A SIMPLIFIED PROCEDURE FOR CALCULATING THE COMPLETE HARMONIC POTENTIAL FUNCTION OF A MOLECULE FROM THE VIBRATIONAL FREQUENCIES

BY

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Synopsis.

A method is described for deriving extremely simple relations between vibrational frequencies and force constants. It is based on the usual F- and G-matrices and on external symmetry coordinates. The translations and rotations are not removed from the symmetry coordinates. Instead a number of simple relations between the force constants are introduced. The calculation of the force constants corresponding to a given set of internal coordinates is discussed.

As examples are discussed: ethylene (with a detailed numerical calculation), acetylene and ethane. In an appendix are given a few hints as to the numerical calculations.

INTRODUCTION

The calculation of the internal potential energy function of a molecule has always been a rather tedious job. In their book "Molecular vibrations" WILSON, DECIUS and CROSS[1] have given a detailed description of a straight-forward method for such calculations mainly based on a previous work by WILSON[2]. This method reduces the labour previously involved in such calculations considerably.

They use exclusively symmetry coordinates composed from internal coordinates. They mention, however, other types of symmetry coordinates, especially those composed from local cartesian coordinates[3]. It is the principal aim of this paper to demonstrate the advantage of a thorough use of such coordinates, leading to a very simple and easily handled method.

In the following is first given a brief decription of the principles of the method and afterwards the details are demonstrated by use of three examples: ethylene, acetylene, and ethane. For the ethylene molecule only a numerical material is presented, more as a demonstration of the method than as a new calculation of this interesting potential function. Finally, a few advices are given as to the numerical calculations.

PRINCIPLES

The process of finding the potential energy function of a molecule in a given set of coordinates consists of the following steps:

1. Construction of a set of symmetry coordinates.
2. Setting up of the G- and F-matrices in these coordinates[4].
3. Expansion of the secular equations connecting force constants and vibrational frequencies.
4. Adjustment of the experimental material to the harmonic approximation.
5. Calculation of the force constants from the adjusted frequencies.

[1] E. BRIGHT WILSON, J. C. DECIUS and PAUL C. CROSS: Molecular vibrations. McGraw-Hill, 1955.
[2] E. BRIGHT WILSON, J. chem. Phys. 7, 1047 (1939), 9, 76 (1941).
[3] E. BRIGHT WILSON, J. C. DECIUS and PAUL C. CROSS, loc. cit. p. 125.
[4] These matrices are defined by $2V = \mathbf{S}'\mathbf{F}\mathbf{S}$ and $2T = \dot{\mathbf{S}}'\mathbf{G}^{-1}\dot{\mathbf{S}}$, where V and T are the potential and the kinetic energy respectively, and $\mathbf{S}$ is the coordinate column matrix, $\mathbf{S}'$ the transposed one.

1*

6. Transcription of the force constants from the symmetry coordinates to a given set of coordinates.

Far the most time consuming step in this procedure is no. 5, the calculation of the force constants from the frequencies. It is therefore essential to use a set of symmetry coordinates giving as simple equations between force constants and frequencies as possible, even if this makes step no. 5 a little more complicated. Also it is of fundamental importance to use a set of symmetry coordinates equally useful for all isotopic species of the molecule in question.

The number of variables and constants.

The potential energy of a molecule with N atoms may be expressed in any $3N-6$ independent internal coordinates corresponding to the $3N-6$ internal degrees of freedom ($3N-5$ for linear molecules). If more than $3N-6$ internal coordinates are used there will exist a number of relations both between the coordinates and between the constants of the function.

The number of force constants in a harmonic potential function depends on the number of normal vibrations in each symmetry class. If a class contains n genuine vibrations there will be $\frac{n}{2}(n+1)$ constants for this class. The total number will be the sum of the number from each class, degenerate classes counting only once.

Below we use a set of $3N$ independent external symmetry coordinates. When the potential function is set up in these coordinates we get too many constants. But the fact that translations and rotations do not contribute to the internal energy yields additional relations between the force constants equal in number to the redundant constants.

From the set of $3N$ coordinates we may pass to a set of $3N-6$ independent internal coordinates. Often the apparent number of force constants increases considerably during this process, but it is reduced to the original number on account of the symmetry properties of the molecule. Usually many of the constants are identical (see p. 24).

It is sometimes seen that the potential function is given in more than $3N-6$ internal coordinates. This is mathematically correct, but a number of relations exist between the coordinates. Thus even the main (diagonal) force constants correspond to complicated deformations of the molecule and the force constants can not be given a physically simple interpretation.

Symmetry coordinates.

Some of the general principles for the construction of the external symmetry coordinates used here have been given by WILSON et al.[1] They are constructed as linear combinations of cartesian displacement coordinates differently oriented for each atom.

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[1] E. BRIGHT WILSON, J. C. DECIUS and PAUL C. CROSS, loc. cit. p. 125 and 117.

If possible, the cartesian coordinate systems are oriented so that the defining unit vectors of one system by all symmetry operations of the group go into the defining vectors of other systems (perhaps with opposite sign), but not into linear combinations. This is always possible for molecules having no degenerate vibrations. Also for molecules having doubly degenerate vibrations such an orientation is possible except for the coordinate systems placed at the atoms lying on the more-than-two-fold axis. These systems are oriented with one vector in the direction of the axis and with the other two perpendicular to it, contributing each one symmetry coordinate to each of the two representative set of coordinates. For molecules with triply degenerate vibrations further complications arises. They will not be treated here.

No attempt is made to separate translations and rotations as special coordinates or to obtain symmetry coordinates not containing such non-genuine vibrations. A total number of $3N$ symmetry coordinates is used, distributed over the symmetry classes according to the number of vibrations (including non-genuine) in the classes.

Each symmetry coordinate contains only displacements of one symmetrically equivalent set of atoms and furthermore only the equivalent displacements of these atoms. They are normalized so that the sum of the squares of the coefficients is unity. The obtained total coefficient matrix is orthogonal.

A detailed description of the procedure of construction is more easily given in connection with the examples to follow.

G- and F-matrices.

The great adventage of these symmetry coordinates is demonstrated when the G-matrix is set up. This is done directly from the symmetry coordinates. The matrix formed represents the G-matrices of all isotopic species of the molecule.

If two symmetry coordinates are given as

and
$$S_p = a_1 x_1 + a_2 x_2 + \ldots + c_1 y_1 + \ldots + e_1 z_1 + \ldots$$
$$S_q = b_1 x_1 + b_2 x_2 + \ldots + d_1 y_1 + \ldots + f_1 z_1 + \ldots ,$$

where x_i, y_i and z_i are the cartesian coordinates of the i'th atom, then the G-matrix element corresponding to these two coordinates is[1]

$$G_{pq} = \sum_{i=1}^{N} \frac{1}{m_i} (a_i b_i + c_i d_i + e_i f_i).$$

As mentioned each symmetry coordinate contains only the displacements of one symmetrically equivalent set of atoms. Furthermore it contains only the symmetrically equivalent displacements of these atoms. Thus we have for instance pure carbon-

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[1] This follows from the equations given by WILSON *et al.* (loc. cit. p. 61, p. 55 and p. 307) as these are equally valid if S_t means a symmetry coordinate.

-x-coordinates or pure hydrogen-z-coordinates. If therefore in the above expressions, say, some of the a'a are different from zero then all c's and e's are zero.

Consequently the only non-zero G-matrix elements are those corresponding to two symmetry coordinates originating in equivalent displacements of a certain equivalent set of atoms, for instance corresponding to two carbon-x-coordinates. As such two symmetry coordinates cannot be in the same class it is immediately seen that the diagonal blocks in the G-matrix (one symmetry class) only contain the diagonal elements, all other elements must be zero.

For isotopic species of full symmetry the G-matrix contains only the diagonal elements, which simply are the reciprocal masses of the atoms. For isotopic species of lower symmetry the diagonal elements are certain linear combinations of the reciprocal masses of the atoms in the originally equivalent sets. But in addition we get a few off-diagonal elements outside the diagonal blocks containing differences between reciprocal masses of originally equivalent atoms. These off-diagonal elements couple the symmetry classes together at lower symmetry.

The F-matrix is set up by filling out the diagonal blocks by suitable symbols for the force constants.

Expansion of the secular equations.

The secular equation may be written as

$$| \mathbf{FG} - \mathbf{E}\lambda | = 0.$$

Wilson[1] has, however, shown that the coefficients in the secular equation

$$x^n - c_1 x^{n-1} + c_2 x^{n-2} - c_3 x^{n-3} + \ldots = 0$$

may be derived directly from the matrices as

$$c_s = \sum G^{(s)} F^{(s)}$$

where $G^{(s)}$ is any s-rowed minor of $|\mathbf{G}|$, $F^{(s)}$ is the corresponding minor of $|\mathbf{F}|$ and the sum is to be taken over all such minors. Naturally this procedure applies to the symmetry classes separately. This rule is very conveniently used in connection with the simple G-matrices obtained here.

The number of non-zero terms in the above sum depends on the off-diagonal elements in the G-matrix. For the isotopic species of full symmetry we have no off-diagonal elements and the only non-zero minors of $|\mathbf{G}|$ are the symmetrical (principal) ones. The number of terms in c_s is then equal to $\binom{n}{s}$ if the G-matrix is of order n, and the total number of terms in all coefficients is $2^n - 1$.

For isotopic species of lower symmetry one or more of the original symmetry classes are coupled together by off-diagonal elements. If all of these elements originate

[1] E. Bright Wilson, J. chem. Phys. **7**, 1047 (1939).

in symmetry coordinates constructed exclusively from equivalent cartesian coordinates at one equivalent set of atoms we only get non-zero terms from symmetrical minors of $|\mathbf{G}|$ and the number of terms is the same as for the above case. This is for instance the case if we have only two off-diagonal terms (one on each side of the diagonal).

If on the other hand two classes are coupled together by symmetry coordinates constructed from different symmetrical sets of cartesian coordinates we get a few terms from unsymmetrical minors of $|\mathbf{G}|$. Let us consider the following example

$$
\mathbf{G} = \left|
\begin{array}{ccc|ccc}
\mu_C & 0 & 0 & 0 & 0 & 0 \\
0 & \frac{1}{2}(\mu_H + \mu_D) & 0 & 0 & \frac{1}{2}(\mu_H - \mu_D) & 0 \\
0 & 0 & \frac{1}{2}(\mu_H + \mu_D) & 0 & 0 & \frac{1}{2}(\mu_H - \mu_D) \\ \hline
0 & 0 & 0 & \mu_C & 0 & 0 \\
0 & \frac{1}{2}(\mu_H - \mu_D) & 0 & 0 & \frac{1}{2}(\mu_H + \mu_D) & 0 \\
0 & 0 & \frac{1}{2}(\mu_H - \mu_D) & 0 & 0 & \frac{1}{2}(\mu_H + \mu_D)
\end{array}
\right\}
\quad
\mathbf{F} = \left\{
\begin{array}{ccc|ccc}
\alpha_1 & \alpha_4 & \alpha_5 & 0 & 0 & 0 \\
\alpha_4 & \alpha_2 & \alpha_6 & 0 & 0 & 0 \\
\alpha_5 & \alpha_6 & \alpha_3 & 0 & 0 & 0 \\ \hline
0 & 0 & 0 & \beta_1 & \beta_4 & \beta_5 \\
0 & 0 & 0 & \beta_4 & \beta_2 & \beta_6 \\
0 & 0 & 0 & \beta_5 & \beta_6 & \beta_3
\end{array}
\right|.
$$

In order to find the non-zero terms we examine all combinations of columns trying to find combinations of rows giving minors different from zero in both $\mathbf{G}$ and $\mathbf{F}$. If we choose the columns no. 2 and no. 6 it is possible to get two non-zero terms, one from a symmetrical minor: $\frac{1}{4}(\mu_H + \mu_D)^2 \alpha_2 \beta_3$ and one from an unsymmetrical minor: $-\frac{1}{4}(\mu_H - \mu_D)^2 \alpha_6 \beta_6$. From columns no. 3 and no. 5 we get: $\frac{1}{4}(\mu_H + \mu_D)^2 \alpha_3 \beta_2$ and: $-\frac{1}{4}(\mu_H - \mu_D)^2 \alpha_6 \beta_6$. But we only get the usual terms from symmetrical minors if we take any other combination, no. 2 and no. 5 or no. 3 and no. 6 or any three of them or all four of them at a time. Thus we only get "odd" terms from these two combinations possibly in connection with columns no. 1 and no. 4. For instance these "odd" terms in c_3 are

$$
-\frac{1}{2}(\mu_H - \mu_D)^2 \mu_C \left[\alpha_6 \begin{vmatrix} \beta_1 & \beta_4 \\ \beta_5 & \beta_6 \end{vmatrix} + \beta_6 \begin{vmatrix} \alpha_1 & \alpha_4 \\ \alpha_5 & \alpha_6 \end{vmatrix}\right].
$$

Also in more complicated cases the number of terms is comparatively small. In practice it is therefore possible in this way to handle matrices with n not more than about 8 "by hand". For larger matrices an electronic computer will often be necessary.

As is well-known the coefficients of the secular equation are certain products of the frequencies. Thus we get directly from the G- and F-matrices the equations connecting force constants (from the F-matrix), masses (from the G-matrix) and frequencies. In those classes which contain translations or rotations we further introduce some relations between the force constants and the geometry of the molecule. These relations are found by multiplying the partial F-matrix by a column matrix made up of the values of the different symmetry coordinates for the non-genuine vibration. This product equals a zero column matrix. The proof for this will be given below (p. 10).

Adjustment of the experimental material.

The real potential function of a molecule written as a polynomium naturally is of a very high order. But for all except very small molecules we are only able to handle a harmonic potential function containing only quadratic terms. This is an approximation and may—according to the type of approximation—lead to many different potential functions for the same molecule, all equally correct.

Before starting the calculations it is therefore necessary first to decide between various ways of making the approximation and secondly to adjust the observed frequencies to be in exact accordance with a harmonic potential function. Thus all isotopic rules (product rule, various sum rules etc.) must be exactly fulfilled by the adjusted frequencies.

Calculation of the force constants.

Three principal problems arise during the calculation of the force constants.

1) A sufficient number of independent frequencies must be known.
2) More than one set of constants may give the same set of frequencies.

Often a decision between the various sets of constants is possible by a mere common-sense analysis of the potential function. In other cases a calculation of the amplitudes may be helpfull. Eventually a comparison of the constants with known constants from similar molecules may be taken into account. No rigorous method is available. It must be emphasized, however, that a satisfactory calculation of further frequencies is by no means a proof of the correctness of the constants.

3) The equations connecting force constants and frequencies are often very complicated.

In many cases it is impossible to solve the equations for the unknown constants, but it is always simple to calculate the frequencies from the constants. Often, therefore, the equations are solved by trial and error. This is also to be done if the isotopic relations connecting the necessary number of frequencies are too complicated to allow an initial adjustment of the observed frequencies.

If the equations are solved by trial and error great care must be taken not to miss possible solutions.

Transcription of the force constants.

The force constants obtained correspond to the symmetry coordinates. In order to make a physical interpretation easier it may be convenient to change from this set of coordinates to another set, usually of internal coordinates.

The potential energy is given as

$$2V = \mathbf{S'FS}$$

using symmetry coordinates (column matrix $\mathbf{S}$). This means

$$2V = \{S_1 S_2 \ldots S_{3N}\} \begin{pmatrix} F_{11} & F_{12} \ldots \ldots F_{1\,3N} \\ F_{12} & F_{22} \ldots \ldots F_{2\,3N} \\ \ldots \ldots \ldots \ldots \ldots \ldots \\ \ldots \ldots \ldots \ldots \ldots \ldots \\ F_{1\,3N} & F_{2\,3N} \ldots F_{3N\,3N} \end{pmatrix} \begin{pmatrix} S_1 \\ S_2 \\ \cdot \\ \cdot \\ S_{3N} \end{pmatrix}$$

or written out

$$2V = F_{11} S_1^2 + 2 F_{12} S_1 S_2 + 2 F_{13} S_1 S_3 + \ldots .$$
$$+ F_{22} S_2^2 + 2 F_{23} S_2 S_3 + \ldots .$$

Note that the diagonal terms in the matrix are twice the "main" force constants, whereas the off-diagonal terms are directly the "interaction" constants.

In terms of a different set of coordinates $I_1, I_2 \ldots I_n$ the potential energy may be written as

$$2V = \mathbf{I'F_1 I}.$$

The problem is to find the connection between $\mathbf{F_1}$ and $\mathbf{F}$.

The symmetry coordinates are given as linear combinations of cartesian coordinates $x_1, x_2 \ldots x_{3N}$, or as

$$\mathbf{S = AX}.$$

It is a simple matter to find the analogous connection between the cartesian coordinates and the new set of coordinates

$$\mathbf{X = BI}.$$

The terms in a column of $\mathbf{B}$ are the values of the cartesian coordinates if the corresponding coordinate I_p is one and all others are zero. From

$$\mathbf{S = (AB)\,I} \text{ and } \mathbf{S' = I'\,(AB)'}$$

it follows that

$$\mathbf{F_1 = (AB)'F(AB)}.$$

The matrix multiplications stated by this formula may be rather lengthy, but they are quite simple. Note that they need only be carried out once, at the end of a calculation.

It is sometimes convenient to express $\mathbf{F}$ as a function of $\mathbf{F_1}$. It may be shown that $[(\mathbf{AB})']^{-1} = [(\mathbf{AB})^{-1}]'$ from which we get

$$\mathbf{F = [(AB)^{-1}]'\,F_1\,(AB)^{-1},}$$

where $(\mathbf{AB})^{-1} = \mathbf{B}^{-1}\mathbf{A}^{-1} = \mathbf{B}^{-1}\mathbf{A}'$ as $\mathbf{A}$ is orthogonal. $\mathbf{B}^{-1}$ may be found either from $\mathbf{B}$ or from the relation

$$\mathbf{I} = \mathbf{B}^{-1}\mathbf{X},$$

but the two matrices found need not be identical, because $\mathbf{B}$ is not uniquely determined if the deformations used include some translation or rotation. This does not, however, influence the result of the calculation, because translations and rotations do not contribute to the internal potential energy.

It is now possible to prove the method for introducing the special nature of the non-genuine vibrations in the calculations. We choose a set of independent, internal coordinates with, say, a translation as the first coordinate. The first column in the matrix $\mathbf{AB}$ will then be the values $(s_1, s_2, \ldots . s_{3N})$ of the symmetry coordinates for the pure translation. The first column of $\mathbf{F}_1$ is then

$$(\mathbf{AB})'\mathbf{F}\begin{Bmatrix} s_1 \\ s_2 \\ . \\ . \\ s_{3N} \end{Bmatrix} = \begin{Bmatrix} 0 \\ 0 \\ . \\ . \\ 0 \end{Bmatrix}$$

equal to a zero matrix because a non-genuine vibration does not contribute to the internal potential energy. This is a system of $3N$ homogenious equations with $(\mathbf{AB})'$ as the coefficient matrix and the elements of the column matrix

$$\mathbf{F}\begin{Bmatrix} s_1 \\ s_2 \\ . \\ . \\ s_{3N} \end{Bmatrix}$$

as the unknowns. The determinant $|\mathbf{AB}|$ of the system of equations is $\neq 0$, as $|\mathbf{A}| = 1$ ($\mathbf{A}$ is orthogonal) and $|\mathbf{B}| \neq 0$ (the coordinates are chosen to be independent). Consequently the system has only one solution

$$\mathbf{F}\begin{Bmatrix} s_1 \\ s_2 \\ . \\ . \\ s_{3N} \end{Bmatrix} = \begin{Bmatrix} 0 \\ 0 \\ . \\ . \\ 0 \end{Bmatrix}$$

This is the equation introduced above (p. 7). Naturally it needs only be applied separately to the classes containing the non-genuine vibrations. If a class contain more than one non-genuine vibration the equation is to be applied to each of the non-genuine vibrations separately.

ETHYLENE

As a first example we shall calculate the potential energy function of the ethylene molecule[1].

At each atom is placed a cartesian coordinate system oriented as shown in Fig. 1. All z-axes are pointing upwards from the plane.
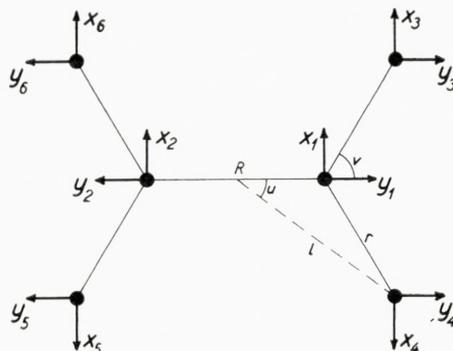

Fig. 1.

The character table of the point group (D_{2h}) is given in Table 1. The method for finding which coordinates contribute to the symmetry coordinates of each class

TABLE 1.

	E	C_z	C_x	C_y	i	σ_{xy}	σ_{yz}	σ_{xz}			Freq. No.
A_g	+1	+1	+1	+1	+1	+1	+1	+1		y_C, y_H, x_H	1, 2, 3
B_{1g}	+1	+1	−1	−1	+1	+1	−1	−1	R_z	y_H, x_C, x_H	5, 6
B_{2g}	+1	−1	+1	−1	+1	−1	+1	−1	R_x	z_C, z_H	8
B_{3g}	+1	−1	−1	+1	+1	−1	−1	+1	R_y	z_H	—
A_u	+1	+1	+1	+1	−1	−1	−1	−1		z_H	4
B_{1u}	+1	+1	−1	−1	−1	−1	+1	+1	T_z	z_C, z_H	7
B_{2u}	+1	1	+1	−1	−1	+1	−1	+1	T_x	y_H, x_C, x_H	9, 10
B_{3u}	+1	−1	−1	+1	−1	+1	+1	−1	T_y	y_C, y_H, x_H	11, 12
y_C	2	0	0	2	0	2	2	0			
y_H	4	0	0	0	0	4	0	0			
x_C	2	0	0	−2	0	2	−2	0			
x_H	4	0	0	0	0	4	0	0			
z_C	2	0	0	−2	0	−2	2	0			
z_H	4	0	0	0	0	−4	0	0			

[1] This has been done previously by many authors. Some of the more recent papers are:
J. Charette and C. Manneback, Ann. soc. sci. Bruxelles, Sér. I **66**, 178 (1952).
R. L. Arnett and B. L. Crawford, J. chem. Phys. **18**, 118 (1950).
B. L. Crawford, J. E. Lancaster and R. G. Inskeep, J. chem. Phys. **21**, 678 (1953).
L. M. Sverdlow and N. L. Pakhomova, Zhur. Eksptl. i Teoret. Fiz. **26**, 64 (1954).

is analogous to that described by WILSON et $al.$[1] We count the number of coordinates within each set which go into themselves under each symmetry operation. These numbers are given below the characters in Table 1, negative numbers correspond to a change of sign of the coordinates. A definite set of coordinates then contribute one symmetry coordinate to a definite class if the sum of products of these numbers and the corresponding characters equals 8, the number of operations in the group. If this sum of products equals zero the set of coordinates does not contribute any symmetry coordinate to the class. The result of this procedure is indicated to the right of the characters in Table 1. Here is further given the non-genuine vibrations and the frequency numbering according to HERZBERG[2].

The symmetry coordinates are constructed as described by WILSON et $al.$[3]. For instance the y_H symmetry coordinate of B_{1g} is found in the following way. The characters for the operations which transfer y_3 into y_3, y_4, y_5 and y_6 are: $+1$, -1, $+1$ and -1. Then the symmetry coordinate is $S_5 = N(y_3 - y_4 + y_5 - y_6)$, where the normalizing factor $N = \frac{1}{2}$. All the symmetry coordinates are given in Table 2. In this table is further indicated the symbols used in the F-matrix.

The G-matrix is constructed as described above (p. 5) and is given in Table 3. It represents the G-matrices of all isotopic species of the ethylene molecule. For

TABLE 2.

	Symmetry Coordinates	F-Matrix		Symmetry Coordinates	F-Matrix
A_g	$S_1 = \frac{1}{\sqrt{2}}(y_1 + y_2)$ $S_2 = \frac{1}{2}(y_3 + y_4 + y_5 + y_6)$ $S_3 = \frac{1}{2}(x_3 + x_4 + x_5 + x_6)$	$\begin{Bmatrix} \alpha_1 \alpha_4 \alpha_5 \\ \alpha_4 \alpha_2 \alpha_6 \\ \alpha_5 \alpha_6 \alpha_3 \end{Bmatrix}$	B_{2u}	$S_{10} = \frac{1}{\sqrt{2}}(x_1 + x_2)$ $S_{11} = \frac{1}{2}(y_3 - y_4 - y_5 + y_6)$ $S_{12} = \frac{1}{2}(x_3 - x_4 - x_5 + x_6)$	$\begin{Bmatrix} \varepsilon_1 \varepsilon_4 \varepsilon_5 \\ \varepsilon_4 \varepsilon_2 \varepsilon_6 \\ \varepsilon_5 \varepsilon_6 \varepsilon_3 \end{Bmatrix}$
B_{1g}	$S_4 = \frac{1}{\sqrt{2}}(x_1 - x_2)$ $S_5 = \frac{1}{2}(y_3 - y_4 + y_5 - y_6)$ $S_6 = \frac{1}{2}(x_3 - x_4 + x_5 - x_6)$	$\begin{Bmatrix} \beta_1 \beta_4 \beta_5 \\ \beta_4 \beta_2 \beta_6 \\ \beta_5 \beta_6 \beta_3 \end{Bmatrix}$	B_{2g}	$S_{13} = \frac{1}{\sqrt{2}}(z_1 - z_2)$ $S_{14} = \frac{1}{2}(z_3 + z_4 - z_5 - z_6)$	$\begin{Bmatrix} \pi_1 \pi_3 \\ \pi_3 \pi_2 \end{Bmatrix}$
B_{3u}	$S_7 = \frac{1}{\sqrt{2}}(y_1 - y_2)$ $S_8 = \frac{1}{2}(y_3 + y_4 - y_5 - y_6)$ $S_9 = \frac{1}{2}(x_3 + x_4 - x_5 - x_6)$	$\begin{Bmatrix} \delta_1 \delta_4 \delta_5 \\ \delta_4 \delta_2 \delta_6 \\ \delta_5 \delta_6 \delta_3 \end{Bmatrix}$	B_{1u}	$S_{15} = \frac{1}{\sqrt{2}}(z_1 + z_2)$ $S_{16} = \frac{1}{2}(z_3 + z_4 + z_5 + z_6)$	$\begin{Bmatrix} \varrho_1 \varrho_3 \\ \varrho_3 \varrho_2 \end{Bmatrix}$
			A_u	$S_{17} = \frac{1}{2}(z_3 - z_4 + z_5 - z_6)$	$\{\sigma_1\}$
			B_{3g}	$S_{18} = \frac{1}{2}(z_3 - z_4 - z_5 + z_6)$	$\{\tau_1\}$

[1] E. BRIGHT WILSON, J. C. DECIUS and PAUL C. CROSS, loc. cit. p. 110.
[2] G. HERZBERG, Infrared and Raman Spectra, van Nostrand, 1945, p. 107.
[3] E. BRIGHT WILSON, J. C. DECIUS and PAUL C. CROSS, loc. cit. p. 118.

TABLE 3. G-Matrix.

		A_g			B_{1g}			B_{3u}			B_{2u}			B_{2g}		B_{1u}		A_u	B_{3g}
		S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}	S_{11}	S_{12}	S_{13}	S_{14}	S_{15}	S_{16}	S_{17}	S_{18}
A_g	S_1	a						c											
	S_2		b			d			e			f							
	S_3			b			d			e			f						
B_{1g}	S_4				a						c								
	S_5		d			b			f			e							
	S_6			d			b			f			e						
B_{3u}	S_7	c						a											
	S_8		e			f			b			d							
	S_9			e			f			b			d						
B_{2u}	S_{10}				c						a								
	S_{11}		f			e			d			b							
	S_{12}			f			e			d			b						
B_{2g}	S_{13}													a		c			
	S_{14}														b		e	f	d
B_{1u}	S_{15}													c		a			
	S_{16}														e		b	d	f
A_u	S_{17}														f		d	b	e
B_{3g}	S_{18}														d		f	e	b

All elements not given are zero.

$$a = \frac{1}{2}(\mu_1 + \mu_2) \qquad c = \frac{1}{2}(\mu_1 - \mu_2) \qquad e = \frac{1}{4}(\mu_3 + \mu_4 - \mu_5 - \mu_6)$$

$$b = \frac{1}{4}(\mu_3 + \mu_4 + \mu_5 + \mu_6) \qquad d = \frac{1}{4}(\mu_3 - \mu_4 + \mu_5 - \mu_6) \qquad f = \frac{1}{4}(\mu_3 - \mu_4 - \mu_5 + \mu_6)$$

species of full symmetry only the diagonal elements are present. For species of lower symmetry we further get some off-diagonal elements, which couple the classes together.

For instance the G-matrices of all four planar classes of ethylene-d_0 are

$$\begin{Bmatrix} \mu_C & 0 & 0 \\ 0 & \mu_H & 0 \\ 0 & 0 & \mu_H \end{Bmatrix}$$

where μ means the reciprocal mass, and the G-matrices of both of the two planar classes of all three ethylene-d_2 are

$$
\begin{vmatrix}
\mu_C & 0 & 0 & 0 & 0 & 0 \\
0 & \tfrac{1}{2}(\mu_H + \mu_D) & 0 & 0 & \tfrac{1}{2}(\mu_H - \mu_D) & 0 \\
0 & 0 & \tfrac{1}{2}(\mu_H + \mu_D) & 0 & 0 & \tfrac{1}{2}(\mu_H - \mu_D) \\
0 & 0 & 0 & \mu_C & 0 & 0 \\
0 & \tfrac{1}{2}(\mu_H - \mu_D) & 0 & 0 & \tfrac{1}{2}(\mu_H + \mu_D) & 0 \\
0 & 0 & \tfrac{1}{2}(\mu_H - \mu_D) & 0 & 0 & \tfrac{1}{2}(\mu_H + \mu_D)
\end{vmatrix}
$$

Before expanding the secular equation it is convenient to designate the minors of $|\mathbf{F}|$ in the following manner

$$a_1 = \alpha_1 \qquad\qquad a_2 = \alpha_2 \qquad\qquad a_3 = \alpha_3$$

$$a_4 = \begin{vmatrix} \alpha_1 & \alpha_4 \\ \alpha_4 & \alpha_2 \end{vmatrix} \qquad a_5 = \begin{vmatrix} \alpha_1 & \alpha_5 \\ \alpha_5 & \alpha_3 \end{vmatrix} \qquad a_6 = \begin{vmatrix} \alpha_2 & \alpha_6 \\ \alpha_6 & \alpha_3 \end{vmatrix}$$

$$a_7 = \begin{vmatrix} \alpha_1 & \alpha_4 & \alpha_5 \\ \alpha_4 & \alpha_2 & \alpha_6 \\ \alpha_5 & \alpha_6 & \alpha_3 \end{vmatrix} \qquad a_8 = \alpha_6 \qquad\qquad a_9 = \begin{vmatrix} \alpha_1 & \alpha_4 \\ \alpha_5 & \alpha_6 \end{vmatrix}$$

and similarly for the other classes.

By expansion according to the above given rule (p. 6) we get for the coefficients of the A_g class of ethylene-d_0:

$$
\begin{aligned}
c_1 &= \mu_C a_1 + \mu_H (a_2 + a_3) \\
c_2 &= \mu_C \mu_H (a_4 + a_5) + \mu_H{}^2 a_6 \\
c_3 &= \mu_C \mu_H{}^2 a_7
\end{aligned}
$$

For the other planar classes we get analogous expressions. For the out-of-plane classes we get

for the B_{2g} class: $c_1 = \mu_C p_1 + \mu_H p_2$, $c_0 = \mu_C \mu_H p_3$
for the B_{1u} class: $c_1 = \mu_C r_1 + \mu_H r_2$, $c_0 = \mu_C \mu_H r_3$
for the A_u class: $c_1 = \mu_H s_1$
for the B_{3g} class: $c_1 = \mu_H l_1$

For ethylene-d_4 we only have to insert μ_D instead of μ_H. The expressions for the coefficients of all the out-of-plane classes of the partly deuterated species are of a similar simplicity. For the planar classes of all three ethylene-d_2 (G-matrix given above) the expressions are also easily found, although they naturally are somewhat more complicated than those given above. The large planar classes of ethylene-d_1 and -d_3 cannot be handled in this way in practice as the matrices are of 12th order.

The translations and rotations yield the following equations (p. 7 and p. 10)

$$\begin{Bmatrix} \beta_1\beta_4\beta_5 \\ \beta_4\beta_2\beta_6 \\ \beta_5\beta_6\beta_3 \end{Bmatrix} \begin{Bmatrix} R \\ -2\sqrt{2}\,l\sin u \\ 2\sqrt{2}\,l\cos u \end{Bmatrix} = \begin{Bmatrix} 0 \\ 0 \\ 0 \end{Bmatrix}$$

$$\begin{Bmatrix} \delta_1\delta_4\delta_5 \\ \delta_4\delta_2\delta_6 \\ \delta_5\delta_6\delta_3 \end{Bmatrix} \begin{Bmatrix} 1 \\ \sqrt{2} \\ 0 \end{Bmatrix} = \begin{Bmatrix} 0 \\ 0 \\ 0 \end{Bmatrix}$$

$$\begin{Bmatrix} \varepsilon_1\varepsilon_4\varepsilon_5 \\ \varepsilon_4\varepsilon_2\varepsilon_6 \\ \varepsilon_5\varepsilon_6\varepsilon_3 \end{Bmatrix} \begin{Bmatrix} 1 \\ 0 \\ \sqrt{2} \end{Bmatrix} = \begin{Bmatrix} 0 \\ 0 \\ 0 \end{Bmatrix}$$

$$\begin{Bmatrix} \pi_1\pi_3 \\ \pi_3\pi_2 \end{Bmatrix} \begin{Bmatrix} R \\ \sqrt{2}\,R + 2\sqrt{2}\,r\cos v \end{Bmatrix} = \begin{Bmatrix} 0 \\ 0 \end{Bmatrix}$$

$$\begin{Bmatrix} \varrho_1\varrho_3 \\ \varrho_3\varrho_2 \end{Bmatrix} \begin{Bmatrix} 1 \\ \sqrt{2} \end{Bmatrix} = \begin{Bmatrix} 0 \\ 0 \end{Bmatrix}$$

$$\{\tau_1\}\,\{1\} = \{0\}$$

The geometrical parameters are indicated in Fig. 1.

From these 14 equations it follows for instance that

$$b_4 = d_4 = e_4 = p_3 = r_3 = t_1 = 0$$

Consequently all the corresponding coefficients in the secular equations vanish reducing the number of coefficients to that of the genuine vibrations.

Within each symmetry class we know for instance that

$$c_1 = \lambda_1 + \lambda_2 + \lambda_3$$
$$c_2 = \lambda_1\lambda_2 + \lambda_1\lambda_3 + \lambda_2\lambda_3$$
$$c_3 = \lambda_1\lambda_2\lambda_3$$

where $\lambda = 4\pi^2 c^2 \nu^2$, ν being the frequency in cm^{-1}. Thus we have an extremely simple system of equations connecting frequencies and force constants.

Calculation of the force constants.

The observed frequencies collected from various authors[1] are given in Table 4. Distances and angle is taken from GALLAWAY and BARKER[2].

[1] R. L. ARNETT and B. L. CRAWFORD, loc. cit.
B. L. CRAWFORD, J. E. LANCASTER and R. C. INSKEEP, loc. cit. with references to earlier litterature.
B. P. STOICHEFF, J. chem. Phys. 21, 755 (1953)..
J. CHARETTE and M. DE HEMPTINNE, Bull. classe sci. Acad. roy. Belg. 37, 436 (1951).
C. COURTOY and M. DE HEMPTINNE, Ann. soc. sic. Bruxelles. Sér. I, 66, 82 (1952).
J. CHARETTE, C. COURTOY and M. DE HEMPTINE, ibid. Sér. I, 67, 122 (1953).
M. DE HEMPTINNE and J. CHARETTE, Bull. classe sci. Acad. roy. Belg. 39, 622 (1953).

After the conclusion of the present calculations T. FELDMAN, J. ROMANKO and H. L. WELSH [Can. J. Phys. 34, 737 (1956)] have published the following values for ethylene-d_0: $\nu_1 = 3026.4$, $\nu_2 = 1622.6$, $\nu_3 = 1342.2$ and $\nu_5 = 3102.5$ cm^{-1}.

[2] W. S. GALLAWAY and E. F. BARKER, J. chem. Phys. 10, 88 (1942). Their values are probably not too correct, but no better values have been published yet. The errors will not influence the results considerably.

TABLE 4.

Observed ⎫
Calculated ⎬ Frequencies in cm⁻¹.
Calculated–Observed ⎭

Freq. No.	-d$_0$	-d$_1$	asym-d$_2$	cis-d$_2$	trans-d$_2$	-d$_3$	-d$_4$
1	3019	3002[2]	3017	2299	2285	2281	2260
	3026		*3009*	*2300*	*2279*		*2253*
	+ 7		− 8	+ 1	− 6		− 7
2	1623	1606	1585	1571	1571	1547	1518
	1630		*1561*	*1574*	*1572*		*1511*
	+ 7		− 24	+ 3	+ 1		− 7
3	1343	1290	1031	1218	1286	1045	985
	1350		*1922*	*1209*	*1284*		*978*
	+ 7		− 9	− 9	− 2		− 7
4	1027	1000	unobs.	unobs.	988	765	726
	1027	*1002*	*889*	*986*	*990*	*764*	*726*
	0	+ 2			+ 2	− 1	0
5	3108	3061	2334	3054	3045	2332	2310
	3110		*2336*	*3057*	*3069*		*2308*
	+ 2		+ 2	+ 3	+ 24		− 2
6	1236[1]	1129	1150	1039[3]	1004	999	1011[4]
	1238		*1155*	*1048*	*1007*		*1009*
	+ 2		+ 5	+ 9	+ 3		− 2
7	949	808	751	842	726	724	720
	950	*807*	*751*	*843*	*722*	*722*	*719*
	+ 1	− 1	0	+ 1	− 4	− 2	− 1
8	947[1]	944	943	763[1]	864[1]	919	785[1]
	951	*951*	*950*	*760*	*870*	*923*	*781*
	+ 4	+ 7	+ 7	− 3	+ 6	+ 4	− 4
9	3106	3096	3093	3059	3065	3049	2345
	3110		*3100*	*3066*	*3040*		*2340*
	+ 4		+ 7	+ 7	− 25		− 5
10	810	713	660	646	678	610	584
	815		*668*	*652*	*664*		*580*
	+ 5		+ 8	+ 6	− 14		− 4
11	2990	2276	2230	2254	2273	2222	2200
	3001		*2236*	*2253*	*2298*		*2189*
	+ 11		+ 6	− 1	+ 25		− 11
12	1444	1401	1384	1342	1299	1289	1078
	1455		*1402*	*1335*	*1280*		*1067*
	+ 11		+ 18	− 7	− 19		− 11

For the sake of clearness the frequencies are given without decimals. Where more accurate values are available these have been used in the calculations.

[1] Liquid frequencies, all others are gas frequencies.

[2] Mean value of resonance doublet 2976–3028.

[3] Either 1034.86 or 1039.34.

[4] From $\nu_6 + \nu_{10} = 1595$.

With the exception of the A_g class the calculations are based on the frequencies of ethylene-d$_0$ and -d$_4$ exclusively. The initial adjustment of the observed frequencies to the harmonic approximation is therefore simply an adjustment to the requirements of the product rules connecting the frequencies of ethylene-d$_0$ and -d$_4$. This may be done in several ways, but in order not to anticipate anything we prefer to smooth out the errors so that all differences between observed and adjusted frequencies are numerically equal in cm^{-1} within each symmetry class. On this basis we get a potential energy function which approximates the real one rather closely within the region of usual amplitudes. The adjusted frequencies are given in Table 4 as calculated values, because a calculation of these frequencies from the force constants naturally leads to exactly the same values again.

It is now a simple matter to find the force constants of all but the A_g class.

TABLE 5.

Force Constants Corresponding to Symmetry Coordinates (in md/Å).

		Set I accepted	Set II rejected			Set I accepted	Set II rejected
	α_1	21.170	21.170		ε_1	9.056	9.056
	α_2	2.150	2.150		ε_2	0.848	0.848
A_g	α_3	4.164	4.164	B_{2u}	ε_3	4.528	4.528
	α_4	− 1.173	− 2.400		ε_4	− 1.950	+ 1.950
	α_5	− 3.482	− 2.783		ε_5	− 6.404	− 6.404
	α_6	+ 1.702	+ 1.702		ε_6	+ 1.379	− 1.379
	β_1	10.435	10.435		π_1	2.239	
	β_2	1.994	4.759	B_{2g}	π_2	0.348	
B_{1g}	β_3	3.781	1.017		π_3	− 0.883	
	β_4	− 1.645	+ 5.617		ϱ_1	0.918	
	β_5	− 5.374	+ 0.179	B_{1u}	ϱ_2	0.459	
	β_6	+ 2.173	+ 1.422		ϱ_3	− 0.649	
	δ_1	5.188	5.188				
	δ_2	2.594	2.594	A_u	σ_1	0.626	
B_{3u}	δ_3	3.571	3.571				
	δ_4	− 3.668	− 3.668	B_{3g}	τ_1	0	
	δ_5	− 2.652	+ 2.652				
	δ_6	+ 1.875	− 1.875				

In the out-of-plane classes we only get one set of constants which are given in Table 5. The frequencies calculated for the partly deuterated compounds are given in Table 4. The fit is satisfactory, the largest difference between calculated and observed frequencies being 7 cm^{-1}.

In each of the three planar classes B_{1g}, B_{3u} and B_{2u} we get two set of constants, both of which are given in Table 5. The question is how to decide between them. As demonstrated below it is of no use to try which set gives the best fit for the frequencies

of the partly deuterated species. The best way seems to be to study the behavior of the molecule at an enforced deformation.

For instance we deform the molecule in such a way that $S_7 = 1$ and all other $S = 0$, which we get for $(y_1, y_2) = (1/\sqrt{2}, -1/\sqrt{2})$, that is we force both carbon atoms to the right. We now wish to find the value of S_9 for which the potential energy is minimum, in other words the natural movements of the hydrogen atoms only allowing them to move in the x-direction. This concerns only the constants of the B_{3u} class. We find the minimum at

$$S_9 = -\frac{\delta_5}{\delta_3} = \begin{cases} +0.742 & \text{(Set I)} \\ -0.742 & \text{(Set II)} \end{cases}$$

$$\text{or } x_3 = x_4 = \begin{cases} +0.371 \\ -0.371 \end{cases} \quad \text{and } x_5 = x_6 = \begin{cases} -0.371 & \text{(Set I)} \\ +0.371 & \text{(Set II)} \end{cases}$$

Naturally, only set I is physically reasonable (see Fig. 1).

In a similar way it is seen that α_6, β_6, δ_6 and ε_6 must be positive, whereas α_4, α_5, β_4, β_5, δ_4, δ_5, ε_4 and ε_5 must be negative. Consequently there is no doubt as to the choice between the solutions in the B_{1g}, B_{3u} and B_{2u} classes.

It is of interest to consider for a moment why we get those different solutions. It is no fault of the mathematical system. By use of different mathematical procedures we get exactly the same solutions. We may say that the ambiguity in the above case of the B_{3u} class is caused by the uncertainty in the definition of x_3, x_4, x_5 and x_6. If we had defined these with opposite sign we had got exactly the same system of equations because the G-matrix is invariant for a change of sign of any symmetry coordinate and because S_9 is not involved in the equations given by the translation. Said in other words: it is clear that a mechanical system of the given structure will oscillate with the given frequencies if its internal forces are described by either of the two set of constants, the difference in forces being again a change of sign of the x-direction. Consequently we are at present forced to anticipate the result of our calculations at least qualitatively in order to decide between the various solutions. In the present example we only need to assume a certain stiffness of the chemical bonds, of which no doubt exists, but in other cases the problem is more serious.

From the obtained constants we are able to calculate the following frequencies:

asym-d_2: ν_5, ν_6, ν_9 and ν_{10} (B_1 class)
cis-d_2: ν_5, ν_6, ν_{11} and ν_{12} (B_1 class)
trans-d_2: ν_9, ν_{10}, ν_{11} and ν_{12} (B_u class)

The expressions for the coefficients of these classes are rather lengthy but not impossible to use for direct calculation. They are, however, easily brought in a more convenient form. As the G-matrix of these classes (shown on p. 14) is very similar to that of the E' class of sym-benzene-d_3 it is to be expected that higher order sum rules approxi-

mately valid for that class[1] would also be approximately valid for the present case. On this basis it is found that the coefficients of, say, the B_1 class of asym-ethylene-d_2 may be written as

$$c_1 = \tfrac{1}{2}(c_1^{BH} + c_1^{BD} + c_1^{EH} + c_1^{ED}),$$

$$c_2 = \tfrac{1}{2}(c_2^{BH} + c_2^{BD} + c_1^{BH} c_1^{ED} + c_1^{EH} c_1^{BD} + c_2^{EH} + c_2^{ED})$$
$$+ \tfrac{1}{4}(\mu_H - \mu_D)^2 (b_2 e_3 + b_3 e_2 - b_6 - e_6 - 2 b_8 e_8),$$

$$c_3 = \tfrac{1}{2}(c_3^{BH} + c_3^{BD} + c_2^{BH} c_1^{ED} + c_2^{BD} c_1^{EH} + c_1^{BH} c_2^{ED} + c_1^{BD} c_2^{EH} + c_3^{EH} + c_3^{ED})$$
$$+ \tfrac{1}{4}\mu_C (\mu_H - \mu_D)^2 (-b_1 e_6 - b_6 e_1 + b_2 e_5 + b_5 e_2 + b_3 e_4 + b_4 e_3 - b_7 - e_7 - 2 b_8 e_9 - 2 b_9 e_8),$$

$$c_4 = \tfrac{1}{2}(c_3^{BH} c_1^{ED} + c_3^{BD} c_1^{EH} + c_2^{BH} c_2^{ED} + c_2^{BD} c_2^{EH} + c_1^{BH} c_3^{ED} + c_1^{BD} c_3^{EH})$$
$$+ \tfrac{1}{4}\mu_C^2 (\mu_H - \mu_D)^2 (b_4 e_5 + b_5 e_4 - b_1 e_7 - b_7 e_1 - 2 b_9 e_9),$$

where c^{BH}, c^{EH}, c^{BD} and c^{ED} mean the coefficients of the B_{1g} and the B_{2u} classes of ethylene-d_0 and ethylene-d_4 respectively. Analogous expressions exist for the other two casses.

By means of these expressions it is a very simple matter to calculate the coefficients and from them to get the frequencies. The result is given in Table 4. It is seen that we get deviations from the observed values up to 25 cm^{-1}. This is not too bad seen in connection with the deviations in ethylene-d_0 and -d_4 ranging up to 11 cm^{-1}. The errors are probably mainly caused by the use of a harmonic potential function although experimental errors and perhaps mis-assignments may contribute somewhat.

Next we pass to the A_g class. Here ethylene-d_0 and -d_4 only yield a total number of five independent frequencies from which to calculate six constants. We are therefore forced to use the frequencies of the partly deuterated compounds. The most direct way would be to adjust the frequencies of asym-d_2 (A_1 class), cis-d_2 (A_1 class) and trans-d_2 (A_g class) to the requirements of the isotopic rules connecting them with the frequencies of -d_0 and -d_4. This is, however, impossible in practice as most of the rules are of an extremely complicated nature. Consequently it is not practicable to use the frequencies of the partly deuterated compounds for a straight-forward calculation of the constants. If we wish not to assume any of the constants there is only one way left: To calculate five of the constants and the frequencies of asym-d_2, cis-d_2 and trans-d_2 as functions of the remaining constant. Apart from the problem of different solutions, the set of constants giving the best fit for the frequencies yields the best approximation to the potential function.

[1] S. BRODERSEN and A. LANGSETH, Mat. Fys. Skr. Dan. Vid. Selsk. 1, no. 1 (1956).

If we calculate α_1, α_3, α_4, α_5 and α_6 as functions of α_2 we get six solutions for each value of α_2. Three and three they are identical except for the sign of α_4, α_5 and α_6, of which we only know that $\alpha_4\alpha_5\alpha_6$ is positive. We have, however, shown above that α_4 and α_5 should be negative and α_6 positive, on which basis we are able to reject four set of solutions. The remaining two sets are shown grafically in Fig. 2 (α_4 and α_5 are chosen positive for a few uninteresting values of α_2 for the sake continuity).
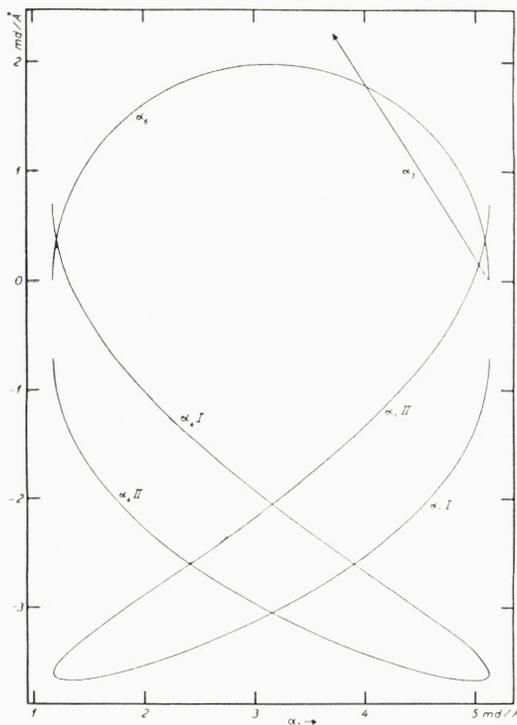
Fig. 2. α_3, α_4, α_5 and α_6 *versus* α_2. α_1 is a constant equal to 21.170 md/Å.

From these constants we calculate the remaining frequencies of asym-d_2, cis-d_2 and trans-d_2 as functions of α_2. The expressions for the coefficients are analogous to those presented above. By inserting the constant terms they are reduced to very simple expressions containing only a_2, a_4, a_8 and a_9. In this way it is possible within a reasonable time to calculate all 15 frequencies for both set of constants and a sufficient number of α_2-values. The differences between these calculated values and the observed ones are plottet in Fig. 3. It is seen that the best fit for both sets is obtained for $\alpha_2 = 2.150$ although this value is not very accurately determined.

Further it is seen that the fit is equally good for both set of constants. It is therefore impossible to decide between the solutions on this basis. Next we try the method demonstrated above. We get the most interesting case by putting $S_1 = 1$ and find the values of S_2 and S_3 in the potential minimum. We get
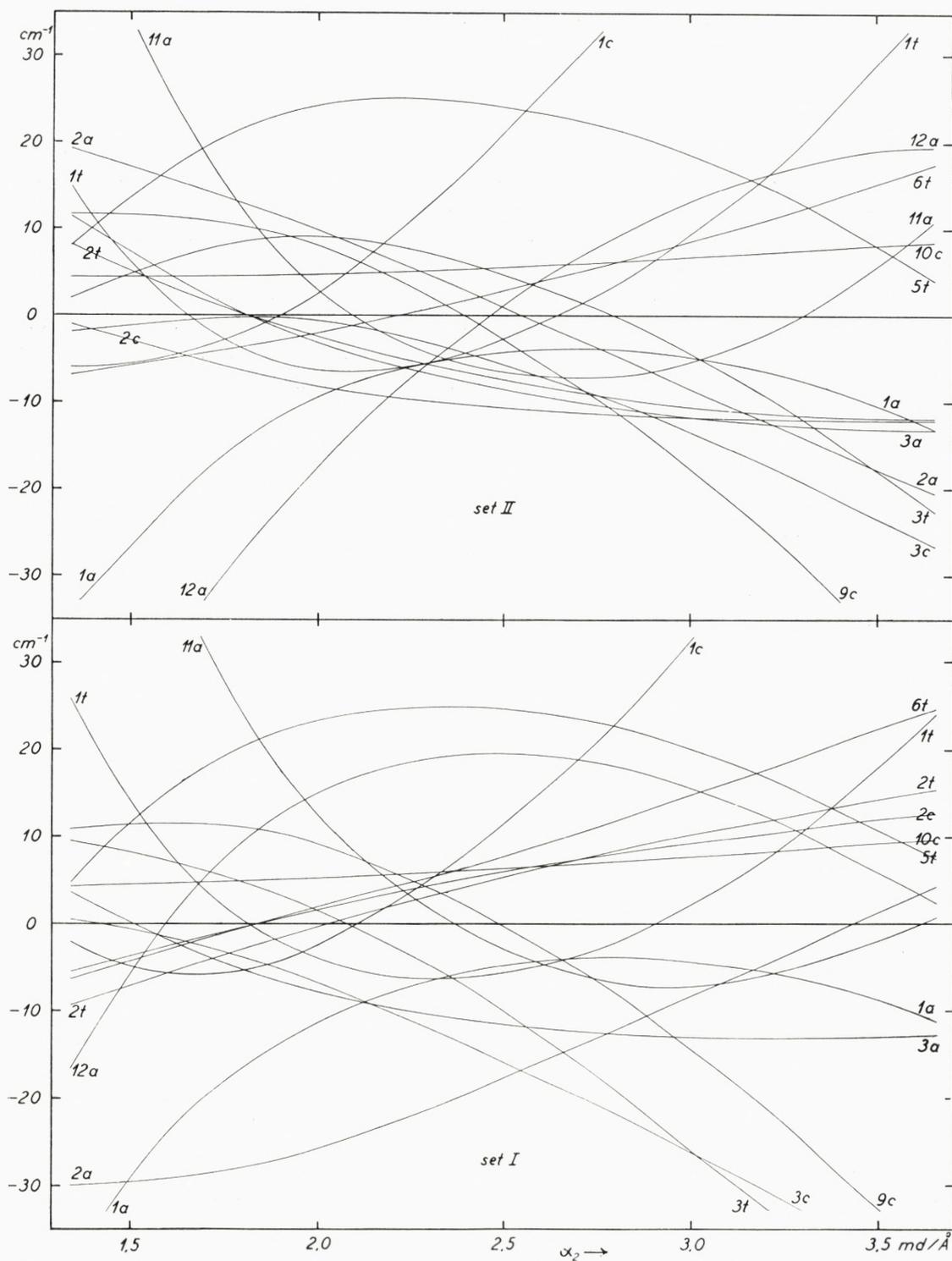
Fig. 3. $\nu_{\text{calc.}} - \nu_{\text{obs.}}$ *versus* α_2, the frequency numbering being indicated on the curves. a, c and t mean asym-d_2, cis-d_2 and trans-d_2 respectively.

for set I: $S_2 = -0.172$ $S_3 = +0.907$
for set II: $S_2 = +0.868$ $S_3 = +0.313$.

In internal coordinates this means that a stretching of the C-C bond of, say, 0.1 Å causes a contraction of the C-H bonds of 0.00033 Å (I) or 0.00007 Å (II) and a decrease of the C-C-H angles of 3°27′ (I) or 1°11′ (II). In both cases the changes in the C-H distances are extremely small, whereas the changes in the angles are appreciable. It seems, however, difficult to make a reliable decision on this basis too. The final choice in favour of set I has been made on basis of a calculation of the form of the normal vibrations (see below).

The final set of constants is given in Table 5 and the calculated frequencies in Table 4. The differences between calculated and observed frequencies are of the usual magnitude. It would have been interesting to calculate the planar frequencies of ethylene-d_1 and -d_3 too, but such a calculation seems—as mentioned above—impossible without the use of an electronic computer.

Transcription of the force constants.

The constants obtained refer to the given set of symmetry coordinates and they correspondingly have a simple physical meaning. It may, however, be convenient to know the constants for a different set of coordinates, especially a set of internal coordinates.
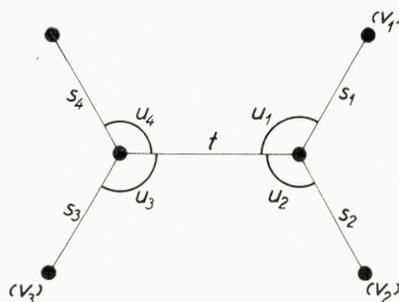
Fig. 4.

As suitable internal coordinates we choose (see Fig. 4).

t = increase of the C-C distance,

s_1, s_2, s_3 or s_4 = increase of the C-H distance,

u_1, u_2, u_3 or u_4 = increase of the C-C-H angle,

v_1, v_2, or v_3 = angle between a C-H bond and the plane of the C atoms and the fourth H atom, all positive upwards from the plane.

Because of the symmetry there is no interaction between in-plane and out-of-plane distortions, and we may therefore treat the constants separately. For the out-of-plane coordinates we get

$$
\mathbf{S} = \mathbf{AX} \quad \text{or} \quad
\begin{Bmatrix} S_{13} \\ S_{14} \\ S_{15} \\ S_{16} \\ S_{17} \\ S_{18} \end{Bmatrix}
=
\begin{Bmatrix}
+\dfrac{1}{\sqrt{2}} & -\dfrac{1}{\sqrt{2}} & 0 & 0 & 0 & 0 \\[4pt]
0 & 0 & +\dfrac{1}{2} & +\dfrac{1}{2} & -\dfrac{1}{2} & -\dfrac{1}{2} \\[4pt]
+\dfrac{1}{\sqrt{2}} & +\dfrac{1}{\sqrt{2}} & 0 & 0 & 0 & 0 \\[4pt]
0 & 0 & +\dfrac{1}{2} & +\dfrac{1}{2} & +\dfrac{1}{2} & +\dfrac{1}{2} \\[4pt]
0 & 0 & +\dfrac{1}{2} & -\dfrac{1}{2} & +\dfrac{1}{2} & -\dfrac{1}{2} \\[4pt]
0 & 0 & +\dfrac{1}{2} & -\dfrac{1}{2} & -\dfrac{1}{2} & +\dfrac{1}{2}
\end{Bmatrix}
\begin{Bmatrix} z_1 \\ z_2 \\ z_3 \\ z_4 \\ z_5 \\ z_6 \end{Bmatrix}
$$

and

$$
\mathbf{X} = \mathbf{BI} \quad \text{or} \quad
\begin{Bmatrix} z_1 \\ z_2 \\ z_3 \\ z_4 \\ z_5 \\ z_6 \end{Bmatrix}
=
\begin{Bmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
r & 0 & 0 \\
0 & r & 0 \\
0 & 0 & r \\
0 & 0 & 0
\end{Bmatrix}
\begin{Bmatrix} v_1 \\ v_2 \\ v_3 \end{Bmatrix}
$$

The potential energy matrix in the new coordinates is then (see p. 9)
$\mathbf{F}_1 = (\mathbf{AB})' \, \mathbf{F} \, (\mathbf{AB}) =$

$$
\begin{Bmatrix}
\dfrac{r^2}{4}\left(+\pi_2+\varrho_2+\sigma_1+\tau_1\right) & \dfrac{r^2}{4}\left(+\pi_2+\varrho_2-\sigma_1-\tau_1\right) & \dfrac{r^2}{4}\left(-\pi_2+\varrho_2+\sigma_1-\tau_1\right) \\[8pt]
\dfrac{r^2}{4}\left(+\pi_2+\varrho_2-\sigma_1-\tau_1\right) & \dfrac{r^2}{4}\left(+\pi_2+\varrho_2+\sigma_1+\tau_1\right) & \dfrac{r^2}{4}\left(-\pi_2+\varrho_2-\sigma_1+\tau_1\right) \\[8pt]
\dfrac{r^2}{4}\left(-\pi_2+\varrho_2+\sigma_1-\tau_1\right) & \dfrac{r^2}{4}\left(-\pi_2+\varrho_2-\sigma_1+\tau_1\right) & \dfrac{r^2}{4}\left(+\pi_2+\varrho_2+\sigma_1+\tau_1\right)
\end{Bmatrix}
$$

By inserting the values from Table 5 we get (in units md Å/rad²):

	v_1	v_2	v_3	
v_1	0.41			
v_2	+0.05	0.41		(symmetrical)
v_3	+0.21	−0.15	0.41	

By use of the same method we get for the in-plane constants (in units md/Å or md/rad or md Å/rad²)

	l	s_1	s_2	s_3	s_4	u_1	u_2	u_3	u_4
l	11.08								
s_1	0.00	4.77							
s_2	0.00	$+0.02$	4.77						
s_3	0.00	$+0.14$	-0.06	4.77					
s_4	0.00	-0.06	$+0.14$	$+0.02$	4.77				
u_1	$+0.82$	-0.03	$+0.29$	$+0.18$	-0.47	1.01			
u_2	$+0.82$	$+0.29$	-0.03	-0.47	$+0.18$	$+0.36$	1.01		
u_3	$+0.82$	$+0.18$	-0.47	-0.03	$+0.29$	-0.01	0.00	1.01	
u_4	$+0.82$	-0.47	$+0.18$	$+0.29$	-0.03	0.00	-0.01	$+0.36$	1.01

The total number of independent force constants is 18, 3 out-of-plane and 15 in-plane. Here we get 15 in-plane constants but 4 out-of-plane constants. Consequently there must be a relation between the out-of-plane constants, which is also found by
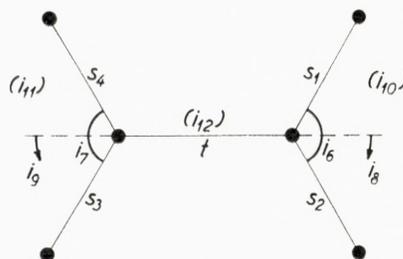

Fig. 5.

inspection ($\tau_1 = 0$). This inconvenience is caused by the unsymmetry in the definition of the out-of-plane internal coordinates. We get, however, correct results by use of these constants, as we only include more or less rotation and translation in the calculations.

Instead of u_1, u_2, u_3, u_4, v_1, v_2 and v_3 we may use other coordinates, for instance those used by CRAWFORD et al.[1] (sketched in Fig. 5):

i_6 or i_7 = r × the increase in H-C-H angle,

i_8 or i_9 = r × the angle between the C-C bond and the bisector of the H-C-H angle (positive to same side),

i_{10} or i_{11} = r cos v × the angle between the C-C bond and the CH_2 plane (positive to same side),

i_{12} = r sin v × the angle of torsion between the CH_2 planes.

This means that we state the movements of the atoms instead of the changes in the angles. For instance $i_6 = 1$ when the two H atoms move to the left perpendicular to the C-H bonds $1/2$ length unit each.

It is not necessary to calculate the new $\mathbf{F}_2$-matrix from the F-matrix again. If

[1] R. L. ARNETT and B. L. CRAWFORD, loc. cit.

C is the matrix connecting the former and the new set of coordinates we get the F_2-matrix as

$$F_2 = C'F_1C.$$

Thus we get (in units md/Å):

	i_{10}	i_{11}	i_{12}
i_{10}	0.81		
i_{11}	+0.11	0.81	
i_{12}	0	0	0.63

	l	s_1	s_2	s_3	s_4	i_6	i_7	i_8	i_9
l	11.08								
s_1	0.00	4.77							
s_2	0.00	+0.02	4.77						
s_3	0.00	+0.14	−0.06	4.77					
s_4	0.00	−0.06	+0.14	+0.02	4.77				
i_6	−0.76	−0.12	−0.12	+0.13	+0.13	0.60			
i_7	−0.76	+0.13	+0.13	−0.12	−0.12	−0.01	0.60		
i_8	0	−0.30	+0.30	+0.61	−0.61	0	0	1.13	
i_9	0	−0.61	+0.61	+0.30	−0.30	0	0	+0.02	1.13

As these coordinates are partially symmetry coordinates certain of the constants are zero on account of symmetry (indicated as 0, those calculated to zero are indicated as 0.00).

On basis of approximately the same experimental material, but a different adjustment etc. CRAWFORD *et al.* give the following values:

	i_{10}	i_{11}	i_{12}
i_{10}	0.80		
i_{11}	+0.12	0.80	
i_{12}	0	0	0.63

	l	s_1	s_2	s_3	s_4	i_6	i_7	i_8	i_9
l	10.90								
s_1	0.00	6.13							
s_2	0.00	+0.04	6.13						
s_3	0.00	+0.05	−0.02	6.13					
s_4	0.00	−0.02	+0.05	+0.04	6.13				
i_6	−0.85	+0.34	+0.34	ass.0	ass.0	0.62			
i_7	−0.85	ass.0	ass.0	+0.34	+0.34	+0.03	+0.62		
i_8	0	+0.94	−0.94	−0.43	+0.43	0	0	1.26	
i_9	0	+0.43	−0.43	−0.94	+0.94	0	0	+0.12	1.26

The large difference between the C-H stretching constants is due to the different methods of adjustment. Grawford *et al.* have aimed at a potential function fitting the "bottom" of the real one. The other differences, especially in the interaction terms between s_1, s_2, s_3, s_4 and i_6, i_7, i_8, i_9, are mainly caused by the fact that we have adjusted the constant of the A_g class to fit the frequencies of the partly deuterated compounds, whereas Crawford *et al.* have assumed a definite constant to equal zero.

A third way of constructing a suitable set of internal constants would be to exchange u_1, u_2, u_3, u_4, v_1, v_2 and v_3 with the corresponding movements of the H atoms analogous to the above principle. The corresponding constants will, however, not be given here, because it is always simple from the above given constants to calculate the potential energy difference corresponding to any given distortion.

Normal vibrations.

On account of the simple form of the G-matrix it is easy to find the G^{-1}-matrix. The unnormalized amplitudes of a normal vibration in the "direction" of the symmetry coordinates are then simply given as the signed minors of an arbitrary row of $|\mathbf{F} - \mathbf{G}^{-1}\lambda|$ for a given λ. For instance we get for the A_g class of ethylene-d_0

$$\mathbf{G}^{-1} = \left\{ \begin{matrix} m_C & 0 & 0 \\ 0 & m_H & 0 \\ 0 & 0 & m_H \end{matrix} \right\} \quad \text{and} \quad \left\{ \mathbf{F} - \mathbf{G}^{-1}\lambda \right\} = \left| \begin{matrix} \alpha_1 - m_C\lambda & \alpha_4 & \alpha_5 \\ \alpha_4 & \alpha_2 - m_H\lambda & \alpha_6 \\ \alpha_5 & \alpha_6 & \alpha_3 - m_H\lambda \end{matrix} \right|$$

The amplitudes are then:

$$l_1 = k \left[\alpha_2\alpha_3 - \alpha_6^2 - (\alpha_2 + \alpha_3) m_H\lambda + (m_H\lambda)^2 \right],$$
$$l_2 = k \left[\alpha_5\alpha_6 - \alpha_3\alpha_4 + \alpha_4 m_H\lambda \right],$$
$$l_3 = k \left[\alpha_4\alpha_6 - \alpha_2\alpha_5 + \alpha_5 m_H\lambda \right],$$

where the normalizing factor k is determined from $\Delta V = \frac{3}{2} hc\nu$.

The results of such calculations for the planar normal vibrations of ethylene-d_0 and -d_4 are given in Table 6 using internal coordinates. It is seen that ν_1 is mainly a C-H stretching, ν_2 mainly a C-C stretching, ν_3 mainly a deformation a.s.o. The only significant difference between the results from the two sets of constants for the A_g class is that of ν_2. According to the constants of set II this vibration (having the well-known double bond frequency) should be a mixture of a C-C stretching and a deformation. On this basis it seems reasonable to reject set II. In principle it should be safer to consider a static case, as demonstrated above, but in this special case the more complicated kinetic one seems to give the only definite argument for rejection[1].

---

[1] Crawford *et al.* have used the same argument.

<div align="center">

TABLE 6.

Amplitudes of Planar Normal Vibrations of Ethylene-d_0 and -d_4.

(in units $10^{-2}\,\text{Å}$ or $10^{-2}\,\text{rad.}$).

</div>

	Freq. No.		t	s_1	u_1
	1	-d_0	-2.06	$+9.27$	$+0.67$
		-d_4	-4.46	$+7.51$	$+1.55$
A_g	2	-d_0	$+8.75$	$+0.98$	$+1.58$
		-d_4	$+8.91$	$+2.46$	-2.27
	3	-d_0	-4.80	-0.23	$+13.36$
		-d_4	-2.00	-0.07	$+11.25$
	5	-d_0	0	$+9.52$	-0.24
		-d_4	0	$+8.25$	-0.82
B_{1g}	6	-d_0	0	-0.68	$+11.99$
		-d_4	0	-0.16	$+9.08$
	9	-d_0	0	$+9.35$	-2.23
		-d_4	0	$+8.05$	-2.20
B_{2u}	10	-d_0	0	$+4.06$	$+18.12$
		-d_4	0	$+3.09$	$+13.61$
	11	-d_0	0	$+9.22$	$+2.04$
		-d_4	0	$+7.75$	$+2.41$
B_{3u}	12	-d_0	0	-2.14	$+12.68$
		-d_4	0	-2.00	$+10.46$
rejected set (II)					
	2	-d_0	$+9.77$	$+1.02$	-9.70
		-d_4	$+8.98$	$+2.44$	-8.08

In the A_g class $s_1 = s_2 = s_3 = s_4$ and $u_1 = u_2 = u_3 = u_4$

In the B_{1g} class $s_1 = -s_2 = s_3 = -s_4$ and $u_1 = -u_2 = u_3 = -u_4$

In the B_{2u} class $s_1 = -s_2 = -s_3 = s_4$ and $u_1 = -u_2 = -u_3 = u_4$

In the B_{3u} class $s_1 = s_2 = -s_3 = -s_4$ and $u_1 = u_2 = -u_3 = -u_4$

Finally it should be remarked that we could equally well have placed the x and y axes in Fig. 1 otherwise. For instance it would also be convenient to place y_3 etc. in the direction of the C-H bonds and x_3 etc. perpendicular to them.

The only differences we get in the above given system are in the equations removing the non-genuine vibrations and in the transcription of the force constants to internal coordinates. In the proposed case the removal of non-genuine vibrations becomes a little more complicated and the transcription a little more easy. Thus the equations and the results for the A_g class separately (for instance Fig. 2, but not Fig. 3) apply to both orientations.

ACETYLENE

As an example of a linear molecule we shall next consider the acetylene molecule. The cartesian coordinate systems are shown in Fig. 6. It is easily seen that the symmetry coordinates are as shown in Table 7. The degeneracy presents the only dif-
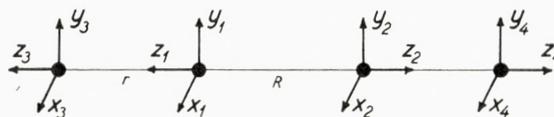
Fig. 6.

ficulty, but in this special case we simply get representative coordinates by interchanging x and y. In Table 7 are further given the non-genuine vibrations, the frequency numbering and the symbols used for the F-matrix.

TABLE 7.

	Symmetry Coordinates	F-Matrix		Freq. No.
Σ_g^+	$S_1 = \dfrac{1}{\sqrt{2}}(z_1 + z_2)$ $S_2 = \dfrac{1}{\sqrt{2}}(z_3 + z_4)$	$\begin{Bmatrix} \alpha_1 \, \alpha_3 \\ \alpha_3 \, \alpha_2 \end{Bmatrix}$		1, 2
$II_{g\,a}$	$S_3 = \dfrac{1}{\sqrt{2}}(x_1 - x_2)$ $S_4 = \dfrac{1}{\sqrt{2}}(x_3 - x_4)$	$\begin{Bmatrix} \beta_1 \, \beta_3 \\ \beta_3 \, \beta_2 \end{Bmatrix}$	R_y	$4\,a$
$II_{g\,b}$	$S_5 = \dfrac{1}{\sqrt{2}}(y_1 - y_2)$ $S_6 = \dfrac{1}{\sqrt{2}}(y_3 - y_4)$	$\begin{Bmatrix} \beta_1 \, \beta_3 \\ \beta_3 \, \beta_2 \end{Bmatrix}$	R_x	$4\,b$
Σ_u^+	$S_7 = \dfrac{1}{\sqrt{2}}(z_1 - z_2)$ $S_8 = \dfrac{1}{\sqrt{2}}(z_3 - z_4)$	$\begin{Bmatrix} \delta_1 \, \delta_3 \\ \delta_3 \, \delta_2 \end{Bmatrix}$	T_z	3
$II_{u\,a}$	$S_9 = \dfrac{1}{\sqrt{2}}(x_1 + x_2)$ $S_{10} = \dfrac{1}{\sqrt{2}}(x_3 + x_4)$	$\begin{Bmatrix} \varepsilon_1 \, \varepsilon_3 \\ \varepsilon_3 \, \varepsilon_2 \end{Bmatrix}$	T_x	$5\,a$
$II_{u\,b}$	$S_{11} = \dfrac{1}{\sqrt{2}}(y_1 + y_2)$ $S_{12} = \dfrac{1}{\sqrt{2}}(y_3 + y_4)$	$\begin{Bmatrix} \varepsilon_1 \, \varepsilon_3 \\ \varepsilon_3 \, \varepsilon_2 \end{Bmatrix}$	T_y	$5\,b$

The G-matrix is given in Table 8. From this we get for all classes of

$$\text{acetylene-d}_0 \begin{Bmatrix} \mu_C & 0 \\ 0 & \mu_H \end{Bmatrix}, \quad \text{of -d}_2 \begin{Bmatrix} \mu_C & 0 \\ 0 & \mu_D \end{Bmatrix}$$

$$\text{and of -d}_1 \begin{Bmatrix} \mu_C & 0 & 0 & 0 \\ 0 & \frac{1}{2}(\mu_H + \mu_D) & 0 & \frac{1}{2}(\mu_H - \mu_D) \\ 0 & 0 & \mu_C & 0 \\ 0 & \frac{1}{2}(\mu_H - \mu_D) & 0 & \frac{1}{2}(\mu_H + \mu_D) \end{Bmatrix}$$

The expressions for the removal of the non-genuine vibrations are

$$\begin{Bmatrix} \beta_1 \beta_3 \\ \beta_3 \beta_2 \end{Bmatrix} \begin{Bmatrix} R \\ R+2r \end{Bmatrix} = \begin{Bmatrix} 0 \\ 0 \end{Bmatrix} \qquad \begin{Bmatrix} \delta_1 \delta_3 \\ \delta_3 \delta_2 \end{Bmatrix} \begin{Bmatrix} 1 \\ 1 \end{Bmatrix} = \begin{Bmatrix} 0 \\ 0 \end{Bmatrix} \qquad \begin{Bmatrix} \varepsilon_1 \varepsilon_3 \\ \varepsilon_3 \varepsilon_2 \end{Bmatrix} \begin{Bmatrix} 1 \\ 1 \end{Bmatrix} = \begin{Bmatrix} 0 \\ 0 \end{Bmatrix}$$

By means of the G-matrix and these equations it is a simple matter to calculate the constants from a set of adjusted frequencies. This will not be done here. The
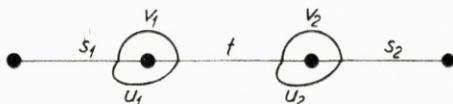

Fig. 7.

TABLE 8. G-Matrix.

| | | Σ_g^+ | | $\Pi_{g\,a}$ | | $\Pi_{g\,b}$ | | Σ_u^+ | | $\Pi_{u\,a}$ | | $\Pi_{u\,b}$ | |
		S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}	S_{11}	S_{12}
Σ_g^+	S_1	a						c					
	S_2		b						d				
$\Pi_{g\,a}$	S_3			a						c			
	S_4				b						d		
$\Pi_{g\,b}$	S_5					a						c	
	S_6						b						d
Σ_u^+	S_7	c						a					
	S_8		d						b				
$\Pi_{u\,a}$	S_9			c						a			
	S_{10}				d						b		
$\Pi_{u\,b}$	S_{11}					c						a	
	S_{12}						d						b

All elements not given are zero.

$$a = \tfrac{1}{2}(\mu_1 + \mu_2) \qquad b = \tfrac{1}{2}(\mu_3 + \mu_4) \qquad c = \tfrac{1}{2}(\mu_1 - \mu_2) \qquad d = \tfrac{1}{2}(\mu_3 - \mu_4)$$

obtained constants may then be recalculated in any other set of coordinates. For instance we may choose the internal coordinates shown in Fig. 7, where t and s mean the increases of the distances and u and v mean the increases of the angles in the zx and the zy planes respectively. By use of these coordinates we get the following F_1-matrix:

	t	s_1	s_2	u_1	u_2	v_1	v_2
t	$\frac{1}{2}(\alpha_1 + \alpha_2 + 2\alpha_3)$	$\frac{1}{2}(\alpha_2 + \alpha_3)$	$\frac{1}{2}(\alpha_2 + \alpha_3)$	0	0	0	0
s_1	$\frac{1}{2}(\alpha_2 + \alpha_3)$	$\frac{1}{2}(\alpha_2 + \delta_2)$	$\frac{1}{2}(\alpha_2 - \delta_2)$	0	0	0	0
s_2	$\frac{1}{2}(\alpha_2 + \alpha_3)$	$\frac{1}{2}(\alpha_2 - \delta_2)$	$\frac{1}{2}(\alpha_2 + \delta_2)$	0	0	0	0
u_1	0	0	0	$\frac{r^2}{2}(\beta_2 + \varepsilon_2)$	$\frac{r^2}{2}(\varepsilon_2 - \beta_2)$	0	0
u_2	0	0	0	$\frac{r^2}{2}(\varepsilon_2 - \beta_2)$	$\frac{r^2}{2}(\beta_2 + \varepsilon_2)$	0	0
v_1	0	0	0	0	0	$\frac{r^2}{2}(\beta_2 + \varepsilon_2)$	$\frac{r^2}{2}(\varepsilon_2 - \beta_2)$
v_2	0	0	0	0	0	$\frac{r^2}{2}(\varepsilon_2 - \beta_2)$	$\frac{r^2}{2}(\beta_2 + \varepsilon_2)$

ETHANE

As a last example we shall discuss how to get the fundamental equations for the ethane molecule, assuming the staggered configuration (D_{3d}). The cartesian coordinate
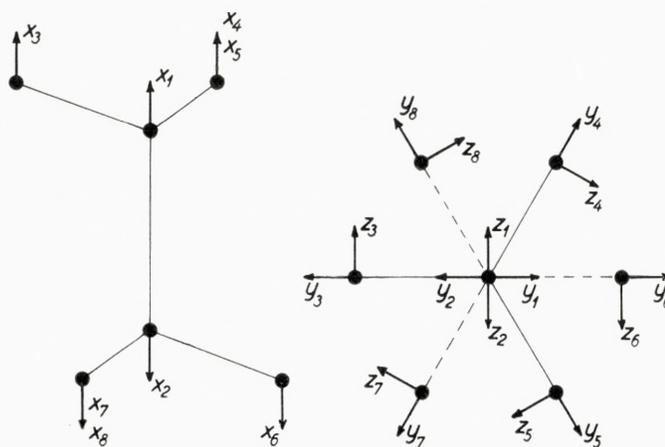

Fig. 8.

TABLE 9.

	E	$2C_3$	$3C_2$	i	$2S_6$	$3\sigma_d$			Freq. No.
A_{1g}	$+1$	$+1$	$+1$	$+1$	$+1$	$+1$		x_C, x_H, y_H	1, 2, 3
A_{2g}	$+1$	$+1$	-1	$+1$	$+1$	-1	R_x	z_H	
E_g	$+2$	-1	0	$+2$	-1	0	$R_{y,z}$	$x_H, y_H, z_H, (y_C, z_C)$	10, 11, 12
A_{1u}	$+1$	$+1$	$+1$	-1	-1	-1		z_H	4
A_{2u}	$+1$	$+1$	-1	-1	-1	$+1$	T_x	x_C, x_H, y_H	5, 6
E_u	$+2$	-1	0	-2	$+1$	0	$T_{y,z}$	$x_H, y_H, z_H, (y_C, z_C)$	7, 8, 9
x_C	2	4	0	0	0	6			
x_H	6	0	0	0	0	6			
y_H	6	0	0	0	0	6			
z_H	6	0	0	0	0	-6			

systems may be chosen as shown in Fig. 8. All x-axis are parallel to the C-C bond, all y- and z-axis are perpendicular to this bond and oriented as shown. The coordinate systems could have been oriented otherwise as discussed for ethylene.

TABLE 10.

	Symmetry Coordinates		Symmetry Coordinates
A_{1g}	$S_1 = \dfrac{1}{\sqrt{2}}(x_1 + x_2)$	A_{1u}	$S_{13} = \dfrac{1}{\sqrt{6}}(z_3 + z_4 + z_5 - z_6 - z_7 - z_8)$
	$S_2 = \dfrac{1}{\sqrt{6}}(x_3 + x_4 + x_5 + x_6 + x_7 + x_8)$		$S_{14} = \dfrac{1}{\sqrt{2}}(x_1 - x_2)$
	$S_3 = \dfrac{1}{\sqrt{6}}(y_3 + y_4 + y_5 + y_6 + y_7 + y_8)$	A_{2u}	$S_{15} = \dfrac{1}{\sqrt{6}}(x_3 + x_4 + x_5 - x_6 - x_7 - x_8)$
A_{2g}	$S_4 = \dfrac{1}{\sqrt{6}}(z_3 + z_4 + z_5 + z_6 + z_7 + z_8)$		$S_{16} = \dfrac{1}{\sqrt{6}}(y_3 + y_4 + y_5 - y_6 - y_7 - y_8)$
$E_{g\,a}$	$S_5 = \dfrac{1}{\sqrt{12}}(-2x_3 + x_4 + x_5 - 2x_6 + x_7 + x_8)$	$E_{u\,a}$	$S_{17} = \dfrac{1}{\sqrt{12}}(-2x_3 + x_4 + x_5 + 2x_6 - x_7 - x_8)$
	$S_6 = \dfrac{1}{\sqrt{12}}(-2y_3 + y_4 + y_5 - 2y_6 + y_7 + y_8)$		$S_{18} = \dfrac{1}{\sqrt{12}}(-2y_3 + y_4 + y_5 + 2y_6 - y_7 - y_8)$
	$S_7 = \dfrac{1}{2}(z_4 - z_5 + z_7 - z_8)$		$S_{19} = \dfrac{1}{2}(z_4 - z_5 - z_7 + z_8)$
	$S_8 = \dfrac{1}{\sqrt{2}}(y_1 + y_2)$		$S_{20} = \dfrac{1}{\sqrt{2}}(y_1 - y_2)$
$E_{g\,b}$	$S_9 = \dfrac{1}{2}(x_4 - x_5 + x_7 - x_8)$	$E_{u\,b}$	$S_{21} = \dfrac{1}{2}(x_4 - x_5 - x_7 + x_8)$
	$S_{10} = \dfrac{1}{2}(y_4 - y_5 + y_7 - y_8)$		$S_{22} = \dfrac{1}{2}(y_4 - y_5 - y_7 + y_8)$
	$S_{11} = \dfrac{1}{\sqrt{12}}(2z_3 - z_4 - z_5 + 2z_6 - z_7 - z_8)$		$S_{23} = \dfrac{1}{\sqrt{12}}(2z_3 - z_4 - z_5 - 2z_6 + z_7 + z_8)$
	$S_{12} = \dfrac{1}{\sqrt{2}}(z_1 + z_2)$		$S_{24} = \dfrac{1}{\sqrt{2}}(z_1 - z_2)$

Table 11. G-Matrix.

	A_{1g}	A_{2g}	$E_{g\,a}$	$E_{g\,b}$	A_{1u}	A_{2u}	$E_{u\,a}$	$E_{u\,b}$
A_{1g}	a b b		i i	k k		e f f	j j	l l
A_{2g}		b	k	$-i$	f		l	$-j$
$E_{g\,a}$	i i k		c c d a	m m $-m$	l	j j	g g h e	n n $-n$
$E_{g\,b}$	k k	$-i$	m m $-m$	d d c a	$-j$	l l	n n $-n$	h h g e
A_{1u}		f	l	$-j$	b		k	$-i$
A_{2u}	e f f		j j	l l		a b b	i i	k k
$E_{u\,a}$	j j l		g g h e	n n $-n$	k	i i	c c d a	m m $-m$
$E_{u\,b}$	l l	$-j$	n n $-n$	h h g e	$-i$	k k	m m $-m$	d d c a

All elements not given are zero.

$$a = \tfrac{1}{2}(\mu_1 + \mu_2)$$

$$b = \tfrac{1}{6}(\mu_3 + \mu_4 + \mu_5 + \mu_6 + \mu_7 + \mu_8)$$

$$c = \tfrac{1}{12}(4\mu_3 + \mu_4 + \mu_5 + 4\mu_6 + \mu_7 + \mu_8)$$

$$d = \tfrac{1}{4}(\mu_4 + \mu_5 + \mu_7 + \mu_8)$$

$$e = \tfrac{1}{2}(\mu_1 - \mu_2)$$

$$f = \tfrac{1}{6}(\mu_3 + \mu_4 + \mu_5 - \mu_6 - \mu_7 - \mu_8)$$

$$g = \tfrac{1}{12}(4\mu_3 + \mu_4 + \mu_5 - 4\mu_6 - \mu_7 - \mu_8)$$

$$h = \tfrac{1}{4}(\mu_4 + \mu_5 - \mu_7 - \mu_8)$$

$$i = \frac{1}{6\sqrt{2}}(-2\mu_3 + \mu_4 + \mu_5 - 2\mu_6 + \mu_7 + \mu_8)$$

$$j = \frac{1}{6\sqrt{2}}(-2\mu_3 + \mu_4 + \mu_5 + 2\mu_6 - \mu_7 - \mu_8)$$

$$k = \frac{1}{2\sqrt{6}}(\mu_4 - \mu_5 + \mu_7 - \mu_8)$$

$$l = \frac{1}{2\sqrt{6}}(\mu_4 - \mu_5 - \mu_7 + \mu_8)$$

$$m = \frac{1}{4\sqrt{3}}(\mu_4 - \mu_5 + \mu_7 - \mu_8)$$

$$n = \frac{1}{4\sqrt{3}}(\mu_4 - \mu_5 - \mu_7 + \mu_8)$$

The character table etc. is given in Table 9. The method used for ethylene for finding which coordinates contribute to the symmetry coordinates of each class is also used here for the x_C, x_H, y_H and z_H coordinates, the total number of operations in the group being 12. The y_C and z_C coordinates are seen each to contribute the remaining symmetry coordinate of the degenerate classes as mentioned above (p. 5).

The symmetry coordinates are given in Table 10. The construction of the symmetry coordinates has been described by WILSON *et al.* for the non-degenerate classes and for one of two degenerate classes. The coordinates for the other degenerate class in this case are constructed from each coordinate of the first set by turning it 120° in a definite direction, multiplying by 2 and adding it to the original one. The resulting coordinate is normalized by multiplication by $\frac{1}{\sqrt{3}}$.

The G-matrix is given in Table 11. It looks somewhat complicated, but for the definite isotopic species many of the elements given are zero and we get matrices of the usual simple appearance.

The non-genuine vibrations are "removed" by use of the usual equations, where the column matrices are for

$$E_g: \begin{Bmatrix} -\varrho \sin u \\ \varrho \cos u \\ \varrho \cos u \\ 1 \end{Bmatrix}, \quad A_u: \begin{Bmatrix} 1 \\ \sqrt{3} \\ \sqrt{3} \end{Bmatrix} \quad \text{and} \quad E_u: \begin{Bmatrix} 0 \\ \sqrt{3} \\ \sqrt{3} \\ \sqrt{2} \end{Bmatrix},$$

where $\varrho = \sqrt{\frac{3}{2}} \frac{R}{r}$, R and r being the distances from the center of gravity to the H and C atoms respectively, and where u is the angle between R and r. Naturally these matrices are identical for two degenerate classes.

The recalculation of the constants in other coordinates is quite simple, but the obtained expressions are too large to be given here.

APPENDIX

For the convenience of the reader a few hints should be given here as to the numerical calculations.

The secular equations are always of the form

$$x^n - c_1 x^{n-1} + c_2 x^{n-2} - c_3 x^{n-3} + \ldots \pm c_n = 0$$

with alternating sign of the coefficients. This may be written as

$$c_n - x \left[c_{n-1} - x \left\{ c_{n-2} - x \left(c_{n-3} \ldots \ldots - x \left[c_2 - x \left\{ c_1 - x \right\} \right] \ldots \right) \right\} \right] = 0.$$

The polynomium may thus be calculated by subtracting x from c_1, multiplying by x, subtracting the result from c_2, multiplying by x and so on. This may be done by use of certain ordinary desk calculators without the need of writing down any intermediate result.

In the calculations considered here it is important in order to limit the necessary number of decimal places to keep all numbers handled in the calculating machine as close to 1 as possible. This may be done in the following way. The unknown in the secular equations λ is given as

$$\lambda = 4 \pi^2 c^2 \nu^2,$$

where ν is the frequency in cm^{-1}. But instead of introducing the correct value of λ at the beginning of the calculations we prefere to use the proportional quantity $\lambda' = (10^{-3}\nu)^2$. In this way we get both numbers round one and a simple relation between λ' and ν. Further we multiply the reciprocal masses by a convenient number in order to get values round 1. When dealing with hydro-carbons we get suitable values by multiplying the reciprocal masses in atomic-weight units by 4. In order to get the constants in the ordinary units (md/Å etc.) we only have to multiply the resulting constants by the appropriate factor, in this case by 2.3554.

The calculations for ethylene reported above have been carried out by means of a Madas calculating machine type 20 AZS using 6 decimal places.

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