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THE POTENTIAL FUNCTION OF METHANE

WITH AN APPENDIX ON ACETYLENE

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THE INTRAMOLECULAR POTENTIAL OF METHANE

I. Introduction.

The first physicist to formulate the general quadratic vibrational function of Methane was JENNY ROSENTHAL.¹ The complete function includes 5 constants. If the numerical values of these 5 constants are known, a precalculation of the vibration frequencies of methane and deuterated methanes can be carried out.

The first calculation of all 5 constants was published by DENNISON and JOHNSON.² At that time only insufficient experimental material from the vibrational analysis of Raman and infrared spectra was available. Hence DENNISON and JOHNSON had to use data from the fine structure of the infrared bands of methane, this resulting in a less accurate determination of the constants as shown below.

Shortly afterwards BARKER and GINSBURG³ published data from the infrared absorption spectrum of CH_3D . This in connexion with the well-known vibration frequencies of methane itself enabled a first calculation of the 5 constants on a pure vibrational basis. However, the calculation could not be carried through without a certain arbitrariness. Due to the method used the constants calculated were sometimes real figures, sometimes imaginary ones.—In 1937 BENEDICT, MORIKAWA, BARNES and TAYLOR⁴ published their great work on the infrared spectra of mixtures of deuterated methanes. In their paper a forthcoming publication is announced where a potential function, including anharmonic terms, would be used. Apparently the paper has not yet been published.

¹ J. ROSENTHAL, Phys. Rev. **45**, 538 (1934).

² DENNISON and JOHNSON, Phys. Rev. **47**, 93 (1935).

³ BARKER and GINSBURG, Phys. Rev. **47**, 641 (1935); J. Chem. Phys. **3**, 668 (1935).

⁴ BENEDICT, MORIKAWA, BARNES and TAYLOR, J. Chem. Phys. **5**, 1 (1937).

As will be seen from what precedes, it will be of importance to have a statement where, firstly, a survey of all the experimental material published is given, and, secondly, this material is utilized for a calculation of the 5 constants in the potential function of methane. The validity of the numerical values should be tested by precalculating the frequencies of all deuterated methanes. We shall here follow the programme sketched, thus for the first time giving a complete survey of the correctness by which we can precalculate the vibration spectra of methane and deuterated methanes, using a quadratic potential function.

Before the calculations are started some words should be said of the method used for attacking the problem. In 1934 HOWARD and BRIGHT WILSON, Jr.¹ demonstrated the use of a general normal-coordinate method, showing the convenience of employing the so-called 'symmetry coordinates'. To derive full advantage of this paper an elementary knowledge of group theory is necessary. This could be acquired by consulting an article by ROSENTHAL and MURPHY.² The two papers just cited should be studied, if necessary, before reading the present paper.

II. Symmetry Considerations.

The methane molecule is placed in an orthogonal xyz coordinate system as shown in double-projection in fig. 1.

The hydrogen atoms are placed in the positions 1, 2, 3, and 4, the carbon atom in the zero point of the coordinate system. The components of the displacement of the carbon atom are denoted by x_0, y_0, z_0 , the corresponding figures for hydrogen no. j are x_j, y_j, z_j .

Geometrically CH_4 and CD_4 belong to the point group T_D . In table I the characters for the normal modes of vibration are given.

The p -axis in the C_3^p -symbol is the line from the carbon atom to $H(1)$.—The symmetry element σ_1 is the plane through $H(1) - C - H(3)$.—Beneath a survey is taken of the ways in

¹ HOWARD and WILSON, Jr., J. Chem. Phys. **2**, 630 (1934).

² ROSENTHAL and MURPHY, Rev. Mod. Phys. **8**, 317 (1936).

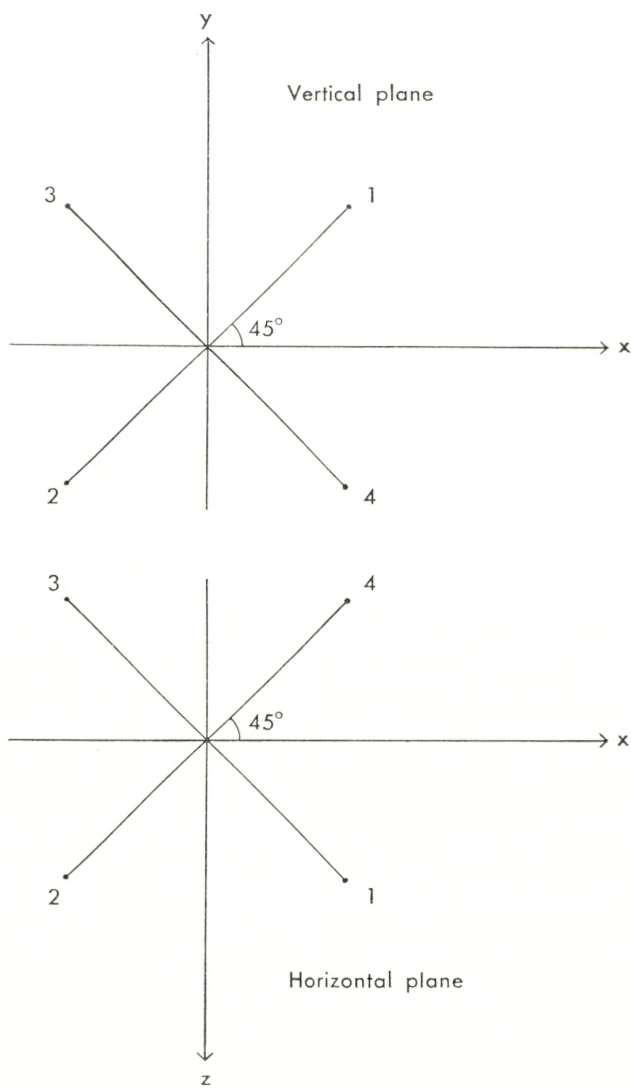


Fig. 1.

Table I.

Covering Operation	E	$8 C_3$	$3 C_2$	$6 \sigma_d$	$6 S_4$	Number of modes	Degree of degeneracy
Symmetry class:							
A_1	1	1	1	1	1	1	1
A_2	1	1	1	-1	-1	0	
E	2	-1	2	0	0	1	2
T_2	3	0	-1	1	1	2	3
T_1	3	0	-1	-1	1	0	
Symmetry elements especially studied:...							
		C_3^p	C_2^x	σ_I	S_4^y		

which the displacement components x_j, y_j, z_j vary during the covering operations of the molecule.

By a rotation of 120° round the p -axis

$$\begin{array}{lll}
 x_0 \rightarrow y_0 & y_0 \rightarrow z_0 & z_0 \rightarrow x_0 \\
 x_1 \rightarrow y_1 & y_1 \rightarrow z_1 & z_1 \rightarrow x_1 \\
 x_2 \rightarrow y_4 & y_2 \rightarrow z_4 & z_2 \rightarrow x_4 \\
 x_3 \rightarrow y_2 & y_3 \rightarrow z_2 & z_3 \rightarrow x_2 \\
 x_4 \rightarrow y_3 & y_4 \rightarrow z_3 & z_4 \rightarrow x_3
 \end{array}$$

By a rotation of 180° round the x -axis

$$\begin{array}{lll}
 x_0 \rightarrow x_0 & y_0 \rightarrow -y_0 & z_0 \rightarrow -z_0 \\
 x_1 \rightarrow x_4 & y_1 \rightarrow -y_4 & z_1 \rightarrow -z_4 \\
 x_2 \rightarrow x_3 & y_2 \rightarrow -y_3 & z_2 \rightarrow -z_3 \\
 x_3 \rightarrow x_2 & y_3 \rightarrow -y_2 & z_3 \rightarrow -z_2 \\
 x_4 \rightarrow x_1 & y_4 \rightarrow -y_1 & z_4 \rightarrow -z_1
 \end{array}$$

By a reflexion in the plane σ_I

$$\begin{array}{lll}
 x_0 \rightarrow z_0 & y_0 \rightarrow y_0 & z_0 \rightarrow x_0 \\
 x_1 \rightarrow z_1 & y_1 \rightarrow y_1 & z_1 \rightarrow x_1 \\
 x_2 \rightarrow z_4 & y_2 \rightarrow y_4 & z_2 \rightarrow x_4 \\
 x_3 \rightarrow z_3 & y_3 \rightarrow y_3 & z_3 \rightarrow x_3 \\
 x_4 \rightarrow z_2 & y_4 \rightarrow y_2 & z_4 \rightarrow x_2
 \end{array}$$

By a 'rotatory reflexion' of 90° round the y -axis

$$\begin{array}{lll}
 x_0 \rightarrow z_0 & y_0 \rightarrow -y_0 & z_0 \rightarrow -x_0 \\
 x_1 \rightarrow z_2 & y_1 \rightarrow -y_2 & z_1 \rightarrow -x_2 \\
 x_2 \rightarrow z_3 & y_2 \rightarrow -y_3 & z_2 \rightarrow -x_3 \\
 x_3 \rightarrow z_4 & y_3 \rightarrow -y_4 & z_3 \rightarrow -x_4 \\
 x_4 \rightarrow z_1 & y_4 \rightarrow -y_1 & z_4 \rightarrow -x_1
 \end{array}$$

We may now pass on to constructing the symmetry co-ordinates.

Symmetry coordinate of the A_1 -class (S_1).

The vibration picture of the totally symmetrical vibration (frequency ν_1) could be drawn immediately as shown in fig. 2 (double-projection).

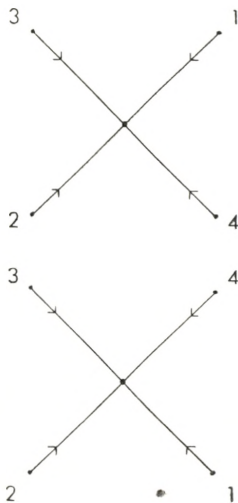


Fig. 2.

In a somewhat loose, but shorthand formulation the amplitude proportions are given by

$$\left. \begin{array}{l}
 x_0 : y_0 : z_0 : x_1 : y_1 : z_1 : x_2 : y_2 : z_2 : x_3 : y_3 : z_3 : x_4 : y_4 : z_4 = \\
 = 0 : 0 : 0 : 1 : 1 : 1 : -1 : -1 : 1 : -1 : 1 : -1 : -1 : 1 : -1. \quad \} (1)
 \end{array} \right.$$

A 'symmetry coordinate' having the symmetry properties of the A_1 -class recorded in table I, is easily seen to be

$$S_1 = x_1 - x_2 - x_3 + x_4 + y_1 - y_2 + y_3 - y_4 + z_1 + z_2 - z_3 - z_4.$$

The conditions that S_1 should be zero for translational and rotational movements of the molecule as a whole, are fulfilled.

Symmetry coordinates of the E -class (S_2 and S_3).

According to table I there is one double degenerate vibration in this class. Our task is to find the vibration pictures of two

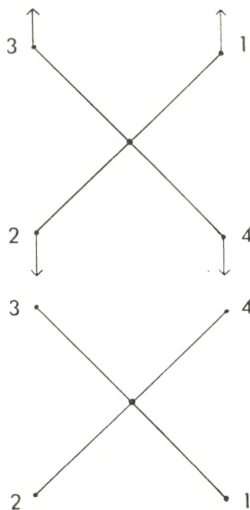


Fig. 3.

mutually orthogonal vibrations, vibrating with the same frequency (ν_{2ab}). To find these vibration pictures one of course makes use of the fact that ν_{2ab} is experimentally found to be a so-called 'hydrogen deformation' frequency ($\nu_{2ab} \sim 1500 \text{ cm}^{-1}$). One of these with symmetry properties as demanded by table I is easily drawn (fig. 3).

An arbitrarily chosen vibration of the E -class, as the one drawn in fig. 3, could generally be conceived as having been formed by a suitable superposition of the two fundamental frequencies ν_{2a} and ν_{2b} of the class + possibly normal vibrations of higher symmetry, that is, in this case the totally symmetrical vibration ν_1 . We first want to see if the vibration of fig. 3 has a totally symmetrical component. Actually it has, as the amplitude proportions

$$\left. \begin{aligned} x_0 : y_0 : z_0 : x_1 : y_1 : z_1 : x_2 : y_2 : z_2 : x_3 : y_3 : z_3 : x_4 : y_4 : z_4 = \\ = 0 : 0 : 0 : 0 : 1 : 0 : 0 : -1 : 0 : 0 : 1 : 0 : 0 : -1 : 0 \end{aligned} \right\} (2)$$

are not orthogonal to (1).

To find the pure *E*-class component

$$x'_0 : y'_0 : z'_0 : x'_1 : y'_1 : z'_1 : x'_2 : y'_2 : z'_2 : x'_3 : y'_3 : z'_3 : x'_4 : y'_4 : z'_4 \quad (3)$$

of the fig. 3 vibration, we must solve the vector equation

$$(1) + (3) = k(2).$$

$k(2)$ stands for a vector, the components of which are found from (2) by multiplying each component by k . This immediately gives the 12 equations:

$$1 + x'_1 = 0 \qquad 1 + y'_1 = k \qquad 1 + z'_1 = 0$$

and so on. The value of k is found by making use of the condition that (1) and (3) should be mutually orthogonal. We find $k = 3$ and consequently

$$(3) = 0 : 0 : 0 : -1 : 2 : -1 : 1 : -2 : -1 : 1 : 2 : 1 : -1 : -2 : 1.$$

The vibration picture becomes (fig. 4):

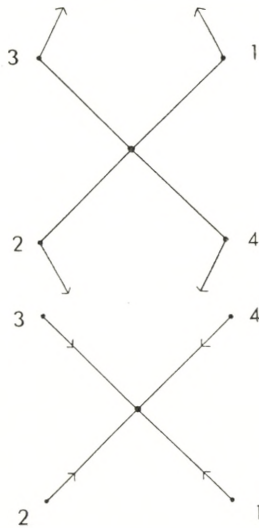


Fig. 4.

Thus, having found one pure E -class vibration we easily find another orthogonal to the first one. The vibrating molecule of fig. 4 is simply turned 120° round the p -axis. After the rotation the molecule of course still vibrates with the same frequency as before. The amplitude proportions are

$$0:0:0:2:-1:-1:-2:1:-1:-2:-1:1:2:1:1. \quad (4).$$

(3) and (4) do not make out a pair of normal vibrations, as they are not mutually orthogonal. But we must be able to form (4) by a superposition of (3) and the corresponding orthogonal normal vibration (5), which means that (5) can be determined by the relation

$$(5) + (3) = k(4).$$

The equation is solved as demonstrated above. The result is that $k = -2$ and

$$(5) = 0:0:0:-3:0:3:3:0:3:3:0:-3:-3:0:-3.$$

Consequently the symmetry coordinates chosen are

$$S_2 = -x_1 + x_2 + x_3 - x_4 - z_1 - z_2 + z_3 + z_4 + 2(y_1 - y_2 + y_3 - y_4)$$

$$S_3 = 3(-x_1 + x_2 + x_3 - x_4 + z_1 + z_2 - z_3 - z_4).$$

Demonstrating that the coordinates above fulfil the requirements of table I we have:

The coordinate S'_2 , having been subjected to a symmetry operation, is denoted by S'_i . By a rotation of 180° round the x -axis

$$S'_2 = S_2$$

$$S'_3 = -S_3,$$

that is, the character (the sum of diagonal elements) is 2, consistent with table I.—By a rotation of 120° round the p -axis

$$S'_2 = -0.5 S_2 + 0.5 S_3$$

$$S'_3 = -1.5 S_2 - 0.5 S_3,$$

which means that the character is -1 as demanded by table I.—In an analogous manner it is shown that the characters are zero by the operations σ_1 and S'_4 .

Symmetry coordinates of the T_2 -class ($S_4, S_5, S_6, S_7, S_8, S_9$).

This class contains two triple-degenerate vibrations. Following a procedure quite analogous to the one sketched above we get for the three components of one of the vibrations

$$\begin{aligned} S_5 &= -4x_0 + (x_1 + x_2 + x_3 + x_4) \\ S_4 &= -4y_0 + (y_1 + y_2 + y_3 + y_4) \\ S_6 &= -4z_0 + (z_1 + z_2 + z_3 + z_4). \end{aligned}$$

The components of the second triple-degenerate vibration are chosen as

$$\begin{aligned} S_7 &= -x_1 - x_2 + x_3 + x_4 - z_1 + z_2 + z_3 - z_4 \\ S_8 &= - z_1 + z_2 - z_3 + z_4 - y_1 - y_2 + y_3 + y_4 \\ S_9 &= -x_1 + x_2 - x_3 + x_4 - y_1 + y_2 + y_3 - y_4. \end{aligned}$$

III. Formulation of the Potential Function.

Wishing to formulate the potential as the quadratic expression commonest possible we write the contribution of the vibrations in the A_1 -class as

$$\mathcal{A}2 V = a_1 S_1^2.$$

The contribution from the E -class is preliminarily written

$$\mathcal{A}2 V = a_2 (S_2^2 + f S_3^2).$$

The constant f can be determined by the condition that $\mathcal{A}2 V$ is invariant during any covering operation of the molecule. Thus by a rotation of 120° round the p -axis

$$\begin{aligned} \mathcal{A}2 V &= a_2 (S_2^2 + f S_3^2) \rightarrow a_2 [(-0.5 S_2 + 0.5 S_3)^2 + \\ &+ f(-1.5 S_2 - 0.5 S_3)^2] = a_2 [S_2^2(0.25 + 2.25 f) + S_3^2(0.25 + 0.25 f) + \\ &+ S_2 S_3(-0.50 + 1.50 f)]. \end{aligned}$$

Identity demands that $f = 1/3$.

Before formulating the potential contribution from the T_2 -class we shortly summarize the symmetry properties of the coordinates.

Coordinate \ Operation	C_2^x	σ_I	S_4^y	C_3^p
S_4'	$-S_4$	S_4	$-S_4$	S_6
S_5'	S_5	S_6	S_6	S_4
S_6'	$-S_6$	S_5	$-S_5$	S_5
S_7'	$-S_7$	S_7	$-S_7$	S_9
S_8'	S_8	S_9	S_9	S_7
S_9'	$-S_9$	S_8	S_8	S_8

Remembering that only symmetry coordinates with common symmetry properties can form 'mixed' products we get

$$A2V = a_3(S_4^2 + S_5^2 + S_6^2) + a_4(S_4S_7 + S_5S_8 + S_6S_9) + a_5(S_7^2 + S_8^2 + S_9^2).$$

The complete quadratic potential function consequently becomes

$$2V = a_1S_1^2 + a_2\left(S_2^2 + \frac{1}{3}S_3^2\right) + a_3(S_4^2 + S_5^2 + S_6^2) + a_4(S_4S_7 + S_5S_8 + S_6S_9) + a_5(S_7^2 + S_8^2 + S_9^2).$$

The simplicity, by which the problems have been solved here, should be compared with the complexity of e. g. ROSENTHAL's paper.¹

¹ J. ROSENTHAL, Phys. Rev. **45**, 538 (1934).

IV. Relations between Force Constants and Vibration Frequencies.

1. CH_4 and CD_4 .

Solving the problem of finding these relation in the usual way by means of the Lagrangian equations a. s. o., we get:

The A_1 -class.

$$z_1 = 4 \pi^2 \nu_1^2 = \frac{12 a_1}{m_H} \quad (\text{I})$$

The E -class.

$$z_2 = 4 \pi^2 \nu_{2ab}^2 = \frac{24 a_2}{m_H} \quad (\text{II})$$

The T_2 -class.

$$\begin{vmatrix} 2 a_3 - \frac{m_H m_C}{2 M(C H_4)} z & a_4 \\ a_4 & 2 a_5 - \frac{m_H}{4} z \end{vmatrix} = 0 \quad (\text{III}).$$

$$\text{Roots: } z_3 = 4 \pi^2 \nu_{3abc}^2; \quad z_4 = 4 \pi^2 \nu_{4abc}^2.$$

2. CH_3D and CHD_3 . (Point group C_{3v}).

Trying to find the relations desired we should first take into consideration the fact that the number of vibrations with different frequencies (6) is another than for methane (4). The classification of the vibrations also becomes different as seen by table II, giving the characters of the normal modes.

In CH_3D the deuterium atom is placed in the 1-position (fig. 1).

As appears from table II, *nine* symmetry coordinates are to be defined. This, of course, could be done by simply starting afresh as was done in the case of CH_4 and CD_4 . But as methane and deuterated methanes are isotopic molecules, they all

Table II.

Covering operations	E	$2 C_3$	$3 \sigma_v$	Number of modes	Degree of degeneracy
Symmetry classes:					
A_1	1	1	1	3	1
E_1	2	-1	0	3	2
Symmetry elements especially studied:.....					
		C_3^p	σ_I		

have the same vibrational potential function, i. e. the one written on page 12. This means that calculations are highly facilitated if the symmetry coordinates U_1, U_2, \dots, U_9 of the CH_3D and CHD_3 molecules could be formulated as functions of the coordinates S_1, S_2, \dots, S_9 . In trying to do this we define that U_1, U_2 , and U_3 should be the symmetry coordinates of the A_1 -class and the rest of the U 's should represent the E_1 -class.

Symmetry coordinates of the A_1 -class.

It is immediately seen that we could put $U_1 = S_1$.—By considering the survey of the symmetry properties of the coordinates S_4, S_5, \dots, S_9 given at page 12, it is soon recognized that we can choose

$$U_2 = S_4 + S_5 + S_6$$

$$U_3 = S_7 + S_8 + S_9.$$

Symmetry coordinates of the E_1 -class.

These coordinates constitute three pairs. According to table II one member of a pair must be symmetrical (+), the other antisymmetrical (−) with respect to the symmetry element σ_I . We therefore arrange the coordinates S_2, S_3, \dots, S_9 in the following way:

$$\begin{array}{llllll} (+) \text{ coordinates:} & S_2 & S_4 & S_7 & (S_5 + S_6) & (S_8 + S_9) \\ (-) \text{ coordinates:} & S_3 & & & (S_5 - S_6) & (S_8 - S_9). \end{array}$$

Taking into account the transformation properties of S_2 and S_3 given at page 10 we find that one pair of degenerate symmetry coordinates are

$$U_4 = S_2 \text{ and } U_5 = S_3.$$

Trying to find the two other pairs we find that a good proposal seems, at a first glance, to be the pair

$$S_5 + S_6 \text{ and } S_5 - S_6.$$

By the operation C_3^P , however, $S_5 + S_6 \rightarrow S_4 + S_5$. This shows that somehow S_4 must enter. Let us try to put $U_6 = fS_4 + (S_5 + S_6)$. U_6 must be orthogonal to the other U 's, of which only $U_2 = S_4 + S_5 + S_6$ comes into consideration (all the other U 's do not depend upon S_4, S_5 , or S_6). The demand for orthogonality gives $f = -2$. $U_6 = -2S_4 + (S_5 + S_6)$. Let U_7 be the symmetry coordinate which constitutes a pair together with U_6 . We try, of course, to put $U_7 = S_5 - S_6$. The necessary conditions, that U_7 should be orthogonal to U_2 and U_6 , are seen to be fulfilled. It only remains to show that the requirement of table II concerning the covering operation C_3^P is satisfied. We have

$$\begin{array}{ll} U_6 = -2S_4 + S_5 + S_6 & U'_6 = -2S_6 + S_4 + S_5 \\ U_7 = S_5 - S_6 & U'_7 = S_4 - S_5. \end{array}$$

This gives

$$\begin{array}{l} U'_6 = -\frac{1}{2}U_6 + \frac{3}{2}U_7 \\ U'_7 = -\frac{1}{2}U_6 - \frac{1}{2}U_7, \end{array}$$

that is, the character is -1 in accordance with table II.

In the same way we find

$$\begin{array}{ll} U_8 = -2S_7 + (S_8 + S_9) \\ U_9 = S_8 - S_9. \end{array}$$

Being in possession of the connexion between the U 's and the S 's we can easily set up the equations of movement a. s. o. The results are :

The A_1 -class.

$$\begin{array}{l}
 2 a \frac{m_C(3 m_H + m_D) + 8 m_H(m_H + m_D)}{24 M(CH_3D)} z \\
 \frac{M(CH_4)(m_D - m_H)}{24 M(CH_3D)} \\
 \frac{(m_H - m_D) m_C}{24 M(CH_3D)} z \\
 \frac{2}{3} a_3 \frac{(3 m_H + m_D) m_C}{24 M(CH_3D)} z \\
 \frac{1}{3} a_4 \frac{(m_H - m_D) m_C}{24 M(CH_3D)} z \\
 \frac{2}{3} a_5 \frac{m_C(m_H + m_D) + 2 m_H(m_H + 3 m_D)}{24 M(CH_3D)} z \\
 = 0 \quad (IV)
 \end{array}$$

Roots: z_1, z_3, z_4 .

The E_1 -class.

$$\begin{array}{l}
 2 a_3 \frac{6(3 m_H + 5 m_D)}{m_H m_D N_1} z \\
 2 a_4 \\
 - a_4 + 18 \frac{m_D - m_H}{m_H m_D N_1} z \\
 12 a_2 + 8 a_5 - \frac{3}{2} m_H z \\
 12 a_2 - 4 a_5 \\
 - a_4 + 18 \frac{m_D - m_H}{m_H m_D N_1} z \\
 12 a_2 + 2 a_5 - 18 \frac{16 m_H m_D + m_C m_H + 3 m_C m_D}{m_H m_D m_C N_1} z \\
 = 0 \quad (V)
 \end{array}$$

where
$$N_1 = \frac{12}{m_H^2 m_D^2} m_C (12 m_H^2 m_D + 5 m_H m_D m_C + 3 m_C m_D^2 + 20 m_H m_D^2).$$

Roots: $z_{2ab}, z_{3ab}, z_{4ab}$.

3. CH_2D_2 . (Point group C_{2v}).

The characters of the vibrations are given in table III. The symmetry element σ_{II} is the plane through $H(2) - C - H(4)$. The deuterium atoms are placed in the 2 and 4 positions (fig. 1).

Table III.

Covering operations	E	C_2	σ_v	σ_d	Number of modes	Degree of degeneracy
Symmetry classes:						
A_1	1	1	1	1	4	1
A_2	1	1	-1	-1	1	1
B_1	1	-1	1	-1	2	1
B_2	1	-1	-1	1	2	1
Symmetry elements especially studied:						
		C_2^y	σ_I	σ_{II}		

By a rotation of 180° round the y -axis (symmetry element C_2^y).

$$\begin{array}{lll}
 x_0 \rightarrow -x_0 & y_0 \rightarrow y_0 & z_0 \rightarrow -z_0 \\
 x_1 \rightarrow -x_3 & y_1 \rightarrow y_3 & z_1 \rightarrow -z_3 \\
 x_2 \rightarrow -x_4 & y_2 \rightarrow y_4 & z_2 \rightarrow -z_4 \\
 x_3 \rightarrow -x_1 & y_3 \rightarrow y_1 & z_3 \rightarrow -z_1 \\
 x_4 \rightarrow -x_2 & y_4 \rightarrow y_2 & z_4 \rightarrow -z_2
 \end{array}$$

By a reflexion in the plane σ_{II}

$$\begin{array}{lll}
 x_0 \rightarrow -z_0 & y_0 \rightarrow y_0 & z_0 \rightarrow -x_0 \\
 x_1 \rightarrow -z_3 & y_1 \rightarrow y_3 & z_1 \rightarrow -x_3 \\
 x_2 \rightarrow -z_2 & y_2 \rightarrow y_2 & z_2 \rightarrow -x_2 \\
 x_3 \rightarrow -z_1 & y_3 \rightarrow y_1 & z_3 \rightarrow -x_1 \\
 x_4 \rightarrow -z_4 & y_4 \rightarrow y_4 & z_4 \rightarrow -x_4
 \end{array}$$

By means of these relations we are able to find out how the previously used symmetry coordinates S_1, S_2, \dots, S_9 vary during the symmetry operations C_2^y, σ_I and σ_{II} , the results being recorded at the top of page 18.

If the symmetry coordinates of the A_1 -class in table III are denoted by R_1, R_2, R_3 and R_4 , we immediately find

$$R_1 = S_1. \quad R_2 = S_2. \quad R_3 = S_4. \quad R_4 = S_7.$$

Coordinate \ Operation	G_2^y	σ_1	σ_{II}
S'_1	S_1	S_1	S_1
S'_2	S_2	S_2	S_2
S'_3	S_3	$-S_3$	$-S_3$
S'_4	S_4	S_4	S_4
S'_5	$-S_5$	S_6	$-S_6$
S'_6	$-S_6$	S_5	$-S_5$
S'_7	S_7	S_7	S_7
S'_8	$-S_8$	S_9	$-S_9$
S'_9	$-S_9$	S_8	$-S_8$

If the symmetry coordinate of the A_2 -class is called R_5 , then

$$R_5 = S_3.$$

The symmetry coordinates of the B_1 -class become

$$R_6 = S_5 + S_6. \quad R_7 = S_8 + S_9.$$

The symmetry coordinates of the B_2 -class similarly are

$$R_8 = S_5 - S_6. \quad R_9 = S_8 - S_9.$$

The relation between vibration frequencies and force constants in the symmetry classes A_2 , B_1 , and B_2 are:

The A_2 -class.

$$z_{2a} = 4 \pi^2 \nu_{2a}^2 = 12 a_2 \frac{m_H + m_D}{m_H m_D}. \tag{VI}$$

The B_1 -class.

$$\left| \begin{array}{cc} \frac{2}{3} a_5 - \frac{8 m_H m_D + m_C (m_H + m_D)}{m_H m_D m_C N_2} z & a_4 + 3 \frac{m_H - m_D}{m_H m_D N_2} z \\ a_4 + 3 \frac{m_H - m_D}{m_H m_D N_2} z & 6 a_3 - 9 \frac{m_H + 3 m_D}{m_H m_D N_2} z \end{array} \right| = 0 \tag{VII}$$

$$N_2 = \frac{6}{m_H^2 m_D^2 m_C} (m_C m_D^2 + 4 m_D m_H^2 + 3 m_C m_H m_D + 12 m_H m_D^2).$$

Roots: z_{3a} , z_{4a} .

The B_2 -class.

$$\left. \begin{aligned} \frac{1}{27} a_5 - 6 \frac{8 m_H m_D + m_C (m_H + m_D)}{m_H m_D m_C N_3} z & - \frac{1}{18} a_4 + 18 \frac{m_H - m_D}{m_H m_D N_3} z \\ - \frac{1}{18} a_4 + 18 \frac{m_H - m_D}{m_H m_D N_3} z & \qquad \frac{1}{3} a_3 - 54 \frac{m_D + 3 m_H}{m_H m_D N_3} z \end{aligned} \right| = 0 \quad (\text{VIII})$$

$$N_3 = \frac{648}{m_H^2 m_D^2 m_C} (4 m_H m_D^2 + 3 m_H m_D m_C + 12 m_D m_H^2 + m_C m_H^2).$$

Roots: z_{3c} , z_{4c} .

V. Numerical Calculation of the Force Constants of the Potential Function.

This calculation we shall carry through by utilizing vibration frequencies from the spectra of CH_4 and CD_4 . Afterwards we shall pass on to precalculating the vibration frequencies of the partly deuterated methanes, everywhere comparing calculated and experimentally observed frequencies.

The Raman spectrum of gaseous CH_4 has been taken by DICKINSON, DILLON, and RASETTI¹ and by BHAGAVANTAM,² the latter taking depolarisation measurements. The Raman spectrum of CD_4 has been reported by McWOOD and UREY.³ The infrared absorption spectrum of methane was studied by VEDDER and MECKE,⁴ by BENEDICT, MORIKAWA, BARNES, and TAYLOR⁵ and by NATH.⁶ Infrared absorption of CD_4 seems to have been studied by BENEDICT, MORIKAWA, BARNES, and TAYLOR.⁵ As the best available experimental material is chosen:

	CH_4	CD_4
ν_1	2915 cm^{-1}	2085 cm^{-1}
ν_{2ab}	1530 —	
ν_{3abc}	3020 —	2258 —
ν_{4abc}	1320 —	988 —

¹ DICKINSON, DILLON, and RASETTI, Phys. Rev. **34**, 582 (1929).

² BHAGAVANTAM, Ind. Jour. Phys. **6**, 595 (1931).

³ McWOOD and UREY, J. Chem. Phys. **3**, 650 (1935); **4**, 402 (1936).

⁴ VEDDER and MECKE. Zeits. f. Physik **86**, 137 (1933).

⁵ BENEDICT, MORIKAWA, BARNES, and TAYLOR, J. Chem. Phys. **5**, 1 (1937).

⁶ NATH, Ind. Jour. Phys. **8**, 581 (1932).

For further details of experimental values see table IV below. In equation (I) page 13 we substitute $\nu_1(CH_4) = 2915 \text{ cm}^{-1}$ and get:

$$a_1 = 4.175 \cdot 10^4 \text{ dyne cm}^{-1}.$$

Subsequently we are able to precalculate $\nu_1(CD_4) = 2068 \text{ cm}^{-1}$. Experimentally $\nu_1(CD_4) = 2085 \text{ cm}^{-1}$.

In equation (II) page 13 $\nu_{2ab}(CH_4) = 1530 \text{ cm}^{-1}$ is substituted. This gives

$$a_2 = 0.5751 \cdot 10^4 \text{ dyne cm}^{-1}.$$

This permits calculating $\nu_{2ab}(CD_4) = 1085 \text{ cm}^{-1}$, which has not yet been observed. (Only $2\nu_{ab} = 2108 \text{ cm}^{-1}$ has been observed. Hence $\nu_{2ab}(CD_4) = 1054$).

Equation (III) page 13 in connexion with the observed frequencies 3020 and 1320 cm^{-1} from the CH_4 -spectrum and 2258 and 988 cm^{-1} from the CD_4 -spectrum gives

$$a_3 = 5.354 \cdot 10^4 \text{ dyne cm}^{-1}; \quad a_4 = \pm 6.590 \cdot 10^4 \text{ dyne cm}^{-1}; \\ a_5 = 4.430 \cdot 10^4 \text{ dyne cm}^{-1}.$$

To solve the problem of the unknown sign of a_4 we pass on to regard the spectra of CH_3D . Assuming $a_4 \geq 0$ we calculate for the vibrations of the A_1 -class:

$a_4 > 0$	$a_4 < 0$	Exp. determined values
1040 cm^{-1}	1307 cm^{-1}	1306.8 cm^{-1}
2712 —	2204 —	2205 —
3005 —	2947 —	2983 —

This definitely shows that $a_4 < 0$, a result which is fully confirmed by all other calculations involving a_4 .

VI. Comparison between Calculated Frequencies and Experimentally Determined Ones.

In table IV a a survey is taken of the experimental results obtained by studying the Raman spectra of methane and deuterated methanes. Table IV b is a corresponding survey of infrared absorption data. In table V experimentally determined frequencies are stated against calculated ones.

Table IV a.
Experimentally determined Raman frequencies of
methane and deuterated methanes.

	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4	Depolarisation measurements for CH_4
ν_1	2914.8	—	2139.0	2141.1	2084.7	$\rho = 0.08$
ν_{2a}	[1535.7]	[1460.8]	1332.9	1299.2	[1054]	
ν_{2b}			[1458.2]			
ν_{3a}	3022.1	—	2974.2	2268.6	2258.0	$\rho = 0.80$
ν_{3b}			—			
ν_{3c}			2199.5	—		
ν_{4a}	—	1330.1	1285.6	[981.7]	—	
ν_{4b}			1033.1			
ν_{4c}			[1157.4]	[1038.3]		
	DICKINSON, DILLON, RASETTI, Phys. Rev. 34 , 582 (1929).	Mc WOOD and UREY, J. Chem. Phys. 3 , 650 (1935), J. Chem. Phys. 4 , 402 (1936).			BHAGAVANTAM, Ind. Jour. Phys. 6 , 595 (1931).	

The frequencies in square brackets have only been found as first over-tones.

A discrepancy between table IV a and IV b is seen in the interpretation of the spectra of CH_3D . The calculation on page 20 above together with the calculations of DENNISON and JOHNSON¹ support the view that the interpretation of the infrared data given by GINSBURG and BARKER is the more correct one.—For reasons to be given below it seems as if the ν_{4a} -frequency in the Raman spectrum of CH_2D_2 should be interchanged with the ν_{4b} or ν_{4c} frequency.—The marks of interrogation in table IV b indicate that the interpretation given is doubtful.

The infrared data of CH_2D_2 found by BARKER and GINSBURG²,

¹ DENNISON and JOHNSON, Phys. Rev. **47**, 93 (1935).

² BARKER and GINSBURG, J. Chem. Phys. **3**, 668 (1935).

Table IVb.

Experimentally determined infrared vibration frequencies
of methane and deuterated methanes.

	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
ν_1	2915	2983	—	—	—
ν_{2a}	1530	1477	—	—	—
ν_{2b}			1450		
ν_{3a}	3020	3031	2255?	2260	2258
ν_{3b}			?		
ν_{3c}			2205	3020?	
ν_{4a}	1320	1156.3	1235?	988	988
ν_{4b}			1035?		
ν_{4c}			1306.8	1035?	
	VEDDER and MECKE, Zeits. f. Phys. 86 , 137 (1933).	GINSBURG and BARKER, J. Chem. Phys. 3 , 668 (1935).	BENEDICT, MORIKAWA, BARNES, TAYLOR, J. Chem. Phys. 5 , 1 (1937).		

BENEDICT *et al.*¹ unfortunately are published in a manner so as to make the assignment of frequencies doubtful. In referring to vibration frequencies of methane and the isotopic molecules two systems have been used: the system of ROSENTHAL, denoting frequencies by ν_1 , ν_{2a} a. s. o., and, in the case of CH_2D_2 , the system of DENNISON, where the frequencies are denoted in accordance with the way in which the electrical moment varies during the vibration, 'M', 'L', or 'G' being put before or after the frequency figures. Unfortunately none of these systems was employed in the papers of BARKER and BENEDICT.—Another circumstance contributing to the confusion as regards the CH_2D_2 -spectrum lies in the fact that undoubtedly the early precalculation of frequencies made by DENNISON has played a more dominant rôle than has purely experimental studies (fine struc-

¹ BENEDICT, J. Chem. Phys. **5**, 1 (1937).

ture of the single bands a. s. o.) by the assignment of frequencies. It seems, however, as if some sort of mistake has got into the paper of DENNISON and JOHNSON. As mentioned the vibrations are classified as 'M', 'L', or 'G' vibrations, this being convenient, because the CH_2D_2 molecule has three unequal moments of inertia. The axis about which the moment of inertia is the least, is denoted by 'L', the axis of middle moment of inertia by 'M' and the axis of greatest moment of inertia by 'G'. A vibration by which the electrical moment varies along the 'L' axis, is called an 'L' vibration a. s. o.—In their paper DENNISON and JOHNSON state that

'L'-frequencies should be at 3013 and 1082 cm^{-1} .
 'G'- — - - - 2227 and 1228 -

It is easy to show that 'L'-frequencies are the frequencies of the B_2 -class (here denoted by ν_{3c} and ν_{4c}), while the 'G'-frequencies are the frequencies of the B_1 -class (here denoted by ν_{3a} and ν_{4a}). By the precalculation of CH_2D_2 -frequencies made in this paper, it is found that

'L'-frequencies should be at 2258 and 1230 cm^{-1} .
 'G'- — - - - 3021 - 1093 -

Fig. 5 a shows the CH_2D_2 molecule in the M, L, G coordinate system, figs. 5 b and 5 c show a 'G' and an 'L' vibration.

As will be seen we must expect to find a hydrogen 'valence' vibration among the 'G'-vibrations, that is, one of the 'G'-vibrations should be located in the neighbourhood of 3000 cm^{-1} . Similarly a deuterium 'valence' vibration must be among the 'L'-vibrations, that is, one of the 'L' vibrations must be near 2200 cm^{-1} . These facts are reproduced best by the calculation made in this paper, while DENNISON and JOHNSON, in their paper, come to the opposite conclusion.

In table V theoretically computed and experimentally found frequency values are compared. By the assignment of frequencies of the CH_2D_2 -spectrum, one has been chosen which is consistent with the frequency values calculated here.

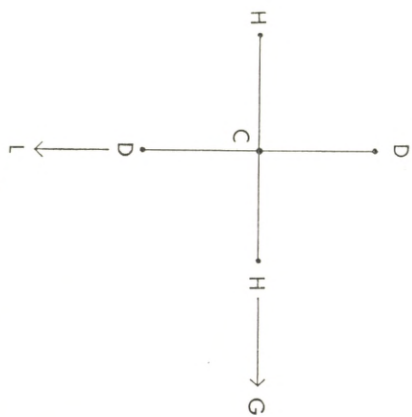
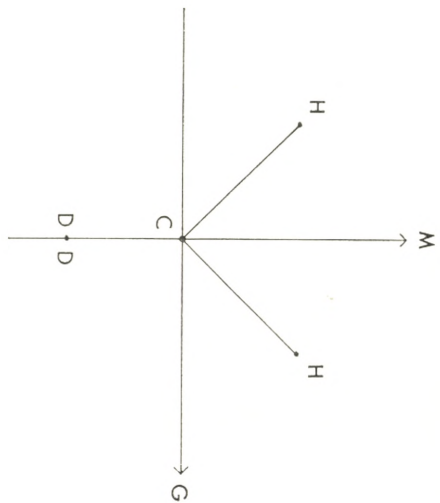


Fig. 5 a.

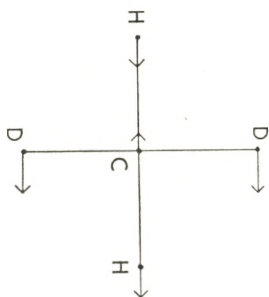
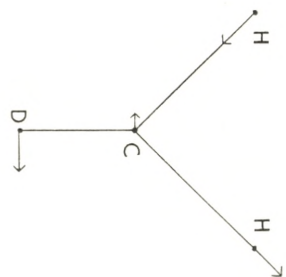


Fig. 5 b.

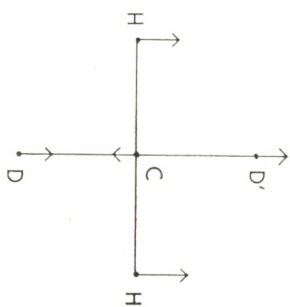
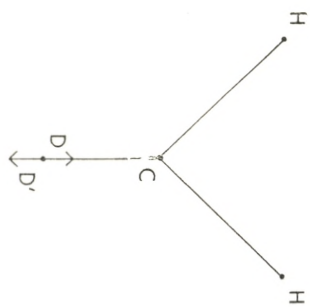


Fig. 5 c.

Table V.

		Calculated by DENNISON	Experimentally determined	Calculated in this paper
CH_4	ν_1	2914	2915	2915
	ν_2	1520	1530	1530
	ν_3	3014	3020	3023
	ν_4	1304	1320	1312
CD_4	ν_1	2061	2085	2068
	ν_2	1075	1054	1085
	ν_3	2227	2258	2258
	ν_4	987	988	988
CH_3D	ν_1	2944	2983	2947
	ν_{2ab}	1460	1477	1458
	ν_{3ab}	3013	3031	3022
	ν_{3c}	2183	2205	2204
	ν_{4ab}	1151	1156	1177
	ν_{4c}	1300	1307	1307
CDH_3	ν_1	2101	2141	2114
	ν_{2ab}	1286	1299	1264
	ν_{3ab}	2222	2260	2292
	ν_{3c}	2992	3000	2998
	ν_{4ab}	1020	988	1020
	ν_{4c}	994	988	1002
CH_2D_2	ν_1	2141	2139	—
	ν_{2a}	1317	1333	1326
	ν_{2b}	1424	1458	—
	ν_{3a}	2227	2974	3021
	ν_{3b}	2969	—	—
	ν_{3c}	3013	—	2258
	ν_{4a}	1228	1038 1090	1093
	ν_{4b}	1019	1033 —	—
	ν_{4c}	1151	1285 1235	1230
			(Raman ¹) (Infrared ²)	

¹ MCWOOD and UREY, *loc. cit.*² BARKER and GINSBURG, *loc. cit.*

VII. Physical Significance of the Results Obtained.

In order to be able to give an account of the above results in a lucid form—which will, at the same time, enable us to make comparisons between methane and other molecules—it is necessary to study the intramolecular forces in some perspicuous cases. In what follows two cases of special simplicity will be examined.

Case 1.

In this case the carbon atom and $H(1)$ are thought to be bound to their equilibrium positions by some imaginary forces. $H(2)$, $H(3)$, and $H(4)$ are given the same displacement along the direction carbon-hydrogen. The situation is illustrated in fig 6.

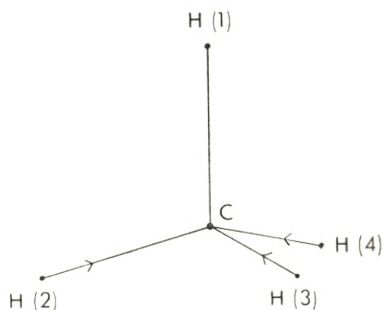


Fig. 6.

The displacements have been chosen so that

$$\begin{array}{llll}
 x_0 = 0 & y_0 = 0 & z_0 = 0 & \\
 x_1 = 0 & y_1 = 0 & z_1 = 0 & S_1 = 9 \quad S_4 = -1 \quad S_7 = 2 \\
 x_2 = -1 & y_2 = -1 & z_2 = 1 & S_2 = 0 \quad S_5 = -1 \quad S_8 = 2 \\
 x_3 = -1 & y_3 = 1 & z_3 = -1 & S_3 = 0 \quad S_6 = -1 \quad S_9 = 2 \\
 x_4 = 1 & y_4 = -1 & z_4 = -1 &
 \end{array}$$

The force acting upon hydrogen atom no. j in the direction of the X -axis (fig. 1) being denoted as $K_{H(j)}(X)$ it is easily shown that

$$K_{H(1)}(X) = -9 a_1 + a_3 - 2 a_4 + 4 a_5 = K_{H(1)}(Y) = K_{H(1)}(Z).$$

$$K_{H(2)}(X) = 9 a_1 + a_3 - a_4 = K_{H(2)}(Y).$$

$$K_{H(2)}(Z) = -9 a_1 + a_3 - 4 a_5$$

$$K_C(X) = 4(a_4 - a_3) = K_C(Y) = K_C(Z).$$

In units of 10^4 dyne cm^{-1} the values of the constants are

$$a_1 = 4.175 \quad a_2 = 0.5751 \quad a_3 = 5.354 \quad a_4 = -6.590 \quad a_5 = 4.430.$$

By insertion of these values we get

$$K_{H(1)}(X) = -1.321 = K_{H(1)}(Y) = K_{H(1)}(Z).$$

By $K_{H(1)}$ we denote the resulting force acting upon $H(1)$. Consequently

$$K_{H(1)} = +1.321\sqrt{3} = 2.288.$$

$$K_{H(2)} = 82.14$$

$$K_C = 79.29$$

The calculation shows that the movements of the hydrogen atoms along the direction carbon-hydrogen take place approximately independently of each other.

Case 2.

As appears from fig. 7 $H(1)$ is displaced perpendicularly to the $C-H(1)$ -direction. All the other atoms are kept in their equilibrium positions. For this displacement $x_1 = z_1 = 1$. $y_1 = -2$. $S_1 = S_3 = 0$ $S_2 = -6$. $S_4 = S_7 = -2$ $S_5 = S_6 = S_7 = S_8 = 1$.

$$\begin{array}{ll} K_{H(1)}(X) = -6 a_2 - a_3 - a_4 - a_5 & K_{H(1)}(Y) = 12 a_2 + 2 a_3 + 2 a_4 + 2 a_5 \\ K_{H(2)}(X) = 6 a_2 - a_3 - 2 a_4 - 3 a_5 & K_{H(2)}(Y) = -12 a_2 + 2 a_3 + a_4 \\ K_{H(3)}(X) = 6 a_2 - a_3 + a_4 + 3 a_5 & K_{H(3)}(Y) = 12 a_2 + 2 a_3 - 2 a_5 \\ K_{H(4)}(X) = -6 a_2 - a_3 + a_5 & K_{H(4)}(Y) = -12 a_2 + 2 a_3 + a_4 \\ K_C(X) = 4 a_3 + 2 a_4 & K_C(Y) = -8 a_3 - 4 a_4 \end{array}$$

$$K_{H(1)}(Z) = -6 a_2 - a_3 - a_4 - a_5$$

$$K_{H(2)}(Z) = -6 a_2 - a_3 + a_5$$

$$K_{H(3)}(Z) = 6 a_2 - a_3 + a_4 + 3 a_5$$

$$K_{H(4)}(Z) = 6 a_2 - a_3 - 2 a_4 - 3 a_5$$

$$K_C(Z) = 4 a_3 + 2 a_4$$

By substitution of numerical values we find

$$K_{H(1)} = 16.27. \quad K_{H(2)} = 5.55. \quad K_{H(3)} = 11.0. \quad K_{H(4)} = 5.55. \quad K_C = 20.18.$$

Movements of the hydrogen atoms perpendicular to the carbon-hydrogen bond could not be considered as being independent of each other.

At the present stage the study of general quadratic potential functions of polyatomic molecules is hardly possible because of the great number of constants involved in the potential function. At present it seems impossible to avoid the use of empirical rules stated with certainty in the case of simple molecules. Such rules would give some relations between the (theoretically independent) force constants. Let us e. g. consider the rule

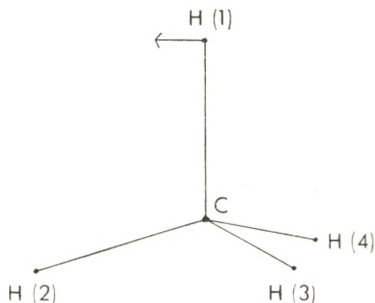


Fig. 7.

stated in *Case 1* for methane. If a more general validity of this rule could be secured, it would be a great help, e. g. in the study of the ethane molecule. It seems natural to assume, however, that deviations from the above rule are more likely to occur in dealing with molecules possessing an electronic structure essentially different from the electronic structure of methane. Here the *acetylene molecule* represents a good test example. In the following chapter a brief treatment of the acetylene molecule is given. The result is that the validity of the rule, stated in *Case 1* for methane, is shown in the case of acetylene, too. The writer hopes to be able to demonstrate the use of this and similar valuable empirical rules in future work.

VIII. Brief Treatment of the Acetylene Molecule.

The distribution of the vibrations of C_2H_2 and C_2D_2 (point group $D_{\infty h}$) has been given by GLOCKLER and MORRELL.¹

Table VI.

Class	Sym.	Antisym.	Number of frequencies	Degree of degeneracy	Vibration frequencies
A_1	C_{∞}, σ_v, i		2	1	$\nu_1 \nu_2$
A_2	$C_{\infty}, \sigma_v,$	i	1	1	ν_3
B_1	σ_v, i	C_{∞}	1	2	$\nu_{4, 5}$
B_2	σ_v	C_{∞}, i	1	2	$\nu_{6, 7}$

Corresponding to the frequency denotation the symmetry coordinates are defined as follows:

$$S_1 = x_0 - x_1.$$

$$S_2 = x_2 - x_3.$$

$$S_3 = x_0 + x_1 - x_2 - x_3.$$

$$S_4 = \frac{r}{R} (y_0 - y_1) - y_2 + y_3.$$

$$S_5 = \frac{r}{R} (-z_0 + z_1) + z_2 - z_3.$$

$$S_6 = y_0 + y_1 - y_2 - y_3.$$

$$S_7 = z_0 + z_1 - z_2 - z_3,$$

the acetylene molecule being placed in the coordinate system as demonstrated in fig. 8.

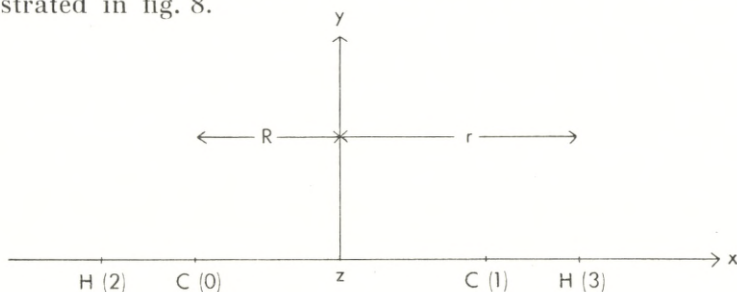


Fig. 8.

¹ GLOCKLER and MORRELL, J. Chem. Phys. **4**, 15 (1936).

Relations between force-constants and vibration frequencies.

The potential contribution of the A_1 -class is formulated as

$$A_2 V = a_1 S_1^2 + a_2 S_2^2 + a_3 S_1 S_2.$$

Consequently the secular equation becomes

$$\begin{vmatrix} 2 a_1 - m_C z & a_3 \\ a_3 & 2 a_2 - m_H z \end{vmatrix} = 0. \quad (1)$$

Roots: z_1 and z_2 .

The A_2 -class.

$$A_2 V = a_4 S_3^2, \quad a_4 = \frac{m_C m_H}{2(m_H + m_C)} z_3. \quad (2)$$

The B_1 -class.

$$A_2 V = a_5 (S_4^2 + S_5^2), \quad a_5 = \frac{m_H m_C}{2 \left(m_C + m_H \left(\frac{r}{R} \right)^2 \right)} z_{4,5}. \quad (3)$$

The B -class.

$$A_2 V = a_6 (S_6^2 + S_7^2), \quad a_6 = \frac{m_H m_C}{2(m_H + m_C)} z_{6,7}. \quad (4)$$

The numerical values of the above-mentioned force constants will now be calculated on the basis of data from Raman and infrared spectra of $C_2 H_2$ and $C_2 D_2$. A good survey of the experimental material available is given by STITT.¹ Beneath the experimentally determined vibration frequencies are stated.

$C_2 H_2$.

$\nu_1 = 1974$ BHAGAVANTAM and RAO, Proc. Ind. Acad. Sci. 3 A, 135 (1936) (R).

GLOCKLER and MORRELL, J. Chem. Phys. 4, 15 (1936) (I).

$\nu_2 = 3372$ The same references as for ν_1 .

$\nu_3 = 3288$ } LEVIN and MEYER, J. Opt. Soc. Am. 16, 137 (1928) (I).

$\nu_{6,7} = 730$ }

$\nu_{4,5} = 612$ MECKE and ZIEGLER, Zeits. f. Phys. 101, 405 (1936) (I).

$C_2 D_2$.

$\nu_1 = 1762$ } GLOCKLER and MORRELL, J. Chem. Phys. 4, 14 (1936) (I).

$\nu_2 = 2700$ }

$\nu_3 = 2428$ } FRED STITT, J. Chem. Phys. 8, 56 (1940) (I).

$\nu_{6,7} = 539$ }

$\nu_{4,5} = 506$ }

(I) = Infrared absorption; (R) = Raman spectrum.

¹ FRED STITT, J. Chem. Phys. 8, 56 (1940).

Calculation of the force-constants and their physical significance.

By means of (1), (2), (3), and (4) we find:

$$\begin{aligned}
 a_1 &= 19.15 \cdot 10^5. & a_2 &= 2.893 \cdot 10^5. & a_3 &= \pm 6.075 \cdot 10^5. \\
 a_4 &= 2.938 \cdot 10^5. & a_5 &= 0.6730 \cdot 10^4. & a_6 &= 1.448 \cdot 10^4 \text{ dyne cm}^{-1}.
 \end{aligned}$$

To check the correctness of these numerical values we shall precalculate the vibrations frequencies of the C_2HD -molecule.

The vibrations of this molecule are distributed on two symmetry-classes, one class of linear vibrations and another of non-linear ones. The secular equation for the linear vibrations is

$$\begin{vmatrix}
 2a_1 - m_C z & & & & & 0 \\
 & a_3 & & & & \\
 & & & & & \\
 a_3 & & 2a_2 - \frac{(m_H + m_D)m_C + 2m_H m_D}{M(C_2HD)} z & & \frac{(m_H - m_D)m_C}{M(C_2HD)} z & \\
 & & & & & \\
 0 & & \frac{(m_H - m_D)m_C}{M(C_2HD)} z & & 2a_4 - \frac{(m_H + m_D)m_C}{M(C_2HD)} z &
 \end{vmatrix} = 0 \quad (5)$$

For the non-linear vibrations I have only evaluated

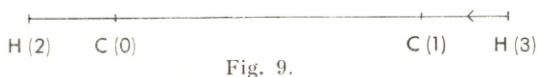
$$\begin{aligned}
 \dot{S}_4 &= \left(\frac{m_H + m_D}{2m_H m_D} + \left(\frac{r}{R} \right)^2 \frac{1}{m_C} \right) \frac{\partial 2T}{\partial \dot{S}_4} + \frac{m_D - m_H}{2m_H m_D} \frac{\partial 2T}{\partial \dot{S}_6} \\
 \dot{S}_6 &= \frac{m_D - m_H}{2m_H m_D} \frac{\partial 2T}{\partial \dot{S}_4} + \left(\frac{1}{m_C} + \frac{1}{2m_H} + \frac{1}{2m_D} \right) \frac{\partial 2T}{\partial \dot{S}_6}
 \end{aligned}$$

in explicit form, omitting to write down the secular equation explicitly.

C_2H_2		C_2HD		C_2D_2	
Calculated	Observed	Calculated	Observed	Calculated	Observed
1985	1974	1851	1851	1747	1762
3366	3372	3332	3340	2710	2700
3288	3288	2576	2560	2420	2428
730	730	674	679	537	539
612	612	518	523	512	506

The table at the bottom of page 31 shows the result of precalculating the complete vibration spectra of C_2H_2 , C_2HD , and C_2D_2 , using the numerical values of the force constants just given. As will be seen from (5) the spectrum of C_2DH does not help us to find the correct sign of a_3 , as only a_3^2 enters.

Having thus demonstrated the correctness of the force-constants we proceed to study the intramolecular forces. $H(3)$ is displaced from its equilibrium position as shown in fig. 9.



We choose $x_3 = -1$ and get $S_1 = S_4 = S_5 = S_6 = S_7 = 0$, $S_2 = S_3 = 1$.

By means of the usual procedure we find

$$K_{C(0)} = -\frac{1}{2}a_3 - a_4; \quad K_{C(1)} = \frac{1}{2}a_3 - a_4; \quad K_{H(2)} = -a_2 + a_4;$$

$$K_{H(3)} = a_2 + a_4.$$

Substituting the numerical values for the force-constants we get

	$a_3 < 0$	$a_3 > 0$
$K_{C(0)} \dots \dots$	0.0989	-5.9761
$K_{C(1)} \dots \dots$	-5.9761	0.0989
$K_{H(2)} \dots \dots$	0.0455	0.0455
$K_{H(3)} \dots \dots$	5.8317	5.8317

Independently of the sign of a_3 it is seen that $K_{H(2)}:K_{H(3)}$ has about the same value as found by the corresponding displacement by methane. The two hydrogen atoms move independently.—As it seems correct to assume that the force acting upon the carbon atom beside the displaced hydrogen atom, is the greater, we see that $a_3 < 0$. This means, however, that beyond the neighbour carbon atom scarcely any effect is exerted by the hydrogen atom attacked. As already mentioned this is the same rule as developed by methane, and it should be mentioned that it is also valid in the case of $H-C \equiv N$, as shown in the present writer's doctor's thesis.¹

¹ B. BAK, Det indremolekylære Potential, Kbhvn. 1943.

IX. Summary.

(1) The equations between vibration frequencies of methane and deuterated methanes have been deduced. It is proposed that the ideas of HOWARD and WILSON in connexion with the group-theoretical tables by ROSENTHAL should be more commonly used in solving vibrational problems.

(2) By means of vibration frequencies from the spectra of CH_4 and CD_4 , numerical values of 5 'harmonic' force constants have been calculated. This makes it possible to precalculate the entire spectra of all the partly deuterated methanes. The agreement between observed and calculated values as a rule is excellent.

(3) Empirical rules which might be of use in dealing with more complex molecules have been looked for, and it is shown that the displacement of a hydrogen atom towards its adjoining carbon atom produces little effect on all the other atoms of the molecule. It is demonstrated that the rule holds good, too, in the case of C_2H_2 and HCN .

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