform. The masses used are C = 12.00, H = 1.008, Cl = 35.46.<sup>24</sup> The formulas for the frequencies of methyl chloride lead to a quartic equation for the constants. Of the four sets of constants which result, only one is satisfactory:  $G_{22} = 3.61 \times 10^5$  dynes/cm.  $G_{12} = 0.560$ ,  $G_{23} = -0.030$ . The other sets have large values of  $G_{12}$ , and for them  $G_{22}$  does not even approximately equal the bond constant  $c$  of Sutherland

<sup>15</sup> See however W. Buchheim, *Physik. Zeits.* **36**, 694 (1935), who shows that a shift in the other direction is possible.

<sup>16</sup> Dr. Ginsburg kindly measured the infrared absorption of chloroform vapor, and obtained the value 3033 cm<sup>-1</sup> for  $\nu_1$ .

<sup>17</sup> Data for HCCL<sub>3</sub> from Kohlrausch, *Der Smekal-Raman Effekt* (1931), p. 116. CCl<sub>4</sub> *ibid.*, p. 305. DCCl<sub>3</sub> R. W. Wood and D. H. Rank, *Phys. Rev.* **48**, 63 (1935); also Redlich and Pordes, *Naturwiss.* **22**, 808 (1934).

<sup>18</sup> K. W. F. Kohlrausch, *Zeits. f. physik. Chemie* **B28**, 340 (1935).

<sup>19</sup> Cf. Horiuchi, *Zeits. f. Physik* **84**, 380 (1933).

<sup>20</sup> Schaefer and Kern, *Zeits. f. Physik* **78**, 609 (1932).

<sup>21</sup> Cabannes and Rousset, *Ann. de physique* **19**, 229 (1933). L. Simons, *Soc. Sci. Fennica, Comm. Phys. math.* **6**, 1-58 (1932). Cf. also reference 18.

<sup>22</sup> L. Pauling and L. O. Brockway, *J. Chem. Phys.* **2**, 867 (1934); Cosslett and de Laszlo, *Nature* **134**, 73 (1934); reference 3.

<sup>23</sup> Mark, *Zeits. f. Electrochemie* **40**, 413 (1934); L. Pauling, *Proc. Nat. Acad. Sci.* **18**, 293 (1932); cf. also references 8 and 9.

<sup>24</sup> Use of this value for the mass of Cl is an approximation, but since the isotope shift for chlorine is very small, it is quite adequate for the present purposes.

TABLE II. *Potential energy constants.* The values given under the headings  $\text{CCl}_4$  and  $\text{CH}_4$  are the constants in the potential energy functions of these molecules when they are treated as though they were of the type  $\text{XYZ}_3$ . The numbers are given to the number of decimal places used in the calculations even though no significance can be attached to the last figure. All quantities are given in dynes  $\times 10^5/\text{cm}$ .

	$\text{CH}_4$	$\text{ClCH}_3$	$\text{HCCl}_3$	$\text{CCl}_4$
$G_{11}$	3.639	3.639	2.850	2.850
$G_{22}$	4.916	3.610	4.916	3.610
$G_{33}$	0.844	0.844	0.819	0.819
$G_{12}$	0.442	0.560	$\begin{smallmatrix} a & -0.482 \\ b & 0 \end{smallmatrix}$	1.421
$G_{13}$	-1.295	-1.295	-1.110	-1.110
$G_{23}$	-0.250	-0.030	$\begin{smallmatrix} a & 0.407 \\ b & 0 \end{smallmatrix}$	-0.661
$G_{44}$	2.876	2.876	1.357	1.357
$G_{55}$	0.657	$\begin{smallmatrix} c & 0.628 \\ d & 0.892 \end{smallmatrix}$	$\begin{smallmatrix} c' & 0.570 \\ d' & 0.555 \end{smallmatrix}$	0.563
$G_{66}$	0.657	0.657	0.563	0.563
$G_{45}$	-0.392	$\begin{smallmatrix} c & -0.360 \\ d & -0.735 \end{smallmatrix}$	$\begin{smallmatrix} c' & -0.155 \\ d' & 0.072 \end{smallmatrix}$	-0.161
$G_{46}$	-0.392	-0.392	-0.161	-0.161
$G_{56}$	0.657	$\begin{smallmatrix} c & 0.013 \\ d & 0.367 \end{smallmatrix}$	$\begin{smallmatrix} c' & 0 \\ d' & 0 \end{smallmatrix}$	0.563

and Dennison<sup>1</sup> ( $c = 3.44$  for  $\text{ClCH}_3$ ) Furthermore, with these other sets it is not possible under the present assumption to correlate the frequencies of carbon tetrachloride and chloroform. The complete set of constants for  $\text{ClCH}_3$  is given in Table II.

With the value  $G_{22} = 3.61$ , the relationship between  $G_{22}$  and  $\bar{A}$ ,  $\bar{B}$ ,  $\bar{D}$ ,  $\bar{E}$  expressed in Eqs. (3), and the four known frequencies, it is possible to obtain the five constants in the general potential function of carbon tetrachloride. Thus the values  $\bar{A} = 3.619$ ,  $\bar{B} = 0.402$ ,  $\bar{C} = 0.256$ ,  $\bar{D} = 0.643$ ,  $\bar{E} = 0.283$  are found. Another possible set is  $\bar{A} = 2.53$ ,  $\bar{B} = 0.840$ ,  $\bar{C} = 0.256$ ,  $\bar{D} = -1.04$ ,  $\bar{E} = 0.283$ , but this has been rejected because it is incompatible with the data for chloroform. The potential function for  $\text{CCl}_4$  determined in this manner shows certain interesting similarities to that for  $\text{CH}_4$ , as may be seen by comparing the values of  $A$ ,  $B$ ,  $C$ ,  $D$ ,  $E$ . Urey and Bradley<sup>25</sup> have given a special potential function for carbon tetrachloride. Their assumption requires<sup>5</sup>  $\bar{D} = 10\bar{B} - 2\bar{C} - 8\bar{E}$ . This relation is not satisfied however, for  $10\bar{B} - 2\bar{C} - 8\bar{E} = 1.243$ , while  $\bar{D} = 0.643$ . The two potential functions seem, therefore, to give rather different descriptions of the molecule.

<sup>25</sup> H. C. Urey and C. A. Bradley, Phys. Rev. **38**, 1969 (1931).

The parallel frequencies of  $\text{HCCl}_3$  may now be investigated. As three frequencies and only two unknown constants are involved, a test of the present assumption is possible. Substitution of the frequencies in Eqs. (4) (in this case barred and unbarred constants are interchanged) leads to equations with imaginary roots. However the real values  $\bar{G}_{12} = -0.482$ ,  $\bar{G}_{23} = 0.407$  give a very close reproduction of the frequencies, as is evident on examination of the values under  $a$  in Table III. If, following Sutherland and Dennison's treatment of the parallel frequencies of methyl chloride, the further assumption that  $\bar{G}_{12}$  and  $\bar{G}_{23}$  are zero is made, the results shown under  $b$  in the table are obtained. These also agree very well with the experimental values, and there is in fact little to choose between the two alternatives. The results with the second are particularly gratifying, since they represent frequencies for chloroform which have been calculated entirely on the basis of data from methane, methyl chloride and carbon tetrachloride. The insensitivity of the frequencies to the values of  $\bar{G}_{12}$  and  $\bar{G}_{23}$  is due to a partial cancelation of terms involving these constants in the equation, and to the fact that the constants themselves usually occur with smaller coefficients than do constants of type  $\bar{G}_{22}$ .

TABLE III. *Experimental and calculated frequencies for  $\text{HCCl}_3$ .*

	CALC. $a$ $G_{12} = -0.482, G_{23} = 0.407$	CALC. $b$ $G_{12}, G_{23} = 0$	OBS. (corr.)
$\nu_1$	3034	3010	3033
$\nu_3$	675	681	683
$\nu_5$	380	388	376

### THE PERPENDICULAR FREQUENCIES

Eqs. (5) for the three perpendicular frequencies of both  $\text{HCCl}_3$  and  $\text{ClCH}_3$  involve three undetermined constants and no further test of the major assumption is possible. However, the constants may be calculated and may then be used to compute the frequencies of the corresponding deuterium compounds. In each case algebraic elimination leads to an equation of the fourth degree, and in each case two of the four sets of constants can be rejected for physical reasons. However, there remain two alternates for  $G_{55}$ ,  $G_{45}$ ,  $G_{56}$  and two for  $\bar{G}_{55}$ ,  $\bar{G}_{45}$ ,  $\bar{G}_{56}$ . These are all listed in Table II, as there seems to be no way at present of rejecting any of them. It is to be noted

in this connection that, while all constants for the perpendicular frequencies should be moderately small (less than  $1 \times 10^5$  dynes/cm), those for cross terms, such as  $G_{45}$ , need not be small compared to those for squared terms in the potential, such as  $G_{55}$ . This is simply a consequence of the way the potential function has been defined (cf. Eq. (8) I).

#### FREQUENCIES OF THE DEUTERIUM DERIVATIVES

It is a simple matter to calculate the frequencies of deuteriochloroform and deutyl chloride with the constants which have been determined. Substitution of the constants, with the mass of deuterium set equal to twice that of hydrogen, in Eqs. (4) or (5) leads to a cubic equation; the three roots are the desired parallel or perpendicular frequencies. The values thus computed are listed in Table IV.  $c$  and  $d$  and  $c'$  and  $d'$  correspond to the two alternate sets of constants in Table II. The frequencies computed for deuteriochloroform agree very well with those observed by Wood and Rank,<sup>17</sup> and this agreement is a further substantiation of the major assumption. For the perpendicular frequencies the agreement is so much better with the set of constants  $d'$  that  $c'$  could be eliminated on this basis.

The frequencies of  $\text{ClCD}_3$  have not yet been observed. The predicted values are given in Table IV. Here the two alternate solutions for the perpendicular constants also yield frequencies which differ considerably, and experimental observations should permit elimination of one of the sets.

TABLE IV. *Computed and observed frequencies of deuterium derivatives in  $\text{cm}^{-1}$ .*

	ClCD <sub>3</sub>		DCCl <sub>3</sub>		Obs. (corr. to gas)
	Calc.		Calc.		
			<i>a</i>	<i>b</i>	
<i>ν</i> <sub>1</sub>	2081		2254	2219	2267
<i>ν</i> <sub>3</sub>	1110		651	659	666
<i>ν</i> <sub>5</sub>	645		377	386	376
			<i>c'</i>	<i>d'</i>	
<i>ν</i> <sub>2</sub>	2253	2231	884	919	916
<i>ν</i> <sub>4</sub>	1059	1135	774	745	753
<i>ν</i> <sub>6</sub>	765	720	269	269	271

#### CONCLUDING REMARKS

The assumption that potential functions within molecular groups are preserved has been validated insofar as it has been possible to test it. It has led to consistent results, and has enabled determination of the general quadratic potential functions for methyl chloride, chloroform and carbon tetrachloride. However, a word of caution is necessary with regard to the potential constants given. Because of anharmonicity, incomplete knowledge of all the gaseous frequencies and the limitations of the primary assumption, these constants cannot be exact. In particular those for cross terms in the potential function are to be considered uncertain, since they are quite sensitive to small changes in the frequencies. But in spite of these reservations it is felt that when the sets of constants are used to calculate frequencies for molecules containing  $\text{CH}_3$  or  $\text{CCl}_3$  groups they will yield good results.