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A COMPLETE RULE FOR
THE VIBRATIONAL FREQUENCIES OF
CERTAIN ISOTOPIC MOLECULES

BY

SVEND BRODERSEN AND A. LANGSETH



København 1958

i kommission hos Ejnar Munksgaard

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Synopsis.

The existence of an isotopic rule in addition to the product rule and the sum rule is demonstrated. This rule allows the calculation of all the frequencies of certain partly isotopically substituted compounds exclusively from the frequencies of the corresponding full-symmetry compounds.

An equation between the secular determinants of the classes in question is a convenient expression for the rule. A detailed description is given of the procedure for setting up this equation. The conditions for the validity of the rule are discussed, the result being roughly that the full-symmetry compounds should be either linear and symmetrical or plane, but of higher symmetry than C_s . Some of the rules are strictly valid within the harmonic approximation (and in fact better); others are based on the further approximation of separating low and high frequencies. In a special chapter the rules are formulated for molecules of some of the more important point groups.

The rule is used to calculate the frequencies of all the partly deuterated species of acetylene and ethylene. The agreement with observed values is at least as good as for calculations based on a harmonic potential function.

I. INTRODUCTION

The vibrational frequencies of isotopic molecules are closely related. From the common potential function one may always calculate all the frequencies of all the isotopic species. The potential function is, however, often unknown and it is of great importance to know all the rules connecting the frequencies of different isotopic species without the use of the potential function.

Of such rules are known the product rule¹ and the sum rule². The former gives one relation between definite frequencies of two isotopic species and the latter gives one relation between definite frequencies of three or more isotopic species. Neither of these, however, allow the calculation of all the frequencies of a definite class, except for very trivial cases. It is the aim of this paper to demonstrate the existence of a further rule allowing in many cases a calculation of all the frequencies of a partially isotopically substituted compound from the frequencies of the corresponding full-symmetry compounds, one "light" and one "heavy".

The treatment of the rule presented in this paper is restricted to the case where each of the atoms in one symmetrically equivalent set is either one or the other of two isotopes. The theory could, however, easily be extended to cases with more than two isotopes. Cases with isotopic substitutions in more than one equivalent set of atoms will not be treated here. Further it should be noted that the rule concerns partially isotopically substituted compounds only, which means that the equivalent set of atoms in question should include at least two atoms.

The validity of the rule and of an approximation sometimes included has been checked by calculations of all the frequencies of all the partly deuterated species of acetylene, ethylene and benzene. The agreement with observed frequencies is excellent. The results for acetylene and ethylene are given in this paper. Those for benzene will be given in a following paper.

Readers not interested in details of the theory may skip the chapters II 3, 4, and 5 (p. 6 to p. 12). A special chapter, II 8 (p. 13), is reserved for a detailed description of the application of the rule to molecules of certain simple symmetries. This description covers most of the cases where the rule is valid, readers interested in other cases are referred to the above mentioned chapters.

¹ O. REDLICH, *Z. phys. Chem. B* **28**, 371 (1935).

² J. C. DECUS and E. B. WILSON, *J. Chem. Phys.* **19**, 1409 (1951).

II. THEORY

1. Hybrid Symmetry Classes.

Before giving a general formulation of the isotopic frequency rule it may be appropriate to define what we shall call a "hybrid symmetry class".

In this paper we shall consider isotopic substitution in one symmetrically equivalent set of atoms by a single isotope only, for instance the substitution of deuterium atoms for the hydrogen atoms in an equivalent set. If all the atoms of the equivalent set in question are either hydrogen or deuterium atoms we speak of a "light", respectively "heavy" compound. Both of these have the same (full) symmetry. If we have as well hydrogen as deuterium atoms in the set we speak of an "intermediate" compound, which will be of lower symmetry.

The symmetry classes of an intermediate compound are always formed by amalgamation of two or more classes of the full-symmetry compounds. Thus, for instance, the A'' class of ethylene- d_1 is formed from the A_{1u} , B_{1u} , B_{2g} and B_{3g} classes of ethylene- d_0 or ethylene- d_4 .

Considering these classes as one composite class, we shall for ethylene- d_0 denote this class by

$$(A_{1u})^{d_0} (B_{1u})^{d_0} (B_{2g})^{d_0} (B_{3g})^{d_0}$$

and for ethylene- d_4 by

$$(A_{1u})^{d_4} (B_{1u})^{d_4} (B_{2g})^{d_4} (B_{3g})^{d_4}.$$

If we take the constituent classes partly from ethylene- d_0 and partly from ethylene- d_4 we may construct a class like, for instance:

$$(A_{1u})^{d_0} (B_{1u})^{d_4} (B_{2g})^{d_0} (B_{3g})^{d_0}.$$

Such a class we shall call a *hybrid class corresponding to the A'' class of ethylene- d_1* .

A hybrid class is not a symmetry class in the usual sense, but in many respects it behaves like an ordinary class. Thus it contains certain symmetry coordinates and frequencies and it can be ascribed a secular determinant, a \mathbf{G} matrix, etc. as discussed further below.

The frequencies of a hybrid class are simply those of the constituent classes. The secular determinant, therefore, is the product of the secular determinants of the constituent classes.

This product may conveniently be formed in the following way. Let us write all expanded secular determinants on the form:

$$x^n - c_1 x^{n-1} + c_2 x^{n-2} - c_3 x^{n-3} + \dots + (-1)^n c_n.$$

If a hybrid class is built up from two classes I and II (of different compounds) with the coefficients c^I and c^{II} we get for the coefficients of the expansion for the hybrid class:

$$\left. \begin{aligned} c_1 &= c_1^I + c_1^{II} \\ c_2 &= c_2^I + c_1^I c_1^{II} + c_2^{II} \\ c_3 &= c_3^I + c_2^I c_1^{II} + c_1^I c_2^{II} + c_3^{II} \\ &\text{etc.} \end{aligned} \right\} \quad (1)$$

If a hybrid class is built up from more than two classes—as in the above case—it is convenient to form the coefficients of the hybrid class by joining the secular determinants of the constituent classes two by two successively.

Concerning the **G** matrix of a hybrid class, see p. 6.

2. General Formulation of the Isotopic Frequency Rule.

In the following we shall show that in certain cases *the secular determinant of a definite class of an intermediate compound may be given as a linear combination of the secular determinants of certain corresponding hybrid classes*. If we again take the A'' class of ethylene- d_1 as an example it may be shown that the secular determinant is given by

$$\begin{aligned} [(A'')^{d_1}] &= \frac{1}{4} [(A_{1u})^{d_4} (B_{1u})^{d_0} (B_{2g})^{d_0} (B_{3g})^{d_0}] \\ &+ \frac{1}{4} [(A_{1u})^{d_0} (B_{1u})^{d_4} (B_{2g})^{d_0} (B_{3g})^{d_0}] \\ &+ \frac{1}{4} [(A_{1u})^{d_0} (B_{1u})^{d_0} (B_{2g})^{d_4} (B_{3g})^{d_0}] \\ &+ \frac{1}{4} [(A_{1u})^{d_0} (B_{1u})^{d_0} (B_{2g})^{d_0} (B_{3g})^{d_4}], \end{aligned} \quad (2)$$

where a class symbol in square brackets means the corresponding secular determinant.

From this equation follows that every coefficient in the secular determinant of the A'' class of ethylene- d_1 is a linear combination of the coefficients of four different hybrid classes. The coefficients of the hybrid classes are in turn given by the coefficients of the light and heavy compounds (Eq. (1)). All coefficients are further closely related to the frequencies by the well-known relations:

$$\left. \begin{aligned} c_1 &= \sum \lambda_i \\ c_2 &= \sum \lambda_i \lambda_j \\ c_3 &= \sum \lambda_i \lambda_j \lambda_k \\ &\text{etc.} \end{aligned} \right\} \quad (3)$$

where $\lambda = 4\pi^2 c^2 \nu^2$. Therefore, *whenever a relation of the form given in (2) exists, it is possible to calculate all the frequencies in that particular class of the intermediate compound directly from the corresponding frequencies of the light and heavy compounds without the use of force constants, geometrical parameters or atomic masses.*

We call such a rule a complete, isotopic rule, because it—contrary to the product rule and the sum rule—allows the calculation of all the frequencies in a given class.

This means that only in cases where no complete rules exist there is a need for further isotopic rules.

In the following will be given the outlines only of a general proof for the existence of complete rules. We shall, however, discuss in detail the conditions for the validity of the rule as well as the principles for setting up the determinantal equation¹.

3. Condition for the Rule Expressed in Terms of Minors of the Isotopic \mathbf{G} Matrices.

The following treatment of the problem is based on the use of external symmetry coordinates as discussed previously by one of the present authors². The advantage of this system is that every single symmetry coordinate is expressed as a linear combination of cartesian displacement coordinates for one symmetrically equivalent set of atoms only. The symmetry coordinates are thus straight away separated corresponding to the different sets of atoms present in the molecule.

As we are only going to discuss cases comprising isotopic substitution in one set of atoms at a time we are conveniently able to divide the symmetry coordinates up into isotopic and non-isotopic coordinates. Correspondingly, we may divide the elements of the \mathbf{G} matrix up into isotopic and non-isotopic ones, as all elements corresponding to one isotopic and one non-isotopic coordinate will vanish identically. The submatrix of \mathbf{G} made up of the isotopic elements only we shall call the isotopic \mathbf{G} matrix.

By expanding the secular determinant in terms of products of minors of $|\mathbf{G}|$ and corresponding minors of $|\mathbf{F}|$ it is seen that only non-vanishing $|\mathbf{G}|$ -minors, the corresponding $|\mathbf{F}|$ -minors of which are also non-vanishing, do contribute to the expansion. As such minors are of special interest for the present problem we shall in the following refer to them as *contributing \mathbf{G} -minors*. They include all principal (symmetrical) minors of \mathbf{G} , but only very few non-principal (unsymmetrical) ones³.

Any minor of $|\mathbf{G}|$ may—just as the \mathbf{G} matrix itself—be divided into an isotopic and a non-isotopic minor. The isotopic minors of the contributing $|\mathbf{G}|$ -minors are identical with the contributing minors of the isotopic \mathbf{G} matrix.

These remarks apply equally well to hybrid classes as to ordinary symmetry classes. The \mathbf{G} matrix of a hybrid class is built up of the \mathbf{G} matrices of the constituent classes as diagonal blocks, all other elements being zero. The \mathbf{G} matrices of all the hybrid classes corresponding to a definite class are different, whereas the \mathbf{F} matrices all are identical with that of the corresponding class of the intermediate compound.

We can now express the condition for the validity of a complete, isotopic frequency rule like (2) in terms of the contributing minors of the isotopic \mathbf{G} matrices of the symmetry classes in question.

¹ Readers may at a first reading skip to p. 12 or even to p. 13.

² SVEND BRODERSEN, Mat. Fys. Skr. Dan. Vid. Selsk. **1**, no. 4. (1957).

³ SVEND BRODERSEN, loc. cit. pag. 7.

Let us expand all the secular determinants in the determinantal equation in terms of minors of $|\mathbf{G}|$ and $|\mathbf{F}|$, but let us furthermore expand all minors of $|\mathbf{G}|$ according to the division in isotopic and non-isotopic minors. All the $|\mathbf{F}|$ -minors as well as all the non-isotopic $|\mathbf{G}|$ -minors are identically the same for all the secular determinants. Consequently, the rule must be valid if the corresponding equation is valid for all isotopic $|\mathbf{G}|$ -minors, these being the only variables.

In other words: *There will exist a complete isotopic frequency rule for a definite class of an intermediate compound if all contributing minors of its isotopic \mathbf{G} matrix may be written as identically the same linear combination of the corresponding minors of certain hybrid classes.*

As a very simple example let us prove the validity of the complete isotopic rule for the B_2 class of asym-ethylene- d_2 :

$$[(B_2)^{as-d_2}] = \frac{1}{2} [(B_{1u})^{d_0} (B_{2g})^{d_4}] + \frac{1}{2} [(B_{1u})^{d_4} (B_{2g})^{d_0}].$$

The \mathbf{G} matrices for the B_2 class and the two hybrid classes are:

$$\begin{pmatrix} \mu_C & 0 & 0 & 0 \\ 0 & \frac{1}{2}(\mu_H + \mu_D) & 0 & \frac{1}{2}(\mu_H - \mu_D) \\ 0 & 0 & \mu_C & 0 \\ 0 & \frac{1}{2}(\mu_H - \mu_D) & 0 & \frac{1}{2}(\mu_H + \mu_D) \end{pmatrix}, \begin{pmatrix} \mu_C & 0 & 0 & 0 \\ 0 & \mu_H & 0 & 0 \\ 0 & 0 & \mu_C & 0 \\ 0 & 0 & 0 & \mu_D \end{pmatrix}, \text{ and } \begin{pmatrix} \mu_C & 0 & 0 & 0 \\ 0 & \mu_D & 0 & 0 \\ 0 & 0 & \mu_C & 0 \\ 0 & 0 & 0 & \mu_H \end{pmatrix}$$

and, hence, the corresponding isotopic \mathbf{G} matrices are:

$$\begin{pmatrix} \frac{1}{2}(\mu_H + \mu_D) & \frac{1}{2}(\mu_H - \mu_D) \\ \frac{1}{2}(\mu_H - \mu_D) & \frac{1}{2}(\mu_H + \mu_D) \end{pmatrix}, \begin{pmatrix} \mu_H & 0 \\ 0 & \mu_D \end{pmatrix}, \text{ and } \begin{pmatrix} \mu_D & 0 \\ 0 & \mu_H \end{pmatrix}.$$

In the isotopic \mathbf{G} matrix of the intermediate compound the three principal minors only are contributing. We may write these as

$$\begin{aligned} \left| \frac{1}{2}(\mu_H + \mu_D) \right| &= \frac{1}{2} |\mu_H| + \frac{1}{2} |\mu_D|, \\ \left| \frac{1}{2}(\mu_H - \mu_D) \right| &= \frac{1}{2} |\mu_D| + \frac{1}{2} |\mu_H|, \text{ and} \\ \begin{vmatrix} \frac{1}{2}(\mu_H + \mu_D) & \frac{1}{2}(\mu_H - \mu_D) \\ \frac{1}{2}(\mu_H - \mu_D) & \frac{1}{2}(\mu_H + \mu_D) \end{vmatrix} &= \frac{1}{2} \begin{vmatrix} \mu_H & 0 \\ 0 & \mu_D \end{vmatrix} + \frac{1}{2} \begin{vmatrix} \mu_D & 0 \\ 0 & \mu_H \end{vmatrix}, \end{aligned}$$

which proves the validity of the determinantal equation.

4. Some Properties of the Minors of Isotopic \mathbf{G} Matrices.

Because of their fundamental importance we shall in the following state certain properties of the minors of the isotopic \mathbf{G} matrix. This will allow us to formulate a simpler condition for the validity of the complete isotopic rule. The following treatment

is limited to deuterated compounds, but may be extended to cases with more than two isotopes.

The symmetry coordinates, being defined as linear combinations of the cartesian displacement coordinates, are given by a coefficient matrix, \mathbf{A} . The isotopic symmetry coordinates are linear combinations of the cartesian coordinates for the atoms in the set in question, the coefficient matrix is a minor of \mathbf{A} which we shall refer to as the isotopic \mathbf{A} matrix, \mathbf{A}^i . Each row of \mathbf{A}^i corresponds to a symmetry coordinate and each column to a cartesian coordinate of a definite atom. To each column is therefore attached the mass of one of the atoms in the set in question. If we consider a definite isotopic molecule we may consequently divide \mathbf{A}^i into minors, one for each isotope, i. e. for a partly deuterated compound into a hydrogen minor \mathbf{A}^H , and a deuterium minor \mathbf{A}^D .

The typical element of the isotopic \mathbf{G} matrix, \mathbf{G}^i , is

$$G_{mn}^i = \sum_t \mu_t a_{mt} a_{nt}, \quad (4)$$

where a_{mt} and a_{nt} are elements of \mathbf{A}^i and μ_t is the reciprocal mass attached to the column no. t . For partly deuterated compounds G_{mn}^i may be written

$$G_{mn}^i = G_{mn}^H \mu_H + G_{mn}^D \mu_D, \quad (5)$$

where G_{mn}^H and G_{mn}^D may be taken as the typical elements of two new matrices, \mathbf{G}^H and \mathbf{G}^D . (Note that \mathbf{A}^H and \mathbf{A}^D are minors of \mathbf{A}^i , whereas \mathbf{G}^H and \mathbf{G}^D are made up of the coefficients of μ_H and μ_D in \mathbf{G}^i).

Any minor of $|\mathbf{G}^i|$ may be written as a homogenous polynomium in μ_H and μ_D of a degree equal to the order of the minor. We shall indicate the expansion of a principal minor, for instance that of the minor corresponding to symmetry coordinates no. 1, 2, and 4, in the following way:

$$|\mathbf{G}_{124}^i| = K_{124}^{H^3} \mu_H^3 + K_{124}^{H^2D} \mu_H^2 \mu_D + K_{124}^{HD^2} \mu_H \mu_D^2 + K_{124}^{D^3} \mu_D^3.$$

For the coefficients of an expanded minor of $|\mathbf{G}^i|$ it is possible to derive the following theorems¹:

1. The sum of the coefficients in a principal minor is equal to 1.
2. The sum of the coefficients in a non-principal minor is equal to 0.
3. Any coefficient in a principal $|\mathbf{G}^i|$ -minor of order n equals the sum of the squares of certain $|\mathbf{A}^i|$ -minors of order n . The coefficient, $K^{H^{n-p}D^p}$, of $\mu_H^{n-p} \mu_D^p$ is equal to the sum over all possible minors with $n-p$ columns from \mathbf{A}^H and p columns from \mathbf{A}^D using the same row (symmetry coordinate) numbers as for the given $|\mathbf{G}^i|$ -minor.
4. Any coefficient in a non-principal $|\mathbf{G}^i|$ -minor is equal to the corresponding sum of binary products of $|\mathbf{A}^i|$ -minors.

¹ It is outside the scope of this paper to give the mathematical proofs for the validity of these rules. They are based on the fact that \mathbf{A} and any minor of it formed by suppressing rows are orthogonal.

5. All the coefficients in a principal $|\mathbf{G}^i|$ -minor may be expressed by the coefficients $K^{H^n}, K^{H^{n-1}}, \dots, K^H$ (or by the coefficients $K^{D^n}, K^{D^{n-1}}, \dots, K^D$) of all the principal minors of the given $|\mathbf{G}^i|$ -minor as follows:

$$\left. \begin{aligned} K^{D^n} &= 1 - \sum K^H + \sum K^{H^2} - \sum K^{H^3} + \dots \\ K^{HD^{n-1}} &= \sum K^H - 2 \sum K^{H^2} + 3 \sum K^{H^3} - \dots \\ K^{H^2 D^{n-2}} &= \sum K^{H^2} - 3 \sum K^{H^3} + 6 \sum K^{H^4} - \dots \\ K^{H^3 D^{n-3}} &= \sum K^{H^3} - 4 \sum K^{H^4} + 10 \sum K^{H^5} - \dots \\ &\text{etc.} \end{aligned} \right\} \quad (6)$$

or the analogous D -expressions. Here, for instance, $\sum K^{H^2}$ is the sum over K^{H^2} of all the principal minors of the given one. The numerical coefficients are the binomial coefficients. All the relations may be written in the general form:

$$K^{H^p D^{n-p}} = \binom{p}{p} \sum K^{H^p} - \binom{p+1}{p} \sum K^{H^{p+1}} + \binom{p+2}{p} \sum K^{H^{p+2}} - \dots \quad (7)$$

or the analogous D -expression.

As an example we may consider the case:

$$\mathbf{A}^i = \begin{pmatrix} & H & & D \\ a_{11} & a_{12} & a_{13} & a_{14} \\ a_{21} & a_{22} & a_{23} & a_{24} \\ a_{31} & a_{32} & a_{33} & a_{34} \\ a_{41} & a_{42} & a_{43} & a_{44} \end{pmatrix}$$

where \mathbf{A}^H has 3 columns and \mathbf{A}^D only 1. For the coefficients of the minor:

$$|\mathbf{G}_{123}^i| = K_{123}^{H^3} \mu_H^3 + K_{123}^{H^2 D} \mu_H^2 \mu_D + K_{123}^{HD^2} \mu_H \mu_D^2 + K_{123}^{D^3} \mu_D^3$$

we get from theorem no. 3:

$$\begin{aligned} K_{123}^{H^3} &= \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix}^2, \\ K_{123}^{H^2 D} &= \begin{vmatrix} a_{11} & a_{12} & a_{14} \\ a_{21} & a_{22} & a_{24} \\ a_{31} & a_{32} & a_{34} \end{vmatrix}^2 + \begin{vmatrix} a_{11} & a_{13} & a_{14} \\ a_{21} & a_{23} & a_{24} \\ a_{31} & a_{33} & a_{34} \end{vmatrix}^2 + \begin{vmatrix} a_{12} & a_{13} & a_{14} \\ a_{22} & a_{23} & a_{24} \\ a_{32} & a_{33} & a_{34} \end{vmatrix}^2, \text{ and} \\ K_{123}^{HD^2} &= K_{123}^{D^3} = 0. \end{aligned}$$

All K^{HD^2} and K^{D^3} vanish, as \mathbf{A}^D has only 1 column. Further we get the following relations from theorem no. 5:

$$\begin{aligned}
K_{123}^{D^3} &= 1 - (K_1^H + K_2^H + K_3^H) + (K_{12}^{H^2} + K_{13}^{H^2} + K_{23}^{H^2}) - K_{123}^{H^3}, \\
K_{123}^{HD^2} &= (K_1^H + K_2^H + K_3^H) - 2(K_{12}^{H^2} + K_{13}^{H^2} + K_{23}^{H^2}) + 3K_{123}^{H^3}, \text{ and} \\
K_{123}^{H^2D} &= (K_{12}^{H^2} + K_{13}^{H^2} + K_{23}^{H^2}) - 3K_{123}^{H^3}
\end{aligned}$$

or the analogous ones, expressing $K_{123}^{H^3}$ and $K_{123}^{H^2D}$ by $\sum K^D$:

$$\begin{aligned}
K_{123}^{H^3} &= 1 - (K_1^D + K_2^D + K_3^D) \text{ and} \\
K_{123}^{H^2D} &= (K_1^D + K_2^D + K_3^D).
\end{aligned}$$

From theorem no. 5 it may be shown that there always exists a scheme comprising all the coefficients of all the principal minors of a given symmetry class. This scheme may be of the form

	S_1	S_2	S_3	S_4	\dots
H	H	H	D	D	\dots
H	H	D	D	H	\dots
H	D	D	H	H	\dots
D	D	D	H	H	\dots
D	D	D	H	H	\dots
D	H	H	H	H	\dots
D	H	H	D	D	\dots
D	H	D	D	D	\dots

All the coefficients of the principal minors of the class in question can be read from the scheme in the following way. The coefficients of, for instance, $|\mathbf{G}_{123}^i|$ are found by use of columns 1, 2, and 3 only. $K_{123}^{H^3}$ is given as the fraction of the total number of rows having H in all three columns: $\frac{1}{8}$, $K_{123}^{H^2D}$ as the fraction of rows having two H and one D in the three columns: $\frac{3}{8}$, and similarly $K_{123}^{HD^2} = \frac{2}{8}$, $K_{123}^{D^3} = \frac{2}{8}$, $K_{34}^{HD} = \frac{5}{8}$, $K_2^D = \frac{3}{8}$ and so on. We shall in the following refer to this scheme as the *coefficient-scheme*.

5. Calculation of the Minors of the \mathbf{G} Matrix and the Setting Up of the Coefficient-Scheme.

The minors of the isotopic \mathbf{G} matrix may be calculated directly from the matrix. This is, however, in most cases a rather tedious method, which can only with advantage be used for the non-principal minors. The principal minors are more easily found by setting up the coefficient-scheme.

This may be done according to theorem no. 5 (page 9) exclusively from the pure H - (or D -) coefficients. These may in turn be calculated either from the \mathbf{A}^H

(or \mathbf{A}^D) matrix by use of theorem no. 3, or as the principal minors of the \mathbf{G}^H (or \mathbf{G}^D) matrix. If only one or two atoms in the set are substituted it is usually simplest to use the \mathbf{A}^H (or \mathbf{A}^D) matrix, as the number of columns and of non-vanishing minors will be small. If more atoms are substituted it will usually be necessary to calculate a number of pure H - (or D -) coefficients from the \mathbf{G}^H (or \mathbf{G}^D) matrix. In both cases the coefficient-scheme is set up rather easily by use of a relatively low number of coefficients. The calculation of a few more coefficients will allow a check on the correctness of the coefficient-scheme.

As the non-isotopic \mathbf{G} matrix is diagonal we get all the principal minors of \mathbf{G} itself almost directly from the coefficient-scheme.

As a simple example we shall construct the coefficient-scheme for the A'' class of ethylene- d_1 . The isotopic coordinates are¹:

$$\begin{aligned} S_{14} &= \frac{1}{2}(z_3 + z_4 - z_5 - z_6) \\ S_{16} &= \frac{1}{2}(z_3 + z_4 + z_5 + z_6) \\ S_{17} &= \frac{1}{2}(z_3 - z_4 + z_5 - z_6) \\ S_{18} &= \frac{1}{2}(z_3 - z_4 - z_5 + z_6). \end{aligned}$$

Assuming the deuterium atom to be no. 3, the different matrices are:

$$\mathbf{A}^i = \begin{pmatrix} +\frac{1}{2} & +\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} \\ +\frac{1}{2} & +\frac{1}{2} & +\frac{1}{2} & +\frac{1}{2} \\ +\frac{1}{2} & -\frac{1}{2} & +\frac{1}{2} & -\frac{1}{2} \\ +\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & +\frac{1}{2} \end{pmatrix} \quad \mathbf{A}^D = \begin{pmatrix} +\frac{1}{2} \\ +\frac{1}{2} \\ +\frac{1}{2} \\ +\frac{1}{2} \end{pmatrix} \quad \mathbf{G}^D = \begin{pmatrix} +\frac{1}{4} & +\frac{1}{4} & +\frac{1}{4} & +\frac{1}{4} \\ +\frac{1}{4} & +\frac{1}{4} & +\frac{1}{4} & +\frac{1}{4} \\ +\frac{1}{4} & +\frac{1}{4} & +\frac{1}{4} & +\frac{1}{4} \\ +\frac{1}{4} & +\frac{1}{4} & +\frac{1}{4} & +\frac{1}{4} \end{pmatrix}$$

$$\mathbf{G}^i = \begin{pmatrix} \frac{1}{4}(3\mu_H + \mu_D) & \frac{1}{4}(\mu_D - \mu_H) & \frac{1}{4}(\mu_D - \mu_H) & \frac{1}{4}(\mu_D - \mu_H) \\ \frac{1}{4}(\mu_D - \mu_H) & \frac{1}{4}(3\mu_H + \mu_D) & \frac{1}{4}(\mu_D - \mu_H) & \frac{1}{4}(\mu_D - \mu_H) \\ \frac{1}{4}(\mu_D - \mu_H) & \frac{1}{4}(\mu_D - \mu_H) & \frac{1}{4}(3\mu_H + \mu_D) & \frac{1}{4}(\mu_D - \mu_H) \\ \frac{1}{4}(\mu_D - \mu_H) & \frac{1}{4}(\mu_D - \mu_H) & \frac{1}{4}(\mu_D - \mu_H) & \frac{1}{4}(3\mu_H + \mu_D) \end{pmatrix}$$

The calculation of the minors of \mathbf{G}^i directly from the matrix is seen to be rather tedious. As \mathbf{A}^D has only one column the coefficients K_{14}^D , K_{16}^D , K_{17}^D and K_{18}^D are the only non-vanishing among the pure D -coefficients. In this special case this is also easily seen from \mathbf{G}^D . All four coefficients are equal to $\frac{1}{4}$. From these data only we may construct the coefficient-scheme as follows: The common denominator for the coefficients is 4 and we arrange the scheme with 4 rows. The first column (corresponding to S_{14}) shall hold one D and three H arbitrarily arranged as $K_{14}^D = \frac{1}{4}$. The second column shall also hold one D and three H as $K_{16}^D = \frac{1}{4}$, but as $K_{14,16}^D = 0$ the D must not be placed in the same row as the D in the first column. Likewise the third and

¹ SVEND BRODERSEN, loc. cit. p. 12.

the fourth column contain one D each in a row not holding any other D . Thus we get the following scheme:

S_{14}	S_{16}	S_{17}	S_{18}
D	H	H	H
H	D	H	H
H	H	D	H
H	H	H	D

where the order of the rows is arbitrary.

6. Condition for the Rule in Terms of the Number of Symmetry Coordinates.

We shall show that it is a sufficient condition for the rule, that none of the classes of the full-symmetry compounds contain more than one isotopic symmetry coordinate each.

In this case the isotopic \mathbf{G} matrix of any hybrid class is diagonal and its coefficient-scheme consists of a single row. The coefficient-scheme of a given class of an intermediate compound may be rather complicated, but all the principal $|\mathbf{G}^i|$ -minors (all contributing minors are principal) may be written as the same linear combination of the corresponding minors of certain hybrid classes. The form of this linear combination, and consequently of the determinantal equation, is immediately given by the coefficient-scheme for the class of the intermediate compound. The form of the hybrid classes are given by the order of H and D in the different rows and the coefficients are given by the number of identical rows, divided by the total number of rows. For instance the coefficient-scheme and the determinantal equation for the A_2 class of ortho-benzene- d_2 are:

B_{2g}	E_u^+	E_g^-
H	H	D
D	H	H
D	H	H
H	D	H
H	D	H
H	D	H

$$[(A_2)^{o-d_2}] = \frac{1}{6} [(B_{2g})^{d_0} (E_u^+)^{d_0} (E_g^-)^{d_6}]$$

$$+ \frac{1}{3} [(B_{2g})^{d_6} (E_u^+)^{d_0} (E_g^-)^{d_0}]$$

$$+ \frac{1}{2} [(B_{2g})^{d_0} (E_u^+)^{d_6} (E_g^-)^{d_0}].$$

Although clearly sufficient, the above given condition need not be a necessary one. We have, however, not been able to find any rules for cases not satisfying the condition. We think, therefore, that it is in fact also a necessary one.

The condition for a complete rule, giving the frequencies of a certain class of an intermediate compound is, that none of the corresponding classes of the full symmetry compounds contain more than one isotopic symmetry coordinate each.

This includes even certain cases in which the isotopic substitution does not affect all the atoms of a set, but divides it into two (or more) sets so that the number of isotopic symmetry coordinates in each symmetry class is reduced to one. Thus, for instance, the frequencies of the planar vibrations of benzene- d_1 are given by those of benzene- d_0 and para-benzene- d_2 in spite of the fact that there are 3 isotopic coordinates in each class of para-benzene- d_2 . In this case, however, D_{2h} is to be considered as the full symmetry, which means that the para-atoms form a symmetrical set with only one isotopic coordinate in each class.

One may feel such a condition to be so strict that complete rules should be too scarce to be of any practical value. In view of the extensive information given by these rules, the number of cases in which they are strictly valid, naturally must be expected to be rather small. It is, however, in many important cases possible to introduce an approximation which considerably increases the number of rules.

7. Approximate Rules.

For deuterated hydrocarbons the rules may—as discussed previously¹—be split into three separate rules: (1) for the hydrogen stretching frequencies, (2) for the deuterium stretching frequencies, and (3) for the remaining lower frequencies. The reason for this is, that the hydrogen and deuterium stretching modes may be given almost exclusively by use of definite isotopic symmetry coordinates, which on the other hand play a secondary role for the modes corresponding to the lower vibrational frequencies. We may therefore split the symmetry coordinates and the coefficient-scheme correspondingly. In many cases this will reduce the number of isotopic symmetry coordinates in each class of the full-symmetry compounds to one, thus producing new complete rules valid within the given approximation and applicable to the three frequency ranges separately. This point will be discussed in detail in our following paper on benzene.

8. Conditions for the Rule in Terms of Molecular Symmetry.

At this point it is possible to go through all the different point groups, setting up all the rules existing. This would, however, require too much space compared to the usefulness of the result. We shall, therefore, confine ourselves to a discussion of some of the more important point groups.

C_1 (*no symmetry at all*). There is only one atom in each equivalent set and no rules exist.

$D_{\infty h}$ (*linear, symmetrical molecules*). All atoms outside the center form sets of two atoms each. Partial isotopic substitution in one of these sets yields a compound of symmetry $C_{\infty v}$. The symmetry classes are:

¹ SVEND BRODERSEN and A. LANGSETH, Mat. Fys. Skr. Dan. Vid. Selsk. **1**, no. 1 (1956), pag. 44.

$D_{\infty h}$	$C_{\infty v}$
Σ_g^+	
Σ_u^+	Σ^+
Π_g	
Π_u	Π

The rules (strictly valid) giving all the frequencies of the $C_{\infty v}$ -molecule are:

$$[(\Sigma^+)^{d_1}] = \frac{1}{2} [(\Sigma_g^+)^{d_0} (\Sigma_u^+)^{d_2}] + \frac{1}{2} [(\Sigma_g^+)^{d_2} (\Sigma_u^+)^{d_0}] \quad (8)$$

$$[(\Pi)^{d_1}] = \frac{1}{2} [(\Pi_g)^{d_0} (\Pi_u)^{d_2}] + \frac{1}{2} [(\Pi_g)^{d_2} (\Pi_u)^{d_0}]. \quad (9)$$

As an example of this point group the acetylene molecule will be discussed below.

C_{2v} (a vertical two-fold axis, C_2 , and two vertical, perpendicular planes, σ_1 and σ_2). The numbers of atoms in the different sets are:

$$\begin{aligned} & \text{on } C_2: 1 \\ & \text{in } \sigma_1 \text{ or } \sigma_2, \text{ but not on } C_2: 2 \\ & \text{elsewhere: 4} \end{aligned}$$

Only the sets of two atoms each give us any rules. Partial substitution in such a set yields a compound of symmetry C_s . The symmetry classes are:

C_{2v}	C_s
A_1	
B_1	A'
A_2	
B_2	A''

The out-of-plane frequencies (A'' -class) are given by a strictly valid rule

$$[(A'')^{d_1}] = \frac{1}{2} [(A_2)^{d_0} (B_2)^{d_2}] + \frac{1}{2} [(A_2)^{d_2} (B_2)^{d_0}]. \quad (10)$$

The in-plane frequencies (A' -class) are given by an approximate rule which for either of the three frequency ranges may be written on the same form:

$$[(A')^{d_1}] = \frac{1}{2} [(A_1)^{d_0} (B_1)^{d_2}] + \frac{1}{2} [(A_1)^{d_2} (B_1)^{d_0}]. \quad (11)$$

C_{2h} (a vertical two-fold axis, C_2 , and a horizontal plane, σ). The number of atoms in the different sets are:

$$\begin{aligned} & \text{both on } C_2 \text{ and in } \sigma: 1 \\ & \text{on } C_2, \text{ but not in } \sigma: 2 \\ & \text{in } \sigma, \text{ but not on } C_2: 2 \\ & \text{elsewhere: 4} \end{aligned}$$

Again, only the sets of two atoms each give us any rules. Partial substitution in the

set on C_2 yields a compound of symmetry C_2 , but in the set in σ , a compound of symmetry C_s . The symmetry classes are:

C_{2h}	C_s	C_2
A_g	A'	A
B_u		B
B_g	A''	A
A_u		A

The frequencies of the classes A'' (out-of-plane) and A (parallel) are given by the strictly valid rules:

$$[(A'')^{d_1}] = \frac{1}{2} [(B_g)^{d_0} (A_u)^{d_2}] + \frac{1}{2} [(B_g)^{d_2} (A_u)^{d_0}] \quad (12)$$

$$[(A)^{d_1}] = \frac{1}{2} [(A_g)^{d_0} (A_u)^{d_2}] + \frac{1}{2} [(A_g)^{d_2} (A_u)^{d_0}]. \quad (13)$$

The other frequencies are given by the approximate rules:

$$[(A')^{d_1}] = \frac{1}{2} [(A_g)^{d_0} (B_u)^{d_2}] + \frac{1}{2} [(A_g)^{d_2} (B_u)^{d_0}] \quad (14)$$

$$[(B)^{d_1}] = \frac{1}{2} [(B_g)^{d_0} (B_u)^{d_2}] + \frac{1}{2} [(B_g)^{d_2} (B_u)^{d_0}]. \quad (15)$$

D_{2h} (three perpendicular planes). The number of atoms in the sets are

- in all three planes: 1
- in two planes: 2
- in one plane only: 4
- elsewhere: 8

Here both the sets of two and of four atoms give us some rules.

Partial substitution in the set in two planes (on a C_2 -axis) gives a compound of symmetry C_{2v} . Partial substitution in the set in one plane only gives compounds of different symmetries: one or three deuterium atoms give C_s , two neighbouring atoms gives C_{2v} and two opposite atoms gives C_{2h} . The C_s -compound may, however, be considered as a partially substituted compound of either the C_{2v} - or the C_{2h} -compounds. The symmetry classes are:

D_{2h}	C_s	C_{2v}	C_{2h}
A_{1g}	A'	A_1	A_g
B_{1u}			B_u
B_{3u}		B_1	A_g
B_{2g}			A_g
B_{3g}	A''	B_2	B_g
B_{2u}			A_u
A_{1u}		A_2	A_u
B_{1g}			B_g

where we have assumed a definite orientation.

All the frequencies of the first C_{2v} -compound are given by the strictly valid rules:

$$[(A_1)^{d_1}] = \frac{1}{2} [(A_{1g})^{d_0} (B_{1u})^{d_2}] + \frac{1}{2} [(A_{1g})^{d_2} (B_{1u})^{d_0}] \quad (16)$$

and the analogous rules for the A_2 , B_1 and B_2 classes.

For the other three compounds we get strictly valid rules for the A'' , A_2 , B_2 , B_g and A_u classes *viz.* the classes with oscillations perpendicular to the plane of the equivalent set in question (often the molecular plane). For the A_2 class we get:

$$[(A_2)^{d_2}] = \frac{1}{2} [(A_{1u})^{d_0} (B_{1g})^{d_4}] + \frac{1}{2} [(A_{1u})^{d_4} (B_{1g})^{d_0}] \quad (17)$$

and analogous for the B_2 , B_g and A_u classes. For the A'' class we get (assuming for instance a tri-deuterocompound):

$$\left. \begin{aligned} [(A'')^{d_3}] &= \frac{1}{4} [(B_{3g})^{d_4} (B_{2u})^{d_4} (A_{1u})^{d_4} (B_{1g})^{d_0}] \\ &+ \frac{1}{4} [(B_{3g})^{d_4} (B_{2u})^{d_4} (A_{1u})^{d_0} (B_{1g})^{d_4}] \\ &+ \frac{1}{4} [(B_{3g})^{d_4} (B_{2u})^{d_0} (A_{1u})^{d_4} (B_{1g})^{d_4}] \\ &+ \frac{1}{4} [(B_{3g})^{d_0} (B_{2u})^{d_4} (A_{1u})^{d_4} (B_{1g})^{d_4}]. \end{aligned} \right\} \quad (18)$$

But as mentioned above we may consider the C_s -compound as a partly substituted C_{2v} - or C_{2h} -compound and use the rules given for these point groups. The result is naturally the same, but the last method is often simpler to use in practice, especially if we wish to calculate the frequencies of all the intermediate compounds. The frequencies of the remaining classes (in-plane) are only given by approximate rules, the form of which are analogous to those for the out-of-plane frequencies.

The ethylene molecule will be discussed below as an example.

D_{6d} (*e. g.* benzene). All the out-of-plane and some of the in-plane frequencies of all eleven partly deuterated compounds are given by strictly valid rules, all the remaining frequencies being given by approximate rules. This case will be dealt with in detail in a following paper.

C_{3v} (*e. g.* methyl halides) and T_d (*e. g.* methane). No complete rules exist.

9. Single-Order Rules.

As mentioned above (p. 5) the complete rule may be resolved into a number of relations each giving one of the coefficients in the expanded secular equation of the given class of the intermediate compound. The first of these relations, giving the coefficient c_1 expressed in terms of first degree in λ , may be called a first-order rule, the next one a second-order rule etc.

If a complete rule does not exist, single-order rules may do. The condition for the validity of a single-order rule is the same as for the complete rule, but only including some of the contributing minors. If the class in question has s non-isotopic

symmetry coordinates and t isotopic ones, the condition for a n -order rule will include only the minors of orders: $n, (n-1), (n-2), \dots, (n-s)$ if $n \leq t$ and of orders $t, (t-1), (t-2), \dots, (n-s)$ if $n \geq t$. This means that the condition for a first-order rule includes only the first order contributing minors of the isotopic \mathbf{G} matrix and these are all principal minors. The condition for a highest-order rule—of order $(s+t)$ —includes only one minor of order t , which is $|\mathbf{G}^t|$ itself.

The first order rules are usually identical with the sum-rules as formulated by DECIUS and WILSON¹. The highest-order rules constitute very convenient expressions for the product rule if we—according to REDLICH²—insert the value of the ratio of frequencies for non-genuine vibrations, if any.

The condition for, say, a second-order rule is that all contributing minors of first and second order can be written as the same linear combination of corresponding minors. This condition is much stricter than those for the first and the highest order rules, and it is in fact almost as strict as the one for the complete rule. The intermediate-order rules are consequently very scarce except for the cases in which the complete rule is valid.

III. EXAMPLES

In the following we shall demonstrate the use of the rule by means of two examples, acetylene and ethylene. In order to show the most convenient method for carrying through such calculations in practice the calculation of the frequencies of acetylene-d₁ is considered in detail. The ethylene molecule is used to discuss the application of the approximate, splitted rules.

1. Acetylene.

This is a linear, symmetrical molecule of point group $D_{\infty h}$. The equations to be used in order to calculate the frequencies of acetylene-d₁ are given on page 14:

$$[(\Sigma^+)^{d_1}] = \frac{1}{2} [(\Sigma_g^+)^{d_0} (\Sigma_u^+)^{d_2}] + \frac{1}{2} [(\Sigma_g^+)^{d_2} (\Sigma_u^+)^{d_0}] \quad (19)$$

$$[(\Pi)^{d_1}] = \frac{1}{2} [(\Pi_g)^{d_0} (\Pi_u)^{d_2}] + \frac{1}{2} [(\Pi_g)^{d_2} (\Pi_u)^{d_0}] \quad (20)$$

The frequencies of acetylene-d₀ and -d₂ are given in Table 1. Taking the squares we get the λ 's leaving out the constant $4\pi^2 c^2$. The coefficients of the classes of both light and heavy compound are simply for the Σ_g^+ class: $c_1 = \lambda_1 + \lambda_2$ and $c_2 = \lambda_1 \lambda_2$ and

¹ J. C. DECIUS and E. B. WILSON, loc. cit. The symmetry condition attached to the stoichiometric condition, introduced by these authors, need not necessarily be fulfilled, as will be demonstrated for the non-planar vibrations of para-benzene-d₂.

² O. REDLICH, loc. cit. quoted by E. B. WILSON, JR., J. C. DECIUS, P. C. CROSS: Molecular Vibrations, Mc Graw-Hill (1955) p. 183.

for the other classes: $c_1 = \lambda$. Now we form the coefficients of the four hybrid classes by means of the expressions given on page 5. They have three and two coefficients respectively equal to the number of frequencies. Next we form the mean values of each coefficient from corresponding hybrid classes, getting according to Eq. (19) and (20) the coefficients of acetylene-d₁. Solving the secular equations with these coefficients we get the frequencies quoted in Table 1.

TABLE 1.
Acetylene. Frequencies in cm^{-1} .

Freq. No.	Sym. Class		-d ₀	-d ₂	-d ₁		
	$D_{\infty h}$	$C_{\infty v}$	Obs. ^a	Obs. ^b	Obs. ^c	Calc.	Calc. — Obs.
1	Σ_g^+	Σ^+	3373.3	2703.56	3335.58	3335.4	-0.2
2			1973.5	1764.71	1853.75	1853.4	-0.4
3			Σ_u^+	3288.4	2439.10	2583.64	2582.6
4	Π_g	Π	611.6	511.38	518.31	519.3	+1.0
5			Π_u	729.2	538.66	ca 679	677.5

a. H. C. ALLEN, E. D. TIDWELL and E. K. PLYLER, J. Research NBS **57**, 213 (1956). M. T. CHRISTENSEN, D. R. EATON, B. A. GREEN and H. W. THOMPSON, Proc. Roy. Soc. London A **238**, 15 (1956). E. F. BELL and H. H. NIELSEN, J. Chem. Phys. **18**, 1382 (1950). ν_3 is given as the mean value of a resonance doublet: 3281.9 and 3294.9 cm^{-1} .

b. R. M. TALLEY and A. H. NIELSEN, J. Chem. Phys. **22**, 2030 (1954).

c. H. C. ALLEN, E. D. TIDWELL and E. K. PLYLER, J. Am. Chem. Soc. **78**, 3034 (1956). The value of ν_3 is from H. M. RANDALL and E. F. BARKER, Phys. Rev. **45**, 124, (1934). A value of 687 cm^{-1} has been given by F. STITT, J. Chem. Phys. **8**, 56 (1940).

The agreement between calculated and observed values is much better than could be expected for a rule based on the harmonic approximation. The reason for this is that the anharmonicity tends to cancel out by this "interpolation" between the frequencies for a light and a heavy compound.

For the value of ν_3 in acetylene-d₀ we have simply used the mean value of the observed doublet: 3281.9 and 3294.9 cm^{-1} . As the interpretation of this doublet is a little in doubt, whereas all the parallel frequencies of acetylene-d₁ and -d₂ are well known, it seems more interesting to calculate the frequencies of -d₀ from those of -d₁ and -d₂. This is in fact possible on basis of the equations given above, but the result is comparatively inaccurate as is to be expected for any extrapolation. It is much better (and easier) to vary the doubtful value of ν_3 and find the best fit for the frequencies of -d₁. This is obtained for $\nu_3 = 3289 \pm 2 \text{ cm}^{-1}$, which seems to prove that the doublet is in fact a resonance doublet with ν_3 contributing a little more to the component of highest frequency than to the other component. This interpretation is confirmed by the intensity and the rotational structure¹.

¹ Reference a of Table 1.

2. Ethylene.

This molecule of point group D_{2h} has five partly deuterated species:

- d₁ and -d₃ of point group C_s
- trans -d₂ of point group C_{2h}
- cis -d₂ of point group C_{2v}
- asym-d₂ of point group C_{2v}

the remaining axis being differently oriented in the last two compounds. The frequencies are distributed over the symmetry classes in the following way:

-d ₀ and -d ₄		asym-d ₂		cis-d ₂		trans-d ₂		-d ₁ and -d ₃	
A_{1g}	1, 2, 3	A_1	1, 2, 3	A_1	1, 2, 3,	A_g	1, 2, 3,	A'	1, 2, 3,
B_{1g}	5, 6		11, 12		9, 10		5, 6		5, 6,
B_{2u}	9, 10	B_1	5, 6,	B_1	5, 6,	B_u	9, 10		9, 10,
B_{3u}	11, 12		9, 10		11, 12		11, 12	11, 12	
A_{1u}	4	B_2	7, 8	B_2	7	B_g	8	A''	4, 7, 8
B_{1u}	7		A_2		4		A_2		
B_{2g}	8								

Equations expressing the frequencies of the partly deuterated compounds in terms of those of -d₀ and -d₄ are given above (p. 15)¹.

The out-of-plane frequencies are easily calculated by means of the strictly valid rules. In order to calculate the in-plane frequencies we have to use the approximate rules based on the separation of the frequencies in 1. low frequencies, 2. deuterium stretching frequencies, and 3. hydrogen stretching frequencies. As the rules are of the same form for all three kinds of frequencies we may handle these either separately or jointly. The result should within the approximation be the same. In practice it is always easiest to handle the frequencies separately.

The low in-plane frequencies (no. 2, 3, 6, 10 and 12) of asym-d₂, cis-d₂ and trans-d₂ are calculated in the usual way. The frequencies of -d₁ and -d₃ are then calculated on basis of the frequencies of any of these compounds and -d₀ or -d₄ using the equations for the point groups C_{2v} or C_{2h} (p. 14). Here we should use the coefficients of the composite classes of the D_{2h} -compounds considered as a compound of lower symmetry. These we get by the same procedure as for hybrid classes (p. 5).

When calculating the high frequencies (no. 1, 5, 9 and 11) separately as deuterium or hydrogen frequencies some of the frequencies to be used are missing, which is, however, a further simplification. For instance the hydrogen frequency of the A_1 class of asym-d₂ is to be calculated from the rule

$$[(A_1)^{asym-d_2}] = \frac{1}{2} [(A_{1g})^{d_0} (B_{3u})^{d_4}] + \frac{1}{2} [(A_{1g})^{d_4} (B_{3u})^{d_0}]. \quad (21)$$

¹ The symbols used here are those of Herzberg (Infrared and Raman Spectra, von Nostrand, 1955). The orientation used on p. 15 is different from this in order to be consistent with our forthcoming paper on benzene.

TABLE 2.

Ethylene.

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	3026	3002	3017	2299	2285	2281	2260
		<i>3005</i>	<i>3008</i>	<i>2303</i>	<i>2285</i>	<i>2284</i>	
		+ 3	- 9	+ 4	0	+ 3	
2	1623	1606	1585	1571	1571	1547	1518
		<i>1595</i>	<i>1581</i>	<i>1554</i>	<i>1561</i>	<i>1539</i>	
		- 11	- 4	- 17	- 10	- 8	
3	1342	1290	1031	1218	1286	1045	985
		<i>1299</i>	<i>1030</i>	<i>1232</i>	<i>1299</i>	<i>1044</i>	
		+ 9	- 1	+ 14	+ 13	- 1	
4	1027	1000	unobs.	unobs.	988	765	726
		<i>1002</i>	<i>889</i>	<i>983</i>	<i>989</i>	<i>767</i>	
		+ 2			+ 1	+ 2	
5	3103	3061	2334	3054	3045	2332	2310
		<i>3059</i>	<i>2328</i>	<i>3047</i>	<i>3065</i>	<i>2331</i>	
		- 2	- 6	- 7	+ 20	- 1	
6	1236	1129	1150	1039	1004	999	1011
		<i>1127</i>	<i>1150</i>	<i>1032</i>	<i>1002</i>	<i>1001</i>	
		- 2	0	- 7	- 2	+ 2	
7	949	808	751	842	726	724	720
		<i>808</i>	<i>753</i>	<i>842</i>	<i>722</i>	<i>722</i>	
		0	+ 2	0	- 4	- 2	
8	947	944	943	763	864	919	785
		<i>948</i>	<i>948</i>	<i>762</i>	<i>870</i>	<i>921</i>	
		+ 4	+ 5	- 1	+ 6	+ 2	
9	3106	3096	3093	3059	3065	3049	2345
		<i>3105</i>	<i>3105</i>	<i>3066</i>	<i>3048</i>	<i>3056</i>	
		+ 9	+ 12	+ 7	- 17	+ 7	
10	810	713	660	646	678	610	584
		<i>717</i>	<i>671</i>	<i>649</i>	<i>661</i>	<i>617</i>	
		+ 4	+ 11	+ 3	- 17	+ 7	
11	2990	2276	2230	2254	2273	2222	2200
		<i>2279</i>	<i>2230</i>	<i>2255</i>	<i>2273</i>	<i>2222</i>	
		+ 3	0	+ 1	0	0	
12	1444	1401	1384	1342	1299	1289	1078
		<i>1401</i>	<i>1384</i>	<i>1354</i>	<i>1298</i>	<i>1299</i>	
		0	0	+ 12	- 1	+ 10	

* For referencies see SVEND BRODERSEN, loc. cit. p. 15.

Here the $-d_0$ classes only contain hydrogen frequencies (no. 1 and 11 resp.) and the hybrid classes consequently contain the same frequencies only. The equation, therefore, simply states that the hydrogen frequency of the A_1 class of asym- d_2 is the mean value of no. 1 and no. 11 of $-d_0$. (Strictly speaking, the mean value should be made from the λ 's, but the difference is usually insignificant for high frequencies).

The frequencies used and the result of the calculation are given in Table 2. The agreement with the observed values is not as good as for acetylene- d_1 , but at least as good as for the frequencies calculated from a complete, harmonic potential function¹. Naturally the agreement could not be expected to be as good for the approximate rules as for the strictly valid ones. A part of the deviation is doubtless due to experimental errors, as well as there may be assignment errors.

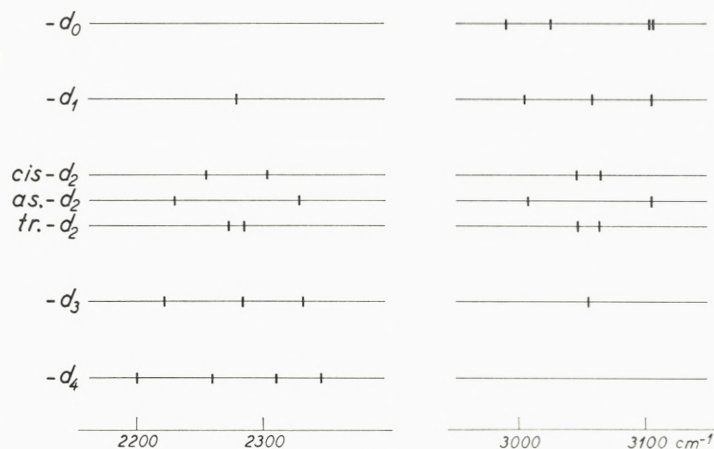


Fig. 1.

The results of the calculations are conveniently illustrated by diagrams analogous to those used previously for sym-benzene- d_3 ². These diagrams are always very useful as illustrations of rules giving a determinant as the mean value of those of two hybrid classes. The calculated high frequencies are sketched in Fig. 1.

¹ SVEND BRODERSEN, loc. cit. p. 16.

² SVEND BRODERSEN and A. LANGSETH, loc. cit. p. 37-39.

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