

no atom transfer, while at the same time satisfying physical evidence regarding symmetry⁷.

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May 1.

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³ Klinkenberg, *Chem. Weekblad*, **35**, 197 (1938).

⁴ *J. Chem. Soc.*, 1093 (1946).

⁵ *Nature*, **159**, 743 (1947).

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⁷ Sutherland, *Proc. Roy. Soc., A*, **141**, 342 (1933).

A General Solution for the Force Constants of Polyatomic Molecules

It is well known that the fundamental vibration frequencies of polyatomic molecules can be predicted with an error of only 1 or 2 per cent by solving the secular equation with force constants obtained from related molecules¹. The reverse process of solving for the constants in terms of the frequencies is, in general, impossible unless some special assumptions are made concerning the force field². The following general solution is therefore of some interest.

The n th order secular equation can be written in matrix form as follows:

$$[dA - \lambda I] = 0. \quad (1)$$

The elements of d are the force constants d_{ij} in the general potential function:

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

The Δ_i are valence-type co-ordinates, expressed in terms of N further co-ordinates z_j :

$$\Delta_i = \sum_{j=1}^N a_{ij} z_j, \quad (3)$$

all possessing any required symmetry properties, and the elements of A (related to the inverse kinetic energy matrix G used by Wilson³), are defined as follows:

$$A_{ij} = A_{ji} = \sum_{k=1}^N a_{ik} a_{jk} \frac{M}{m_k}, \quad (4)$$

m_k being the mass for the co-ordinate z_k and M some arbitrary mass, introduced in order that the A_{ij} shall be pure numbers. I is the unit matrix, and the quantity λ is defined as follows:

$$\lambda = 4\pi^2 \nu^2 c^2 M, \quad (5)$$

ν being the frequency of vibration in cm.^{-1} and c the velocity of light in cm. sec.^{-1} . The $(N-n)$ null vibrations factorize out, giving (1). If the subscripts are ordered so that Δ_i is the approximate normal co-ordinate for ν_i , corresponding to the vibrational assignment, and if $\nu_1 > \nu_2 > \dots > \nu_n$, then the proposed general solution for the constants is obtained by equating to zero all elements below the diagonal of the determinant (1), thus reducing it to the product of n linear factors, and substituting λ_1 to λ_n in order in the n diagonal elements; that is:

$$\left. \begin{aligned} \sum_{i=1}^n A_{ki} d_{ki} - \lambda_k &= 0, (k = 1, 2 \dots n). \\ \sum_{i=1}^n A_{qi} d_{pi} &= 0, (p > q). \end{aligned} \right\} \quad (6)$$

The corresponding (unnormalized) normal co-ordinates are given by:

$$z_i^{\nu k} = \sum_{j=1}^k a_{ji} \frac{M}{m_i} {}^k A_{kj} \quad (7)$$

$$\Delta_p^{\nu k} = \sum_{j=1}^k A_{pj} {}^k A_{kj}, (= 0 \text{ for } p < k). \quad (8)$$

where ${}^k A_{kj}$ are first minors of the k th order determinant formed from the first k rows and columns of the matrix A . The normal co-ordinate for ν_i involves only the co-ordinates Δ_i to Δ_n ; the method, in effect, factorizes out the frequencies in descending order, the molecule increasing in rigidity as factorization proceeds. If only the constants for the m lowest frequencies are required, only elements in the last m rows of (1) need be considered, without introducing any fresh approximation.

The above solution is found to give surprisingly good results with actual examples, and is easy to apply. For molecules in which all the fundamentals fall into the category of 'group vibrations', factorization of the secular equation will clearly give a close approximation; where $(\nu_i - \nu_{i+1})$ is small and Δ_i and Δ_{i+1} overlap, the approximation will not be so close, since the normal co-ordinate for ν_{i+1} would then certainly involve Δ_i ; but only the constants d_{ii} , $d_{i(i+1)}$ and $d_{(i+1)(i+1)}$ will be much affected. The constants obtained in (6) are always real, and the normal co-ordinates defined in (7) and (8) correspond to the vibrations having idealized geometrical forms; thus, in valence vibrations the atomic displacement vectors lie directly along the appropriate valence bonds. Interactions which would normally be discarded are here generally found to be negligibly small; their retention gives the unambiguous solution.

The method can obviously be adapted to predict vibration frequencies, by substituting constants only in the diagonal elements of (1); the inconsistency in the force field can then be estimated by evaluating terms below the diagonal.

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² Glockler and Tung, *J. Chem. Phys.*, **13**, 388 (1945).

³ Wilson, *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 76 (1941).

Study of the Action of Ultra-violet Light on Urease by Means of the Ultracentrifuge

THE action of ultra-violet light on serum albumin has been studied with the ultracentrifuge by Svedberg and Brohult¹ and by Sanigar, Krejci, and Kraemer². Irradiation of serum albumin at room temperature and at 0° C. causes the formation of low-molecular substances and a general inhomogenization of the protein.

It seemed worth while to perform a similar experiment with a protein having enzymatic activity in order to see if inhomogenization accompanies loss of activity, or is a process resulting from the absorption of quanta beyond those required on the average for inactivation. For irradiation, monochromatic light of 2537 Å. was used, at which a quantum yield of inactivation of 0.000926 has been found³. Inactiva-