THE POTENTIAL
FUNCTION OF ETHANE

BY

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CONTENTS

I. Introduction.

In dealing with the problem of finding the coefficients of the general quadratic potential function of molecules for the internal degrees of freedom it is usually found, that the experimental material available is insufficient for a determination of all the force-constants. The well-known 'valence-force' and 'central-force' models are generally applied means of avoiding this difficulty. However, the use of these models very often is evidently wrong, e. g. as demonstrated by the author as regards benzene[1].

In order to find some relations between the theoretically independent force-constants of the general quadratic potential function, based upon less rigorous assumptions than those laid down in the valence-force or central-force systems, the author looked for such rules in the case of HCN, CH_4 and C_2H_2[2] and succeeded in putting forward an 'empirical rule' valid for the three molecules mentioned: If one or more hydrogen atoms connected with the same carbon atom are displaced towards the adjoining carbon atom, the forces acting upon the other atoms of the molecule could as a good approximation be put equal to zero.

To see if a more general validity of this rule could be stated, the potential function of ethane was investigated. Ethane is the prototype of alifatic hydrocarbons with a carbon-chain, which means that the results obtained are of more than special interest. The result of the investigation of ethane may be briefly summarized as follows:

As far as only vibrations, non-degenerate with respect to the threefold axis of ethane, are considered, the 'empirical rule' helps to find a set of force-constants which are probably correct. But

[1] B. BAK, Det Kgl. Danske Vidensk. Selskab, mat.-fys. Medd. XXII, 9 (1945).
[2] B. BAK, ibid. XXII, 16 (1946).

in the case of degenerate vibrations the application of the rule gives false results. This, of course, means that the rule should be handled with much care as its domain of validity is undetermined.

Even if only a partial knowledge of the potential function of ethane is obtained, such knowledge is of importance, too. It can be foreseen that during the next years the study of the spectra of the partially deuterated ethanes will be among the principal means by which to decide finally whether ethane has the D_{3d} or the D_{3h} configuration[1]. For the interpretation of those spectra even a partial knowledge of the potential function of ethane is of importance as all isotopic molecules obey the same potential function.

II. Symmetry Considerations.

The problem of finding the correct stereochemical model of ethane has been the subject of numerous papers during this decade. It seems to be a firmly established result that no free rotation occurs around the carbon-carbon bond, but that three intermediate positions of minimum potential energy exist. It has not, however, been decided whether the D_{3d} or the D_{3h} configuration is the more correct one. The mathematical technique and the subsequent discussion of the vibrational spectra are approximately the same in both cases, as will appear from the following treatment.

1. Symmetry Coordinates and Potential Function for the D_{3d} Model.

Fig. 1 shows in double projection how the ethane molecule is placed in an xyz-coordinate system.

In table I the characters of the normal modes of vibration for molecules of the ethane type (point group D_{3d}) are given.

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[1] A discussion of this problem is given by H. MARK in his book: 'Physical Chemistry of High Polymeric Systems', p. 53, New York 1940.
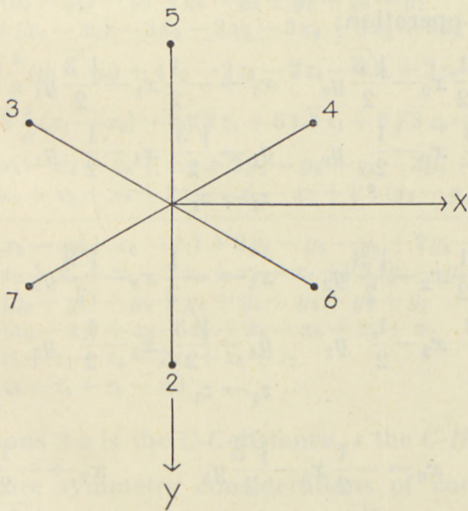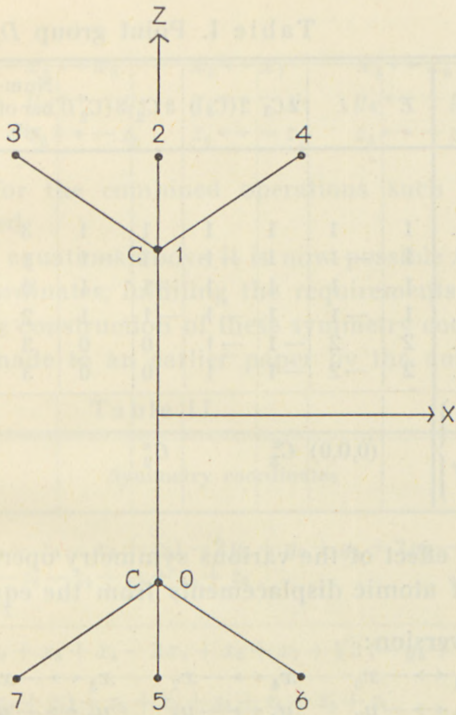
Fig. 1.

Table I. Point group D_{3d}.

Covering operation	E	i	$2\,C_3$	$2\,(C_3\,i)$	$3\,C_2'$	$3\,(C_2'\,i)$	Number of vib.	Zero freq.	Degree of deg.	Spect. activ.	Frequency desig.
Symmetry class											
A_{1g}	1	1	1	1	1	1	3		1	R	$\nu_1\,\nu_2\,\nu_3$
A_{1u}	1	-1	1	-1	1	-1	1		1		ν_4
A_{2g}	1	1	1	1	-1	-1	0	R_z	1		
A_{2u}	1	-1	1	-1	-1	1	2	T_z	1	I	$\nu_5\,\nu_6$
E_g	2	2	-1	-1	0	0	3	$R_x R_y$	2	R	$\nu_7\,\nu_8\,\nu_9$
E_u	2	-2	-1	1	0	0	3	$T_x T_y$	2	I	$\nu_{10}\,\nu_{11}\,\nu_{12}$
Symmetry elements particularly studied		$(0,0,0)$	C_3^z		C_2^x						

The effect of the various symmetry operations on the components of atomic displacements from the equilibrium position is:

The inversion:

$$x_1 \leftrightarrow -x_0 \qquad x_4 \leftrightarrow -x_7 \qquad x_3 \leftrightarrow -x_6 \qquad x_2 \leftrightarrow -x_5$$
$$y_1 \leftrightarrow -y_0 \qquad y_4 \leftrightarrow -y_7 \qquad y_3 \leftrightarrow -y_6 \qquad y_2 \leftrightarrow -y_5$$
$$z_1 \leftrightarrow -z_0 \qquad z_4 \leftrightarrow -z_7 \qquad z_3 \leftrightarrow -z_6 \qquad z_2 \leftrightarrow -z_5$$

The C_3^z-operation:

$$x_0 \to -\frac{1}{2}x_0 - \frac{\sqrt{3}}{2}y_0 \qquad x_1 \to -\frac{1}{2}x_1 - \frac{\sqrt{3}}{2}y_1 \qquad x_2 \to -\frac{1}{2}x_4 - \frac{\sqrt{3}}{2}y_4$$
$$y_0 \to \frac{\sqrt{3}}{2}x_0 - \frac{1}{2}y_0 \qquad y_1 \to \frac{\sqrt{3}}{2}x_1 - \frac{1}{2}y_1 \qquad y_2 \to \frac{\sqrt{3}}{2}x_4 - \frac{1}{2}y_4$$
$$z_0 \to z_0 \qquad z_1 \to z_1 \qquad z_2 \to z_4$$

$$x_3 \to -\frac{1}{2}x_2 - \frac{\sqrt{3}}{2}y_2 \qquad x_4 \to -\frac{1}{2}x_3 - \frac{\sqrt{3}}{2}y_3 \qquad x_5 \to -\frac{1}{2}x_7 - \frac{\sqrt{3}}{2}y_7$$
$$y_3 \to \frac{\sqrt{3}}{2}x_2 - \frac{1}{2}y_2 \qquad y_4 \to \frac{\sqrt{3}}{2}x_3 - \frac{1}{2}y_3 \qquad y_5 \to \frac{\sqrt{3}}{2}x_7 - \frac{1}{2}y_7$$
$$z_3 \to z_2 \qquad z_4 \to z_3 \qquad z_5 \to z_7$$

$$x_6 \to -\frac{1}{2}x_5 - \frac{\sqrt{3}}{2}y_5 \qquad x_7 \to -\frac{1}{2}x_6 - \frac{\sqrt{3}}{2}x_6$$
$$y_6 \to \frac{\sqrt{3}}{2}x_5 - \frac{1}{2}y_5 \qquad y_7 \to \frac{\sqrt{3}}{2}x_6 - \frac{1}{2}y_6$$
$$z_6 \to z_5 \qquad z_7 \to z_6.$$

The C_2^x-operation:

$$x_0 \leftrightarrow x_1 \qquad x_2 \leftrightarrow x_5 \qquad x_3 \leftrightarrow x_7 \qquad x_4 \leftrightarrow x_6$$
$$y_0 \leftrightarrow -y_1 \qquad y_2 \leftrightarrow -y_5 \qquad y_3 \leftrightarrow -y_7 \qquad y_4 \leftrightarrow -y_6$$
$$z_0 \leftrightarrow -z_1 \qquad z_2 \leftrightarrow -z_5 \qquad z_3 \leftrightarrow -z_7 \qquad z_4 \leftrightarrow -z_6.$$

The equations for the combined operations such as $(C_2 i)$ are easily constructed.

By means of the equations above it is now possible to find a set of symmetry coordinates, fulfilling the requirements of table I. As to details in the construction of these symmetry coordinates reference must be made to an earlier paper by the author[1].

Table II.

Symmetry class	Symmetry coordinates
A_{1g}	$S_1 = \sqrt{3}\,(x_3 - x_4 - x_6 + x_7) - 2\,y_2 + y_3 + y_4 + 2\,y_5 - y_6 - y_7$ $S_2 = -z_2 - z_3 - z_4 + z_5 + z_6 + z_7$ $S_3 = z_0 - z_1$
A_{1u}	$S_4 = -2\,x_2 + x_3 + x_4 - 2\,x_5 + x_6 + x_7 + \sqrt{3}\,(-y_3 + y_4 - y_6 + y_7)$
A_{2u}	$S_5 = -3\,(z_0 + z_1) + z_2 + z_3 + z_4 + z_5 + z_6 + z_7$ $S_6 = \sqrt{3}\,(x_3 - x_4 + x_6 - x_7) - 2\,y_2 + y_3 + y_4 - 2\,y_5 + y_6 + y_7$
E_g	$S_{7a} = -b\,(y_0 - y_1) - y_2 - y_3 - y_4 + y_5 + y_6 + y_7$ $S_{7b} = -3\,b\,(x_0 - x_1) - 3\,x_2 - 3\,x_3 - 3\,x_4 + 3\,x_5 + 3\,x_6 + 3\,x_7$ $S_{8a} = 4\,\sqrt{2}\,\dfrac{s}{a}\,(y_1 - y_0) + 4\,z_2 - 2\,z_3 - 2\,z_4 - 4\,z_5 + 2\,z_6 + 2\,z_7$ $S_{8b} = 12\,\sqrt{2}\,\dfrac{s}{a}\,(x_1 - x_0) - 6\,\sqrt{3}\,z_3 + 6\,\sqrt{3}\,z_4 + 6\,\sqrt{3}\,z_6 - 6\,\sqrt{3}\,z_7$ $S_{9a} = \sqrt{3}\,(x_3 - x_4 - x_6 + x_7) + 2\,y_2 - y_2 - y_3 - 2\,y_5 + y_6 + y_7$ $S_{9b} = -2\,x_2 + x_3 + x_4 + 2\,x_5 - x_6 - x_7 + \sqrt{3}\,(y_3 - y_4 - y_6 + y_7)$
E_u	$S_{10a} = \sqrt{3}\,(x_3 - x_4 + x_6 - x_7) + 2\,y_2 - y_3 - y_4 + 2\,y_5 - y_6 - y_7$ $S_{10b} = -2\,x_2 + x_3 + x_4 - 2\,x_5 + x_6 + x_7 + \sqrt{3}\,(y_3 - y_4 + y_6 - y_7)$ $S_{11a} = -3\,(y_0 + y_1) + y_2 + y_3 + y_4 + y_5 + y_6 + y_7$ $S_{11b} = -3\,(x_0 + x_1) + x_2 + x_3 + x_4 + x_5 + x_6 + x_7$ $S_{12a} = -2\,z_2 + z_3 + z_4 - 2\,z_5 + z_6 + z_7$ $S_{12b} = \sqrt{3}\,(z_3 - z_4 + z_6 - z_7)$

In these definitions $2\,a$ is the C-C-distance, s the C-H-distance and $b = \dfrac{3\,a + s}{a}$. Pure symmetry considerations of course only determines each symmetry coordinate except an arbitrary factor,

[1] B. Bak, Det Kgl. Danske Vidensk. Selskab, mat.-fys. Medd. XXII, 16 (1946).

but the factors used in the above expressions are chosen so as to make the potential energy function as simple as possible.

As the potential function must be invariant during any covering operation of the molecule, we find that:

$$2V = a_1 S_1^2 + a_2 S_2^2 + a_3 S_3^2 + a_4 S_1 S_2 + a_5 S_1 S_3 + a_6 S_2 S_3 + a_7 S_4^2 +$$

$$+ a_8 S_5^2 + a_9 S_6^2 + a_{10} S_5 S_6 + a_{11} (S_{7a}^2 + S_{7b}^2) + a_{12} (S_{8a}^2 + S_{8b}^2) +$$

$$+ a_{13} (S_{9a}^2 + S_{9b}^2) + a_{14} (S_{7a} S_{8a} + S_{7b} S_{8b}) + a_{15} (S_{7a} S_{9a} + S_{7b} S_{9b}) +$$

$$+ a_{16} (S_{8a} S_{9a} + S_{8b} S_{9b}) + a_{17} (S_{10a}^2 + S_{10b}^2) + a_{18} (S_{11a}^2 + S_{11b}^2) +$$

$$+ a_{19} (S_{12a}^2 + S_{12b}^2) + a_{20} (S_{10a} S_{11a} + S_{10b} S_{11b}) + a_{21} (S_{10a} S_{12a} + S_{10b} S_{12b}) +$$

$$+ a_{22} (S_{11a} S_{12a} + S_{11b} S_{12b}).$$

2. Symmetry Coordinates and Potential Function for the D_{3h}-Model.

Fig. 2 shows how the ethane molecule is placed in the coordinate system if belonging to the D_{3h} point group.

In table III the characters of the normal modes of vibration are given.

Table III. Point group D_{3h}.

Covering operation	E	σ_h	$2 C_3$	$2 S_3$	$3 C_2$	$3 \sigma_v$	Number of vib.	Zero freq.	Degree of deg.	Spect. activ.	Frequency desig.
Symmetry class											
A_1'	1	1	1	1	1	1	3		1	R	$\nu_1 \nu_2 \nu_3$
A_2'	1	1	1	1	—1	—1	0	R_z	—		
A_1''	1	—1	1	—1	1	—1	1		1		ν_4
A_2''	1	—1	1	—1	—1	1	2	T_z	1	I	$\nu_5 \nu_6$
E'	2	2	—1	—1	0	0	3	$T_x T_y$	2	RI	$\nu_7 \nu_8 \nu_9$
E''	2	—2	—1	1	0	0	3	$R_x R_y$	2	R	$\nu_{10} \nu_{11} \nu_{12}$
Symmetry elements particularly studied		σ_z	C_3^z	S_3^z	C_2^y	σ_x					

The effects of the various symmetry operations on the components of atomic displacements from the equilibrium positions are:
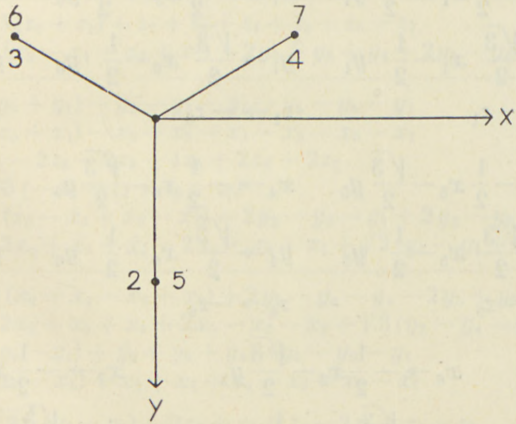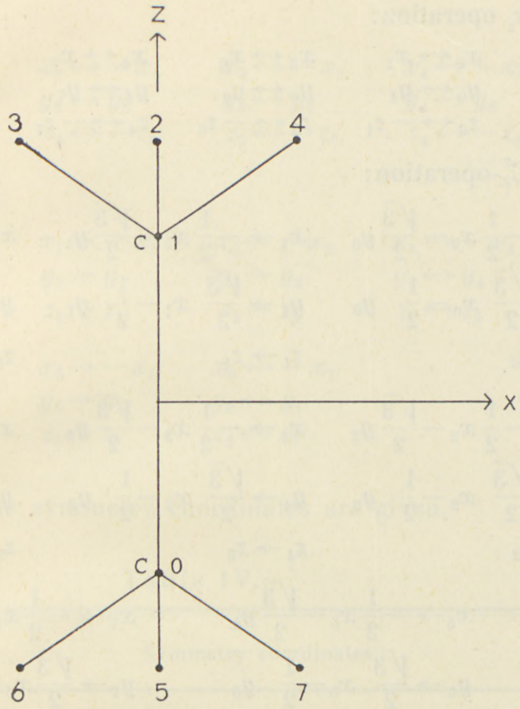
Fig. 2.

The σ_z operation:

$$x_0 \leftrightarrow x_1 \qquad x_3 \leftrightarrow x_6 \qquad x_4 \leftrightarrow x_7 \qquad x_2 \leftrightarrow x_5$$
$$y_0 \leftrightarrow y_1 \qquad y_3 \leftrightarrow y_6 \qquad y_4 \leftrightarrow y_7 \qquad y_2 \leftrightarrow y_5$$
$$z_0 \leftrightarrow -z_1 \qquad z_3 \leftrightarrow -z_6 \qquad z_4 \leftrightarrow -z_7 \qquad z_2 \leftrightarrow -z_5$$

The C_3^z-operation:

$$x_0 \to -\frac{1}{2}x_0 - \frac{\sqrt{3}}{2}y_0 \qquad x_1 \to -\frac{1}{2}x_1 - \frac{\sqrt{3}}{2}y_1 \qquad x_2 \to -\frac{1}{2}x_4 - \frac{\sqrt{3}}{2}y_4$$

$$y_0 \to \frac{\sqrt{3}}{2}x_0 - \frac{1}{2}y_0 \qquad y_1 \to \frac{\sqrt{3}}{2}x_1 - \frac{1}{2}y_1 \qquad y_2 \to \frac{\sqrt{3}}{2}x_4 - \frac{1}{2}y_4$$

$$z_0 \to z_0 \qquad\qquad z_1 \to z_1 \qquad\qquad z_2 \to z_4$$

$$x_3 \to -\frac{1}{2}x_2 - \frac{\sqrt{3}}{2}y_2 \qquad x_4 \to -\frac{1}{2}x_3 - \frac{\sqrt{3}}{2}y_3 \qquad x_5 \to -\frac{1}{2}x_7 - \frac{\sqrt{3}}{2}y_7$$

$$y_3 \to \frac{\sqrt{3}}{2}x_2 - \frac{1}{2}y_2 \qquad y_4 \to \frac{\sqrt{3}}{2}x_3 - \frac{1}{2}y_3 \qquad y_5 \to \frac{\sqrt{3}}{2}x_7 - \frac{1}{2}y_7$$

$$z_3 \to z_2 \qquad\qquad z_4 \to z_3 \qquad\qquad z_5 \to z_7$$

$$x_6 \to -\frac{1}{2}x_5 - \frac{\sqrt{3}}{2}y_5 \qquad x_7 \to -\frac{1}{2}x_6 - \frac{\sqrt{3}}{2}y_6$$

$$y_6 \to \frac{\sqrt{3}}{2}x_5 - \frac{1}{2}y_5 \qquad y_7 \to \frac{\sqrt{3}}{2}x_6 - \frac{1}{2}y_6$$

$$z_6 \to z_5 \qquad\qquad z_7 \to z_6.$$

The S_3^z-operation:

$$x_0 \to -\frac{1}{2}x_1 - \frac{\sqrt{3}}{2}y_1 \qquad x_1 \to -\frac{1}{2}x_0 - \frac{\sqrt{3}}{2}y_0 \qquad x_2 \to -\frac{1}{2}x_7 - \frac{\sqrt{3}}{2}y_7$$

$$y_0 \to \frac{\sqrt{3}}{2}x_1 - \frac{1}{2}y_1 \qquad y_1 \to \frac{\sqrt{3}}{2}x_0 - \frac{1}{2}y_0 \qquad y_2 \to \frac{\sqrt{3}}{2}x_7 - \frac{1}{2}y_7$$

$$z_0 \to -z_1 \qquad\qquad z_1 \to -z_0 \qquad\qquad z_2 \to -z_7$$

$$x_3 \to -\frac{1}{2}x_5 - \frac{\sqrt{3}}{2}y_5 \qquad x_4 \to -\frac{1}{2}x_6 - \frac{\sqrt{3}}{2}y_6 \qquad x_5 \to -\frac{1}{2}x_4 - \frac{\sqrt{3}}{2}y_4$$

$$y_3 \to \frac{\sqrt{3}}{2}x_5 - \frac{1}{2}y_5 \qquad y_4 \to \frac{\sqrt{3}}{2}x_6 - \frac{1}{2}y_6 \qquad y_5 \to \frac{\sqrt{3}}{2}x_4 - \frac{1}{2}y_4$$

$$z_3 \to -z_5 \qquad\qquad z_4 \to -z_6 \qquad\qquad z_5 \to -z_4$$

$$x_6 \to -\frac{1}{2}x_2 - \frac{\sqrt{3}}{2}y_2 \qquad x_7 \to -\frac{1}{2}x_3 - \frac{\sqrt{3}}{2}y_3$$

$$y_6 \to \frac{\sqrt{3}}{2}x_2 - \frac{1}{2}y_2 \qquad y_1 \to \frac{\sqrt{3}}{2}x_3 - \frac{1}{2}y_3$$

$$z_6 \to -z_2 \qquad\qquad z_7 \to -z_3$$

The C_2^y-operation:

$$x_0 \leftrightarrow -x_1 \qquad x_2 \leftrightarrow -x_5 \qquad x_3 \leftrightarrow -x_7 \qquad x_4 \leftrightarrow -x_6$$
$$y_0 \leftrightarrow y_1 \qquad y_2 \leftrightarrow y_5 \qquad y_3 \leftrightarrow y_7 \qquad y_4 \leftrightarrow y_6$$
$$z_0 \leftrightarrow -z_1 \qquad z_2 \leftrightarrow -z_5 \qquad z_3 \leftrightarrow -z_7 \qquad z_4 \leftrightarrow -z_6$$

The σ_x-operation:

$$x_0 \rightarrow -x_0 \qquad x_1 \rightarrow -x_1 \qquad x_2 \rightarrow -x_2 \qquad x_3 \leftrightarrow -x_4$$
$$y_0 \rightarrow y_0 \qquad y_1 \rightarrow y_1 \qquad y_2 \rightarrow y_2 \qquad y_3 \leftrightarrow y_4$$
$$z_0 \rightarrow z_0 \qquad z_1 \rightarrow z_1 \qquad z_2 \rightarrow z_2 \qquad z_3 \leftrightarrow z_4$$

$$x_5 \rightarrow -x_5 \qquad x_6 \leftrightarrow -x_7$$
$$y_5 \rightarrow y_5 \qquad y_6 \leftrightarrow y_7$$
$$z_5 \rightarrow z_5 \qquad z_6 \leftrightarrow z_7$$

In table IV the symmetry coordinates are given.

Table IV.

Symmetry class	Symmetry coordinates
A_1'	$\begin{aligned} S_1 &= \sqrt{3}\,(x_3 - x_4 + x_6 - x_7) - 2y_2 + y_3 + y_4 - 2y_5 + y_6 + y_7 \\ S_2 &= -z_2 - z_3 - z_4 + z_5 + z_6 + z_7 \\ S_3 &= z_0 - z_1 \end{aligned}$
A_1''	$S_4 = -2x_2 + x_3 + x_4 + 2x_5 - x_6 - x_7 + \sqrt{3}\,(-y_3 + y_4 + y_6 - y_7)$
A_2''	$\begin{aligned} S_5 &= -3\,(z_0 + z_1) + z_2 + z_3 + z_4 + z_5 + z_6 + z_7 \\ S_6 &= \sqrt{3}\,(x_3 - x_4 - x_6 + x_7) - 2y_2 + y_3 + y_4 + 2y_5 - y_6 - y_7 \end{aligned}$
E'	$\begin{aligned} S_{7a} &= 3\,(y_0 + y_1) - y_2 - y_3 - y_4 - y_5 - y_6 - y_7 \\ S_{7b} &= 3\,(x_0 + x_1) - x_2 - x_3 - x_4 - x_5 - x_6 - x_7 \\ S_{8a} &= 4z_2 - 2z_3 - 2z_4 - 4z_5 + 2z_6 + 2z_7 \\ S_{8b} &= 2\sqrt{3}\,(-z_3 + z_4 + z_6 - z_7) \\ S_{9a} &= \sqrt{3}\,(x_3 - x_4 + x_6 - x_7) + 2y_2 - y_3 - y_4 + 2y_5 - y_6 - y_7 \\ S_{9b} &= -2x_2 + x_3 + x_4 - 2x_5 + x_6 + x_7 + \sqrt{3}\,(y_3 - y_4 + y_6 - y_7) \end{aligned}$
E''	$\begin{aligned} S_{10a} &= \sqrt{3}\,(x_3 - x_4 - x_6 + x_7) + 2y_2 - y_3 - y_4 - 2y_5 + y_6 + y_7 \\ S_{10b} &= -2x_2 + x_3 + x_4 + 2x_5 - x_6 - x_7 + \sqrt{3}\,(y_3 - y_4 - y_6 + y_7) \\ S_{11a} &= b\,(y_0 - y_1) + y_2 + y_3 + y_4 - y_5 - y_6 - y_7 \\ S_{11b} &= b\,(x_0 - x_1) + x_2 + x_3 + x_4 - x_5 - x_6 - x_7 \\ S_{12a} &= 2\sqrt{2}\,\frac{s}{a}\,(y_0 - y_1) - 2z_2 + z_3 + z_4 - 2z_5 + z_6 + z_7 \\ S_{12b} &= 2\sqrt{2}\,\frac{s}{a}\,(x_0 - x_1) + \sqrt{3}\,(z_3 - z_4 + z_6 - z_7) \end{aligned}$

D_{3d} con-figuration	$\begin{vmatrix} 2a_1 - \dfrac{m_H}{12}\varkappa & a_4 & a_5 \\[2mm] a_4 & 2a_2 - \dfrac{m_H}{3}\varkappa & a_6 \\[2mm] a_5 & a_6 & 2a_3 - m_C\varkappa \end{vmatrix} = 0$	$a_7 = $ $\dfrac{m_H}{24}\varkappa$	$\begin{vmatrix} 2a_8 - \dfrac{m_H m_C}{3(m_C + 3m_H)}\varkappa & a_{10} \\[2mm] a_{10} & 2a_9 - \dfrac{m_H}{12}\varkappa \end{vmatrix} = 0$
	Roots: $\varkappa_1$ $\varkappa_2$ $\varkappa_3$	$\varkappa_4$	$\varkappa_5$ $\varkappa_6$
Symmetry class	A_{1g}	A_{1u}	A_{2u}
Symmetry class	A'_1	A''_1	A''_2
D_{3h} con-figuration	Same as above	Same as above	Same as above
	Roots: $\varkappa_1$ $\varkappa_2$ $\varkappa_3$	$\varkappa_4$	$\varkappa_5$ $\varkappa_6$

V.

$$\begin{vmatrix} 2a_{11} - \dfrac{32\left(\frac{s}{a}\right)^2 m_H + 24 m_C}{N_1 m_H m_C}\varkappa & a_{14} + \dfrac{4\sqrt{2}\,sb}{N_1 a m_C}\varkappa & a_{15} \\[2ex] a_{14} + \dfrac{4\sqrt{2}\,sb}{N_1 a m_C}\varkappa & 2a_{12} - \dfrac{m_H b^2 + 3 m_C}{N_1 m_H m_C}\varkappa & a_{16} \\[2ex] a_{15} & a_{16} & 2a_{13} - \dfrac{m_H}{12}\varkappa \end{vmatrix} = 0$$

$$N_1 = \frac{m_H\left(24 b^2 + 96\left(\frac{s}{a}\right)^2\right) + 72 m_C}{m_C m_H^2}$$

$$\varkappa_7 \qquad \varkappa_8 \qquad \varkappa_9$$

$$\begin{vmatrix} 2a_{17} - \dfrac{m_H}{12}\varkappa & a_{20} & a_{21} \\[2ex] a_{20} & 2a_{18} - \dfrac{m_H m_C}{3M}\varkappa & a_{22} \\[2ex] a_{21} & a_{22} & 2a_{19} - \dfrac{m_H}{6}\varkappa \end{vmatrix} = 0$$

$$M = \text{mass of } CH_3.$$

$$\varkappa_{10} \qquad \varkappa_{11} \qquad \varkappa_{12}$$

$$E_g \qquad\qquad\qquad\qquad E_u$$

$$E'' \qquad\qquad\qquad\qquad E'$$

$$\begin{vmatrix} 2a_{17} - \dfrac{m_H}{12}\varkappa & a_{20} & a_{21} \\[2ex] a_{20} & 2a_{18} - \dfrac{8\left(\frac{s}{a}\right)^2 m_H + 6 m_C}{N_2 m_H m_C}\varkappa & a_{22} + \dfrac{2\sqrt{2}\,sb}{N_2 a m_C}\varkappa \\[2ex] a_{21} & a_{22} + \dfrac{2\sqrt{2}\,sb}{N_2 a m_C}\varkappa & 2a_{19} - \dfrac{m_H b^2 + 3 m_C}{N_2 m_H m_C}\varkappa \end{vmatrix} = 0$$

$$N_2 = \frac{m_H\left(6 b^2 + 24\left(\frac{s}{a}\right)^2\right) + 18 m_C}{m_C m_H^2}.$$

$$\varkappa_{10} \qquad \varkappa_{11} \qquad \varkappa_{12}$$

$$\begin{vmatrix} 2a_{11} - \dfrac{m_H m_C}{3M}\varkappa & a_{14} & a_{15} \\[2ex] a_{14} & 2a_{12} - \dfrac{m_H}{24}\varkappa & a_{16} \\[2ex] a_{15} & a_{16} & 2a_{13} - \dfrac{m_H}{12}\varkappa \end{vmatrix} = 0$$

$$M = \text{mass of } CH_3.$$

$$\varkappa_7 \qquad \varkappa_8 \qquad \varkappa_9$$

The symmetry coordinates of table IV have been chosen in such a way that the potential function is formulated exactly as in the case of the D_{3d}-model, given on page 8. Formally one can operate with the same potential function in both models but it should be remembered that the physical meaning of the force-constants is not the same in the two cases.

III. Relations between Force-Constants and Vibration Frequencies.

These equations are found in the usual way by means of the Lagrangian equations. The results are given in table V.

As appears from table V the symmetry coordinates have been chosen so as to make all calculations in the non-degenerate classes formally identical. This is a great advantage because this paper mainly deals with these classes. In the degenerate classes there are differences, but there are also fundamental similarities between the equations to be solved.

IV. Numerical Calculations.

1. Experimental Material.

Infrared and Raman data have been published by many authors.

Infrared data.

LEVIN and MAYER, Journ. Opt. Soc. Am. **16**, 137 (1928)	(C_2H_6)
BENEDICT, MORIKAWA, BARNES, and TAYLOR, J. Chem. Phys. **5**, 1 (1937)	(-)
BARTHOLOMÉ and KARWEIL, Naturwis. **25**, 476 (1937)	(-)
CRAWFORD, AVERY, and LINNETT, J. Chem. Phys. **6**, 682 (1938)	(-)
FRED. STITT, J. Chem. Phys. **7**, 297 (1939)	(C_2D_6)

Raman data.

DAURE, Trans. Far. Soc. **25**, 825 (1929)	(C_2H_6)
BHAGAVANTAM, Ind. Journ. Phys. **6**, 595 (1932)	(-)

Lewis and Houston, Phys. Rev. 44, 903 (1933)   (C_2H_6)
Bhagavantam, Proc. Ind. Acad. Sci. A, 2, 86 (1935)   (-)
Glockler and Renfrew, J. Chem. Phys. 6, 295 (1938)   (-)
Glockler and Renfrew, J. Chem. Phys. 6, 409 (1938)   (-)
Crawford, Avery, and Linnett, J. Chem. Phys. 6, 682 (1938)   (-)
Goubeau and Karweil, Zeits. Phys. Chem. B, 40, 376 (1938)   (-)
Fred Stitt, J. Chem. Phys. 7, 297 (1939)   (C_2D_6)

Fred Stitt was the first to find the very important data from C_2D_6. These highly facilitate the assignment of frequencies. A careful examination of all the available literature reveals that the assignment of frequencies made by Stitt must be considered as far the most probable at present. In table VI the results of Stitt, therefore, are given.

Table VI.

D_{3d} configuration	C_2H_6	C_2D_6	D_{3h} configuration
ν_1	993	852	ν_1
ν_2	1375	1158	ν_2
ν_3	2925	2115	ν_3
ν_4	310	—	ν_4
ν_5	1380	1072	ν_5
ν_6	2925	2100	ν_6
ν_{10}	827	601	ν_7
ν_{11}	1465	1102	ν_8
ν_{12}	2980	2237	ν_9
ν_7	1170	970	ν_{10}
ν_8	1460	1055	ν_{11}
ν_9	2960	2225	ν_{12}

2. Discussion of Various Models.

The frequencies of table VI deviate from the 'harmonical' frequencies of the molecule (the frequencies for zero amplitude). In cases where this deviation could be experimentally determined it has been shown that the harmonical frequencies are roughly about 2 per cent. higher than those experimentally determined for vibrations in which hydrogen and carbon atoms take part.

The deviation is of course greater in the case of C_2H_6 than in the case of C_2D_6 because of the greater amplitudes in the former case. To give an impression of the size of the deviations the 'product rule' of TELLER can be used. The results are given in table VII.

Table VII.

D_{3d}	D_{3h}	Product rule ratio calc.	Experimentally determined
A_{1g}	A'_1	2.00	1.92
A_{1u}	A''_1	1.41	—
A_{2u}	A''_2	1.83	1.79
E_g	E''	2.36	2.22
E_u	E'	2.58	2.44

In papers where force-constants are calculated the experimentally determined frequencies are generally used as if they were 'harmonical', that is, a molecular model carrying out harmonical vibrations with the experimentally determined frequencies is considered, and it is postulated that the conditions of force in such a model are approximately the same as in the real molecule. In the papers hitherto published by the author[1] this procedure has met with no difficulties. In the present case, however, difficulties arise in the degenerate symmetry classes. If the experimentally determined frequencies are used in the calculations in the usual way, imaginary force-constants result. This means that in the case of ethane a model corresponding to those used at the description of other molecules such as benzene, methane, and acetylene does not exist. To get a model with real values of the force-constants we must alter the experimentally determined frequencies slightly before starting the calculations. The set of frequencies used must of course obey the above-mentioned product rule, and they should deviate as little as possible from the experimental ones. But as such correction of the frequencies could be carried through in many different ways, the important question arises what rôle this arbitrariness plays for the numerical size of the force-constants. In this paper we shall try to

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[1] loc. cit.

give a partial answer to this problem by making some of the calculations on the basis of two different sets of frequencies that are to be considered beforehand of equal correctness.

The more fundamental problem concerning the difference between the various models and the 'real' molecule cannot be answered until a description of the vibrating molecule by means of a potential function involving higher powers of the symmetry coordinates has been given. But there is no possibility of giving such a description at the present stage of chemical physics.

3. Force-Constants of the Non-Degenerate Classes.

Solving the determinantal equations of the non-degenerate classes with respect to the unknown force-constants we get the eleven equations:

$$a_3 \qquad = \frac{m_C}{2}\left(2\sum_1^3 x_i' - \sum_1^3 x_i\right) \tag{1}$$

$$a_2 + 4\,a_1 \qquad = \frac{m_H}{3}\left(\sum_1^3 x_i - \sum_1^3 x_i'\right) \tag{2}$$

$$a_4^2 - 4\,a_1 a_2 \qquad = \frac{m_D m_H^2}{36\,(m_D - m_H)}\left(2\sum_1^3 x_i' x_j' - \sum_1^3 x_i x_j\right)(i \neq j) \tag{3}$$

$$\begin{aligned}4\,a_2 a_3 + 16\,a_1 a_3 -\\ -\,4\,a_5^2 - a_6^2\end{aligned} \qquad = \frac{m_H m_C}{3}\left(4\sum_1^3 x_i' x_j' - \sum_1^3 x_i x_j\right)(i \neq j) \tag{4}$$

$$\begin{aligned}4\,a_1 a_2 a_3 + a_4 a_5 a_6 -\\ -\,a_1 a_6^2 - a_2 a_5^2 - a_3 a_4^2\end{aligned} \qquad = \begin{cases} \dfrac{x_1 x_2 x_3 m_C m_H^2}{72} & \tag{5}\\[2ex] \dfrac{x_1' x_2' x_3' m_C m_D^2}{72} & \tag{6} \end{cases}$$

$$a_7 \qquad = \frac{m_H}{24}\,x_4 \tag{7}$$

$$a_8 \qquad = \frac{m_C + 3\,m_H}{3\,(m_D - m_H)}\left(2\,(x_5' + x_6') - (x_5 + x_6)\right) \tag{8}$$

$$a_9 \qquad = \frac{m_H}{24}\left(\varkappa_5 + \varkappa_6 + \frac{m_C + 3m_H}{3(m_D - m_H)}\left(\varkappa_5 + \varkappa_6 - 2(\varkappa_5' + \varkappa_6')\right)\right) \qquad (9)$$

$$4\,a_8 a_9 - a_{10}^2 \quad = \begin{cases} \dfrac{\varkappa_5 \varkappa_6 m_C m_H^2}{36\,(m_C + 3m_H)} & (10) \\[2mm] \dfrac{\varkappa_5' \varkappa_6' m_C m_D^2}{36\,(m_C + 3m_D)} & (11) \end{cases}$$

where $\varkappa_i = 4\pi^2 \nu_i^2$, ν_i being one of the frequencies of the ethane molecule

and $\varkappa_i' = 4\pi^2 \nu_i'^2$, ν_i' being one of the frequencies of the hexa-deuteroethane molecule.

By insertion of the numerical values from table VI we get the equations

$$\begin{aligned}
a_3 &= 57.85 \cdot 10^4 \\
4\,a_1 + a_2 &= 9.618 \cdot 10^4 & (12) \\
a_4^2 - 4\,a_1 a_2 &= -11.64 \cdot 10^8 & (13) \\
4\,a_2 a_3 + 16\,a_1 a_3 - 4\,a_5^2 - a_6^2 &= 1988 \cdot 10^8 & (14) \\
4\,a_1 a_2 a_3 + a_4 a_5 a_6 - a_1 a_6^2 - a_2 a_5^2 - a_3 a_4^2 &= (5.412 + 5.902)\frac{1}{2} \cdot 10^{14} = 5.657 \cdot 10^{14}. & (15)
\end{aligned}$$

$a_7 = 0.02467 \cdot 10^4$; $a_8 = 2.5732 \cdot 10^4$; $a_9 = 1.7651 \cdot 10^4$; $a_{10} = \pm\, 2.318 \cdot 10^4$.

All force-constants are measured in dyne cm^{-1}.

The equations (12) — (15) represent 4 equations with 5 unknowns. It is therefore impossible to find their numerical value without making any physical assumption. We now want to use the 'empirical' rule cited on page 3.

The hydrogen atoms numbers 2, 3 and 4 are displaced towards $C\,(1)$. The amplitude components are:

$$x_2 = 0 \qquad\qquad y_2 = -\frac{2\sqrt{2}}{3} \qquad\qquad z_2 = -\frac{1}{3}$$

$$x_3 = \frac{\sqrt{6}}{3} \qquad\qquad y_3 = \frac{\sqrt{2}}{3} \qquad\qquad z_3 = -\frac{1}{3}$$

$$x_4 = -\frac{\sqrt{6}}{3} \qquad\qquad y_4 = \frac{\sqrt{2}}{3} \qquad\qquad z_4 = -\frac{1}{3}.$$

By insertion of these values in the definition equations for the symmetry coordinates we get:

$$S_1 = 4\sqrt{2}; \quad S_2 = 1; \quad S_5 = -1; \quad S_6 = 4\sqrt{2}.$$

The remaining symmetry coordinates are equal to zero. If we denote the force acting upon X-atom number i in the direction of the U-axis by $K_{X(i)}(U)$, we may write:

$$K_{H(5)}(Z) = -a_2 - 2\sqrt{2}\,a_4 + a_8 - 2\sqrt{2}\,a_{10}$$
$$K_{H(5)}(Y) = -8\sqrt{2}\,a_1 - a_4 + 8\sqrt{2}\,a_9 - a_{10}$$
$$K_{H(5)}(X) = 0$$
$$K_{C(0)}(Z) = -2\sqrt{2}\,a_5 - \frac{1}{2}a_6 - 3a_8 + 6\sqrt{2}\,a_{10}.$$

Putting these forces equal to zero we get the three equations:

$$a_4 + a_{10} = \frac{a_8 - a_2}{2\sqrt{2}} \tag{1, f}$$

$$a_4 + a_{10} = 8\sqrt{2}\,(a_9 - a_1) \tag{2, f}$$

$$4\sqrt{2}\,a_5 + a_6 + 6a_8 - 12\sqrt{2}\,a_{10} = 0. \tag{3, f}$$

('f' means: derived on physical assumption).

Now $(1, f)$, $(2, f)$ and (12) are three equations with three unknowns. We solve them and find

$$a_1 = 1.764 \cdot 10^4 \qquad a_2 = 2.560 \cdot 10^4 \qquad a_4 = \pm 2.318 \cdot 10^4.$$

But a_4 can also be determined from (13) and the values just obtained for a_1 and a_2. We find $a_4 = \pm 2.528 \cdot 10^4$. The consistency between the two ways of calculating a_4 must be considered as a verification of the 'empirical rule' in the present case.

(14) now gives a relation between a_5^2 and a_6^2. $4a_5^2 + a_6^2 = 237 \cdot 10^8$. Another relation between the same two constants is available in $(3, f)$. Here two cases arise, dependent upon the sign of a_{10}. The calculations, however, show that $a_{10} < 0$ means that a_5 becomes imaginary. As this possibility must be excluded on physical grounds it only remains that

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$$a_5 = 5.950 \cdot 10^4 \quad \text{and} \quad a_6 = -9.763 \cdot 10^4 \quad \text{(case 1)}$$
$$\text{or}$$
$$a_5 = 1.559 \cdot 10^4 \quad \text{and} \quad a_6 = 15.07 \cdot 10^4 \quad \text{(case 2)}.$$

The remaining two possibilities for the numerical values of the force-constants are:

	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8	a_9	a_{10}
(Case 1)	1.764	2.559	57.85	−2.528	5.950	−9.762	0.0236	2.5732	1.7651	2.318
(Case 2)	1.764	2.559	57.85	−2.528	1.559	15.07	0.0236	2.5732	1.7651	2.318

A choice between these two possibilities can be made by means of (15). We write (15) as

$$4\,a_1 a_2 a_3 - a_3 a_4^2 - 565.7 \cdot 10^{12} = -a_4 a_5 a_6 + a_1 a_6^2 + a_2 a_5^2.$$

In both cases the left-hand side has the value $109.8 \cdot 10^{12}$. In case 1 the right-hand side becomes $111.9 \cdot 10^{12}$, in case 2, $466.7 \cdot 10^{12}$. Thus case 1 must be the correct one and the numerical conformity found is a new confirmation of the validity of the empirical rule in the present case.

We finish this chapter by comparing the experimentally determined frequencies of the non-degenerate vibrations of ethane and hexadeuteroethane with frequencies calculated on the basis of the force-constants of case (1) above.

	Experimentally determined	Calculated in this paper
ν_1	993	1037
ν_2	1375	1344
ν_3	2925	2925
ν_5	1380	1395
ν_6	2925	2917
ν_1'	852	805
ν_2'	1158	1203
ν_3'	2115	2108
ν_5'	1072	1060
ν_6'	2100	2106

4. Effect of the Choice of Model.

In order to see what effect the choice of model has on the numerical values of the force-constants the preceding calculations are repeated on the basis of slightly altered frequency values. At the choice of these values there is an infinite number of possibilities. A special interest would be connected with a model the vibration frequencies of which were derived from the experimental ones by correcting them for anharmonicity. But such correction could not be carried through at present. As the anharmonicity as a rule is greater at hydrogen- than at deuterium-vibrations I have arbitrarily chosen to consider a model with hydrogen frequencies which are 2 per cent. higher than the corresponding values of table VI except in the A_{2u}-class, where only 1 per cent. is added[1]. The deuterium frequencies are taken over without change.

	Theoretical product rule ratio	Ratio for frequencies chosen
A_{1g}	2.00	2.04
A_{2u}	1.83	1.83

The frequency values chosen are more in harmony with the product rule than the experimentally determined ones. But the author wants to stress, that this should not be considered a sign that the molecular model to be built up on the basis of such corrected values is a better approximation to the 'real' molecule, not even if we had succeeded in finding the true 'harmonical' frequencies.

By means of the slightly altered frequency values the calculation of a new set of force-constants could be made in exactly the same way as was shown on pages 18—20. Beneath the force-constants of this second model (model 2) are compared with the force-constants of the model first considered (model 1).

	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8	a_9	a_{10}
Model 1	1.764	2.560	57.85	—2.528	5.950	—9.762	0.0236	2.573	1.765	2.318
Model 2	2.084	2.160	41.76	—1.449	2.898	—6.072	0.0240	1.756	2.072	1.229
Deviation per cent. of middle number	8.3	8.5	16.5	27.2	34.6	23.4	1.0	19.0	7.8	31.0

[1] If 2 per cent. are added in this symmetry class, imaginary force-constants result.

Table VIII.

S_i	$\dfrac{\partial 2V}{\partial S_i}$	Value of $\dfrac{\partial 2V}{\partial S_i}$ for displacement considered	$\dfrac{\partial S_i}{\partial y_0}$	$\dfrac{\partial S_i}{\partial z_0}$	$\dfrac{\partial S_i}{\partial x_3}$
S_1	$2a_1S_1 + a_4S_2 + a_5S_3$	$8\sqrt{2}\,a_1 + a_4 = \alpha$			$\sqrt{3}$
S_2	$a_4S_1 + 2a_2S_2 + a_6S_3$	$4\sqrt{2}\,a_4 + 2a_2 = \beta$			
S_3	$a_5S_1 + a_6S_2 + 2a_3S_3$	$4\sqrt{2}\,a_5 + a_6 = \gamma$		1	
S_4	$2a_7S_4$	0			1
S_5	$2a_8S_5 + a_{10}S_6$	$-2a_8 + 4\sqrt{2}\,a_{10} = \delta$	-3		
S_6	$a_{10}S_5 + 2a_9S_6$	$-a_{10} + 8\sqrt{2}\,a_9 = \varepsilon$			$\sqrt{3}$
S_{7a}	$2a_{11}S_{7a} + a_{14}S_{8a} + a_{15}S_{9a}$	$4\sqrt{2}\,a_{11} - 4a_{14} - 4\sqrt{2}\,a_{15} = A$	$-b$		
S_{8a}	$a_{14}S_{7a} + 2a_{12}S_{8a} + a_{16}S_{9a}$	$2\sqrt{2}\,a_{14} - 8a_{12} - 4\sqrt{2}\,a_{16} = B$	$-4\sqrt{2}\,\dfrac{s}{a}$		
S_{9a}	$a_{15}S_{7a} + a_{16}S_{8a} + 2a_{13}S_{9a}$	$2\sqrt{2}\,a_{15} - 4a_{16} - 8\sqrt{2}\,a_{13} = C$			$\sqrt{3}$
S_{10a}	$2a_{17}S_{10a} + a_{20}S_{11a} + a_{21}S_{12a}$	$-8\sqrt{2}\,a_{17} - 2\sqrt{2}\,a_{20} + 2a_{21} = D$			
S_{11a}	$a_{20}S_{10a} + 2a_{18}S_{11a} + a_{22}S_{12a}$	$-4\sqrt{2}\,a_{20} - 4\sqrt{2}\,a_{18} + 2a_{22} = E$	-3		
S_{12a}	$a_{21}S_{10a} + a_{22}S_{11a} + 2a_{19}S_{12a}$	$-4\sqrt{2}\,a_{21} - 2\sqrt{2}\,a_{22} + 4a_{19} = F$			
		Equation number:	(1)	(2)	(3)

As is seen the 'cross product constants' of the potential function (a_4, a_5, a_6 and a_{10}) are rather badly determined.

5. Attempt to Calculate Force-Constants of Degenerate Classes.

Solving the determinantal equation of e. g. the E_u-class we find that

$$2a_{17} + a_{19} = 2.207 \cdot 10^4$$
$$8a_{17}a_{18} + 4a_{18}a_{19} - 2a_{20}^2 - a_{22}^2 = 51.33 \cdot 10^8$$
$$a_{21}^2 - 4a_{17}a_{19} = 3.233 \cdot 10^8$$
$$4a_{17}a_{18}a_{19} + a_{20}a_{21}a_{22} - a_{17}a_{22}^2 - a_{18}a_{21}^2 - a_{19}a_{20}^2 = 5.240 \cdot 10^{12}$$
$$a_{18} = 5.657 \cdot 10^4$$

This is easily seen to be insufficient knowledge if we want to find the numerical values of the force-constants $a_{19} - a_{22}$. In order to get more information of the force-constants we use the 'empirical rule', displacing a single hydrogen atom towards its

		D_{3d}						D_{3h}								
$\dfrac{\partial S_i}{\partial y_3}$	$\dfrac{\partial S_i}{\partial z_3}$	$\dfrac{\partial S_i}{\partial y_5}$	$\dfrac{\partial S_i}{\partial z_5}$	$\dfrac{\partial S_i}{\partial x_6}$	$\dfrac{\partial S_i}{\partial y_6}$	$\dfrac{\partial S_i}{\partial z_6}$	$\dfrac{\partial S_i}{\partial y_0}$	$\dfrac{\partial S_i}{\partial z_0}$	$\dfrac{\partial S_i}{\partial x_3}$	$\dfrac{\partial S_i}{\partial y_3}$	$\dfrac{\partial S_i}{\partial z_3}$	$\dfrac{\partial S_i}{\partial y_5}$	$\dfrac{\partial S_i}{\partial z_5}$	$\dfrac{\partial S_i}{\partial x_6}$	$\dfrac{\partial S_i}{\partial y_6}$	$\dfrac{\partial S_i}{\partial z_6}$
1		2		$-\sqrt{3}$	-1				$\sqrt{3}$	1			-2	$\sqrt{3}$	1	
	-1	1				1					-1		1			1
$-\sqrt{3}$			1	$-\sqrt{3}$			1		1	$-\sqrt{3}$				-1	$\sqrt{3}$	
	1	1				1		-3			1		1			1
1	-2		$\sqrt{3}$	1					$\sqrt{3}$	1			2	$-\sqrt{3}$	-1	
-1	1			1			3			-1			-1			-1
	-2	-4			2					0	-2		-4			2
-1	-2		$-\sqrt{3}$	1					$\sqrt{3}$	-1			2	$\sqrt{3}$	-1	
-1	2		$\sqrt{3}$	-1					$\sqrt{3}$	-1			-2	$-\sqrt{3}$	1	
1	1			1			b				1			-1		-1
	1	-2				1	$2\sqrt{2}\,\dfrac{s}{a}$				1		-2			1
(4)	(5)	(6)	(7)	(8)	(9)	(10)										

adjoining carbon atom and putting the forces acting upon all the other atoms equal to zero. Thus,

$$x_2 = 0 \qquad y_2 = -2\sqrt{2} \qquad z_2 = -1,$$

and consequently

$$S_1 = 4\sqrt{2}; \quad S_2 = 1; \quad S_5 = -1;$$

$$S_6 = 4\sqrt{2}; \quad S_{7a} = 2\sqrt{2}; \quad S_{8a} = -4;$$

$$S_{9a} = -4\sqrt{2}; \quad S_{10a} = -4\sqrt{2}; \quad S_{11a} = -2\sqrt{2}; \quad S_{12a} = 2,$$

whether the stereochemical model is D_{3h} or D_{3d}. All other $S_i = 0$.

Table VIII gives a good survey of the way in which to find the relations that could be derived by means of the 'empirical rule'. These relations could all be written in the general form:

$$-2K_{X(i)}(U) = \frac{\partial 2V}{\partial u_i} = \sum_{0}^{7} \frac{\partial 2V}{\partial S_i} \frac{\partial S_i}{\partial u_i}.$$

The ten equations that can be derived from table VIII
are (D_{3d}):

$$A \cdot b + 4\sqrt{2}\,\frac{s}{a}\,B \qquad\qquad + 3\,E \qquad\quad = 0 \qquad (1)$$

$$\gamma - 3\,\delta \qquad\qquad\qquad\qquad\qquad\qquad\qquad = 0 \qquad (2)$$

$$\alpha \qquad\quad + \varepsilon \qquad\qquad\quad + C\ +D \qquad\qquad\quad = 0 \qquad (3)$$

$$\alpha \qquad\quad + \varepsilon - A \qquad\qquad - C\ -D + E \qquad\quad = 0 \qquad (4)$$

$$-\beta\ +\delta \qquad\qquad\quad\ -2\,B \qquad\qquad\qquad +F = 0 \qquad (5)$$

$$2\,\alpha \qquad\quad -2\,\varepsilon + A \qquad\quad -2\,C + 2\,D + E \qquad\quad = 0 \qquad (6)$$

$$\beta\ +\delta \qquad\qquad\qquad -4\,B \qquad\qquad\qquad -2\,F = 0 \qquad (7)$$

$$-\alpha \qquad\quad + \varepsilon \qquad\qquad\quad -C\ +D \qquad\qquad\quad = 0 \qquad (8)$$

$$-\alpha \qquad\quad + \varepsilon + A \qquad\qquad + C\ -D + E \qquad\quad = 0 \qquad (9)$$

$$\beta\ +\delta \qquad\qquad\qquad +2\,B \qquad\qquad\qquad\ +F = 0 \qquad (10)$$

By eliminating the unknown quantities A—F from these equations it could immediately be tested, whether they are correct or not. We get:

$$A = -E; \quad B = \frac{1}{4\sqrt{2}}\,E; \quad C = \frac{1}{2}\,E; \quad D = \frac{1}{2}\,E; \quad F = \frac{-1}{2\sqrt{2}}\,E$$

and finally derive the following three equations between the wellknown quantities α, β, γ, δ, and ε:

$$-\alpha + \varepsilon = 0 \qquad\qquad (4, f)$$
$$\beta + \delta = 0 \qquad\qquad (5, f)$$
$$\gamma - 3\,\delta = 0 \qquad\qquad (6, f)$$
$$\alpha + \varepsilon = \sqrt{2}\,(\beta - \delta) \qquad (7, f)$$

Here $(4, f)$, $(5, f)$ and $(6, f)$ simply are identical with the earlier derived equations $(2, f)$, $(1, f)$ and $(3, f)$ (page 19). The consequences of these three equations were shown to be correct. However, $(7, f)$ is certainly wrong. By insertion of the numerical values of the force-constants given on page 21 (model 1) the left-hand side becomes $+35 \cdot 10^4$ while the right-hand side becomes $-24 \cdot 10^4$. This definite inequality is furthermore seen to be independent of the choice of model.

Table IX gives exactly the same result.

6. Difficulties of Further Physical Treatment.

At a first glance it seems peculiar that the first use of the empirical rule made in this paper gives correct results, while the use of the rule just made above leads to at least one false
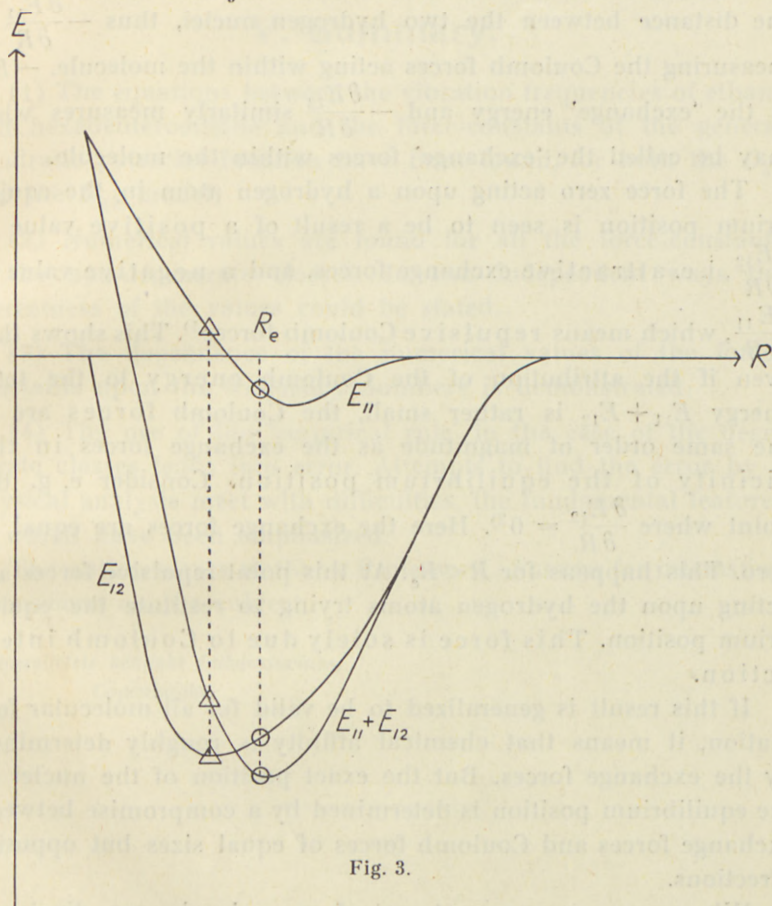

Fig. 3.

equation. *A priori* one would reason that the disturbance of the molecule made by displacing *one* hydrogen atom must be much less than by displacing *three*. If, however, one tries to penetrate deeper into the problem great difficulties are at once met with.

We start with drawing the attention to the original paper by HEITLER and LONDON[1] and by SIUGURA[2] on the prototype of

1) HEITLER and LONDON, Zeits. f. Physik, **44**, 455 (1927).
2) SIUGURA, ibid. **45**, 484 (1927).

molecules, the hydrogen molecule. Fig. 3 reproduces the essential features in a figure from the paper of SIUGURA.

E_{11} is the 'Coulomb' integral, which corresponds to the classical interaction energy between the two hydrogen atoms. R is the distance between the two hydrogen nuclei, thus $-\dfrac{\partial E_{11}}{\partial R}$ is measuring the Coulomb forces acting within the molecule. $-E_{12}$. is the 'exchange' energy and $-\dfrac{\partial E_{12}}{\partial R}$ similarly measures what may be called the 'exchange' forces within the molecule.

The force zero acting upon a hydrogen atom in the equilibrium position is seen to be a result of a p o s i t i v e value of $\dfrac{\partial E_{12}}{\partial R}$, i. e. a t t r a c t i v e exchange forces, and a n e g a t i v e value of $\dfrac{\partial E_{11}}{\partial R}$, which means r e p u l s i v e Coulomb forces[1]. This shows that even if the attribution of the Coulomb e n e r g y to the total energy $E_{11} + E_{12}$ is rather small, the Coulomb f o r c e s are of the same order of magnitude as the exchange forces in the vicinity of the equilibrium position. Consider e. g. the point where $\dfrac{\partial E_{12}}{\partial R} = 0$[2]. Here the exchange forces are equal to zero. This happens for $R < R_e$. At this point repulsive forces are acting upon the hydrogen atoms trying to restitute the equilibrium position. T h i s f o r c e i s s o l e l y d u e t o C o u l o m b i n t e r a c t i o n.

If this result is generalized to be valid for all molecular formation, it means that chemical affinity is roughly determined by the exchange forces. But the exact position of the nuclei in the equilibrium position is determined by a compromise between exchange forces and Coulomb forces of equal sizes but opposite directions.

When one or more atoms of a molecule are displaced from the equilibrium position, the problem, therefore, is to account for the hange in two great forces, exchange and Coulomb forces. Consequently it generally lies beyond the reach of qualitative arguing to give reasons why e. g. the 'empirical rule' could be used with success in one case and not in the other.

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[1] Points marked with circles.
[2] Points marked with triangles.

In future work the author hopes to be able to carry through a quantitative or semi-quantitative treatment of this and similar problems.

V. Summary.

(1) The equations between the vibration frequencies of ethane and hexadeuteroethane and the force-constants of the general quadratic potential function have been found, for both the D_{3d} and the D_{3h} model.

(2) Numerical values are found for all the force-constants of the non-degenerate classes. In two independent ways the correctness of the values could be stated.

(3) The dependence of the numerical values of the force-constants upon the frequency numbers is demonstrated.

(4) The use of the 'empirical rule' in the case of the degenerate classes leads into error. Attempts to find the error by a physical analysis meet with difficulties, the fundamental features of which have been emphasized.

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