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Citation: *The Journal of Chemical Physics* **17**, 1026 (1949); doi: 10.1063/1.1747108

View online: <http://dx.doi.org/10.1063/1.1747108>

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Developments in the Theory of the Secular Equation for Molecular Vibrations

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(Received December 16, 1948)

A general solution for the secular equation is obtained, giving the force constants and normal coordinates, for any molecule, in terms of the fundamental vibration frequencies and molecular constants. The solution is based on the reduction of the secular determinant to Jacobian canonical form; it is shown to have a simple physical interpretation. Methods are developed which enable adjustments to be made to the standard solution as required. The theory is fully illustrated by several worked examples.

I. INTRODUCTION

THE process of calculating the force constants in the potential function for a given molecule from its fundamental vibration frequencies is one determined to some considerable extent by individual preference. One usually carries over as many constants as possible from related molecules and adjusts the whole set to fit the observed frequencies, introducing interaction constants where the adjustment required appears unreasonable. This process involves a series of trial-and-error calculations. As data on various related molecules accumulate, it is in principle possible to adjust the values of the force constants to obtain sets which are mutually consistent, so that any variations from an accepted "normal" value can be taken as having physical significance. In practice, there is usually considerable ambiguity, and values differing by amounts up to 10 percent may be obtained for a given force constant by investigators using different force fields on the same molecule. It would therefore be useful to have available a procedure for obtaining a set of force constants characteristic of each molecule, corresponding to some ideal solution, and for making adjustments to this solution as required. Such a procedure is worked out in the present investigation.

II. THE DERIVATION OF THE SECULAR EQUATION

The secular equation can be expressed in several different forms which, for the sake of completeness, will be derived here from first principles. For a molecule with n vibrational degrees of freedom, in which the motions are assumed to be simple harmonic, the potential energy V can be written as a general quadratic function of n valence-type displacement coordinates Δ_i as follows:

$$2V = \sum_{i=1}^n \sum_{j=1}^n d_{ij} \Delta_i \Delta_j, \quad (1)$$

where the d_{ij} are force constants, the matrix $d = [d_{ij}]$ being symmetric. The n internal coordinates can be expressed in terms of $N(N = n + 6)$ Cartesian displace-

ment coordinates z_j ,

$$\Delta_i = \sum_{j=1}^N a_{ij} z_j, \quad (2)$$

where the coefficients a_{ij} are determined by the geometry of the system; they are conveniently written in the form of a matrix $a = [a_{ij}]$ of order $n \times N$. The equations of motion are

$$(\partial V / \partial z_k) - \lambda m_k z_k = 0, \quad (k = 1 \text{ to } N), \quad (3)$$

where m_k is the mass corresponding to the displacement coordinate z_k , the latter being assumed to be a sinusoidal function of the time, and λ is related to one of the normal vibrational frequencies ν of the system as,

$$\lambda = 4\pi^2 \nu^2. \quad (4)$$

The system of N linear and homogeneous Eqs. (3) in z_1 to z_N requires that the determinant of the coefficients shall vanish. This condition leads to the first form of the secular equation, which can be written as

$$|a'da - \lambda m| = 0, \quad (5)$$

where a' is the transpose of a , and m the diagonal matrix $[m_1 m_2 \cdots m_N]$. The general element of the matrix $b = a'da$ is

$$b_{ij} = \sum_{k=1}^n \sum_{m=1}^N a_{ki} a_{mj} d_{km}. \quad (6)$$

The determinant in Eq. (5) is symmetric and of order N ; the N roots of the equation in λ include the $(N - n)$ zero frequencies of translation and rotation, and the relative displacements $z_1(\nu_k)$ to $z_N(\nu_k)$ in the k th normal mode are given by first minors of any row of the determinant in Eq. (5), with the appropriate root λ_k substituted.

A second form of the equation is obtained by applying the transformation

$$R_p' = \sum_{i=1}^N (|N_a|_{pi} / |N_a|) R_i, \quad (7)$$

giving rows R_p' of a new determinant in terms of rows R_i of Eq. (5); the elements $|N_a|_{pi}$ are first minors of the determinant $|N_a|$ formed from the N th-order square matrix N_a of the coefficients a_{ij} in Eq. (2), in which the last $(N - n)$ rows are from the "null coordinates" expressing the conditions for no translation and

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no rotation (where these are not included in any symmetry properties possessed by the coordinates Δ_i).^a The secular equation now has the following form:

$$|da - \lambda(Na^{-1})'m| = 0, \quad (8)$$

where $(Na^{-1})'$ is the reciprocal of the transpose of Na , and the product da is regarded as a square matrix of order $N \times N$ whose last $(N-n)$ rows consist of zero elements. The general element in Eq. (8) is as follows:

$$b_{ij}' = \sum_{k=1}^n a_{kj} d_{ik} - (|Na|_{ij} / |Na|) \lambda m_j, \quad (9)$$

the first term being zero in the last $(N-n)$ rows. Eq. (8) is again of order N and, since Eq. (7) involves only the rows of Eq. (5), the relative displacements $z_1(\nu_k)$ to $z_N(\nu_k)$ are again given by first minors of any row.

By means of a further transformation giving columns C_q'' of a new determinant in terms of columns C_j' of Eq. (8), as follows:

$$C_q'' = \sum_{j=1}^N a_{qj}(M/m_j)C_j', \quad (10)$$

a third form of the secular equation is obtained, which can be written

$$|dA - \lambda I| = 0, \quad (11)$$

where the elements of the symmetric matrix A are derived from the rows of a in Eq. (2) according to the scheme,

$$A_{ij} = \sum_{k=1}^N a_{ik} a_{jk} (M/m_k). \quad (12)$$

I is the unit matrix, and the quantity λ is redefined as

$$\lambda = 4\pi^2 \sigma^2 c^2 M, \quad (13)$$

σ being now a normal vibration frequency in cm^{-1} and c the velocity of light in cm sec^{-1} . M is an arbitrary mass (usually chosen to be one of the m_k 's), introduced in order that the A_{ij} shall be dimensionless quantities of convenient magnitude. Equation (11) is of order n , the $(N-n)$ null vibrations having been factored out. A is identical with the kinetic energy matrix G of Wilson,¹ apart from the factor M included here for convenience in application; the symbol G is not used in order to avoid confusion. The general element of the matrix $B = dA$ is

$$B_{ij} = \sum_{k=1}^n A_{jk} d_{ik}. \quad (14)$$

The transformation in Eq. (10) leads to the expressions for the relative displacements occurring in any normal

^a If the molecule possesses elements of symmetry, the coordinates Δ_1 to Δ_n are chosen to satisfy the symmetry requirements of the n normal modes in a given symmetry class. Equation (11) is then the symmetry factor of the secular equation for this class of vibration. The total secular equation is the product of all such factors, one from each class.

¹ E. B. Wilson, Jr., J. Chem. Phys. 7, 1047 (1939); 9, 76 (1941).

mode:

$$z_j = \sum_{i=1}^n a_{ij}(M/m_i)D_{ki}, \quad (15)$$

$$\Delta_i = \sum_{j=1}^n A_{ij} D_{kj}, \quad (16)$$

where the D_{ki} and D_{kj} are first minors of the k th row of the secular determinant in Eq. (11), k having any value from 1 to n .

III. THE SOLUTION OF THE SECULAR EQUATION FOR THE FORCE CONSTANTS

The second-degree equation has been dealt with at some length in a recent investigation.² It was found possible to obtain equations giving the complete range of allowed values for the force constants, and to relate these with the forms of vibration and with the potential energy distributions. Formulas were obtained for various singular and related solutions, and it was shown that one of the solutions in which the secular determinant in the form given in Eq. (11) was reduced to the product of its diagonal elements gave reasonable results. No such general treatment is possible with equations of higher degree, but it would be of interest to examine the solution corresponding to the second-degree case, in which the matrix $B = dA$ is reduced to Jacobian canonical form. With the determinant $|B|$ reduced to the product of its diagonal elements, since a given diagonal element B_{kk} is a function of the force constants d_{kj} , ($j = 1$ to n), the root $\lambda_k = B_{kk}$ can be regarded as a group frequency characteristic of the coordinate Δ_k , corrected for interaction with the remainder of the molecule. The conditions for the reduction are^{2a}

$$\sum_{i=1}^n A_{ki} d_{ki} - \lambda_k = 0, \quad (k = 1, 2, \dots, n), \quad (17)$$

$$\sum_{i=1}^n A_{qi} d_{pi} = 0, \quad (p > q), \quad (18)$$

where λ_k is derived from the vibration frequency assigned to the normal mode determined primarily by Δ_k . By analogy with the second-degree case,² the subscripts are ordered so that $\nu_1 > \nu_2 > \dots > \nu_n$. The solution of these $\frac{1}{2}n(n+1)$ linear simultaneous equations gives all the elements of d . For convenience, we introduce two subsidiary matrices e and h , with elements as defined:

$$e_{ij} = i|A|_{ji}, \quad (=0 \text{ for } i > j), \quad (19)$$

$$h_{ij} = \sum_{k=1}^j A_{ik} e_{kj}, \quad (=0 \text{ for } i < j). \quad (20)$$

In the above, $i|A|_{ji}$ is a first minor^b of the j th row of

² P. Torkington, J. Chem. Phys. 17, 357 (1949).

^{2a} P. Torkington, Nature 162, 370, 607 (1948).

^b Throughout, unless otherwise stated, the term "minor" refers to the minor with proper algebraic sign, the first minor being identical with a cofactor; a presubscript is used to indicate the order of a determinantal element, subscripts referring to derived minors.

the j th-order determinant $|A|$ derived from the first j rows and columns of A ; h_{ij} is an unsigned minor of order $(i-j)$ with respect to $|A|$. The general solution for the force constants is found to be

$$d_{ij} = \sum_{k=i}^n (e_{ik}e_{jk}/e_{kk}h_{kk})\lambda_k, \quad (i > j). \quad (21)$$

If, before solving for the constants, the k highest frequencies are factored out by Wilson's method,¹ the same formula applies, the subscripts now referring to elements of the reduced d and A matrices, and λ_1 to λ_n being replaced by λ_{k+1} to λ_n ; nothing is gained here, therefore, by making this initial reduction. The non-diagonal elements of d will in general be small compared with the diagonal elements; several obvious approximations arise from Eq. (21). In the next section, methods will be given for eliminating all small interaction constants by adjusting the remainder.

If the λ_k are disregarded, the elements of the series in Eq. (21) are seen to be the terms of a general Schweinsian expansion; because of this fact, the force constants d_{ij} , ($i > j$), can be expressed in terms of λ_i and of the differences $(\lambda_i - \lambda_k)$, as

$$d_{ij} = ({}^n|A|_{ij}/{}^n|A|)\lambda_i - \sum_{k=i+1}^n (e_{ik}e_{jk}/e_{kk}h_{kk})(\lambda_i - \lambda_k). \quad (22)$$

The upper non-diagonal elements of the matrix $B = dA$ follow from Eq. (22):

$$B_{ij} = \sum_{k=i}^j (e_{ik}h_{jk}/e_{kk}h_{kk})\lambda_k, \quad (=0 \text{ for } i > j). \quad (23)$$

An alternative form of Eq. (23) is convenient,

$$B_{ij} = - \sum_{k=i+1}^j (e_{ik}h_{jk}/e_{kk}h_{kk})(\lambda_i - \lambda_k), \quad (=0 \text{ for } i > j). \quad (24)$$

The normal coordinates corresponding to the solution for the force constants in Eq. (21) can now be found. For the k th normal mode, $(B_{kk} - \lambda_k = 0)$, the first k members of the first minors D_{ki} of the k th row of the secular determinant in Eq. (11) are found to be proportional to the corresponding elements e_{ik} of the matrix e defined in Eq. (19); $D_{k,k+1}$ to D_{kn} become zero. Thus,

$$D_{k1}:D_{k2}:\cdots:D_{kk}:D_{k,k+1}\cdots D_{kn}::e_{1k}:e_{2k}:\cdots:e_{kk}:0:\cdots:0. \quad (25)$$

With the above ratios for the minors, the relative atomic displacements describing the geometrical form of a given normal mode are

$$z_j(\nu_k) = (M/m_j) \sum_{i=1}^k a_{ij}e_{ik}, \quad (26)$$

and the components in the displacements from the

coordinates Δ_1 to Δ_n ,

$$\Delta_i(\nu_k) = h_{ik}, \quad (=0 \text{ for } i < k). \quad (27)$$

The quantities defined in Eqs. (26) and (27) are the coefficients in the linear transformations giving the displacements z_j and Δ_i in terms of the (unnormalized) normal coordinate for ν_k .² To normalize them, the total potential energy in Eq. (1) is required in terms of the displacements Δ_i as defined in Eq. (27). It is found that

$$2V(\nu_k) = e_{kk}h_{kk}\lambda_k. \quad (28)$$

The potential energy distribution for any given normal mode can now be obtained; the following relations are found to hold:

$$\sum_{i=1}^n V_{ki}(\nu_k) = 1, \quad (29)$$

$$\sum_{i=1}^n V_{mi}(\nu_k) = 0, \quad (m \neq k), \quad (30)$$

where $V_{ij}(\nu_k)$ is the fraction of the total potential energy in the term $d_{ij}\Delta_i\Delta_j$, for the k th normal mode, and d_{ij} and d_{ji} are counted separately.

The solution dealt with in this section has a simple physical interpretation. The displacement for ν_k involves only the coordinates Δ_k to Δ_n ; thus the reduction of the matrix $B = dA$ to Jacobian canonical form causes the fundamental vibration frequencies to factor out in order of decreasing magnitude, the molecule increasing in rigidity as factorization proceeds. (Compare Taylor and Pitzer.³) The force constants d_{ij} are expressed in terms of λ_i to λ_n only (where i is greater than j); they are derived from the rows of the subsidiary matrix e in a manner analogous to that in which the A_{ij} are derived from a . The solution is always real, and it is found that the normal coordinates correspond to the vibrations having idealized geometrical forms; thus, in valence vibrations, the atomic displacement vectors in general lie along the appropriate valence bonds. This last fact is readily seen in the case of ν_1 , for which $z_j \propto (a_{ij}/m_j)$.

IV. VARIATIONS FROM THE STANDARD SOLUTION

The standard solution derived in the last section gives all the elements of the matrix d as explicit functions of minors of A and of the vibration frequencies. In practice, many of the nondiagonal elements of d will be found to have small values, this applying to most which would normally be discarded before solving for the constants. To eliminate them, we require the various

² The linear transformation giving the (unnormalized) normal coordinates is found to be $\eta_i = \sum_{j=1}^i e_{ji}\Delta_j$, where η_i is the normal coordinate for the i th normal mode.

³ W. J. Taylor and K. S. Pitzer, J. Research Nat. Bur. Stand. 38, 1 (1947).

derivatives ($\partial\lambda_k/\partial d_{ij}$); in this section, these quantities will also be obtained as explicit functions of minors of $|A|$.

Consider the general expanded form of the secular equation of order n ,

$$\lambda^n - c_1\lambda^{n-1} + c_2\lambda^{n-2} \dots + (-1)^{n-1}c_{n-1}\lambda + (-1)^nc_n = 0. \quad (31)$$

The coefficients c_1 to c_n are related to the matrix B of Eq. (14) as

$$c_i = sp_i |B|, \quad (32)$$

where sp_i stands for the sum of all principal minors of order i . c_i is also the i th elementary symmetric function of the n roots λ_1 to λ_n of Eq. (31). For small variations of the coefficients c_i , the corresponding variations in any root λ_k are governed by the relation,

$$(\partial\lambda_k/\partial c_i) = (|\sigma|_{ik}/|\sigma|), \quad (33)$$

where $|\sigma|$ is the Jacobian of c_1 to c_n with regard to λ_1 to λ_n , and $|\sigma|_{ik}$ is the cofactor of the element σ_{ik} ; the general element σ_{ij} is the $(i-1)$ th symmetric function minus all terms involving λ_j , the first row consisting of unit elements. The minors of the Jacobian are found to have the form

$$|\sigma|_{ik} = (-1)^{i+k}\lambda_k^{n-i} \prod_{p,q} (\lambda_p - \lambda_q), \quad (p < q; p, q \neq k). \quad (34)$$

The Jacobian itself is the difference-product of λ_1 to λ_n :

$$|\sigma| = \prod_{i,j} (\lambda_i - \lambda_j), \quad (i < j). \quad (35)$$

It follows that

$$(\partial\lambda_k/\partial c_i) = (-1)^{i+1}\lambda_k^{n-i} \prod_p (\lambda_k - \lambda_p)^{-1}, \quad (p \neq k). \quad (36)$$

The variations in the coefficients c_i may be expressed in terms of variations in the elements B_{ij} , using (32) and the usual rule for differentiating determinants; for diagonal elements,

$$(\partial c_i/\partial B_{jj}) = sp_{i-1} |B|, \quad (=1 \text{ for } i=1), \quad (37)$$

where the subscript j denotes the omission of all minors involving B_{jj} . If products of non-diagonal elements are neglected, the expressions for frequency-variation can be shown to be those derived from the following first approximation to the roots of the secular equation,

$$\lambda_k = B_{kk} + \sum_{i=1}^n [B_{ki}B_{ik}/(B_{kk} - B_{ii})], \quad (i \neq k). \quad (38)$$

This approximation is suitable when ν_k is a group frequency known to be practically independent of the remainder of the molecule; the series following the summation sign is the first-order perturbation term for the kinetic coupling. Where this is known to be slight,^{3a} interaction terms may be neglected and Eq. (38) re-

duces to

$$\lambda_k = d_{kk} \{ A_{kk} + \sum_{i=1}^n [A_{ik}^2/(\lambda_k - \lambda_i)] d_{ii} \}, \quad (i \neq k), \quad (39)$$

where approximate values suffice for the d_{ii} and $(\lambda_k - \lambda_i)$. Equation (39) can be used to predict the shifts in a group frequency caused by coupling of the group to different residues, or to estimate variations in a group force constant caused by electronic interaction with different environments.

From Eq. (14),

$$(\partial B_{mk}/\partial d_{ij}) = \begin{cases} A_{kj} & \text{for } m=i, \\ 0 & \text{for } m \neq i, \end{cases} \quad (40)$$

$$(\partial B_{im}/\partial A_{kj}) = \begin{cases} d_{ij} & \text{for } m=k, \\ 0 & \text{for } m \neq k, \end{cases} \quad (41)$$

where d_{ij} and d_{ji} are counted separately. From Eq. (41), possible errors introduced by uncertainties in the molecular dimensions may be estimated and equations for the isotope effect obtained. Thus, for replacement of the mass m_p by an isotope, the increments in the elements A_{ij} are

$$\Delta A_{ij} = -a_{ip}a_{jp}(M/m_p)(\Delta m_p/m_p), \quad (42)$$

and the associated increments in the elements of B as

$$\Delta B_{ij} = -a_{jp}(M/m_p)(\Delta m_p/m_p) \sum_{k=1}^n a_{kp}d_{ik}. \quad (43)$$

If we ignore non-diagonal elements of d and B , the following expression is obtained for the frequency-shifts:

$$\Delta\lambda_k = -a_{kp}^2 d_{kk}(M/m_p)(\Delta m_p/m_p), \quad (44)$$

and, as a first approximation,

$$(\Delta\lambda_k/\lambda_k) = -(a_{kp}^2/A_{kk})(M/m_p)(\Delta m_p/m_p). \quad (45)$$

Where ν_k is a group frequency, Eq. (45) will give a good approximation; where the coordinates Δ_k and Δ_j overlap to any considerable extent (i.e., where (A_{kj}/A_{kk}) and (A_{kj}/A_{jj}) are of the order of unity), the approximation corresponding to Eq. (44) will be obtained by including terms for d_{jj} and d_{kj} , d_{jk} from B_{kk} , B_{jj} and B_{jk} , B_{kj} .

In favorable cases, where the first term of Eq. (21) gives a good approximation for the constant d_{ij} , the errors introduced by uncertainties in the molecular dimensions are readily estimated,

$$d_{ij}^0 = (e_{ji}^0/h_{ii}^0)\lambda_i, \quad (i > j), \quad (46)$$

$$(\Delta d_{ij}/d_{ij}^0) = (\Delta e_{ji}/e_{ji}^0) - (\Delta h_{ii}/h_{ii}^0), \quad (47)$$

where e^0 and h^0 refer to the model with conventional dimensions (e.g., with angles for exact trigonal and tetrahedral hybrid structures), and the variations correspond to possible variations in these dimensions. The errors caused by uncertainties in the vibration frequencies (such as differences between infra-red and Raman

^{3a} P. Torkington, Nature 164, 113 (1949)..

frequencies), may be evaluated directly from the series in Eq. (21); the approximation given in Eq. (46) serves well enough for the main (square term) constants.

For the standard solution obtained in the last section, it is possible to give explicit expressions for the derivatives $(\partial\lambda_k/\partial d_{ij})$. We first require the variations with respect to the B_{ij} . The following relations are found to hold:

$$(\partial\lambda_k/\partial B_{kj}) = (e_{jk}/e_{kk}), \quad (=0 \text{ for } j > k) \quad (48)$$

$$(\partial\lambda_k/\partial B_{ik}) = (h_{ik}/h_{kk}), \quad (=0 \text{ for } i < k) \quad (49)$$

$$(\partial\lambda_k/\partial B_{ij}) = (\partial\lambda_k/\partial B_{ik})(\partial\lambda_k/\partial B_{kj}), \quad (50)$$

where e and h are the matrices which define the force constants and normal coordinates. (See Eqs. (19) and (20)). The general expression for the variation of a given vibration frequency with any particular force constant, counting d_{ij} and d_{ji} separately, is then

$$(\partial\lambda_k/\partial d_{ij}) = (h_{ik}h_{jk}/e_{kk}h_{kk}), \quad (=0 \text{ for } k > i \text{ or } j). \quad (51)$$

The derivatives for any particular λ_k therefore form the elements of a symmetric matrix of order $(n-k+1)$, derived from A . The standard d matrix obtained by applying the formula given in Eq. (21) may now be suitably adjusted, or partially diagonalized. The increments

$$\Delta\lambda_k = -\sum_{i,j} (\partial\lambda_k/\partial d_{ij})d_{ij}$$

produced by removing interaction constants d_{ij} are found (remembering that d_{ij} and d_{ji} are counted separately), and the necessary increments $\Delta d_{kk} = -[\Delta\lambda_k/(\partial\lambda_k/\partial d_{kk})]$ required to restore the λ_k to their initial values calculated. In the latter process, use is made of the fact that the $(\partial\lambda_k/\partial d_{ij})$ matrices increase in order from ν_n to ν_1 ; the balancing increments Δd_{kk} give rise to further variations in λ_1 to λ_{k-1} , which must be estimated and added to the increments already found. The d_{kk} are therefore adjusted in the order $k=n-1$ to 1, proceeding from λ_{n-1} to λ_1 . The balancing adjustments need not necessarily be carried out on the diagonal elements d_{kk} ; λ_k will usually prove to be most sensitive to d_{kk} , and hence the adjustment required will be a minimum, but in principle it may be performed on any element with a non-zero derivative $(\partial\lambda_k/\partial d_{ij})$.

By means of the above procedure, small non-diagonal elements of d (e.g., these corresponding to zero elements of A), may be removed, and the remainder adjusted to fit data from related molecules. The removal of the larger interaction constants will naturally introduce some degree of approximation; these are often associated with pairs of overlapping coordinates, for which a complete treatment is developed in the following section.

V. TREATMENT OF OVERLAPPING COORDINATES

Where the coordinates Δ_k and Δ_m ($k < m$), overlap to any considerable extent, and the frequency-difference

$(\nu_k - \nu_m)$ is small, the standard solution of Section III will not be satisfactory, since it prohibits Δ_k from taking part in ν_m . This difficulty may be overcome, without introducing any new principle, by replacing Δ_k and Δ_m by two linear combinations of these coordinates, defined as

$$\left. \begin{aligned} \Delta_k' &= p_{kk}\Delta_k + p_{km}\Delta_m \\ \Delta_m' &= p_{mk}\Delta_k + p_{mm}\Delta_m \end{aligned} \right\}, \quad (52)$$

where the ratios (p_{km}/p_{kk}) and (p_{mk}/p_{mm}) are less than unity, to agree with the approximate vibrational assignment. A is then replaced by A' , where the elements of A' are

$$\left. \begin{aligned} A_{kk}' &= p_{kk}^2 A_{kk} + 2p_{kk}p_{km}A_{km} + p_{km}^2 A_{mm} \\ A_{km}' &= p_{kk}p_{mk}A_{kk} + p_{km}p_{mm}A_{mm} \\ &\quad + (p_{kk}p_{mm} + p_{km}p_{mk})A_{km} \\ A_{mm}' &= p_{mk}^2 A_{kk} + 2p_{mk}p_{mm}A_{km} + p_{mm}^2 A_{mm} \\ A_{ki}' &= p_{kk}A_{ki} + p_{km}A_{mi}, \quad (i \neq k, m). \\ A_{mi}' &= p_{mk}A_{ki} + p_{mm}A_{mi}, \quad (i \neq k, m). \\ A_{ij}' &= A_{ij}, \quad (i, j \neq k, m). \end{aligned} \right\}. \quad (53)$$

In the standard solution of $|d'A' - \lambda I| = 0$ (d' being the force constant matrix going with A'), there is no component from Δ_k' in the displacement for ν_m . It follows from Eq. (52) that the initial coordinate Δ_k will take part in ν_m . The treatment can be simplified by taking $p_{kk} = p_{mm} = 1$, $p_{mk} = 0$, and replacing p_{km} by p , which can be regarded as a parameter which in particular determines the extent to which Δ_k takes part in ν_m . Only the case $m = k+1$ will be considered here; this includes all important examples, and there is no particular difficulty in extending the treatment to the general case.

The matrices e' and h' giving the force constants d_{ij}' and the normal coordinates in terms of the coordinates $\Delta_1 \cdots \Delta_k' \cdots \Delta_n$ are readily obtained from A' (see Eqs. (19) and (20)), using Eq. (53). These may now be transformed to e and h , from which are derived the force constants d_{ij} now associated with the initial valence coordinates, and the normal coordinates in terms of these coordinates. The relation between the two sets of force constants is:

$$\left. \begin{aligned} d_{i,k+1} &= d_{i,k+1}' + pd_{ik}', \quad (i \neq k+1) \\ d_{k+1,k+1} &= d_{k+1,k+1}' + 2pd_{k,k+1}' + p^2 d_{kk}' \\ d_{ij} &= d_{ij}', \quad (i, j \neq k+1) \end{aligned} \right\}, \quad (54)$$

these relations going with the transformations

$$\left. \begin{aligned} e_{k+1,i} &= e_{k+1,i}' + pe_{ki}', \quad (i=1 \text{ to } n) \\ &\quad (=0 \text{ for } i < k) \\ e_{mi} &= e_{mi}', \quad (i=1 \text{ to } n, m \neq k+1) \\ &\quad (=0 \text{ for } i < m) \end{aligned} \right\}. \quad (55)$$

$$\left. \begin{aligned} h_{ki} &= h_{ki}' - ph_{k+1,i}', \quad (i=1 \text{ to } n) \\ &\quad (=0 \text{ for } i > k+1) \\ h_{mi} &= h_{mi}', \quad (i=1 \text{ to } n, m \neq k) \\ &\quad (=0 \text{ for } i > m) \end{aligned} \right\}. \quad (56)$$

It is found that e and h can be written as

$$\begin{aligned} e &= e^0 + p e'' \\ h &= h^0 + p h'' \end{aligned} \quad (57)$$

where e^0 and h^0 are the matrices for the standard solution with the initial coordinates, and e'' and h'' have non-zero elements in the k th and $(k+1)$ th columns only, as

$$\left. \begin{aligned} e_{ik}'' &= -(e_{k,k+1}^0)_{ki}, \quad (i=1 \text{ to } k-1). \\ e_{kk}'' &= 0 \\ e_{k+1,k}'' &= e_{kk}^0 \end{aligned} \right\} \quad (58a)$$

$$e_{i,k+1}'' = -(h_{k+1,k+1}^0)_{ki}, \quad (i=1 \text{ to } k+1). \quad (58b)$$

$$\left. \begin{aligned} h_{ik}'' &= (h_{i,k+1}^0)_{kk}, \quad (i=k+1 \text{ to } n). \\ h_{kk}'' &= h_{k+1,k}^0 \end{aligned} \right\} \quad (59a)$$

$$\left. \begin{aligned} h_{i,k+1}'' &= (h_{i,k+2}^0)_{k+2,k}, \quad (i=k+2 \text{ to } n). \\ &= 0 \text{ for } i < k \text{ and } i = k+1. \end{aligned} \right\} \quad (59b)$$

where the subscripts p, q in $(e_{ij}^0)_{pq}$ and $(h_{ij}^0)_{pq}$ refer to minors derived from the determinantal elements e_{ij}^0 and h_{ij}^0 ; (see Eqs. (19) and (20)). In the series expansions for the force constants, in Eq. (21), ${}^k|A|$ must be replaced by ${}^k|A'|$ where it occurs in the denominator of the coefficients of λ_k and λ_{k+1} ; ${}^k|A'|$ can be expressed in terms of p and of minors of $|A|$ as

$${}^k|A'| = {}^k|A| - 2p({}^{k+1}|A|)_{k+1,k} + p^2({}^{k+1}|A|)_{kk}. \quad (60)$$

${}^k|A|$ must also be replaced by ${}^k|A'|$ where it occurs in Eq. (28) from which are obtained the normalization factors for use with e and h .

If desired, the values of p may be chosen to satisfy suitable arbitrary conditions. Two such conditions, with the corresponding solutions for p , are given,

$$(a) \quad (\Delta_k/\Delta_{k+1})(\nu_k) = (\Delta_{k+1}/\Delta_k)(\nu_{k+1}).$$

$$p^2 + p[(h_{kk}^0 + h_{k+1,k}''')/h_{k+1,k}^0] + 1 = 0, \quad (61)$$

$$(b) \quad V_{k,k+1}(\nu_k) = V_{k,k+1}(\nu_{k+1}).$$

$$\begin{aligned} p^2 + p[(h_{kk}^0/h_{k+1,k}^0)\{1 + (\lambda_k/\lambda_{k+1})\} \\ + (h_{k+1,k}^0/h_{k+1,k}''')\{1 - (\lambda_k/\lambda_{k+1})\}] \\ + (h_{kk}^0/h_{k+1,k}''') = 0, \end{aligned} \quad (62)$$

where $(\Delta_i/\Delta_j)(\nu_m)$ is the ratio of the components from the coordinates Δ_i and Δ_j in the displacement for ν_m , and $V_{ij}(\nu_m)$ is the fraction of the potential energy in the term $d_{ij}\Delta_i\Delta_j$ for the m th normal mode. Both Eqs. (61) and (62) always have real roots. Equation (62) also satisfies the conditions $V_{kk}(\nu_k) = V_{k+1,k+1}(\nu_{k+1})$, $V_{kk}(\nu_{k+1}) = V_{k+1,k+1}(\nu_k)$, in the case $k+1=n$; here Δ_k and Δ_{k+1} are the only two coordinates having components in the displacements for ν_k and ν_{k+1} , and there are consequently analogies with the second-degree equation which lead to the existence of related singular solutions.² The above conditions relating the potential energy terms are also satisfied by the two values of p

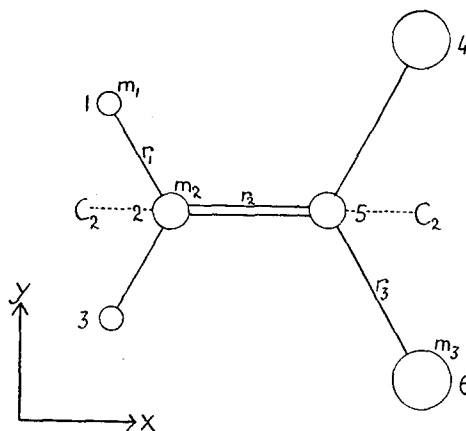


FIG. 1. Coordinates for vinylidene chloride.

which are roots of the equation which is obtained by interchanging the signs of the terms $(\lambda_k/\lambda_{k+1})$ in Eq. (62) if the following additional condition is satisfied:

$$\begin{aligned} [(\lambda_k - \lambda_{k+1})^2/(\lambda_k\lambda_{k+1})] \\ \geq 4[(h_{k+1,k}^0)^2/(e_{kk}^0h_{k+1,k+1}^0)]. \end{aligned} \quad (63)$$

d may be reduced, or adjusted, in the manner already described; the quantities $(\partial\lambda_m/\partial d_{ij})$ are related to e' and h' in the same manner as $(\partial\lambda_m/\partial d_{ij})$ are related to e^0 and h^0 (see Eq. (51)) and $(\partial\lambda_m/\partial d_{ij})$ may be found from $(\partial\lambda_m/\partial d_{ij})$, using Eq. (54). The introduction of the parameter p allows of an alternative treatment, as follows. For small values of p (where for generality $p_{k,k+1}$ is written for p , as in Eq. (52));

$$\begin{aligned} (\partial d_{ij}/\partial p_{k,k+1}) \\ = \sum_{m=k}^{k+1} [(e_{im}^0 e_{jm}'' + e_{jm}^0 e_{im}'')/(e_{mm}^0 h_{mm}^0)] \lambda_m \end{aligned} \quad (64)$$

(where $e_{kk}'' = 0$, and $e_{ik}'' = e_{i,k+1}'' = 0$ for $i > k+1$);

$$\begin{aligned} [\partial \Delta_i(\nu_j)/\partial p_{k,k+1}] &= h_{ij}'', \\ &= 0 \text{ for } j \begin{cases} \leq k \\ > k+1 \end{cases}, i < k, \text{ and } i = j = k+1. \end{aligned} \quad (65)$$

$$\begin{aligned} [\partial z_i(\nu_j)/\partial p_{k,k+1}] &= (M/m_i) \sum_{q=1}^{k+1} a_{qi} e_{qj}'', \\ &= 0 \text{ for } j \begin{cases} \leq k \\ > k+1 \end{cases}. \end{aligned} \quad (66)$$

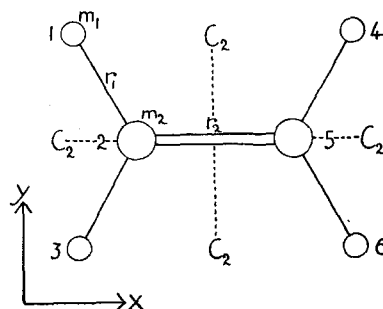


FIG. 2. Coordinates for ethylene.

Equation (64) enables d to be adjusted to correspond to the introduction of one or more small parameters $p_{k,k+1}$; or, conversely, one can estimate the value of $p_{k,k+1}$ required to produce any desired increment in any chosen d_{ij} . Equations (65) and (66) enable the deviations of the displacement vectors from the ideal to be expressed in terms of $p_{k,k+1}$. Equation (65) can also be used to adjust the energy fractions V_{ij} .

VI. EXAMPLES ON THE APPLICATION OF THE METHODS

A. The Class A_1 Vibrations of Vinylidene Chloride

The vinylidene chloride molecule falls into the symmetry point group C_{2v} ; the class A_1 normal vibrations arise from a fifth-order factor in the secular equation. The matrix a for a suitable set of coordinates Δ_i of the required symmetry,⁴ and the derived matrix A , are given below for the coordinates z_j , see Fig. 1.

$$\begin{array}{c}
 \begin{array}{c} z_j = \\ \Delta_1 = \Delta r_{12} + \Delta r_{23} \dots \dots \dots \\ \Delta_2 = \Delta r_{25} \dots \dots \dots \\ \Delta_3 = r_1(\Delta \theta_{13} - \Delta \theta_{15} - \Delta \theta_{35}) \dots \\ \Delta_4 = \Delta r_{45} + \Delta r_{56} \dots \dots \dots \\ \Delta_5 = r_3(\Delta \theta_{46} - \Delta \theta_{24} - \Delta \theta_{26}) \dots \end{array}
 \end{array}
 \begin{array}{c}
 \begin{array}{c} a \\ \begin{array}{cccccc} x_1, x_3 & y_1, -y_3 & x_2 & x_5 & x_4, x_6 & y_4, -y_6 \end{array} \\ \begin{bmatrix} -(1/2) & (\sqrt{3}/2) & 1 & \cdot & \cdot & \cdot \\ \cdot & \cdot & -1 & 1 & \cdot & \cdot \\ \sqrt{3} & 1 & -2\sqrt{3} & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & -1 & (1/2) & (\sqrt{3}/2) \\ \cdot & \cdot & \cdot & 2\sqrt{3} & -\sqrt{3} & 1 \end{bmatrix} \end{array}
 \end{array}
 \begin{array}{c}
 \begin{array}{c} \dots \nu_{CH_2^s} \\ \dots \nu_{CC} \\ \dots \delta_{CH_2^s} \\ \dots \nu_{CCl_2^s} \\ \dots \delta_{CCl_2^s} \end{array}
 \end{array}
 \end{array}$$

$$\begin{array}{c}
 \begin{array}{c} A (M=m_2) \\ \begin{bmatrix} (1+2\mu_1) & -1 & -2\sqrt{3} & 0 & 0 \\ & 2 & 2\sqrt{3} & -1 & 2\sqrt{3} \\ & & 4(3+2\mu_1) & 0 & 0 \\ & & & (1+2\mu_3) & -2\sqrt{3} \\ & & & & 4(3+2\mu_3) \end{bmatrix} \end{array}
 \end{array}
 \begin{array}{c}
 \begin{array}{c} \dots \nu_{CH_2^s} \\ \dots \nu_{CC} \\ \dots \delta_{CH_2^s} \\ \dots \nu_{CCl_2^s} \\ \dots \delta_{CCl_2^s} \end{array}
 \end{array}
 \end{array}$$

where $\mu_1 = (m_2/m_1)$, $\mu_3 = (m_2/m_3)$, and the angles are taken as 120° . With the coordinates chosen, e and h become

$$\begin{array}{c}
 \begin{array}{c} e \\ \begin{bmatrix} 1 & 1 & 2\sqrt{3} & A_{33}' & -2\sqrt{3}A_{33}'A_{44}' \\ 0 & A_{11} & -2\sqrt{3}A_{11}' & A_{13}' & -2\sqrt{3}A_{44}'A_{13}' \\ 0 & 0 & A_{11}'' & -2\sqrt{3}A_{11}' & 12A_{11}'A_{44}' \\ 0 & 0 & 0 & D & 2\sqrt{3}A_{11}'A_{33}' \\ 0 & 0 & 0 & 0 & D' \end{bmatrix} \end{array}
 \end{array}$$

$$\begin{array}{c}
 \begin{array}{c} h \\ \begin{bmatrix} A_{11} & 0 & 0 & 0 & 0 \\ -1 & A_{11}'' & 0 & 0 & 0 \\ -2\sqrt{3} & 2\sqrt{3}A_{11}' & D & 0 & 0 \\ 0 & -A_{11} & 2\sqrt{3}A_{11}' & D' & 0 \\ 0 & 2\sqrt{3}A_{11} & -12A_{11}' & -2\sqrt{3}A_{11}'A_{33}' & D'' \end{bmatrix} \end{array}
 \end{array}$$

where $A_{11}' = (A_{11} - 1)$, $A_{11}'' = (2A_{11} - 1)$
 $A_{33}' = (A_{33} - 12)$
 $A_{44}' = (A_{44} - 1)$
 $A_{13}' = (A_{11}A_{33} - 12)$
 $D = (A_{33}A_{11}'' - 12A_{11})$, $D' = (A_{44}D - A_{13}')$, $D'' = \{A_{55}D' + 12(12A_{11}' + A_{33}' - A_{44}A_{13}')\}$

The fundamental frequencies are⁴ 3035, 1620, 1395, 605, and 295 cm^{-1} , assigned to ν_1 to ν_5 in the order given. With these values, the standard d matrix becomes

$$\begin{array}{c}
 \begin{array}{c} d \\ \begin{bmatrix} 2.641 & 0.3931 & 0.0088 & 0.0380 & -0.0041 \\ & 10.64 & -0.2551 & 1.057 & -0.1134 \\ & & 0.1368 & -0.0329 & 0.0035 \\ & & & 2.452 & 0.1415 \\ & & & & 0.1016 \end{bmatrix} \end{array}
 \end{array}
 \times 10^5 \text{ dynes/cm.}$$

⁴ It is the usual practice to include a normalizing factor in the symmetry coordinate, so that the constant going with any particular coordinate is identical with the valence force constant. These factors would take the following values here: for Δ_1 and Δ_4 , $(1/\sqrt{2})$; for Δ_3 and Δ_5 , $(1/\sqrt{3})$; for Δ_2 , 1. Since the constants refer only to vibrations in one particular symmetry class, it is considered preferable not to normalize the coordinates, but to obtain the valence force constants by combining components from the different symmetry classes. Thus, the C-H stretching constant will be $(d_{11} + d_{55})$, where d_{55} is the constant going with the coordinate $\Delta_5 = \Delta r_{12} - \Delta r_{23}$, of symmetry B_2 .

⁴ H. W. Thompson and P. Torkington, Proc. Roy. Soc. A184, 21 (1945).

The components in the displacements are given below; the elements $\Delta_i(\nu_j)$ are obtained from h by dividing the elements in the j th column by h_{ij} . The elements N_j in the row vector N are the normalizing factors for the appropriate columns of $\Delta_i(\nu_j)$, i.e., $N_j = \Delta_j(\nu_j)$, (in tenths of an angstrom), for the first vibrational level.

$$\begin{array}{c}
 j = \\
 N_j
 \end{array}
 \begin{array}{ccccc}
 1 & 2 & 3 & 4 & 5 \\
 \hline
 [0.2625 & 0.1010 & 0.7816 & 0.1264 & 0.4159] \times 10^{-9} \text{ cm} \\
 \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ -0.040 & 1 & 0 & 0 & 0 \\ -0.140 & 1.696 & 1 & 0 & 0 \\ 0 & -0.5103 & 0.0168 & 1 & 0 \\ 0 & 1.768 & -0.0581 & -1.392 & 1 \end{bmatrix}
 \end{array}
 \Delta_i(\nu_j)$$

The potential energy distribution is as given below; the elements are percentages of the total potential energy in each mode:

$$\begin{array}{c}
 i \backslash k \\
 \begin{array}{cc}
 1 & 2 \\
 \hline
 1 & [100.65 & -0.60 & -0.05 & 0 & 0] \\
 2 & [& 0.66 & -0.05 & 0 & 0] \\
 3 & [& & 0.10 & 0 & 0] \\
 4 & [& & & 0 & 0] \\
 5 & [& & & & 0]
 \end{array}
 \end{array}
 \begin{array}{c}
 i \backslash k \\
 \begin{array}{ccc}
 3 & 4 & 5 \\
 \hline
 3 & [100.56 & -0.41 & -0.15] \\
 4 & [& 0.51 & -0.10] \\
 5 & [& & 0.25]
 \end{array}
 \end{array}
 \begin{array}{c}
 i \backslash k \\
 \begin{array}{ccc}
 1 & 2 & 3 \\
 \hline
 1 & [112.39 & -4.57 & -5.70 & -2.12] \\
 2 & [& 4.16 & 0.30 & 0.11] \\
 3 & [& & 6.74 & -1.35] \\
 4 & [& & & 3.35]
 \end{array}
 \end{array}$$

The $[[V_{ij}(\nu_k)]]$ matrices are symmetric, d_{ij} and d_{ji} being counted separately; the energy term $d_{ij}\Delta_i\Delta_j$ is thus twice the matrix element given.

The relative atomic displacements, derived from e and h, are

$$\begin{array}{c}
 z_j = x_1 (= x_3) \quad y_1 (= -y_3) \quad x_2 \quad x_5 \quad x_4 (= x_6) \quad y_4 (= -y_6) \\
 \begin{array}{cccccc}
 \nu_1 \cdots & -1 & \sqrt{3} & 2\mu_2 & 0 & 0 & 0 \\
 \nu_2 \cdots & -1 & \sqrt{3} & -4 & 2(2+\mu_2) & 0 & 0 \\
 \nu_3 \cdots & 1 & (1+\mu_2)/\sqrt{3} & -\mu_2 & -\mu_2 & 0 & 0 \\
 \nu_4 \cdots & -1 & 0 & -1 & -1 & (1+\mu_2)\mu_3 & \sqrt{3}(1+\mu_2)\mu_3 \\
 \nu_5 \cdots & 1 & 0 & 1 & 1 & -(1+\mu_2)\mu_3 & \{1+\mu_3(1+\mu_2)\}/\sqrt{3}
 \end{array}
 \end{array}$$

where $\mu_2 = (m_1/m_2)$, $\mu_3 = (m_2/m_3)$.

The main features of the standard general solution are well illustrated by the above data. The potential energy distribution agrees with the vibrational assignment; the energy in ν_i is found mainly in the square term $\frac{1}{2}d_{ii}\Delta_i^2$. The simple form of the atomic displacement vectors should be noted; in the stretching vibrations, the displacement vectors of the appropriate atoms lie directly along the valence bonds.

The quantities $(\partial\lambda_k/\partial d_{ij})$ are given below as matrices characteristic of each normal mode.

$$\begin{array}{c}
 i \backslash k \\
 \begin{array}{cc}
 1 & 2 \\
 \hline
 1 & [24.81 & -1 & -2\sqrt{3} & 0 & 0] \\
 2 & [& 0.040 & 0.140 & 0 & 0] \\
 3 & [& & 0.484 & 0 & 0] \\
 4 & [& & & 0 & 0] \\
 5 & [& & & & 0]
 \end{array}
 \end{array}
 \begin{array}{c}
 i \backslash k \\
 \begin{array}{ccc}
 3 & 4 & 5 \\
 \hline
 3 & [101.1 & 1.70 & -5.88] \\
 4 & [& 0.028 & -0.099] \\
 5 & [& & 0.341]
 \end{array}
 \end{array}
 \begin{array}{c}
 i \backslash k \\
 \begin{array}{ccc}
 1 & 2 & 3 \\
 \hline
 1 & [1.96 & 3.32 & -1 & 2\sqrt{3}] \\
 2 & [& 5.64 & -1.70 & 5.88] \\
 3 & [& & 0.510 & -1.77] \\
 4 & [& & & 6.12]
 \end{array}
 \end{array}$$

As in the $V_{ij}(\nu_k)$ matrices, d_{ij} and d_{ji} are counted separately; for interaction constants, $(\partial\lambda_k/\partial d_{ij})$ is twice the

appropriate matrix element. Using the above quantities, the small non-diagonal elements d_{13} , d_{14} , d_{15} , d_{34} , and d_{35} may be eliminated from d , the balancing increments having the values:

$$\Delta d_{11} = -0.0024, \quad \Delta d_{22} = +0.081, \quad \Delta d_{33} = -0.0015, \quad \times 10^5 \text{ dynes/cm.}$$

The elimination of the remaining interaction constants will introduce some degree of approximation; d_{23} and d_{45} are larger than the main constants d_{33} and d_{55} , respectively, and experience has shown that in such cases d_{ij} cannot in general be reduced to zero without making ν_i and ν_j complex. The increments required to balance the elimination of d_{12} and d_{24} are

$$\Delta d_{11} = -0.0314, \quad \Delta d_{22} = -1.06, \quad \times 10^5 \text{ dynes/cm,}$$

giving

$$d_{11} = 2.607, \quad d_{22} = 9.66, \quad \times 10^5 \text{ dynes/cm,}$$

which values agree reasonably well with similar constants in ethylenic molecules where the term in the potential energy corresponding to the interaction $\Delta r_{CH} \cdot \Delta r_{CC}$ is neglected. Application of Eq. (39) to the C—H stretching vibration gives $d_{11} = 2.60 \times 10^5$ dynes/cm.

B. The Class A_g Vibrations of Ethylene

The ethylene molecule falls into the symmetry point group V_h ; the totally symmetric vibrations arise from a cubic factor in the secular equation. The matrices a and A for a suitable set of symmetry coordinates (see Fig. 2), are given:^{e,5}

$$a \quad z_j = \begin{matrix} x_1, x_3, -x_4, -x_6 & y_1, -y_3, y_4, -y_6 & x_2, -x_5 \end{matrix}$$

$$\begin{bmatrix} \Delta_1 = \Delta r_{12} + \Delta r_{23} + \Delta r_{45} + \Delta r_{56} & \dots & \dots & \dots \\ \Delta_2 = \Delta r_{25} & \dots & \dots & \dots \\ \Delta_3 = r_1(\Delta\theta_{13} + \Delta\theta_{46} - \Delta\theta_{15} - \Delta\theta_{24} - \Delta\theta_{26} - \Delta\theta_{35}) & \dots & \dots & \dots \end{bmatrix} \begin{bmatrix} -(1/2) & (\sqrt{3}/2) & 1 \\ 0 & 0 & -1 \\ \sqrt{3} & 1 & -2\sqrt{3} \end{bmatrix} \begin{bmatrix} \dots \nu_{CH_2}^s \\ \dots \nu_{CC} \\ \dots \delta_{CH_2}^s \end{bmatrix}$$

$$A \quad (M = m_2)$$

$$\begin{bmatrix} 2(1+2\mu) & -2 & -4\sqrt{3} \\ & 2 & 4\sqrt{3} \\ & & 8(3+2\mu) \end{bmatrix} \begin{bmatrix} \dots \nu_{CH_2}^s \\ \dots \nu_{CC} \\ \dots \delta_{CH_2}^s \end{bmatrix}$$

where $\mu = (m_2/m_1)$.

If Δ_2 is replaced by $\Delta_2' = \Delta_2 + p\Delta_3$, the matrices e and h , from which are derived the force constants going with the initial set of coordinates in the standard solution for the new set, and the normal coordinates in terms of these initial coordinates, have the form:

$$e \quad \begin{bmatrix} 1 & 2(1+2\sqrt{3}p) & -32\mu p \\ 0 & 2(1+2\mu) & -16\mu\{\sqrt{3}+4(2+\mu)p\} \\ 0 & 2(1+2\mu)p & 8\mu(1+2\sqrt{3}p) \end{bmatrix} \quad h \quad \begin{bmatrix} 2(1+2\mu) & 0 & 0 \\ -2 & 8\mu(1+2\sqrt{3}p) & -128\mu^2 p \\ -4\sqrt{3} & 16\mu\{\sqrt{3}+4(2+\mu)p\} & 128\mu^2 \end{bmatrix}$$

The quantity ${}^2|A'|$, which occurs in the denominator of the coefficients of λ_2 and λ_3 in the series for the d_{ij} , and in the normalization factors for the potential energy, is

$${}^2|A'| = 8\mu\{1+4\sqrt{3}p+8(2+\mu)p^2\}.$$

The Cartesian components of the atomic displacement vectors are given below as functions of p :

$$z_j = \begin{matrix} x_1 & y_1 & x_2 \end{matrix}$$

$$\begin{bmatrix} \nu_1 \dots \\ \nu_2 \dots \\ \nu_3 \dots \end{bmatrix} \begin{bmatrix} -1 & \sqrt{3} & (2/\mu) \\ (1-4\sqrt{3}\mu p) & -\{\sqrt{3}+4(2+\mu)p\} & 4(1+2\sqrt{3}p) \\ (\sqrt{3}+8p) & 1 & 8p \end{bmatrix}$$

With $p=0$, the displacements are those for the standard solution. In this case, the displacement vectors of the hydrogen atoms lie along the C—H bonds in both ν_1 and ν_2 , and the C=C bond remains rigid in ν_3 . It should

^e Gallaway and Barker (see reference 5) obtained a value $119^\circ 55'$ for the angle \widehat{HCH} in ethylene; the round figure of 120° is used here.

⁵ W. S. Gallaway and E. F. Barker, J. Chem. Phys. 10, 88 (1942).

be noted that a small component from Δ_2 in the displacement for ν_3 has here a much greater effect on the potential energy distribution determining the assignment than the same component from Δ_3 in the displacement for ν_2 , since the force constants for the square terms involving these two coordinates are of very different orders of magnitude ($d_{22} \sim 150d_{33}$); the rigidity of the C=C bond in the standard solution for ν_3 is therefore not such a crude approximation as might appear at first sight. The introduction of the parameter p has no effect on the form of the vibration ν_1 , but causes the displacement vectors of the hydrogen atoms in ν_2 and ν_3 to shift from their ideal directions. The shift $\Delta\beta_i$ in ν_i is

$$\begin{cases} \Delta\beta_2 = [\arctan(|y_1/x_1|)(\nu_2) - (\pi/3)] \\ \Delta\beta_3 = [\arctan(|x_1/y_1|)(\nu_3) - (\pi/3)] \end{cases}$$

It is found that these angles can be expressed in terms of p as follows:

$$\begin{cases} \tan\Delta\beta_2 = 2[(1+2\mu)/(1+2\sqrt{3}p)]p \\ \tan\Delta\beta_3 = [2/(1+2\sqrt{3}p)]p \end{cases}$$

The values of p corresponding to the solution $V_{22}(\nu_2) = V_{33}(\nu_3)$, $V_{22}(\nu_3) = V_{33}(\nu_2)$, $V_{23}(\nu_2) = V_{23}(\nu_3)$, are the roots of the quadratic equation:

$$p^2 + \frac{1}{2}\{(\lambda'/\sqrt{3}) - (\sqrt{3}\lambda'')/[2(2+\mu)]\}p + [8(2+\mu)]^{-1} = 0,$$

where $\lambda' = [(\lambda_2/\lambda_3) + 1]$, $\lambda'' = [(\lambda_2/\lambda_3) - 1]$.

The assignment for ethylene is as follows:⁶

$$\nu_1 = 3019.3, \quad \nu_2 = 1623.3, \quad \nu_3 = 1342.4, \text{ cm}^{-1}.$$

These figures are used, uncorrected for anharmonicity since only an empirical correction is possible,⁷ to give the following standard solution ($p=0$):

d

$$\begin{bmatrix} 1.314 & 0.3911 & 0 \\ & 10.507 & -0.2316 \\ & & 0.06686 \end{bmatrix} \times 10^5 \text{ dynes/cm}$$

[[$V_{ij}(\nu_k)$]]

$i \backslash k$	1	2	3
1	101.214	-1.214	0
2		1.314	-0.100
3			0.100

] 108.267 -8.267] [100.000]

Solving the equation giving the values of p corresponding to analogous potential energy distributions in ν_2 and ν_3 , we obtain $p = -0.01315$ and -0.6833 . The solutions for these two values are:

(a) $p = -0.01315$. ($\Delta\beta_2 = -34^\circ 22'$, $\Delta\beta_3 = -1^\circ 35'$).

d

$$\begin{bmatrix} 1.314 & 0.3946 & -0.0017 \\ & 10.745 & -0.2751 \\ & & 0.06744 \end{bmatrix} \times 10^5 \text{ dynes/cm}$$

[[$V_{ij}(\nu_k)$]]

$i \backslash k$	1	2	3
1	101.207	-1.225	0.018
2		1.344	-0.119
3			0.101

] 108.668 -5.832] 2.996 -5.832] 108.668

⁶ G. Herzberg, *Infra-red and Raman Spectra of Polyatomic Molecules* (D. van Nostrand Company, Inc., New York, 1945).

⁷ J. E. Kilpatrick and K. S. Pitzer, *J. Research Nat. Bur. Stand.* **38**, 191 (1947).

(b) $p = -0.6833$. ($\Delta\beta_2 = 87^\circ 42'$, $\Delta\beta_3 = 45^\circ 0'$).

$$\begin{bmatrix} 1.309 & 0.2640 & 0.0024 \\ & 7.503 & -0.2751 \\ & & 0.09658 \end{bmatrix} \times 10^5 \text{ dynes/cm}$$

$$[[V_{ij}(\nu_k)]]$$

$i \backslash k$	1	2	2
1	100.845	-0.819	-0.026
2		0.938	-0.119
3			0.145

$$\begin{bmatrix} 2.996 & -5.832 \\ & 108.668 \end{bmatrix} \begin{bmatrix} 108.668 & -5.832 \\ & 2.996 \end{bmatrix}$$

Solution (b) is given for the sake of completeness; it is seen to correspond to a reversed assignment of ν_2 and ν_3 . It may be noted that in solution (a) the displacement vectors of the hydrogen atoms are much more sensitive to p in ν_2 than in ν_3 . The small interaction constant d_{13} may be eliminated if desired; the balancing increment to d_{11} is negligible. The larger constant d_{12} , which effectively maintains the displacement vectors of the hydrogen atoms along the C-H bonds in ν_1 , may also be eliminated here without introducing any appreciable error, since $(\partial\lambda_1/\partial d_{11}) \gg (\partial\lambda_1/\partial d_{12})$; the balancing increment is $\Delta d_{11} = -0.032 \times 10^5$ dynes/cm.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 17, NUMBER 11 NOVEMBER, 1949

Isothermal Compositional Order-Disorder.*

I. Superstructure Solid Solutions in a Salt System

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(Received January 17, 1949)

Solid solutions in the system, $\text{NH}_4\text{Cl}-\text{MnCl}_2-\text{H}_2\text{O}$, exhibit properties characteristic of order-disorder in alloys. Disordered solid solutions are indistinguishable in structure from that of ammonium chloride. Order is revealed by superstructure formation. The familiar compositions A_3B and AB appear as end-members of the ordered solid solution series. Crystal symmetry alteration from cubic to tetragonal results from ordering. Tetragonality is intimately related to the state of order. Though increase in "solute" content produces significant lattice distortion, superstructure unit cell volumes are constant.

Despite their unusual properties, the ordered salt solid solutions exhibit a normal Vegard's law relationship.

The salt system's features resemble those of a low temperature isotherm across Shockley's theoretical phase diagram for alloy

order-disorder transformation and are regarded as experimental verification of Shockley's qualitative predictions. A concept of isothermal, compositional order-disorder is used in presenting the results.

Demonstration of a two-phase region, wherein ordered and disordered solid solutions coexist in equilibrium, provides a basis for resolving the controversy over whether the phase rule governs order-disorder transformations.

Identity of the order-disorder phenomenon in metal and salt systems was further shown by producing the disordered state of salt solutions from the ordered by thermal and cold-working methods. In both instances, order was spontaneously restored with aging at room temperature.

INTRODUCTION

IN essence, the research to be described consists of x-ray diffraction and phase rule studies of a salt system, $\text{NH}_4\text{Cl}-\text{MnCl}_2-\text{H}_2\text{O}$, equilibrated at 25°C . From the results of this investigation, there is developed evidence that the solid solutions occurring in this system exhibit properties known to characterize the order-disorder phenomenon in alloys.¹ It is one of the

purposes of this paper to set forth these properties along with the data therefor.

It is a further purpose to show that the salient features of this salt system resemble those deduced from a low temperature isotherm drawn across Shockley's phase diagram² for alloy order-disorder transformation. The resemblances between the experimentally determined salt system phase diagram and the theoretically based diagram of Shockley point up an aspect of perhaps major importance; in that, both reveal a two-phase region wherein ordered and disordered state solid solutions coexist at equilibrium. Thereby is provided a

* Based upon material presented before the joint meeting of the American Society for X-Ray and Electron Diffraction and the Electron Microscope Society of America, the Mellon Institute and the University of Pittsburgh, Pittsburgh, Pennsylvania, December 5-7, 1946.

¹ F. C. Nix and W. Shockley, *Rev. Mod. Phys.* **10**, 1-71 (1938).

² W. Shockley, *J. Chem. Phys.* **6**, 130 (1938).