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The Raman Effect

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FOREWORD

THIS review was written with the following considerations in mind: The first aim was the construction of a summary which would interest the average physicist whose main endeavor, however, lies in other directions, but who wishes to have a broad acquaintance with the general field of physics in all of its many ramifications. From this point of view it was necessary to include certain sections well known to the specialist. However, this procedure seemed justified, for so far no review on the Raman effect has been offered in the pages of this journal. In order to develop the subject consistently and to save the reader time and effort, certain sections have been rendered perhaps in more detail than is customary in such articles. Nevertheless, it was felt preferable to err on the side of detailed development rather than brevity in order to assure the rendition of a complete and comprehensive account.

The second aim in writing this paper was the coverage of this field of research from July, 1939 to July, 1942. The subject is thereby brought from Hibben's monograph (IV)* of 1939 and Kohlrausch's complementary volume (V) of 1938 up to date. From this point of view the topic was to be outlined for the research workers in the field, and it is hoped that a perusal of these pages will repay investigators who use the Raman effect in their own work, either for its own sake or as a tool for the solution of other problems. The literature of the Raman effect is very extensive and up to the present has been extremely active. Hibben lists about 2000 references, and the present review is based on 500 papers, the greatest number having appeared in the last three years. It is also our aspiration in writing this survey to summarize the research in the last three years for the use of the specialists.

Another thought was the belief that this report, following at this time the monographs mentioned above, will come at the end of a period of investigation on the Raman effect. A great number of scientists have changed their work and are helping in the total war effort. A period of war research will make it impossible for many workers to continue their usual labors for years to come.

*Numbers in parentheses designate references in the bibliography at the end of this article.

I. THEORY OF THE RAMAN EFFECT

1. Introduction

Sir C. V. Raman discovered the scattering of light with change in frequency on February 28, 1928 (355). The shifts in frequency depend upon the substance used. The differences in wave number between the incident radiation and the scattered light are intimately connected with the energy states of the molecules. These energy differences relate to the vibrational and rotational energy levels. No "electronic" Raman effect has been discovered with certainty. Elastic scattering of radiation by matter without attendant frequency shift has been known for a long time as "Rayleigh" or "Tyndall" scattering and explains, for example, the blue color of the sky. But the "Raman effect" had not been observed, mainly because of the small probability of occurrence of the individual interactions between radiation and molecules. The phenomenon was predicted by Smekal (425) on the old quantum theory. He reasoned on the basis of energy and momentum considerations that a quantum of light of frequency ν could interact by an inelastic collision with a molecule in energy state E_p . Conservation of energy demands

$$h\nu + E_p = h\nu' + E_q, \quad (1)$$

where $h\nu'$ is the energy of the scattered photon and E_q is some other definite energy state of the molecule after the interaction. If $\nu' < \nu$ the lines of scattered radiation are "Stokes" lines, and if $\nu < \nu'$, they are called "anti-Stokes" lines. The corresponding acts can be written

$$\begin{aligned} M + h\nu &\rightarrow M^* + h\nu'; & \nu' < \nu \\ \text{and} & & \\ M^* + h\nu &\rightarrow M + h\nu''; & \nu'' > \nu \end{aligned} \quad (2)$$

(M = ground state of the molecule; M^* = excited state). From the point of view of the chemist, these changes can be considered forward and backward reactions, and on the principle of microscopic reversibility, they are readily understood. The similarity to the Compton effect is seen from the corresponding equation for x-ray scattering

$$E_0 + h\nu \rightarrow E_f + h\nu', \quad (3)$$

where E_0 represents the electron of nearly zero energy in the scattering substance, E_f refers to

the Compton electrons, $h\nu$ is the incident x-ray, and $h\nu'$ is the scattered radiation of lesser frequency. The "inverse" Compton effect predicted on the principle of microscopic reversibility has not yet been discovered. It involves the interaction of a fast electron with a light or x-ray quantum, the electron losing some energy and the quantum leaving the impact region with higher frequency.

The Raman frequencies are given by

$$\nu' - \nu = (E_q - E_p)/h. \quad (4)$$

It must be pointed out that the interaction is not the simple act of fluorescence, where a quantum of one frequency is absorbed by the fluorescing molecule and another one of different frequency is emitted. In the case of fluorescence the incoming radiation must be actually absorbed by the interacting molecule while so definite an absorption act is not necessary in the Raman effect. To be sure there is involved a "third level" of the scattering molecule, but the incoming radiation need only fulfill the condition that

$$h\nu > E_n - E_k,$$

where ν is the frequency of the incident radiation and E_n, E_k are two energy states of the molecule. In more detail the Raman acts can be written

$$\begin{array}{l} M + h\nu \leftrightarrow M^{**} \\ \frac{M^{**} \leftrightarrow M^* + h\nu'}{M + h\nu \leftrightarrow M^* + h\nu'} \end{array} \quad (5)$$

where M^{**} is the third level involved in the interaction.

2. Wave Mechanics

Since the advent of wave mechanics it has become necessary to be able to discuss any atomic phenomenon on the basis of these principles. If theoretical physicists should be unable to "explain" any new observation on the basis of the theory fashionable at a given time, they will naturally have to revise their theoretical notions. In the case of the Raman effect Placzek (IX) considered the phenomenon on a semi-wave mechanical basis. In order to give a derivation of a scattering equation involving frequency shifts he postulated, using the old idea of the correspondence principle, that the radiation coming

from a material system is determined in classical manner by the time dependence or time variation of an electric moment. Any system of particles is described by the time-dependent Schroedinger equation

$$\begin{aligned} [H_0 + (h/2\pi i)(\partial/\partial t)]\Psi^0(q, t) &= 0, \\ [H_0^* - (h/2\pi i)(\partial/\partial t)]\Psi^{0*}(q, t) &= 0, \end{aligned} \quad (6)$$

where the energy operator H_0 is derived from the classical Hamiltonian by replacing all momenta by the operation $(h/2\pi i)(\partial/\partial t)$, q representing all coordinates. The other symbols have their usual meaning. The general solution is

$$\Psi^0 = \sum_r a_r \psi_r \cdot \exp [(-2\pi i/h)E_r t]. \quad (7)$$

a_r are constants, ψ_r are wave functions independent of the time, and E_r is the energy of the r th state of the system. If the molecule is in its k th state

$$\Psi_k^0 = \psi_k \cdot \exp [(-2\pi i/h)E_k t]. \quad (8)$$

A light wave, of wave-length large in comparison to atomic dimensions, of frequency different from the proper vibrations of the molecule and incident upon the system, can be described by its electric vector F :

$$F = A^* \exp(2\pi i\nu t) + A \exp(-2\pi i\nu t). \quad (9)$$

A is a complex vector and ν is the frequency of the incoming radiation. The energy of the system will be changed by the perturbing influence of the external field. The perturbation is

$$H_1 = -F \sum e_j r_j = -\mu F, \quad (10)$$

where e_j is the electronic charge of the j th particle, r_j is its position, and $\mu = \sum e_j r_j$. The perturbed Schroedinger equation is

$$\begin{aligned} [H_0 + H_1 + (h/2\pi i)(\partial/\partial t)]\Psi(q, t) &= 0, \\ [H_0^* + H_1 - (h/2\pi i)(\partial/\partial t)]\Psi^*(q, t) &= 0. \end{aligned} \quad (11)$$

The perturbed system in the state k has the solution

$$\Psi = \Psi_k^0 + \Psi_k^{(1)}$$

which yields

$$\begin{aligned} [H_0 + (h/2\pi i)(\partial/\partial t)]\Psi_k^{(1)} &= \mu F \Psi_k^0, \\ [H_0^* - (h/2\pi i)(\partial/\partial t)]\Psi_k^{(1)*} &= \mu F \Psi_k^{0*}. \end{aligned} \quad (12)$$

The solution for the perturbing functions is

$$\begin{aligned} \Psi_k^{(1)} = \sum_r \psi_r [& \{ (A \cdot \mu_{kr}) / (h\nu_{rk} - h\nu) \} \\ & \exp \{ - (2\pi i / h) (E_k + h\nu) t \} \\ & + \{ (A^* \cdot \mu_{kr}) / (h\nu_{rk} + h\nu) \} \\ & \cdot \exp \{ - (2\pi i / h) (E_k - h\nu) t \}], \quad (13) \end{aligned}$$

where

$$\mu_{kr} = \int \psi_r^* \mu \psi_k d\tau$$

and the summation is carried over the unperturbed function ψ_r . The electric moment of the perturbed state is

$$\int (\Psi_k^0 + \Psi_k^{(1)})^* \mu (\Psi_k^0 + \Psi_k^{(1)}) d\tau.$$

Substitution and multiplication yield a variety of terms. The first one is independent of the time and refers to the permanent dipole of the molecule, the second one has the same time dependency and frequency as the incident light and produces coherent scattering. This term is

$$\mu_{kk}^{(1)} = F_{kk} \cdot \exp(-2\pi i \nu t) + F_{kk}^* \cdot \exp(2\pi i \nu t), \quad (14)$$

where

$$\begin{aligned} F_{kk} = \sum_r [& \{ (A \mu_{kr}) \cdot \mu_{rk} \} / (h\nu_{rk} - h\nu) \\ & + \{ \mu_{kr} \cdot (A \mu_{rk}) \} / (h\nu_{rk} + h\nu)]. \quad (15) \end{aligned}$$

The classical intensity (I) of radiation of this electric moment is

$$I = \{ (64\pi^4 \nu^4) / (3c^3) \} \cdot |F_{kk}|^2. \quad (16)$$

So far no transition of the molecule and therefore no frequency shift of the scattered radiation was involved, only the k th state and its interaction with the incoming light.

If the molecule should, however, make the transition from level k to n , then its resulting electric moment while under the influence of the radiation is

$$\int (\Psi_n^0 + \Psi_n^{(1)})^* \mu (\Psi_k^0 + \Psi_k^{(1)}) d\tau.$$

Multiplication after the appropriate substitution yields the sum

$$\begin{aligned} & \mu_{kn} \cdot \exp(-2\pi i \nu_{kn} t) \\ & + \sum_r [\{ (A \mu_{kr}) \cdot \mu_{rn} \} / (h\nu_{rk} - h\nu)] \\ & \cdot \exp \{ -2\pi i (\nu_{kn} + \nu) t \} \\ & + \sum_r [\{ \mu_{kr} \cdot (A \mu_{rn}) \} / (h\nu_{rn} + h\nu)] \\ & \cdot \exp \{ -2\pi i (\nu_{kn} + \nu) t \} + \dots \quad (17) \end{aligned}$$

The first term refers to the spontaneous emission of a quantum and *the next two terms correspond to scattered radiation of frequency $\nu + \nu_{kn}$* subject to the condition

$$\nu + \nu_{kn} > 0 \quad \text{or} \quad E_n < E_k + h\nu.$$

The final energy of state E_n can be greater or less than the energy of the initial state E_k . In the first instance the scattered radiation is of longer, and in the second case, it is of shorter wave-length than the incident light. (Stokes and anti-Stokes lines.) *The interaction of radiation and matter whereby the molecule makes a transition between energy states (k, r, n) constitutes the Raman effect.* The intensity of scattered radiation is

$$I_{kn} = [\{ (64\pi^4) (\nu + \nu_{kn})^4 \} / (3c^3)] \cdot |F_{kn}|^2, \quad (18)$$

where

$$\begin{aligned} F_{kn} = \sum_r [& \{ (A \mu_{kr}) \cdot \mu_{rn} \} / (h\nu_{rk} - h\nu) \\ & + \{ \mu_{kr} \cdot (A \mu_{rn}) \} / (h\nu_{rn} + h\nu)] \quad (19) \end{aligned}$$

and $|F_{kn}|$ is the magnitude of the oscillating electric moment. It is seen that the interaction requires not only the states k and n , but also all the other quantum states r of the unperturbed system. Two levels (k and n) can exhibit a Raman transition only if another one exists which itself can combine with them (third common level rule).

3. Selection Rules

Following Placzek it is customary to consider the scattering in relation to the nuclear motions of the molecule. It is the electrons which interact with the incident radiation, but the resulting energy changes must be taken up by the nuclei, presupposing a coupling of the motions of these two kinds of particles. The scattering caused by the electrons at any instant is to be related to the nuclear position at that instant. The dipole moment (μ) induced in a molecule by the static field F is usually given as

$$\mu = \alpha F, \quad (20)$$

where α is the polarizability of the molecule. The induced moment and the field are vectors, and the polarizability connecting them is a tensor quantity:

$$\begin{aligned}
M_x &= \alpha_{xx}E_x + \alpha_{xy}E_y + \alpha_{xz}E_z, \\
M_y &= \alpha_{yx}E_x + \alpha_{yy}E_y + \alpha_{yz}E_z, \\
M_z &= \alpha_{zx}E_x + \alpha_{zy}E_y + \alpha_{zz}E_z.
\end{aligned} \quad (21)$$

Since α is a symmetric tensor, only six of the nine components are distinct. From Eqs. (9), (15), and (19), it can be seen how the complex amplitudes A and F_{kn} are connected with the induced moment. If the indices ρ, σ are related to the Cartesian coordinates x, y, z , then in general

$$(F_\rho)_{kn} = \sum_\sigma (C_{\rho\sigma})_{kn} \cdot A_\sigma, \quad (22)$$

where

$$\begin{aligned}
(C_{\rho\sigma})_{kn} &= \sum_r [\{(\mu_\sigma)_{kr} \cdot (\mu_\rho)_{rn}\} / (h\nu_{rk} - h\nu) \\
&\quad + \{(\mu_\rho)_{kr} \cdot (\mu_\sigma)_{rn}\} / (h\nu_{rn} + h\nu)]
\end{aligned} \quad (23)$$

for coherent scattering $k=n$ and from Eq. (14)

$$\begin{aligned}
(\mu_\rho)_{kk}^{(1)} &= \sum_\sigma [(C_{\rho\sigma})_{kk} \cdot A_\sigma \{\exp(-2\pi i\nu t)\} \\
&\quad + (C_{\rho\sigma})_{kk}^* \cdot A_\sigma^* \{\exp(+2\pi i\nu t)\}].
\end{aligned} \quad (24)$$

Since

$$(\mu_\sigma)_{kr} = (\mu_\sigma)_{rk}^* \quad (25)$$

it follows that

$$(C_{\rho\sigma})_{kk} = (C_{\sigma\rho})_{kk}^* \quad (26)$$

For the static case ($\nu=0$) Eq. (24) becomes

$$(\mu_\rho)_{kk}^{(1)} = \sum_\sigma (C_{\rho\sigma})_{kk} \cdot F_\sigma \quad (27)$$

But the induced moment μ mentioned [Eq. (20)] is just this quantity and therefore

$$(C_{\rho\sigma})_{kk} = \alpha_{\rho\sigma}^{(k)} \quad (28)$$

or the polarizability. Hence the Raman effect depends on the change of induced electric moment during a transition and therefore also on the change in polarizability of the molecule. Since the state of a molecule in a given electronic level can be described by a wave function which is the product of two factors, one of which refers to the nuclei only, the induced moment can be expressed by

$$\begin{aligned}
\mu_{nn'}^{(1)} &= F \int \psi_n(q) \{\alpha_{\rho\sigma}(q)\} \psi_{n'}(q) dq \\
&= \langle (\alpha_{\rho\sigma})_{nn'} \rangle_{\mathcal{N}} \cdot F,
\end{aligned} \quad (29)$$

where $\psi_n, \psi_{n'}$ are nuclear wave functions (vibration and rotation), q represents the coordinates, and $\langle (\alpha_{\rho\sigma})_{nn'} \rangle_{\mathcal{N}}$ is the average value of the polarizability:

$$\langle (\alpha_{\rho\sigma})_{nn'} \rangle_{\mathcal{N}} = \int \psi_n(q) \{\alpha_{\rho\sigma}(q)\} \psi_{n'}(q) dq. \quad (30)$$

The separate components of the polarizability from Eqs. (23) are

$$\begin{aligned}
(\alpha_{\rho\sigma})_{lm} &= \sum_r \left[\left\{ \int \psi_l \cdot \mu_\sigma \cdot \psi_r d\tau \right. \right. \\
&\quad \times \left. \left. \int \psi_r \cdot \mu_\rho \cdot \psi_m d\tau \right\} / (h\nu_{rl} - h\nu) \right] \\
&\quad + \sum_r \left[\left\{ \int \psi_l \cdot \mu_\rho \cdot \psi_r d\tau \right. \right. \\
&\quad \times \left. \left. \int \psi_r \cdot \mu_\sigma \cdot \psi_m d\tau \right\} / (h\nu_{rm} + h\nu) \right].
\end{aligned} \quad (31)$$

It is important next to determine the effect of molecular symmetry on the components of the polarizability, and to this end it is necessary to investigate the behavior of $\alpha_{\rho\sigma}(q)$ in respect to symmetry operations.

The total vibrational wave function of a molecule can be written as a product

$$\psi_n(q) = \prod_{s=1}^{3N-6} \psi_{n_s}(q_s), \quad (32)$$

where the ψ are Hermitian orthogonal functions. In the Raman effect the most common transition is from the ground state to the next vibrational level, hence the n_s will change by unity ($n = n' \pm 1$). Since the Hermitian functions are even or odd depending on whether n is even or odd, the product $\psi_n(q) \cdot \psi_{n'}(q)$ must be an odd function of q . A matrix element $\{ \langle (\alpha_{\rho\sigma})_{nn'} \rangle_{\mathcal{N}} \}$ [Eq. (30)] can be different from zero only if its value remains unchanged during a symmetry operation. And conversely, in order that it will be zero, its value must change. Hence if the polarizability component $\{ [\alpha_{\rho\sigma}(q)] \}$ in (30) remains even during a covering operation, $\langle (\alpha_{\rho\sigma})_{nn'} \rangle_{\mathcal{N}}$ will be zero because the product of the vibrational wave functions changes sign. In order to determine the symmetry properties of $\alpha_{\rho\sigma}(q)$, it is only necessary to note how the expression (31) changes when such an operation is performed. If a molecule has a plane of symmetry perpendicular to the σ axis, the integrals [Eq. (31)] will transform as the σ coordinate transforms:

$$\sigma \rightarrow -\sigma; \quad \rho \rightarrow \rho \quad (33)$$

and

$$(\mu_\sigma)_{kn} \rightarrow -(\mu_\sigma)_{kn}; \quad (\mu_\rho)_{kn} \rightarrow (\mu_\rho)_{kn}$$

and $\alpha_{\rho\sigma}(q)$ will transform as the product of coordinates

$$\sigma\rho \rightarrow -\sigma\rho; \quad \sigma\sigma \rightarrow \sigma\sigma; \quad \rho\rho \rightarrow \rho\rho.$$

For the three Cartesian coordinates

$$\begin{aligned} \alpha_{ii} &\rightarrow \alpha_{ii}; & \alpha_{xy} &\rightarrow -\alpha_{xy}; \\ \alpha_{yz} &\rightarrow \alpha_{yz}; & \alpha_{xz} &\rightarrow -\alpha_{xz}. \end{aligned} \quad (34)$$

The components of the electric moment transform as the related coordinate, and the components of the polarizability transform as the product of the respective coordinates. The vibrations of the molecule must be either symmetrical or antisymmetrical with respect to the plane of reflection. If the vibration is symmetrical, then

$$\begin{aligned} & q \rightarrow q \\ \text{and} \quad \alpha_{ii}(q) &= \alpha_{ii}(q); & \alpha_{xy}(q) &= -\alpha_{xy}(q); \\ \alpha_{yz}(q) &= \alpha_{yz}(q); & \alpha_{xz}(q) &= -\alpha_{xz}(q). \end{aligned} \quad (35)$$

If the vibration is antisymmetrical

$$\begin{aligned} & q \rightarrow -q \\ \text{and} \quad \alpha_{ii}(q) &= \alpha_{ii}(-q); & \alpha_{xy}(q) &= -\alpha_{xy}(-q), \\ \alpha_{yz}(q) &= \alpha_{yz}(-q); & \alpha_{xz}(q) &= -\alpha_{xz}(-q). \end{aligned} \quad (36)$$

In the first case $\alpha_{xy}(q)$ and $\alpha_{xz}(q)$ vanish because they are odd functions of q , and in the second case $\alpha_{ii}(q)$ and $\alpha_{yz}(q)$ vanish because they are even functions of q .

In the infra-red the electric vector is of interest and it transforms as the corresponding coordinate: For the reflection plane just considered

$$M_x \rightarrow -M_x; \quad M_y \rightarrow M_y; \quad M_z \rightarrow M_z. \quad (37)$$

For symmetric vibrations

$$\begin{aligned} M_x(q) &= -M_x(q); & M_y(q) &= M_y(q); \\ M_z(q) &= M_z(q); \end{aligned} \quad (38)$$

and only the x component vanishes. For anti-symmetric vibrations

$$\begin{aligned} M_x(q) &= -M_x(-q); & M_y(q) &= M_y(-q); \\ M_z(q) &= M_z(-q); \end{aligned} \quad (39)$$

and the last two mentioned vanish. The two cases cited are compared in Table I. In some

TABLE I. Behavior of the components of polarizability and electric moment with symmetry operations.

Symmetry	Vibration type	Raman	Infra-red
Plane	sym.	$\alpha_{xy} = \alpha_{xz} = 0$	$M_x = 0$
Plane	antisym.	$\alpha_{ii} = \alpha_{yz} = 0$	$M_y = M_z = 0$

cases certain lines or transitions may be entirely forbidden in either the Raman effect or the infra-red, and the selection rules are not the same for the two spectral regions. Hence for a complete investigation it is necessary to obtain both types of spectra. In the manner indicated Placzek (IX) has derived selection rules for all symmetry classes and the tables given by Wilson (485) and Kohlrausch (V) are based on his work.

4. Depolarization Factor

In order to calculate intensities and polarization properties of Raman lines, it is necessary to evaluate the components of the polarizability [Eq. (30)]. They must be given in their dependence on the coordinates and even though the functional relations are unknown, they can at least be expressed by a series development:

$$\alpha_{\rho\sigma}(q) = (\alpha_{\rho\sigma})_0 + (\partial\alpha_{\rho\sigma}/\partial q)_0 q + \dots \quad (40)$$

so that

$$\begin{aligned} (\alpha_{\rho\sigma})_{nn'} &= (\alpha_{\rho\sigma})_0 + (\partial\alpha_{\rho\sigma}/\partial q)_0 \int \psi_n(q) \\ & \quad q \cdot \psi_{n'}(q) dq + \dots \end{aligned} \quad (41)$$

showing that the Raman effect depends on the change in polarizability of the molecule as it vibrates through the equilibrium position. It is customary to represent the deformability of any molecule by the "polarizability ellipsoid" in which the main components ($\alpha_1, \alpha_2, \alpha_3$) are directed along the principal axes. Variations are then represented by changes in shape and/or rotation of the ellipsoid. The tensor can further be divided into two parts, the linear average value

$$a = \frac{1}{3}(\alpha_1' + \alpha_2' + \alpha_3'); \quad \alpha_i' = (\partial\alpha_i/\partial q)_0 \quad (42)$$

and the anisotropic part

$$b = \frac{1}{2} \left[\sum_{i,k} (|\alpha_i' - \alpha_k'|)^2 \right]^{\frac{1}{2}}. \quad (43)$$

In terms of these quantities the depolarization factor (ρ_n) is defined below. It is the ratio of

the intensity $[I(\sigma)]$ of the scattered radiation which has the same direction as the incident ray to the intensity of scattered light $[I(\pi)]$ moving at right angles to the incident beam and to the direction of observation which is usually 90° to the initial direction. If unpolarized radiation is used to excite the Raman lines, then

$$\rho_n = I(\sigma)/I(\pi) = (6b^2)/(45a^2 + 7b^2). \quad (44)$$

Raman lines are depolarized ($d\phi$) when a^2 is zero and ρ_n is $6/7$ which is the case for unsymmetrical fundamentals. For symmetric vibrations Raman lines are polarized (ϕ) and $0 < \rho_n < 6/7$. The most intense Raman shifts are the so-called "breathing vibrations," which are symmetric to all symmetry elements. In the cubic system they have $\rho_n = 0$. The measurement of this depolarization factor is of great help in allocating lines to modes of motion and analyses of Raman spectra must include this ratio of parallel and perpendicular components of the scattered radiation. Detailed treatment of this important topic was given by Cabannes (I, 55), Kohlrausch (V), Placzek (IX), and Stuart (XII). From the theory of polarizability as developed by Placzek (IX), Levin (259) derived a relation for the temperature variation of the index of refraction at constant density and its connection with the ratio of the intensity of Rayleigh scattering and Raman scattering of the second order. Available experimental results do not contradict the theory.

5. Anharmonicity

In the usual approximate treatment used in Raman studies the molecule is considered to be a system of linear harmonic oscillators, and the total energy W of such vibrators is

$$W = \sum_{j=1}^{3N-6} (v_j + \frac{1}{2}) h\nu_j. \quad (45)$$

This expression is, however, inaccurate and for the complete analysis of the vibrations of a molecule it may be amplified by considering the molecule a non-rotating anharmonic oscillator. The total energy is then given in the form

$$W = \sum_k \omega_k (n_k + \frac{1}{2}) + \sum_{k \leq l} X_{kl} (n_k + \frac{1}{2})(n_l + \frac{1}{2}). \quad (46)$$

For a triatomic molecule this expression is

$$\begin{aligned} W = \text{const.} &+ [\omega_1 + X_{11} + \frac{1}{2}X_{21} + \frac{1}{2}X_{31}]n_1 \\ &+ X_{11}n_1^2 + X_{21}n_2n_1 \\ &+ [\omega_2 + X_{22} + \frac{1}{2}X_{21} + \frac{1}{2}X_{32}]n_2 \\ &+ X_{22}n_2^2 + X_{32}n_3n_2 \\ &+ [\omega_3 + X_{33} + \frac{1}{2}X_{32} + \frac{1}{2}X_{31}]n_3 \\ &+ X_{33}n_3^2 + X_{31}n_3n_1. \quad (47) \end{aligned}$$

The nine quantities ω_k and X_{kl} have been determined, for example, by Bonner (44) for water vapor from the infra-red absorption bands and by King (214) for deuterium oxide. In the Raman effect only three fundamentals are obtained, and the anharmonicity factors cannot be determined. A complete analysis of a molecular vibration spectrum is therefore impossible. However, the observed Raman frequencies are useful in many other investigations even though they do not represent the fundamental vibrational constants of the molecule. Thermodynamic quantities can be calculated with sufficient accuracy, and force constants of chemical bonds can be obtained which, even though they are not correct, help in advancing our knowledge of the binding forces in molecules.

In order to obtain the anharmonic constants by the Raman effect, overtones would have to be observed. They are, however, usually very weak in relation to the fundamentals. For example, Bhagavantam (36) has calculated that the intensity of the fundamental frequency may be from 150–500 times that of the overtone in hydrogen halides, oxygen, and nitrogen. Redlich (369) has studied the anharmonicity of C–H vibration and the product rule (Section 16) where the application of the latter was impaired to some extent by the error due to the anharmonicity of these hydrogen vibrations. The same author (370) points out that the data available for calculation of anharmonicity factors are as a rule insufficient, and he tried to find some general relations which would reduce the number of these coefficients. He neglects cross terms of higher order than the second containing stretching coordinates of different non-equivalent groups. For example, two C–H groups in the same molecule are equivalent. A similar assumption concerning cross terms containing bending and bending-stretching coordinates is considered,

though it may not hold as rigorously. A single stretching coordinate may possibly be approximated by a Morse function, and the relation between anharmonicity and energy of dissociation of diatomic molecules is extended to the polyatomic case.

6. Fermi Resonance

If the number of Raman lines for a given molecule has been determined from the selection rules as based on symmetry, it may still be found that the experimentally obtained number does not agree with the predictions made from theory. Some of the allowed shifts may be too weak to show on the spectrum plate in the time of exposure. On the other hand, overtones and combination lines may appear on the plate in certain cases. This difficulty is found rather frequently and adds to the uncertainty of locating the fundamental frequencies. Still another complication may occur as, for example, in carbon dioxide and carbon tetrachloride. Quantum mechanical resonance splitting may happen between vibrations of different types. If a given fundamental of one class is nearly equal to an overtone of a frequency of another class, these two vibrations may cause the appearance of two lines. The question was first discussed by Fermi (123) in the case of carbon dioxide.

7. Tunnel Effect

Another reason for the appearance of doublets where only one fundamental frequency was expected rests on the shape of the potential energy curve. It may contain two minima as, for example, in ammonia which may have two possible equilibrium positions for the nitrogen atom in relation to the plane of the three hydrogens. The two potential minima refer to two models of the molecule which are mirror images with the hydrogen plane the reflecting surface. The case of ammonia has been studied by many writers on quantum mechanical basis, for example, Glockler and Wall (162). Another similar problem arises with the hydrogen fluoride ion where the hydrogen nucleus can take up two equilibrium positions in the neighborhood of the two fluorine nuclei by passing through a potential barrier. This condition results in a system

of double energy states leading to the splitting of an otherwise single fundamental as shown by Glockler and Evans (149). In phosphine and arsine a similar effect should be found since their structure is somewhat like ammonia and Sutherland, Lee, and Wu (446) find the barrier to be about the same height as in ammonia (2000 cm^{-1}), but the frequency of inversion is 1000 times less than in this gas.

II. VIBRATIONS OF POLYATOMIC MOLECULES

8. Theory of Small Vibrations

A molecule consisting of N atoms possesses $3N$ degrees of freedom of which 3 belong to the translation of the system as a whole, 3 to its rotation in space, and $3N-6$ can be regarded as internal degrees of freedom. The latter correspond to vibrations of the component atoms. A linear molecule has only two rotational degrees of freedom and hence possesses $3N-5$ vibrations. For convenience of the dynamical treatment of the molecule a Cartesian coordinate system is selected in such a way that the total linear and angular momenta of the molecule are zero in this coordinate system. Such a set of axes will rotate and move in space as the molecule rotates or moves. In the present treatment it is assumed that there is no interaction between rotation and vibration, and the latter can be investigated by supposing the above defined set of axes is fixed in space. If the atoms are at rest, not subject to any accelerations, the coordinates of the atoms are called the equilibrium coordinates and the i th atom is in its equilibrium position (a_i, b_i, z_i) . The equilibrium distance (r_{ij}) between the i th and j th atom is then

$$r_{ij} = [(a_i - a_j)^2 + (b_i - b_j)^2 + (c_i - c_j)^2]^{\frac{1}{2}} \quad (48)$$

If the two atoms undergo small displacements such that the coordinates are now

$$a_i + x_i, \quad b_i + y_i, \quad \text{and} \quad c_i + z_i,$$

where x_i, y_i, z_i represent their components, then the new interatomic distance is

$$s_{ij} = [(a_i + x_i - a_j - x_j)^2 + (b_i + y_i - b_j - y_j)^2 + (c_i + z_i - c_j - z_j)^2]^{\frac{1}{2}} \quad (49)$$

If small quantities $(x_i - x_j)^2$, etc., are neglected

and if the direction cosines are

$$\alpha_{ij} = (a_i - a_j)/r_{ij}, \quad \beta_{ij} = (b_i - b_j)/r_{ij}, \quad (50)$$

and

$$\gamma_{ij} = (c_i - c_j)/r_{ij}, \quad (51)$$

then

$$\Delta_{ij} = \alpha_{ij}(x_i - x_j) + \beta_{ij}(y_i - y_j) + \gamma_{ij}(z_i - z_j), \quad (52)$$

where the quantity Δ_{ij} is the change of the i - j th distance from equilibrium.

Nothing has been said regarding the forces causing these displacements and their detailed nature is not known any too well. It can be said, however, that for a given electronic state the potential energy depends on the position of the nuclei. Two different force fields have been considered: "valency" and "central" forces. In the first case they are thought to act along chemical bonds and to oppose bending of the angles of directed bonds, while central forces are said to act between any pair of atoms, irrespective of the chemical structure of the molecule. It is further assumed for simplicity that the interactions are harmonic in nature. Constraints along bonds are of the same nature in both cases, but they are different when changes in angles take place.

In the case of central forces, the potential energy will be given approximately by

$$V \doteq \frac{1}{2} \sum_{ij} \sum_{mn} k_{ijmn} \cdot \Delta_{ij} \cdot \Delta_{mn}, \quad (53)$$

where the k_{ijmn} are Hooke's law force constants. For valency forces a similar expression holds, only some of the terms will be replaced by changes in the valence angles.

As long as displacements are small, linear relationships exist between changes of angles and changes of distances. As an illustration, consider a triatomic non-linear molecule, with chemical bonds between atoms 1 and 2 and atoms 2 and 3 and a valence angle θ between them. In the notation used above, we find

$$r_{13}^2 = r_{12}^2 + r_{23}^2 - 2r_{12}r_{23} \cos \theta \quad (54)$$

and

$$s_{13}^2 = s_{12}^2 + s_{23}^2 - 2s_{12}s_{13} \cos(\theta + \Delta\theta) \quad (55)$$

by the cosine law. To the order of small quantities adopted above, it is found that

$$s_{ij}^2 \doteq r_{ij}^2 + 2r_{ij} \cdot \Delta_{ij} \quad (56)$$

and since

$$\cos(\theta + \Delta\theta) \doteq \cos \theta - \Delta\theta \sin \theta$$

it follows that

$$r_{13} \cdot \Delta_{13} = (r_{12} - r_{23} \cos \theta) \Delta_{12} + (r_{23} - r_{12} \cos \theta) \Delta_{23} + r_{12} r_{23} \sin \theta \cdot \Delta\theta. \quad (57)$$

By means of this equation certain of the Δ_{ij} can be eliminated to give a potential energy consistent with a valency force field as was pointed out by Wall (478).

The kinetic energy (T) of the system is

$$2T = \sum_l m_l (\dot{x}_l^2 + \dot{y}_l^2 + \dot{z}_l^2), \quad (58)$$

where m_l = mass of l th atom and

$$\dot{x}_l = dx_l/dt; \quad \text{etc.}$$

The Lagrangian equations of motion are now obtained:

$$d(\partial L / \partial \dot{q}_k) / dt - \partial L / \partial q_k = 0 \quad (59)$$

where $L = T - V$ and q_k is any coordinate. But

$$\partial L / \partial \dot{x}_l = m_l \dot{x}_l \quad (60)$$

and omitting cross terms in the potential energy we have

$$\partial L / \partial x_l = - \sum_{ij} k_{ij} \cdot \Delta_{ij} (\partial \Delta_{ij} / \partial x_l), \quad (61)$$

where

$$\partial \Delta_{ij} / \partial x_l = \alpha_{ij} (i=l); \quad = -\alpha_{ij} (j=l); \quad = 0 (l \neq i \neq j).$$

Therefore

$$m_l \ddot{x}_l = - \sum_{ij} k_{ij} \Delta_{ij} (\partial \Delta_{ij} / \partial x_l) \quad (62)$$

or

$$\ddot{x}_l = \sum_{ij} A_{lij} \Delta_{ij}; \quad A_{lij} = -k_{ij} (\partial \Delta_{ij} / \partial x_l) / m_l. \quad (63)$$

Similar expressions result for the other coordinates:

$$\ddot{y}_l = \sum_{ij} B_{lij} \Delta_{ij}; \quad \ddot{z}_l = \sum_{ij} C_{lij} \Delta_{ij}. \quad (64)$$

But

$$\ddot{\Delta}_{ij} = \alpha_{ij} (\ddot{x}_i - \ddot{x}_j) + \beta_{ij} (\ddot{y}_i - \ddot{y}_j) + \gamma_{ij} (\ddot{z}_i - \ddot{z}_j) \quad (65)$$

and substitution yields

$$\ddot{\Delta}_{ij} = \sum_{kl} [\alpha_{ij} (A_{ikl} - A_{jkl}) + \beta_{ij} (B_{ikl} - B_{jkl}) + \gamma_{ij} (C_{ikl} - C_{jkl})] \Delta_{kl} \quad (66)$$

or

$$\ddot{\Delta}_{ij} = \sum_{kl} G_{ijkl} \Delta_{kl}, \quad (67)$$

where

$$G_{ijkl} = \alpha_{ij}(A_{ikl} - A_{jkl}) + \beta_{ij}(B_{ikl} - B_{jkl}) + \gamma_{ij}(C_{ikl} - C_{jkl}). \quad (68)$$

If the motion is simple harmonic

$$\ddot{\Delta}_{ij} = -4\pi^2\nu^2\Delta_{ij} = -\lambda\Delta_{ij} \quad (69)$$

and

$$\sum_{kl} (G_{ijkl} + \lambda\delta_{ij}^{kl})\Delta_{kl} = 0, \quad (70)$$

where

$$\delta_{ij}^{kl} = 1 \quad (kl \text{ is } ij) \quad \text{and} \quad \delta_{ij}^{kl} = 0 \quad (kl \text{ is not } ij).$$

For each displacement Δ_{ij} there will be one equation, and the whole array constitutes a set of simultaneous homogeneous linear equations. In order that they be satisfied the determinant of the coefficients must be zero:

$$\begin{vmatrix} \lambda + G_{1212} & G_{1213} & \cdots & G_{12mn} \\ G_{1312} & \lambda + G_{1313} & \cdots & G_{13mn} \\ \vdots & \vdots & \ddots & \vdots \\ G_{mn12} & G_{mn13} & \cdots & \lambda + G_{mnmn} \end{vmatrix} = 0. \quad (71)$$

The roots of the determinantal or secular equation will give the desired frequencies. If the roots appear only once the corresponding frequency is said to be non-degenerate. If a root appears twice the degree of degeneracy is two, etc. In the solution of this equation the geometry of the molecule will be portrayed in the symmetry properties of the determinantal equation. They furnish valuable assistance in reducing the secular equation by allowing factorization.

9. Symmetry of Secular Equation

The symmetry property of the determinantal equation has been studied by Wall (478) and Glockler and Wall (163). They considered the non-degenerate frequencies of acetylene, ethane, methyl acetylene, dimethyl acetylene, and diacetylene, using a simple valency force field, involving no cross terms. The secular equation for methyl acetylene is as follows:

$$\begin{vmatrix} \lambda + A & B & C & 0 & 0 & 0 & 0 \\ D & \lambda + E & F & 0 & 0 & 0 & 0 \\ G & -3B & \lambda - 6C & H & 0 & 0 & 0 \\ 0 & 0 & 3C & \lambda - 2H & 3C & 0 & 0 \\ 0 & 0 & 0 & H & \lambda - 6C & -3B & G \\ 0 & 0 & 0 & 0 & F & \lambda + E & D \\ 0 & 0 & 0 & 0 & C & B & \lambda + A \end{vmatrix} = 0. \quad (75)$$

$$\begin{vmatrix} \lambda + A & B & C & 0 & 0 \\ D & \lambda + E & F & 0 & 0 \\ G & -3B & \lambda - 6C & H & 0 \\ 0 & 0 & 3C & \lambda - 2H & I \\ 0 & 0 & 0 & H & \lambda + J \end{vmatrix} = 0. \quad (72)$$

$k =$ force constant,

$m =$ mass,

$\nu =$ vibration frequency,

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

$A = -k_{CH}(1/3m_C + 1/m_H)$,

$B = 2 \cdot 8^{1/2} \cdot k_{CCH} \cdot r_{CH}/3m_C$,

$C = k_{CC}/3m_C$,

$D = 8^{1/2} \cdot k_{CH}/3m_C r_{CH}$,

$E = -2k_{CCH}(8/3m_C + 1/m_H)$,

$F = 8^{1/2} \cdot k_{CC}/3m_C r_{CH}$,

$G = k_{CH}/m_C$,

$H = k_{C=C}/m_C$,

$I = k_{=CH}/m_C$,

$J = -k_{=CH}(1/m_C + 1/m_H)$.

The equation for acetylene is

$$\begin{vmatrix} \lambda + J & H & 0 \\ I & \lambda - 2H & I \\ 0 & H & \lambda + J \end{vmatrix} = 0 \quad (73)$$

and for ethane

$$\begin{vmatrix} \lambda + A & B & C & 0 & 0 \\ D & \lambda + E & F & 0 & 0 \\ G & -3B & \lambda - 6C & -3B & G \\ 0 & 0 & F & \lambda + E & D \\ 0 & 0 & C & B & \lambda + A \end{vmatrix} = 0. \quad (74)$$

The expression for methyl acetylene contains a certain part which comes from the acetylene determinant and a portion related to the ethane equation. This is related to the fact that a methyl group is attached to the acetylene kernel ($-C \equiv C-$). Similarly the dimethyl acetylene equation contains these same features, and the ethane portion is, of course, doubled since there are two methyl groups in the molecule:

The last case considered was diacetylene with an ethane (C—C) linkage in the center of the molecule. The secular equation portrays this fact

$$\begin{vmatrix} \lambda+J & H & 0 & 0 & 0 \\ I & \lambda-2H & 3C & 0 & 0 \\ 0 & H & \lambda-6C & H & 0 \\ 0 & 0 & 3C & \lambda-2H & I \\ 0 & 0 & 0 & H & \lambda+J \end{vmatrix} = 0. \quad (76)$$

These secular equations are therefore simply mathematical formulae of these molecules in another language than the usual chemical notation. It is of interest to recall certain matrix considerations made by Balandin (21, 22).

10. Normal Coordinates

In a molecule having N atoms there are $N(N-1)/2$ different distances and the same number of displacements. Since there are $3N-6$ degrees of freedoms only this number of distances can be independent. In a five atom molecule there are 10 distances and only nine degrees of freedom. The tenth distance (i.e., the redundant coordinate) can be gotten from the others by simple geometric means as a linear combination. Furthermore it is easily seen that a non-degenerate system having n displacements (Δ_{ij}) and hence n frequencies (λ) will have $n(n+1)/2$ terms in the potential energy expression given above. These terms are only the quadratic ones, and a more complete form of potential energy should have cubic and possibly quartic terms. There are already more quadratic terms than there are constants (i.e., frequencies) to determine them. Hence it is important to express both the kinetic and potential energy by the so-called "normal" coordinates (Q_i). In them the kinetic and potential energies are sums of squared terms:

$$2T = \sum \dot{Q}_i^2 \quad \text{and} \quad 2V = \sum \lambda_i Q_i^2 \quad (77)$$

and no cross terms appear. The λ in the expression for V are the same as the roots of the determinantal equation. For a molecular problem solved by normal coordinates, the off-diagonal members of the secular equations would all be zero.

11. Valency Force Field

In the usual approximate treatment of vibration problems the potential energy is expressed

by some convenient displacement coordinates, preferably of the valency force type, because of their connection with the chemical structure of the molecule. Only such cross terms are included as can be determined from the number of frequencies obtainable. If an isotopic molecule is available, it helps greatly because a greater number of force constants can then be calculated. In the Raman effect only certain of the fundamental frequencies are obtained, depending on the symmetry properties of the molecule, and none of the rotational details appears, except in special cases. On the other hand the infra-red spectrum under large dispersion will furnish the individual rotation lines of a band. However, band centers will give the vibration levels, and hence it is possible by the use of Raman and infra-red spectra to obtain all of the fundamental vibrations unless of course the selection rules for a given structure should forbid the appearance of a given frequency. It is always to be hoped that later investigation will give the rotational details. In the Raman effect and especially in the infra-red, overtones and combination tones are observed, usually as weaker lines and bands. In the early stages of Raman spectroscopy there was a great deal of guess work involved in the determination of the fundamentals of a given molecule. However, as the number of compounds investigated increased, the analysis of Raman spectra became somewhat easier to carry out.

In any case it is of importance to study in each instance the molecular vibration problem and to set up a potential energy expression. As an example the valency force field gives in the case of a triatomic molecule (H_2O) the following expressions for the kinetic (T) and potential energies (V):

$$2T = \sum_i m_i \dot{q}_i^2, \quad (78)$$

where $q_i = x_i \cdots y_3$ are Cartesian coordinates and

$$2V = c_1(\Delta_{12}^2 + \Delta_{13}^2) + c_2(r \cdot \Delta\eta)^2 + 2c_3(r \cdot \Delta\eta)(\Delta_{12} + \Delta_{13}) + 2c_4 \cdot \Delta_{12} \cdot \Delta_{13}, \quad (79)$$

where Δ_{12} , Δ_{13} are the changes in r , the OH bond distance, $\Delta\eta$ refers to the change in valence angle, c_1 is the OH bond force constant, c_2 is the valency angle bending force constant, and the last two terms are cross terms involving interactions between stretching and bending. The respective

force constants are c_3 and c_4 . Application of Lagrange's equations of motion yields the determinant

$$\begin{vmatrix} \lambda+A & D & B \\ C & \lambda+E & C \\ B & D & \lambda+A \end{vmatrix} = 0, \quad (80)$$

where

$$A = -c_1/\mu + c_3(\sin \alpha)/M - c_4(\cos \alpha)/M,$$

$$B = -c_1(\cos \alpha)/M + c_3(\sin \alpha)/M - c_4/\mu,$$

$$C = c_1(\sin \alpha)/M - 2c_3(1/\mu - (\cos \alpha)/M) + c_4(\sin \alpha)/M,$$

$$D = c_2(\sin \alpha)/M - c_3(1/\mu + (\cos \alpha)/M),$$

$$E = -2c_2(1/\mu - (\cos \alpha)/M) + 2c_3(\sin \alpha)/M.$$

The secular equation yields

$$\begin{aligned} \lambda_1 + \lambda_2 &= -A - B - E; \\ \lambda_1 \cdot \lambda_2 &= E(A + C) - 2CD; \quad \lambda_3 = B - A. \end{aligned} \quad (81)$$

These expressions allow the determination of three of the five unknown quantities (c_1 , c_2 , c_3 , c_4 , and α). Three frequencies are known from Raman spectra and/or the infra-red. The valence angle α can be obtained from electron diffraction experiments as outlined by Brockway (49). In order to test the method stated below, the valence angle of water was taken from Dennison's (105) complete analysis of the infra-red spectrum of the water vapor molecule ($\alpha = 104^\circ 31'$). The three fundamental frequencies are given by him as: $\omega_1 = 3825.32$, $\omega_2 = 1653.91$, and $\omega_3 = 3935.59$ cm^{-1} . With these frequencies all the possible real values of the constants have been obtained and are shown in the ellipses of Fig. 1. It was

TABLE II. Valence field force constants of the water vapor molecule (megadynes/cm).

c_1	c_2	c_3	c_4	Reference
0.696	0.0379	0.004	0.0165	Van Vleck and Cross (461)
0.8233	0.0752	—	-0.00757	Bonner (44)
0.8423	2.049	0.04047	-0.01015	Shaffer and Newton (412)
0.8386	0.0766	0.02343	-0.00991	Glockler (138)
0.8428	0.07678	0.02521	-0.01051	Dennison (105)
0.8269	0.07632	0.02346	-0.00585	King (213)

first assumed that the cross term c_4 could be neglected. However, this assumption led to imaginary values of c_2 and c_3 . By taking various values of c_4 the curves of Fig. 1 could easily be constructed. It is also seen that a simple valency

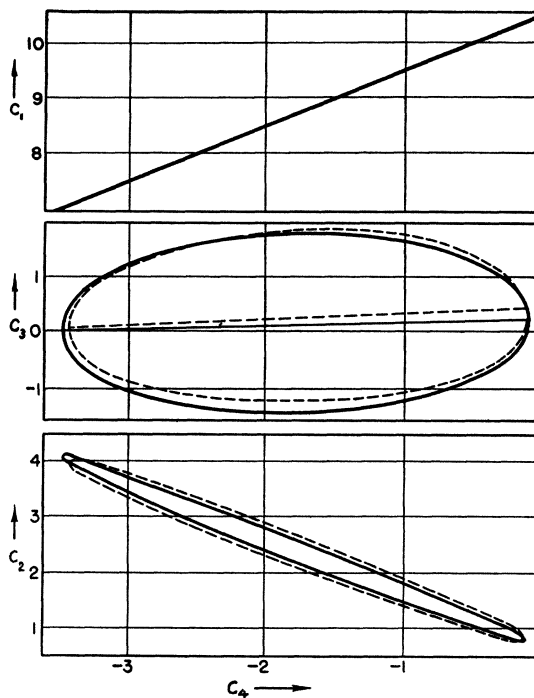


FIG. 1. Relations between force constants of the water vapor molecule [Glockler (138)]. Constants are given in megadynes/cm.

potential (containing only squared terms) is unsatisfactory. There are now more equations than unknowns, and no single consistent set of the force constants c_1 and c_2 can be found. However, the end points of greatest curvature of the ellipses are single valued and one of these sets checks the values given by Bonner (44), Dennison (105), Shaffer and Newton (412), and King (213) as shown in Table II. By the use of these force constants (line 4 of Table II) the three fundamental frequencies of heavy water (D_2O) have been calculated and are compared with the experimental values mentioned by Dennison (Table III).

The condition of single value for the end points of greatest curvature of the ellipses in Fig. 1 leads to the following equations for the force constants:

$$\begin{aligned} c_1 &= \lambda_3/2C + (C\lambda_1)/[2(AC - B^2)], \\ c_2 &= \lambda_2/2C + (B^2\lambda_3)/[2C(AC - B^2)], \\ c_3 &= (B\lambda_1)/[2(AC - B^2)], \\ c_4 &= c_1 - \lambda_3/C, \end{aligned} \quad (82)$$

where

$$A = 1/\mu + (\cos \alpha)/M; \quad 1/\mu = 1/m + 1/M;$$

$$B = (\sin \alpha)/M; \quad m = \text{mass of end atom};$$

$$C = 1/\mu - (\cos \alpha)/M; \quad M = \text{mass of central atom}.$$

These equations yield the force constants shown in Table IV. For comparison the values given by Wu (XIV) are shown, and it is seen that they check satisfactorily. Even though the method is an approximation, it is very simple to apply and gives results as good as is warranted from our present knowledge of Raman lines.

The dotted ellipses in Fig. 1 apply to heavy water (D_2O) and have been calculated from the data given by Dennison (105) as mentioned in Table III. It is seen that the ellipses for light and heavy water cross very near the point of greatest curvature, and hence it can be understood why the force constants for light water apply to deuterium oxide.

TABLE III. Calculated frequencies of deuterium oxide vapor molecule.

	Experiment (cm^{-1}) [from Dennison (105)]	Calculation (cm^{-1}) [Glockler (138)]
ω_3	2883.79	2883.5
ω_1	2758.06	2758.9
ω_2	1210.25	1212.9

12. Group Theory

The symmetry properties of molecules allow the factorization of the determinantal equation, and the applications of group theory have been of the greatest service in determining the classes of frequencies and certain of their properties. The subject has been discussed by Mulliken (293) in connection with the electronic structure of molecules and by Placzek (IX) in its application to the Raman effect. Rosenthal and Murphy (385) have summarized this topic and Kohlrausch (V) gives complete tables from which the number of vibrations of a molecule and the selection rules can be determined. Brester (46) initiated these ideas by algebraic methods, and Wigner (482) applied the methods of group theory. Molecules are systems of points and as such constitute a space group. They may possess certain elements of symmetry such as rotational

axes, reflection planes, and a point of inversion. The related covering operations form the members of a group. Each such element can be referred to an analytical expression known as its representation. They are matrices and are called "irreducible" in case they possess diagonal elements only. Wigner found that there are as many types of fundamental frequencies for a given molecule as the corresponding "group" has irreducible representations or classes and the number of the linearly independent fundamental vibrations of a certain frequency is given by the order of the representation. The physically important quantity is the sum of the diagonal elements of the irreducible representation, called the character [$X(R)$] of the representation:

$$X(R) = \pm u_R(1 + 2 \cos \varphi_R). \quad (83)$$

φ_R is the angle of rotation of the operator R (upper sign for pure rotation, lower one for rotation-reflection) and u_R is the number of equilibrium positions (i.e., atoms) not changed by the operation R . $X(R)$ is a linear combination of the characters $X^{(i)}(R)$ of the various irreducible representations of the group:

$$X(R) = a_1' X^{(1)}(R) + a_2' X^{(2)}(R) + \dots \quad (84)$$

Here the coefficients a_1' , a_2' (which are positive

TABLE IV. Valency field force constants for triatomic molecules [G =Glockler (138); W =Wu (XIV)].

	c_1	c_2	c_3	c_4	Ref.
H_2S	0.3941	0.0468	0.0056	-0.0017	G
	0.402	0.048	0.000	-0.012	W
CO_2	1.5335	0.0571	0.000	0.1052	G
	1.59	0.058	0.000	0.106	W
SO_2	1.0409	0.1070	0.1347	0.048	G
	0.991	0.0820	0.0000	-0.009	W
CS_2	0.7456	0.0233	0.0000	0.0593	G
	0.755	0.0240	0.0000	0.067	W
COS	1.5216	0.0364	0.0000	0.0602	G
	0.7402				
	1.340	—	—	—	W
	0.835				

whole numbers or zero) show how many fundamental vibrations of the system belong to the various representations $D^{(1)}(R)$, $D^{(2)}(R)$, \dots

The numbers a_1', a_2', \dots can also be calculated by the explicit expression

$$a_p' = \frac{1}{h} \sum_R X(R) \cdot X^{(p)}(R), \quad (85)$$

where the sum must be carried over all h elements of the group (G). Ordinary translation and rotation are included. If they are removed, there is obtained for the number of fundamental frequencies of the various types (a):

$$\begin{aligned} S(R) &= a_1 X^{(1)}(R) + a_2 X^{(2)}(R) + \dots \\ &= (u_R - 2)(1 + 2 \cos \varphi_R); \text{ pure rotation} \\ &= -u_R(1 + 2 \cos \varphi_R); \\ &\hspace{10em} \text{rotation-reflection} \end{aligned} \quad (86)$$

or the explicit formula

$$\begin{aligned} a_p &= \frac{1}{h} \sum_R X^{(p)}(R) \cdot S(R) \\ &= \sum' (u_R - 2)(1 + 2 \cos \varphi_R) \\ &\quad - \sum'' u_R(1 + 2 \cos \varphi_R). \end{aligned} \quad (87)$$

The characters of the irreducible representations of most symmetry groups have been determined by Bethe (35).

In order to illustrate the use of these equations their application to methane is of interest. The symmetry group of this molecule is the tetrahedral group T_d . It consists of the operations of unity (E), four threefold rotation axes C_3 (8 group elements), three twofold rotation axes C_2 (3 elements), six reflection planes σ_d (6 elements), and three fourfold rotation-reflection axes S_4 (6 elements). The characters of the five irreducible representations are shown in Table V.

TABLE V. Characters of the five irreducible representations of the tetrahedral group T_d .

T_d	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$
$X^{(1)}$	1	1	1	1	1
$X^{(2)}$	2	-1	2	0	0
$X^{(3)}$	3	0	-1	1	-1
$X^{(4)}$	3	0	-1	-1	1
$X^{(5)}$	1	1	1	-1	-1

The quantities needed for further calculation are given in Table VI. In order to determine μ_R , the symmetry operation indicated is carried out and the atoms which do not move are counted. Their

sum is the desired quantity. The total number of group elements (h) is twenty-four. The five coefficients a_p can be obtained from Eq. (87). Each one is a sum of five terms of the type $S(R) \times X^{(p)} \times n$, where n is the number of group elements, for example,

$$a_1 = (1/24)[9 \times 1 \times 1 + 0 \times 1 \times 8 + 1 \times 1 \times 3 + 3 \times 1 \times 6 - 1 \times 1 \times 6] \quad (88)$$

and

$$a_1 = 1; \quad a_2 = 1; \quad a_3 = 2; \quad a_4 = 0; \quad a_5 = 0,$$

which gives one single frequency, one doubly degenerate one and two trebly degenerate vibrations. There are altogether $1 + 2 + 2 \times 3 = 9$ frequencies which checks the number of internal degrees of freedom for a five-atom molecule: $3 \times 5 - 6 = 9$. Four distinct frequencies are to be expected to be observable in this case.

The calculation can also be carried out by applying these equations to equivalent points or to the single atoms, i.e., the carbon atom and the hydrogen atoms of methane separately as shown in Tables VII and VIII. It is necessary to end the

TABLE VI. Values of pertinent quantities for symmetry group T_d .

T_d	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$
μ_R	5	2	1	3	1
φ_R	0	$2\pi/3$	π	π	$2\pi/4$
$\pm(1 + 2 \cos \varphi_R)$	3	0	-1	1	-1
$X(R)$	15	0	-1	3	-1
$S(R)$	9	0	1	3	-1

tables with $X(R)$ and subtract rotation and translation characters from one of them.

The calculation of the coefficients a_p is the same

$$a_1 = (1/24)[3 \times 1 \times 1 + 0 - 1 \times 1 \times 3 + 1 \times 1 \times 6 - 1 \times 1 \times 6] \quad (89)$$

and

$$a_1 = a_2 = a_4 = a_5 = 0; \quad a_3 = 1.$$

Hence there is one frequency which is treble. The coefficients a_p are $a_1 = 1; a_2 = 1; a_3 = 2; a_4 = 1; a_5 = 0$. If translation and rotation (a_3 and a_4) are taken away there remains one single frequency (a_1), one double (a_2), and one treble one (a_3). Hence the sum of frequencies for the two types of equivalent atoms (carbon and hydrogen)

is the same as before. Nowadays the tables of Kohlrausch (V) permit the analysis to be carried out without any calculations at all, but it is of some interest to see how these tables were constructed.

Wilson (485) gives tables of the numbers, degeneracies, and symmetries of the normal modes

TABLE VII. Carbon atom.

T_d	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$
u_R	1	1	1	1	1
φ_R	0	$2\pi/3$	π	π	$2\pi/4$
$\pm(1+2\cos\varphi_R)$	3	0	-1	1	-1
$X(R)$	3	0	-1	1	-1
$S(R)$	3	0	-1	1	-1

TABLE VIII. Hydrogen atoms.

T_d	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$
u_R	4	1	0	2	0
φ_R	0	$2\pi/3$	π	π	$2\pi/4$
$\pm(1+2\cos\varphi_R)$	3	0	-1	1	-1
$X(R)$	12	0	0	2	0

of vibration for a number of the common molecular types. The selection rules are also included as well as the polarization properties of the Raman lines.

13. Symmetry Coordinates

In studying a molecular vibration problem, normal coordinates would be most satisfactory because the determinantal equation would have diagonal terms only. Although it is usually not an easy matter to find the normal coordinates, it is very desirable to choose such a set that will at least be in accordance with the symmetry requirements, even though their use should involve cross terms in the kinetic and potential energy expressions. Such coordinates will allow the determinantal equation to be factored to the maximum extent, and Howard and Wilson (188) call them "symmetry coordinates." Edgell (110) applied the methods of Wilson (493, 495) to the methylene halides, which belong to the space group C_{2v} . Their character table is given in Table IX. The internal coordinates chosen were the changes in length of interatomic distance $r_{H(1)}$, $r_{H(2)}$, $r_{X(3)}$, $r_{X(4)}$ and the changes in valence angles α (HCH), β (XCX) and γ_{13} , γ_{14} , γ_{23} , and γ_{24}

TABLE IX. Character table for symmetry group C_{2v} .

C_{2v}	E	C_2^z	σ_x	σ_y	Raman	Infra-red	Frequencies
A_1	1	1	1	1	p	a	$\nu_1\nu_2\delta_1\delta_2$
A_2	1	1	-1	-1	d^2p	ia	δ
B_1	1	-1	1	-1	d^2p	a	$\nu_3\delta_3$
B_2	1	-1	-1	1	d^2p	a	$\nu_4\delta_4$

(Fig. 2). There are ten internal coordinates, but only nine degrees of freedom, hence one coordinate is redundant. One of the angles can be obtained from the others, since their sum must be constant. By the method of Wilson one of the symmetry coordinates is obtained from this condition and later ignored, whereby the redundancy is eliminated without destroying the symmetry. The following linear combinations of internal coordinates will be symmetry coordinates for the irreducible representation A_1 since they transform into themselves under all operations of the group:

$$\begin{aligned} R_1 &= (1/\sqrt{2})(r_{H(1)} + r_{H(2)}), \\ R_2 &= (1/\sqrt{2})(r_{X(3)} + r_{X(4)}), \\ R_3' &= \alpha, \\ R_4' &= \beta, \\ R_5' &= (1/2)(\gamma_{13} + \gamma_{14} + \gamma_{23} + \gamma_{24}). \end{aligned} \quad (90)$$

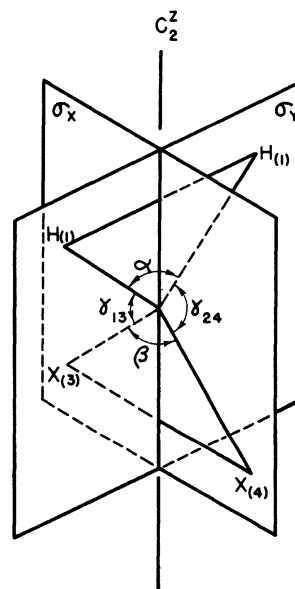


FIG. 2. Symmetry elements and internal coordinates of the methylene halides (CH_2X_2) [Edgell (110)].

These symmetry coordinates are orthogonal, normalized, and have been formed from equivalent internal coordinates only. There are four vibrations of type A_1 and five linearly inde-

TABLE X. Symmetry properties of coordinate R_5 .

	E	C_2^z	σ_x	σ_y
$\gamma_{13} \rightarrow$	γ_{13}	γ_{24}	γ_{14}	γ_{23}
$\gamma_{24} \rightarrow$	γ_{24}	γ_{13}	γ_{23}	γ_{14}
$\gamma_{14} \rightarrow$	γ_{14}	γ_{23}	γ_{13}	γ_{24}
$\gamma_{23} \rightarrow$	γ_{23}	γ_{14}	γ_{24}	γ_{13}
$C(R_5)$	$(+1)R_5$	$(+1)R_5$	$(-1)R_5$	$(-1)R_5$

pendent combinations, hence one of this set must be the redundant coordinate. In terms of the internal coordinates the constancy of angles is expressed by

$$\alpha + \beta + \sum \gamma_{ij} = 0$$

or written as a normalized symmetrical coordinate

$$R_C = (1/\sqrt{6})(\alpha + \beta + \gamma_{13} + \gamma_{14} + \gamma_{23} + \gamma_{24}) = 0 \quad (91)$$

$$= (1/\sqrt{6})(R_3' + R_4' + 2R_5') = 0.$$

The primed coordinates combine into 2 coordinates orthogonal to R_C and to each other:

$$R_3 = (1/\sqrt{2})(R_3' - R_4') = (1/\sqrt{2})(\alpha - \beta) \quad (92)$$

and

$$R_4 = (1/\sqrt{3})(R_3' + R_4' - R_5') = (1/\sqrt{3})[\alpha + \beta - (1/2)(\gamma_{13} + \gamma_{14} + \gamma_{23} + \gamma_{24})]. \quad (93)$$

Only one vibration is of type A_2 and its symmetry coordinate must transform into itself under the operation C_2^z (character +1) and into its negative under $\sigma_x(-1)$ and $\sigma_y(-1)$:

$$R_5 = (1/2)(\gamma_{13} - \gamma_{14} - \gamma_{23} + \gamma_{24}). \quad (94)$$

It is easily verified that R_5 has the desired symmetry properties as can be seen from Table X. The two symmetry coordinates for type B_1 are

$$R_6 = (1/\sqrt{2})(r_{X(3)} - r_{X(4)}), \quad (95)$$

$$R_7 = (1/2)(\gamma_{13} - \gamma_{14} + \gamma_{23} - \gamma_{24}) \quad (96)$$

and for type B_2

$$R_8 = (1/\sqrt{2})(r_{H(1)} - r_{H(2)}), \quad (97)$$

$$R_9 = (1/2)(\gamma_{13} + \gamma_{14} - \gamma_{23} - \gamma_{24}). \quad (98)$$

14. Kinetic Energy Matrix

Further application of Wilson's methods of calculation to the methylene halides will give the kinetic energy matrix from which the secular equation can be obtained. The internal coordinates r_k are linear combinations of the Cartesian coordinates (x_i):

$$r_k = \sum_{i=1}^{3n} B_{ki} x_i, \quad (99)$$

but they also can be described by using two vectors \mathbf{g}_t and \mathbf{s}_{kt} (with components x_i and B_{ki} , respectively):

$$r_k = \sum_{t=1}^n \mathbf{s}_{kt} \cdot \mathbf{g}_t. \quad (100)$$

The kinetic energy matrix

$$G_{kk'} = \sum_{i=1}^{3n} \mu_i B_{ki} B_{k'i}; \quad (\mu_i = \text{mass}_i^{-1}) \quad (101)$$

is written in terms of these vectors

$$G_{kk'} = \sum_{t=1}^n \mu_t \mathbf{s}_{kt} \cdot \mathbf{s}_{k't}. \quad (102)$$

This form has the advantage of not requiring a coordinate system. Furthermore the vectors \mathbf{s}_{kt} can be expressed in terms of unit vectors $[\mathbf{r}(d)]$ along the chemical bonds:

$$\mathbf{s}_{kt'} = \mathbf{r}(d) \quad \text{and} \quad \mathbf{s}_{kt} = -\mathbf{r}(d) \quad (103)$$

between the atoms t' and t . Changes in angle (φ) between atoms $t' - t - t''$ ($t = \text{apex atom}$) have the following vectors: For the end atoms

$$\mathbf{s}_{kt'} = (\cos \varphi \cdot \mathbf{r}(d') - \mathbf{r}(d'')) / (d' \sin \varphi), \quad (104)$$

$$\mathbf{s}_{kt''} = (\cos \varphi \cdot \mathbf{r}(d'') - \mathbf{r}(d')) / (d'' \sin \varphi)$$

and for the apex atom

$$\mathbf{s}_{kt} = [(d' - d'' \cos \varphi) \cdot \mathbf{r}(d') + (d'' - d' \cos \varphi) \cdot \mathbf{r}(d'')] / (d' d'' \sin \varphi). \quad (105)$$

The equilibrium distance between atoms t' and t is d' and between atoms t'' and t it is d'' . The unit vectors $\mathbf{r}(d')$ and $\mathbf{r}(d'')$ point away from the apex atom (t). They will be directed from the carbon atom to the hydrogen and halogen atoms (Fig. 2). The equilibrium distance C-H and C-X will be designated d_H and d_X . Tetrahedral angles are assumed for all the angles:

$$\cos \alpha = \cos \beta = \cos \gamma = -\frac{1}{3} \quad (106)$$

and

$$\sin \alpha = \sin \beta = \sin \gamma = -4/(3\sqrt{2}). \quad (107)$$

The \mathbf{s}_{kt} vectors are:

For hydrogen (H_1):

$$\begin{aligned} \mathbf{s}_{r(1)H(1)} &= \mathbf{r}_1, \\ \mathbf{s}_{\alpha; H(1)} &= -\sqrt{2}(\mathbf{r}_1 + 3\mathbf{r}_2)/(4d_H), \\ \mathbf{s}_{\gamma(13)H(1)} &= -\sqrt{2}(\mathbf{r}_1 + 3\mathbf{r}_3)/(4d_H), \\ \mathbf{s}_{\gamma(14)H(1)} &= -\sqrt{2}(\mathbf{r}_1 + 3\mathbf{r}_4)/(4d_H). \end{aligned} \quad (108)$$

For halogen (X_3):

$$\begin{aligned} \mathbf{s}_{r(3)X(3)} &= \mathbf{r}_3, \\ \mathbf{s}_{\beta; X(3)} &= -\sqrt{2}(\mathbf{r}_3 + 3\mathbf{r}_4)/(4d_X), \\ \mathbf{s}_{\gamma(13)X(3)} &= -\sqrt{2}(\mathbf{r}_3 + 3\mathbf{r}_1)/(4d_X), \\ \mathbf{s}_{\gamma(23)X(3)} &= -\sqrt{2}(\mathbf{r}_3 + 3\mathbf{r}_2)/(4d_X). \end{aligned} \quad (109)$$

For carbon (C):

$$\mathbf{s}_{r(i), C} = -\mathbf{r}_i; \quad i = 1, 2, 3, 4.$$

$$\begin{aligned} \mathbf{s}_{\alpha; C} &= \sqrt{2}(\mathbf{r}_1 + \mathbf{r}_2)/d_H, \\ \mathbf{s}_{\beta; C} &= \sqrt{2}(\mathbf{r}_3 + \mathbf{r}_4)/d_X, \end{aligned} \quad (110)$$

$$\begin{aligned} \mathbf{s}_{\gamma(ij)C} &= (\sqrt{2}/4) \{ (3/d_X + 1/d_H) \mathbf{r}_i \\ &+ (3/d_H + 1/d_X) \mathbf{r}_j \}, \quad ij = 13, 14, 23, 24. \end{aligned}$$

Utilizing the symmetry situation leads to the introduction of a new set of vectors

$$\mathbf{S}_j^{(t)} = \sum_k U_{jk} \mathbf{s}_{kt}, \quad (111)$$

where the U_{jk} are defined through the symmetry coordinates

$$R_j = \sum_k U_{jk} r_k. \quad (112)$$

In terms of these new vectors the energy matrix $G_{ll'}$ will, on account of symmetry, break into diagonal blocks just like the secular equation and the separate blocks correspond to the various irreducible representations of the group:

$$G_{ll'} = \frac{1}{d} \sum_p \mu_p g_p \sum_a^d \mathbf{S}_{la}^{(t)} \cdot \mathbf{S}_{l'a}^{(t)}. \quad (113)$$

g_p = number of equivalent atoms in the p th set,
 d = degeneracy (2 or 3),
 t = any atom of the p th set.

It is only necessary to form one $\mathbf{S}^{(t)}$ for one atom of each set of equivalent atoms. As an example $\mathbf{S}_4^{(H_1)}$ of the A_1 representation may be

considered. The corresponding symmetry coordinate is

$$R_4 = (1/\sqrt{3})[\alpha + \beta - (1/2)(\gamma_{13} + \gamma_{14} + \gamma_{23} + \gamma_{24})]. \quad (114)$$

Hence

$$U_{4\alpha} = U_{4\beta} = 1/\sqrt{3} \quad (115)$$

and

$$\begin{aligned} U_{4\gamma(13)} &= U_{4\gamma(14)} = U_{4\gamma(23)} \\ &= U_{4\gamma(24)} = -(1/(2\sqrt{3})). \end{aligned} \quad (116)$$

Therefore

$$\begin{aligned} A_1^{(1)} \mathbf{S}_4^{(H_1)} &= U_{4\alpha} \cdot \mathbf{s}_{\alpha H(1)} + U_{4\beta} \cdot \mathbf{s}_{\beta H(1)} \\ &+ U_{4\gamma(13)} \cdot \mathbf{s}_{\gamma(13)H(1)} + U_{4\gamma(14)} \cdot \mathbf{s}_{\gamma(14)H(1)} \\ &+ U_{4\gamma(23)} \cdot \mathbf{s}_{\gamma(23)H(1)} + U_{4\gamma(24)} \cdot \mathbf{s}_{\gamma(24)H(1)} \\ &= (1/\sqrt{3})[-\sqrt{2}(\mathbf{r}_1 + 3\mathbf{r}_2)/(4d_H) \\ &- (1/2)\{-\sqrt{2}(\mathbf{r}_1 + 3\mathbf{r}_3)/(4d_H)\} \\ &- (1/2)\{-\sqrt{2}(\mathbf{r}_1 + 3\mathbf{r}_4)/(4d_H)\}] \\ &= \sqrt{6}(\mathbf{r}_3 + \mathbf{r}_4 - 2\mathbf{r}_2)/(8d_H). \end{aligned} \quad (117)$$

The $\mathbf{S}_j^{(t)}$ vectors are summarized as follows:

$$\begin{aligned} A_1: \quad \mathbf{S}_1^{(H)} &= \mathbf{r}_1/\sqrt{2}, \\ \mathbf{S}_2^{(H)} &= 0, \\ \mathbf{S}_3^{(H)} &= -(\mathbf{r}_1 + 3\mathbf{r}_2)/(4d_H), \\ \mathbf{S}_4^{(H)} &= \sqrt{6}(\mathbf{r}_3 + \mathbf{r}_4 - 2\mathbf{r}_2)/(8d_H), \\ \mathbf{S}_1^{(X)} &= 0, \\ \mathbf{S}_2^{(X)} &= \mathbf{r}_3/\sqrt{2}, \\ \mathbf{S}_3^{(X)} &= (\mathbf{r}_3 + 3\mathbf{r}_4)/(4d_X), \\ \mathbf{S}_4^{(X)} &= \sqrt{6}(\mathbf{r}_1 + \mathbf{r}_2 - 2\mathbf{r}_4)/(8d_X), \\ \mathbf{S}_1^{(C)} &= -(\mathbf{r}_1 + \mathbf{r}_2)/\sqrt{2}, \\ \mathbf{S}_2^{(C)} &= -(\mathbf{r}_3 + \mathbf{r}_4)/\sqrt{2}, \\ \mathbf{S}_3^{(C)} &= (\mathbf{r}_1 + \mathbf{r}_2)/d_H - (\mathbf{r}_3 + \mathbf{r}_4)/d_X, \\ \mathbf{S}_4^{(C)} &= (\sqrt{6}/4)[1/d_H - 1/d_X] \\ &\quad \times (\mathbf{r}_1 + \mathbf{r}_2 - \mathbf{r}_3 - \mathbf{r}_4). \end{aligned} \quad (118)$$

$$\begin{aligned} A_2: \quad \mathbf{S}_1^{(H)} &= 3\sqrt{2}(\mathbf{r}_4 - \mathbf{r}_3)/(8d_H), \\ \mathbf{S}_1^{(X)} &= 3\sqrt{2}(\mathbf{r}_2 - \mathbf{r}_1)/(8d_X), \\ \mathbf{S}_1^{(C)} &= 0. \end{aligned} \quad (119)$$

$$\begin{aligned} B_1: \quad \mathbf{S}_1^{(H)} &= 0, \\ \mathbf{S}_2^{(H)} &= 3\sqrt{2}(\mathbf{r}_4 - \mathbf{r}_3)/(8d_H), \\ \mathbf{S}_1^{(X)} &= \mathbf{r}_3/\sqrt{2}, \\ \mathbf{S}_2^{(X)} &= -\sqrt{2}(3\mathbf{r}_1 + 3\mathbf{r}_2 + 2\mathbf{r}_3)/(8d_X), \\ \mathbf{S}_1^{(C)} &= (\mathbf{r}_4 - \mathbf{r}_3)/\sqrt{2}, \\ \mathbf{S}_2^{(C)} &= -(\sqrt{2}/4)[3/d_H + 1/d_X](\mathbf{r}_4 - \mathbf{r}_3). \end{aligned} \quad (120)$$

$$\begin{aligned}
B_2: \quad \mathbf{S}_1^{(H)} &= \mathbf{r}_1/\sqrt{2}, \\
\mathbf{S}_2^{(H)} &= -\sqrt{2}(2\mathbf{r}_1+3\mathbf{r}_3+3\mathbf{r}_4)/(8d_H), \\
\mathbf{S}_1^{(X)} &= 0, \\
\mathbf{S}_2^{(X)} &= 3\sqrt{2}(\mathbf{r}_2-\mathbf{r}_1)/(8d_X), \\
\mathbf{S}_1^{(C)} &= (\mathbf{r}_2-\mathbf{r}_1)/\sqrt{2}, \\
\mathbf{S}_2^{(C)} &= -(\sqrt{2}/4)[3/d_X+1/d_H](\mathbf{r}_2-\mathbf{r}_1).
\end{aligned} \tag{121}$$

It is now possible to form the G matrices for the various representations. The element in the j th row and j' th column is

$$G_{jj'} = \sum_p \mu_p g_p \mathbf{S}_j^{(p)} \cdot \mathbf{S}_{j'}^{(p)}. \tag{122}$$

($g_H=2$; $g_X=2$; $g_C=1$.) The summation is over all the p kinds of atoms. Hence when the $\mathbf{S}^{(p)}$ vectors of the A_1 representations are used

$$\begin{aligned}
G_{11} &= 2(\mathbf{S}_1^{(H)} \cdot \mathbf{S}_1^{(H)})/m_H \\
&\quad + 2(\mathbf{S}_1^{(X)} \cdot \mathbf{S}_1^{(X)})/m_X + (\mathbf{S}^{(C)} \cdot \mathbf{S}^{(C)})/m_C \\
&= 2(\mathbf{r}_1/\sqrt{2})(\mathbf{r}_1/\sqrt{2})/m_H \\
&\quad + [(\mathbf{r}_1+\mathbf{r}_2)/\sqrt{2}] \cdot [(\mathbf{r}_1+\mathbf{r}_2)/\sqrt{2}]/m_C \\
&= 1/m_H + 2/(3m_C).
\end{aligned} \tag{123}$$

It should be noted that $\mathbf{r}_i \cdot \mathbf{r}_j = 1$ ($i=j$) and $\mathbf{r}_i \cdot \mathbf{r}_j = -\frac{1}{3}$ ($i \neq j$). The energy matrices are symmetrical:

A_1 matrix:

$$\begin{vmatrix} A & B & -C & -D \\ & E & C & D \\ & & F & G \\ & & & H \end{vmatrix}, \tag{124}$$

where

$$\begin{aligned}
A &= 1/m_H + 2/(3m_C), \\
B &= -2/(3m_C), \\
C &= 2\sqrt{2}(1/d_H+1/d_X)/(3m_C), \\
D &= 2\sqrt{3}(1/d_H-1/d_X)/(3m_C), \\
E &= 1/m_X + 2/(3m_C), \\
F &= [1/(m_H d_H^2) + 1/(m_X d_X^2)] \\
&\quad + 4(1/d_H+1/d_X)^2/(3m_C), \\
G &= (\sqrt{6}/2)[1/(m_H d_H^2) - 1/(m_X d_X^2)] \\
&\quad + (2\sqrt{6})(1/d_H^2 - 1/d_X^2)/(3m_C), \\
H &= (3/2)[1/(m_H d_H^2) + 1/(m_X d_X^2)] \\
&\quad + 2(1/d_H - 1/d_X)^2/(m_C).
\end{aligned}$$

A_2 matrix:

$$G_{11} = (3/2)[1/(m_H d_H^2) + 1/(m_X d_X^2)]. \tag{125}$$

B_1 matrix:

$$\begin{vmatrix} I & J \\ & K \end{vmatrix}, \tag{126}$$

where

$$\begin{aligned}
I &= 1/m_X + 4/(3m_C), \\
J &= -2(3/d_H+1/d_X)/(3m_C), \\
K &= 3/(2m_H d_H^2) + 1/(2m_X d_X^2) \\
&\quad + (3/d_H+1/d_X)^2/(3m_C).
\end{aligned}$$

B_2 matrix:

$$\begin{vmatrix} L & M \\ & N \end{vmatrix}, \tag{127}$$

where

$$\begin{aligned}
L &= 1/m_H + 4/(3m_C), \\
M &= -2(3/d_X+1/d_H)/(3m_C), \\
N &= 1/(2m_H d_H^2) + 3/(2m_X d_X^2) \\
&\quad + (3/d_X+1/d_H)^2/(3m_C).
\end{aligned}$$

The secular equations have the form

$$|F - G\lambda| = \begin{vmatrix} F_{11} - (G^{-1})\lambda & F_{12} - (G^{-1})\lambda & \dots \\ F_{21} - (G^{-1})\lambda & F_{22} - (G^{-1})\lambda & \dots \\ \dots & \dots & \dots \end{vmatrix} = 0 \tag{128}$$

and the potential energy expression in terms of internal coordinates and containing all the terms of any importance is

$$\begin{aligned}
2V &= k_H(r_{H(1)}^2 + r_{H(2)}^2) + k_X(r_{X(3)}^2 + r_{X(4)}^2) \\
&\quad + k_\alpha(d_H\alpha)^2 + k_\beta(d_H\beta)^2 \\
&\quad + k_\gamma[(d_X\gamma_{13})^2 + (d_X\gamma_{14})^2 + (d_X\gamma_{23})^2 + (d_X\gamma_{24})^2] \\
&\quad + 2[k_\beta d_X^2\beta + k_\alpha d_H d_X\alpha](\gamma_{13} + \gamma_{14} + \gamma_{23} + \gamma_{24}) \\
&\quad + 2k_{\alpha\beta}d_H d_X\alpha\beta \\
&\quad + 2k_{HX}(r_{H(1)} + r_{H(2)})(r_{X(3)} + r_{X(4)}) \\
&\quad + 2k_{HH}r_{H(1)}r_{H(2)} + 2k_{XX}r_{X(3)}r_{X(4)} \\
&\quad + 2k_{X\gamma}d_X[r_{X(3)}(\gamma_{14} + \gamma_{24}) + r_{X(4)}(\gamma_{13} + \gamma_{23})] \\
&\quad + 2k'_{X\gamma}d_X[r_{X(3)}(\gamma_{13} + \gamma_{23}) + r_{X(4)}(\gamma_{14} + \gamma_{24})] \\
&\quad + 2[(k_{X\alpha}d_H\alpha + k_{X\beta}d_X\beta)(r_{X(3)} + r_{X(4)})] \\
&\quad + 2k_{\gamma\gamma}d_X^2(\gamma_{13}\gamma_{24} + \gamma_{14}\gamma_{23}) \\
&\quad + 2k_{\gamma\gamma}'d_X^2(\gamma_{13}\gamma_{23} + \gamma_{14}\gamma_{24}) \\
&\quad + 2k_{\gamma\gamma}''d_X^2(\gamma_{13}\gamma_{14} + \gamma_{23}\gamma_{24}).
\end{aligned} \tag{129}$$

If the potential energy be expressed in terms of the symmetry coordinates, it becomes

$$2V = \sum_{i,j} F_{ij} R_i R_j, \quad (130)$$

where the F_{ij} as functions of the force constants in Eq. (129) can be determined because in matrix notation

$$R = U r \quad \text{and} \quad r = U' R, \quad (131)$$

where U' is the transpose matrix. The F matrices are symmetrical ($F_{ij} = F_{ji}$) and their elements are:

A_1 matrix:

$$\begin{aligned} F_{11} &= k_H + k_{HH}, \\ F_{12} &= 2k_{HX}, \\ F_{22} &= k_X + k_{XX}, \\ F_{23} &= k_{X\alpha} d_H + k_{X\beta} d_X, \\ F_{24} &= (2/\sqrt{6})(k_{X\alpha} d_H + k_{X\beta} d_X \\ &\quad - k_{X\gamma} d_X - k_{X\gamma}' d_X), \\ F_{33} &= (1/2)(k_{\alpha} d_H^2 + k_{\beta} d_X^2 - 2k_{\alpha\beta} d_H d_X), \\ F_{34} &= (1/\sqrt{6})(k_{\alpha} d_H^2 - k_{\beta} d_X^2 \\ &\quad + 2k_{\beta\gamma} d_X^2 - 2k_{\alpha\gamma} d_H d_X), \\ F_{44} &= (1/3)[k_{\alpha} d_H^2 + k_{\beta} d_X^2 + k_{\gamma} d_X^2 \\ &\quad - 4d_X(k_{\beta\gamma} d_X + k_{\alpha\gamma} d_H) + 2k_{\alpha\beta} d_H d_X \\ &\quad + d_X^2(k_{\gamma\gamma} + k_{\gamma\gamma}' + k_{\gamma\gamma}'')]. \end{aligned} \quad (132)$$

A_2 matrix:

$$F_{11} = d_X^2(k_{\gamma} + k_{\gamma\gamma} - k_{\gamma\gamma}' - k_{\gamma\gamma}''). \quad (133)$$

B_1 matrix:

$$\begin{aligned} F_{11} &= k_X - k_{XX}, \\ F_{12} &= \sqrt{2} d_X (k_{X\gamma}' - k_{X\gamma}), \\ F_{22} &= d_X^2 (k_{\gamma} - k_{\gamma\gamma} + k_{\gamma\gamma}' - k_{\gamma\gamma}''). \end{aligned} \quad (134)$$

B_2 matrix:

$$\begin{aligned} F_{11} &= k_H - k_{HH}, \\ F_{12} &= 0, \\ F_{22} &= d_X^2 (k_{\gamma} - k_{\gamma\gamma} - k_{\gamma\gamma}' + k_{\gamma\gamma}''). \end{aligned} \quad (135)$$

The secular equations can now be determined in expanded form as shown by Wilson (493). They are particularly simple for the A_2 , B_1 , and B_2 vibrations:

$$A_2: \quad \lambda = G_{11} F_{11}. \quad (136)$$

B_1 and B_2 :

$$\begin{aligned} \lambda^2 - (G_{11} F_{11} + G_{22} F_{22} + 2G_{12} F_{12}) \lambda \\ + (G_{11} G_{22} - G_{12}^2) (F_{11} F_{22} - F_{12}^2) = 0, \end{aligned} \quad (137)$$

where $\lambda = 4\pi^2\nu^2$.

15. Splitting of High Frequencies

Wilson (493, 495) has pointed out that the secular equation can be reduced by one degree if one of the vibrations in a symmetry group is a C-H vibration. This is done by splitting off this high frequency from the lower ones. The procedure involves the use of a "reduced" G matrix with an F matrix in which the rows and columns corresponding to the C-H coordinate have been omitted. This action is equivalent to setting the C-H force constant equal to infinity and is particularly helpful in the case of the methylene chlorides since it reduces the A_1 secular equation from a quartic to a cubic equation. Since the A_1 matrix involves the C-H coordinate only once, the element of the j th row and j' th column of the reduced matrix (G^0) is given by

$$G_{jj'}^0 = G_{jj'} - (G_{j1} \cdot G_{1j}) / G_{11}, \quad (138)$$

where R_1 is the C-H coordinate. The B_2 vibrations also contain the C-H frequency, and hence it may be split out. Thus the lower frequency is given by

$$\lambda = G_{22}^0 F_{22}^0. \quad (139)$$

The results of this analysis as applied to CH_2X_2 are given in Section 17.

16. Isotope Effect

While Salant and Rosenthal (401) and Rosenthal (384) had studied the special case of the vibrational isotope effect for tri- and tetra-atomic molecules, and Wilson (486) gave a perturbation method, Teller (450) and Redlich (368) have shown that in general the product of the frequencies of a certain molecule divided by the similar product for the same molecule with isotopic atoms, is independent of the potential energy function and depends only on the masses and the geometric situation of the case. Wilson (495) found that this "product rule" can be shown to be true by using his kinetic energy

matrices G , where the frequency quotient is obtained in somewhat different form. The constant term of the secular equation or in any of its factors is given by the products of the determinants $|G|$ and $|F|$ belonging to the respective energy and force constant matrices. The constant term is the product of the roots of the equation. Since the force constants of two isotopic molecules are the same

$$(\prod_{\lambda\lambda})/(\prod_{\lambda\lambda})' = |G|/|G'|. \quad (140)$$

The primes refer to the isotope species, λ has its usual meaning, and the product contains all λ 's of the same symmetry class as the factor G .

TABLE XI. Force constants of methylene chloride [Edgell (110)].

Type	mega-dyne/cm	Type	mega-dyne/cm
C—Cl	0.359	(C—Cl)(C—Cl)	0.065
C—H	0.489	(C—Cl)(ClCCl)	0.022
H—C—H	0.460	(ClCCl)(HCCl)	0.0574
Cl—C—Cl	0.480	(HCH)(HCCl)	0.0563
H—C—Cl	0.214	(HCCl)(HCCl)	-0.0028
		(HCCl)'(HCCl)'	-0.0011

Wilson makes the useful suggestion that the above equation be applied to the low frequencies independent of the "split off" high ones. It is only necessary to use the reduced matrices G^0 , whereby the product rule can be applied separately to the high and low frequencies.

In the case of acetylenes the carbon isotope shifts have been observed lately by Cleveland and Murray (79). Menzies (275) determined the isotope abundance ratio for chlorine by studying the intensity of the symmetric breathing vibration of carbon tetrachloride. Herzberg (181) showed that the weak Raman line 2062 cm^{-1} near the strong line at 2092 cm^{-1} is due to HC^{13}N and not to HNC .

17. Force Constants

One of the most important applications of the Raman effect is the treatment of molecular vibrations by the theory of small vibrations and the resultant determination of the force constants of bond stretching and valency angle deformation. Even though the usual calculations are made with the observed frequencies and are in

error by as much as 10 percent if anharmonicity is neglected, still they are of great interest to chemists as they give the relative strength of chemical bonds, at least in rough measure. As Wu and Kiang (504) point out in the case of acetylene, the C—H bond force constant is 0.624 megadyne/cm with the zeroth-order frequencies, the observed fundamentals uncorrected for anharmonicity give 0.585 megadyne/cm. Similarly the $\text{C}\equiv\text{C}$ bond force constant in acetylene is 1.72 and 1.559 megadynes/cm, respectively. In order to determine the zeroth-order frequencies a great deal of information regarding the infra-red spectrum is necessary, and experiments in the Raman effect are not refined enough to furnish all the needed detail. Almost all present-day values are, therefore, only approximations to be corrected at a later date as more exact measurements of bands become available.

One of the most interesting features relating to bond force constants is the fact that a given bond, for example, the carbon-carbon bond, has the same force constant in many organic compounds. It is possible, therefore, to analyze more complex molecules by "carrying over" the force constants from simpler ones to the more complicated cases. In this manner a larger number of the cross term constants can be determined. However, there is always the danger that the actual value of a given force constant in a complex molecule may be somewhat different from the one transferred from the simple structure and

TABLE XII. Observed and calculated frequencies of methylene chloride [Edgell (110)].

Type	Assignment	Frequencies (cm^{-1})		
		Observed	Calculated	% dev.
A_1	ν_2	2985	2970	—
	δ_2	1266	1267	0.1
	ν_1	700	698	-0.3
	δ_1	284	285	0.4
A_2	δ	1149	1149	0.0
B_1	δ_3	1429	1436	0.5
	ν_3	737	737	0.0
B_2	ν_4	3046	3031	-0.5
	δ_4	898	897	-0.1

hence the cross term constants may be incorrect and the interaction of bonds is therefore not described properly. The fact that a given set of assumed and calculated force constants will reproduce those frequencies not used in their

TABLE XIII. Normal coordinate treatment of molecules [cf. Hibben (IV); Kohlrausch (V); Sutherland (444)].

Substance	References
C ₂ H ₄ to C ₂ D ₄	Hemptinne and Manneback (180); Bernard and Manneback (32)
C ₂ D ₆	Stitt (436)
<i>n</i> -aliphatic chains	Barriol (25)
C ₂ H ₂ , C ₂ HD, C ₂ D ₂	Wu and Kiang (504); Wu (502); Stitt (438)
B ₃ N ₃ H ₆	Crawford and Edsall (95)
methylhalides	Slawsky and Dennison (424); Crawford and Brinkley (94); Linnett (262)
CH ₃ -O-CH ₃	Crawford and Joyce (96)
CH ₃ -C≡CH	Crawford (89)(92); Linnett (263)
CH ₃ -C≡C-CH ₃	Crawford (90); Linnett (263)
C ₆ H ₆	Bernard, Manneback, and Verleysen (33)
(CH ₃) ₄ C; (CH ₃) ₄ Si	Silver (418)(419)
(CH ₃) ₃ X; X=P, As, Sb, Bi	Rosenbaum, Rubin, and Sandberg (383)
C ₂ H ₆ X; X=Cl, Br, I, OH	Cross and Van Vleck (101)
HN ₃	Davis (103)
HCN; CH ₃ CN	Crawford and Brinkley (94); Linnett (262)
CH ₂ Cl ₂ ; Y-CH ₂ -X	Edgell (110); Wagner (476)
CCl ₃ X; X=H, D, F	Edgell (110); Rosenthal and Voge (386); Voge and Rosenthal (465)
Thiophosgene (X ₂ YZ)	Duchesne (107)
Cyclopropane	Saksena (393)
C ₂ H ₅ OH; C ₂ H ₅ OD; C ₂ D ₅ OD	Mizusima <i>et al.</i> (286)
Aliphatic cyclic compounds	Saksena (398)
Urea and guanidinium	Kellner (207)
C ₆ H ₄ X ₂ ; X=H, CH ₃ , Cl, Br	Kohlrausch and Paulson (237)
HNO ₃ ; CH ₃ NO ₂	Chédin (63)

determination is no guarantee of their correctness. An infinite set of constants could be found to satisfy the mathematical relations involved. However, one would expect, for example, that the force constant of O-H in water should be nearly the same as for the diatomic radical "OH" itself. The same argument applies, of course, to other cases. In most of the molecules summarized the observed frequencies have been used, and force constants are carried over from simple to more complex molecules. The agreement between calculated and observed frequencies is better than expected.

In case a bond force constant is unusual, it may be assumed that resonance exists between several possible configurations of the molecule. Double bonds and triple bonds have, of course, their own specific values. However, the influence of neighboring atoms must always be kept in mind.

As an illustration it is interesting to cite the calculations of Edgell (110) on methylene chloride (Fig. 2). He used five force constants obtained with other molecules and calculated six interaction constants (Table XI). The comparison between the calculated and observed frequencies is satisfactory (Table XII). There are three checks on the potential energy expression used (Section 14); namely, ν_2 , ν_4 , and δ_3 , the latter

being the most significant. The modes of vibration are given by Wu (XIV). In Table XIII the molecules which have been studied by the normal coordinate treatment since 1938 are listed. It is seen that the field has been very active and in every case the theory of small vibrations as outlined has been used.

18. Interatomic Distance

Badger (18) discovered an empirical relation between the force constant (k_e) of a chemical bond and the interatomic distance (R_e):

$$R_e = (C_{ij}/k_e)^{1/3} - d_{ij}, \quad (141)$$

where C_{ij} and d_{ij} are constants which vary, however, with the row in the periodic table to which the bonded atoms belong. Sutherland (443, 445) considered "Badger's rule" as well as several variations by other writers and attempted to establish a theoretical basis for these empirical relations. He assumed that the potential energy (V) of a diatomic molecule can be expressed by

$$V = \alpha/(R^m) - \beta/(R^n). \quad (142)$$

α and β are constants, m and n integers, and R is the interatomic distance. The first derivative of the potential in respect to R yields the force acting between the particles. It vanishes at the

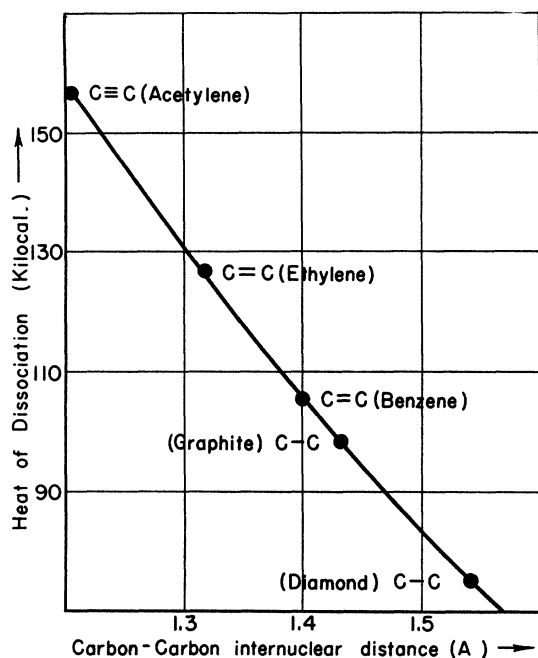


FIG. 3. Heats of dissociation and internuclear distances of carbon-carbon bonds [Fox and Martin (128)].

equilibrium distance R_e :

$$(dV/dR)_{R=R_e} = 0 \quad \text{or} \quad m\alpha = n\beta R_e^{m-n}. \quad (143)$$

The second derivative evaluated at R_e yields the force constant

$$k_e = m\alpha(n-m)/R_e^{m+2} = n\beta(n-m)/R_e^{n+2}. \quad (144)$$

If $m=1$ a relation very similar to Badger's results, if R_e is replaced by an effective internuclear distance: $R_e - d_{ij}$. The dissociation energy (D) is the value of the potential energy at R_e :

$$D = [\alpha(n-m)]/[R_e^m \cdot n] = (k_e R_e^2)/(mn). \quad (145)$$

The ratio $D/(k_e R_e^2)$ or the product mn should be a constant for molecules of the same class, i.e., with nearly the same exponents m and n . Sutherland finds the relations reasonably satisfactory for a series of molecules like O_2 , S_2 , SO , CN , and NO . He points out that a fairly accurate estimate can be made of the dissociation energy and the internuclear distance from the force constant of a chemical bond for which the Raman line is known.

Similar considerations were made by Fox and Martin (128) who calculated heats of dissociation

of C-H and C-C bonds on the assumption that all C-H linkages have the same heat value. They obtained smooth curves (Fig. 3) between heats of dissociation and internuclear distance or the force constants of these bonds. They also determined the order of several carbon-carbon bonds (1 for C-C, 2 for C=C, and 3 for C≡C bond) such as the bond in graphite and in benzene. The respective bond orders are 1.45 and 1.62. The values were obtained by the methods of quantum mechanics by Penney (336) (Fig. 4). Fox and Martin (128) applied Eq. (145) of Sutherland to the general carbon-carbon bond with results shown in Table XIV. They also observed that a relation $k_e R_e^5 = \text{constant}$ gave even better results than $k_e R_e^6 = \text{constant}$ (Morse-Clark) for carbon-carbon linkages. Equation (145) combined with the fifth power expression yields $D R_e^3 = \text{constant}$ showing that D varies as the three-fifths power of k_e . They compare the potential used by Sutherland [Eq. (142)] written in the form

$$V = D \left[\frac{n}{m-n} \right] \cdot \left[\left(\frac{R_e}{R} \right)^m - \left(\frac{m}{n} \right) \left(\frac{R_e}{R} \right)^n \right] \quad (146)$$

with the usual Morse function

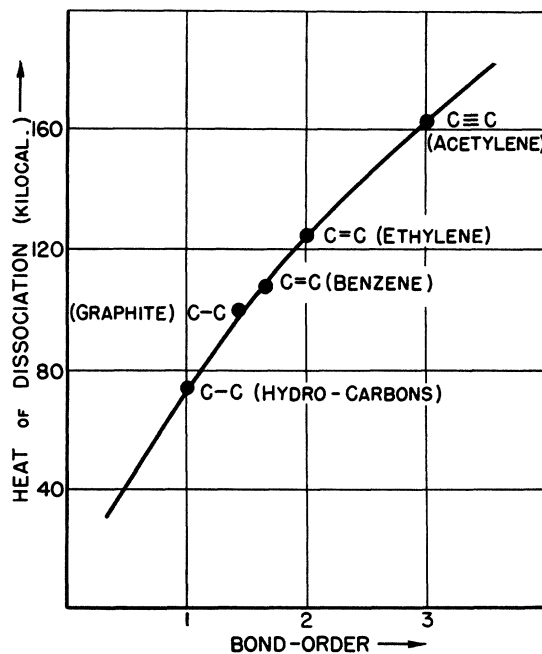


FIG. 4. Heats of dissociation and bond-order of the carbon-carbon linkage [Fox and Martin (128)].

$$V = D[\exp(-2a(R-R_e)) - 2\exp(-a(R-R_e))], \quad (147)$$

where a is a constant for each bond. By expanding these functions and evaluating them for small values of $R-R_e$ (near the equilibrium position) they obtain

$$\text{and } V = D[-1 + \{mn(R-R_e)^2\}/(2R_e^2)] \quad (148)$$

$$V = D[-1 + a^2(R-R_e)^2]. \quad (149)$$

These two Hooke's law potentials are equal provided $a^2 = (mn)/(2R_e^2)$ or $a = 3.22/R_e$. Thus the Morse function can be written

$$U/D = [\exp(-6.44(R/R_e - 1)) - 2\exp(-3.22(R/R_e - 1))]. \quad (150)$$

From the value of " a " chosen it follows that both potentials fit at the equilibrium distance, but agreement elsewhere depends on the individual values of m and n . Equal values give the best fit (Fig. 5). Considering $m-n$ a small quantity (δ)

TABLE XIV. Force constant, internuclear distance, and heat of dissociation of carbon-carbon bonds (128).

Bond	k_e (mega-dyne/cm)	R_e (Å)	D (kcal./mole)	$\frac{k_e R_e}{D} = mn$
C≡C	1.56	1.204	161	20.5
C=C	0.98	1.33	125.1	20.2
C _{ar} -C _{ar}	0.76	1.40	105.3	20.6
C-C	0.44	1.555	71.8	21.6

allows one to write Eq. (146) thus:

$$U/D = (n/\delta)(R_e/R)^m \{1 - (m/n)(R/R_e)^\delta\} \quad (151)$$

which on expansion and by use of $mn = 20.7$ (Table XIV) gives

$$U/D = (R_e/R)^{4.55} \{4.55 \ln(R_e/R) - 1\}. \quad (152)$$

Similar interesting studies were made by Clark and his co-workers (65-68) and extended by the introduction of a group number N ($N = \text{sum of outer electrons}$) and a period or sub-period constant (k_{qr}). A relation of the form

$$k_e R_e^x N^y = k_{qr} \quad (153)$$

is supported by theoretical considerations. Newing's work (316-317) would make $x = 6$ most likely and a reciprocal-exponential poten-

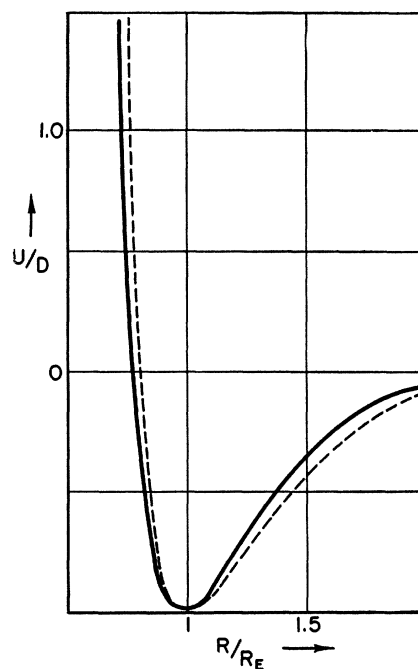


FIG. 5. General Morse function for carbon-carbon bonds. Full curve: Eq. (150) (Morse type). Broken curve: Eq. (152) [Fox and Martin (128)].

tial would indicate $y = \frac{1}{2}$ or $\frac{3}{2}$ with the exponent of the repulsive term of the type aR^{-4} .

The reciprocal-exponential potential was first suggested by Linnett (260) and examined in detail:

$$V = a/R^m - b \exp(-nR), \quad (154)$$

where a and b are constant and m and n integers. Expressions were obtained interrelating the observable quantities: force constant (k_e), equilibrium molecular distance (R_e), heat of dissociation (D), and the anharmonicity correction ($\omega_e x_e$). The relations involved were tested on a large number of diatomic molecules. Linnett (261) extended these calculations enabling him to fix values of the constants a , b , m , and n so that now a good estimate can be made of R_e from observed values of the vibration frequency and D and $\omega_e x_e$ can be obtained approximately.

Glockler and Evans (148) found that Badger's rule held very well for hydrides of the first row elements if these elements were divided into three groups, distinguished by different values of the constants A and B in the relation

$$k_e = A(R_e - B)^{-3} \text{ megadyne/cm}, \quad (155)$$

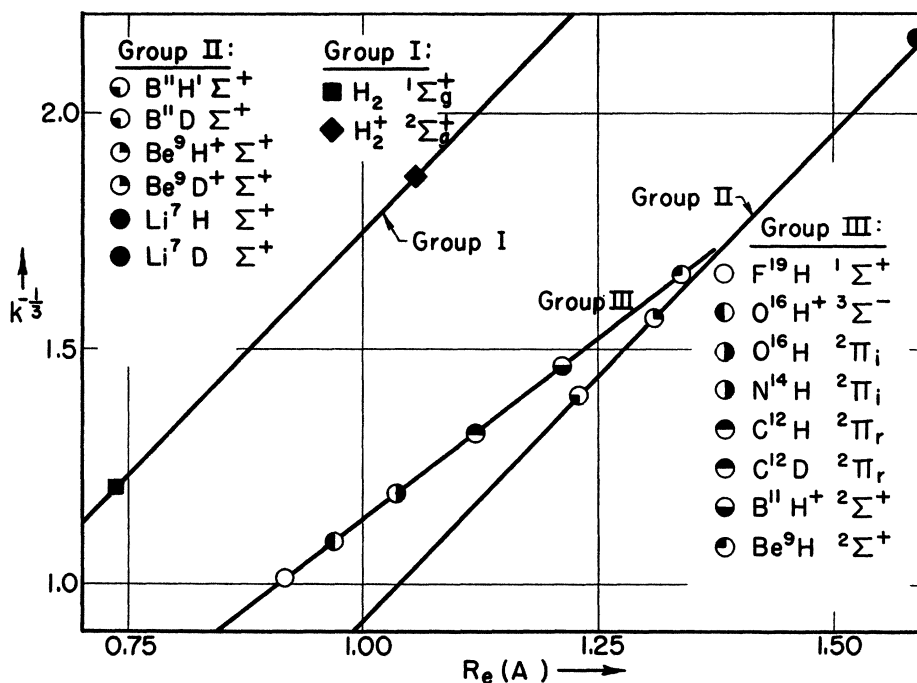


FIG. 6. Badger's rule for first row element hydrides. (Group I: $A=0.1152$, $B=0.1555$; Group II: $A=0.1187$, $B=0.5443$; Group III: $A=0.3003$, $B=0.2385$) [Glockler and Evans (148)].

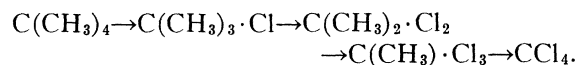
where R_e is the equilibrium distance in angstroms (Fig. 6). The reciprocal-exponential potential was used by Glockler and Baker (142, 144) in a study of the cyanogen radical in various compounds and spectroscopic states. The heat of dissociation was calculated for the radical in its various combinations.

It seems very likely that much interesting information will be brought forth and many instructive connections will be established between various molecular quantities by systematic investigations of this kind. It may be possible that internuclear distances of gaseous molecules can be obtained from Raman spectra with greater accuracy than by the conventional method of electron diffraction (49).

19. Spectral Series

A very helpful method of locating fundamental frequencies is the determination of the Raman spectra of a series of related compounds which differ only by the continued substitution of a given atom or which show some other progressive change in their composition. For example,

Kohlrausch and Wagner (242) studied the transition $\text{CH}_4 \rightarrow \text{CH}_3\text{X} \rightarrow \text{CH}_2\text{X}_2 \rightarrow \text{CHX}_3 \rightarrow \text{CX}_4$ and Wagner (477) discussed the group



Glockler and Leader (154) investigated halo-methanes as shown in Figs. 7-9. The characteristic C-H vibration is always found at about 3000 cm^{-1} and the C-F vibration at about 1065 cm^{-1} if the compounds contain a lone fluorine atom. One might expect to find a similar constant line corresponding to the C-Cl bond in the series CHBr_2Cl , CHBrClF , and CHClF_2 . While this is not the case, it should be noted that in this series the chlorine atom is not always the lightest atom. In order that a trihalomethane molecule show a valency vibration characteristic of a given halogen, this atom must be the only one of its kind and also the lightest one in the molecule. The characteristic C-X vibrations are given in Table XV. In a study of the Raman spectrum of fluoroform Glockler and Edgell (145) had occasion to consider several appropriate

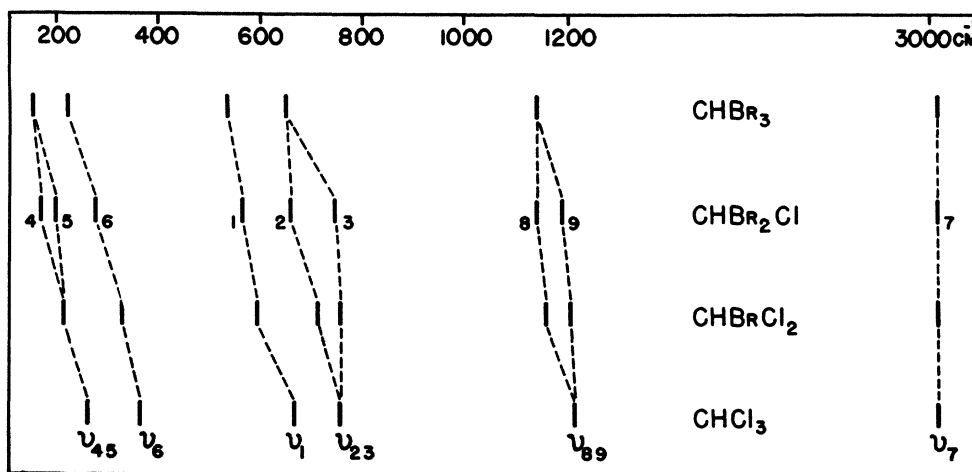


FIG. 7. The spectral sequence $\text{CHBr}_3 \rightarrow \text{CHCl}_3$ [Glockler and Leader (154)].

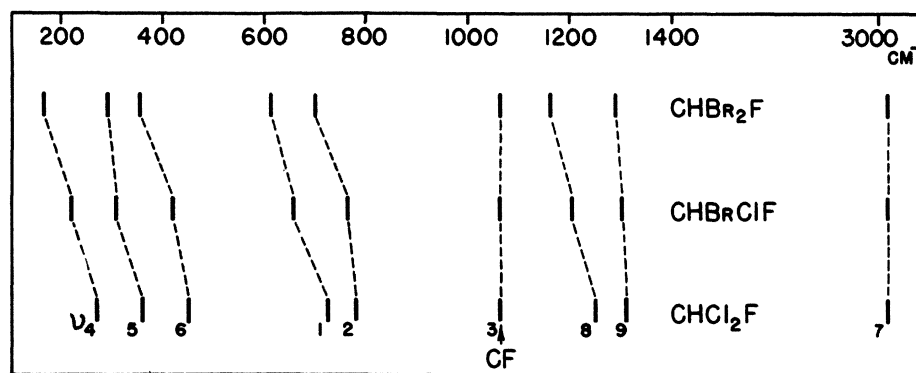


FIG. 8. The spectral sequence $\text{CHBr}_2\text{F} \rightarrow \text{CHCl}_2\text{F}$ [Glockler and Leader (154)].

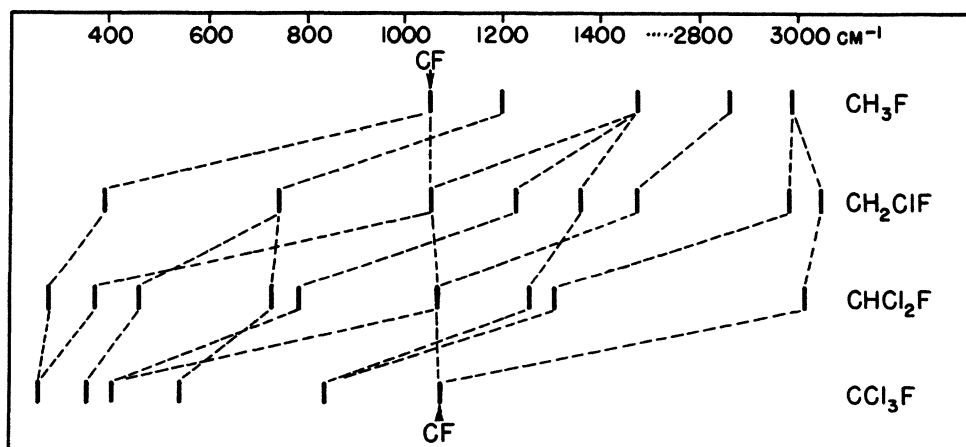


FIG. 9. The spectral sequence $\text{CH}_3\text{F} \rightarrow \text{CCl}_3\text{F}$ [Glockler and Leader (154)].

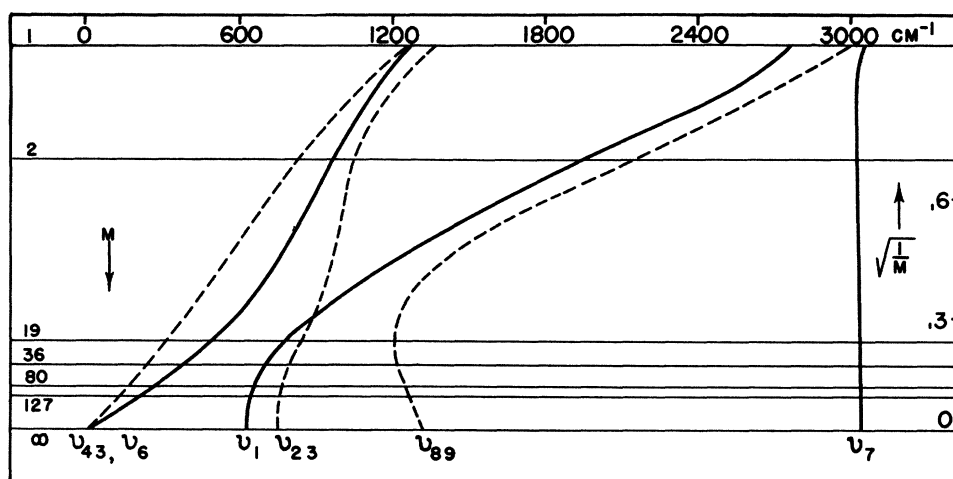
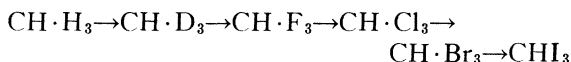


FIG. 10. Theoretical trends in the fundamental vibrations of the molecule CHX_3 under influence of change in mass of X atom: — parallel vibrations; - - - perpendicular vibrations [Glockler and Edgell (145)].

series such as



and



The system of fundamental vibrations of fluoroform must naturally fit into both sequences. Another very helpful graph can be obtained by calculating the frequencies from known force constants, etc., and obtaining the theoretical trend of the Raman lines as a function of mass as shown in Fig. 10 for the CHX_3 sequence. Even approximate calculation will furnish a very helpful datum when comparison with experiment is made, as can be seen on contrasting Figs. 10 and 11. The same investigators also found that the presence of more than one of the lightest halogen atoms modifies the characteristic vibration only slightly. In CHClBr_2 , the chlorine vibration is 750 cm^{-1} . In passing to CHClBrF and CHCl_2F fluorine becomes the lightest atom present and the C-F vibration (*ca.* 1065 cm^{-1}) appears. The addition of another fluorine atom to form CHClF_2 only slightly changes the C-F vibration which becomes 1099 cm^{-1} . The inner consistency of a set of these spectral series offers a strong argument for the correctness of assignments made by their use. Kahovec and Wagner (203), Wu (503), and Lecomte (257) concerned

themselves with such related groupings of halo-methanes. A series of methylene derivatives (CH_2XY) is shown in Fig. 12.

20. Vibration-Rotation Energy

In the Raman effect the rotational structure of the energy level system of molecules does not come into evidence as it does in the infra-red bands. The mathematical theory of vibration and rotation levels has, however, been worked out by Wilson and Howard (496). They obtained the exact kinetic energy on classical basis and derived from it the quantum-mechanical Hamiltonian operator. By studying perturbation

TABLE XV. The characteristic C-X vibrations.

Substance	Bond	cm^{-1}	Av. cm^{-1}
CHCl_3	C-H	3020	3018
CHCl_2F		3014	
CHBr_2F		3017	
CHBrCl_2		3020	
CH_3F	C-F	1048	1050
CH_2ClF		1046	
CHCl_2F		1065	
CCl_3F		1067	730
CH_3Cl	C-Cl	732	
CH_2ClBr		726	
CHBr_2Cl		750	
CBr_3Cl		734	
CH_3Br	C-Br	610	
CH_2IBr		616	618
CH_2Br_2		637	
CHCl_2Br		610	
CH_3I	C-I	532	532

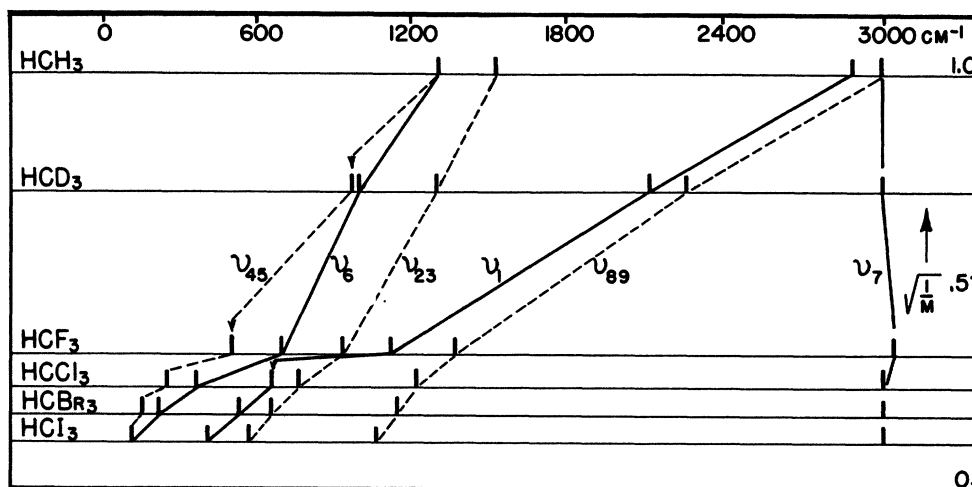


FIG. 11. The spectral sequence CHX_3 : — parallel vibrations; --- perpendicular vibrations [Glockler and Edgell (145)].

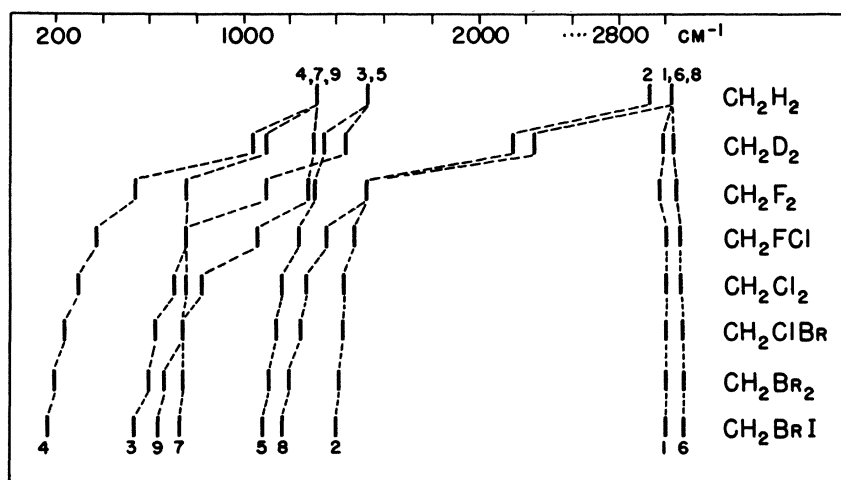


FIG. 12. Spectral sequence of methylene halides (CH_2XY) [Glockler and Leader (154)].

methods they took into account the change of moment of inertia with vibration, the coupling of rotation and oscillation, and centrifugal stretching effects. If the last term is neglected the secular equation for the rotational energy levels reduces to the Wang (479) form for the asymmetric top except that "effective moments of inertia" must be used in place of equilibrium moments of inertia. Wilson (487) further pointed out that the use of the Wang equation is not justified in case either of the vibrational states involved in the transition is perturbed by another one of nearly the same energy. The effect of

centrifugal distortion of semi-rigid asymmetrical molecules has been dealt with by Wilson (489) by an approximate quantum-mechanical treatment. Interaction of vibration and rotation in two-dimensionally slightly anisotropic molecules was considered by Nielsen (318), while Silver and Shaffer (420) dealt with the planar YX_3 model to the second approximation including cubic and quartic anharmonic terms of the potential energy, the Coriolis interaction between the degenerate oscillations and the total angular momentum, the dependence of the moments of inertia upon the vibrational state, and the centrifugal expansion

terms. Similar treatment of the YX_3 and XY_3Z molecular models is given by Shaffer (410–411) and by Shaffer and Nielsen (414) for YX_2 molecules. Wu and Kiang (504), Wu (502), and Shaffer and Nielsen (413) studied the complete potential energy function of linear molecules Y_2X_2 like acetylene and found expressions for their rotation-vibration energies. In connection with an investigation of electronic spectra and structures of AB_2 molecules, Mulliken (294) dealt with the species classification and the rotational energy pattern of such non-linear triatomic molecules. Nielsen (319) considered the vibration-rotation energies of polyatomic molecules of N atoms by the method of Wilson and Howard (496).

III. THERMODYNAMIC PROPERTIES

21. Thermodynamic Functions

It is customary to calculate thermodynamic functions of polyatomic molecules from spectrographic data by assuming that the partition functions can be separated into three factors, corresponding to the separation of the energy into translational, rotational, and vibrational parts. Commonly the rotational partition function is calculated for a molecule assumed to be a rigid rotator, the effect of distortion due to rotation being neglected. Wilson (488) pointed out that this effect may not be a negligible correction in the case of light molecules with weak binding restoring forces and Stephenson and McMahon (431) computed the rotational contribution to the partition function of the water molecule. By comparing them with those of the rigid rotator they found the stretching contributions, which check well with Wilson's theoretical results.

In the considerations made here the simple picture is used throughout and the energy of a molecule is thought to be made up of three parts: translational, rotational, and vibrational energy. Usually molecules are then considered rigid rotators and simple harmonic oscillators. On this approximate basis the determination of thermodynamic functions is very satisfactory in most cases.

From statistical mechanics (VI, VII) it is known that the entropy S of a molecular system can be written as a sum

$$S = S_{tr} + S_{rot} + S_{vib} + S_{el} + S_{spin}, \quad (156)$$

where the individual terms refer to the translational, rotational, vibrational, electronic, and spin contributions to the entropy. Similarly the other thermodynamic functions can be separated in this way and one can speak of the translational, vibrational contribution to the heat capacity (C), the free energy (F), etc. The translational entropy is given by the well-known Sackur-Tetrode equation and the spin entropy is neglected in the usual calculations because in chemical application it cancels out. Since most molecules remain in their electronic ground state in the temperature range usually dealt with, the contribution to the entropy due to the electronic state need not be considered. If ϵ_0 and ϵ_i are the sum of the rotational and vibrational energies of one molecule, and A_0 and A_i the number of molecules in the lowest and the i th quantum state, then it follows from the Maxwell-Boltzmann distribution law that

$$A_i = A_0 \exp \{ -(\epsilon_i - \epsilon_0)/kT \}. \quad (157)$$

If for convenience the energy for the lowest state can be taken as zero, then the total number of molecules in a mole is

$$N = A_0 \sum \exp (-\epsilon_i/kT). \quad (158)$$

If p_i molecules have very nearly the same energy (p_i = statistical weight) then

$$N = A_0 \sum p_i \exp (-\epsilon_i/kT). \quad (159)$$

The total energy of the system is

$$E = N \sum p_i \epsilon_i \exp (-\epsilon_i/kT) / \sum p_i \exp (-\epsilon_i/kT). \quad (160)$$

Let the quantity $\sum p_i \exp (-\epsilon_i/kT)$ be Q (state sum). Then it can be shown that

$$E - E_0 = RT^2(d \ln Q/dT). \quad (161)$$

The heat capacity

$$C = dE/dT = R d(T^2 d \ln Q/dT)/dT. \quad (162)$$

The entropy

$$S - S_0 = \int_0^T (dE/dT) d \ln T = R \{ \ln (Q/Q_0) + T(d \ln Q/dT) \} \quad (163)$$

and the free energy

$$F = E_0 - RT(\ln Q - N_0) \quad (164)$$

(E_0 = energy of system at 0°K; N_0 = Avogadro's number).

The sum Q can be written as a product

$$Q = Q_{\text{vib}} \cdot Q_{\text{rot}}; \quad Q_{\text{vib}} = \sum p_{i,v} \exp(-\epsilon_{i,v}/kT); \quad (165)$$

$$Q_{\text{rot}} = \sum p_{i,r} \exp(-\epsilon_{i,r}/kT).$$

If the various vibrational and rotational levels $\epsilon_{i,v}$ and $\epsilon_{i,r}$ are known the state sum Q can be calculated. *The vibrational levels of a molecule are obtained from the fundamental frequencies as observed in the Raman effect or in infra-red absorption.* It is in this connection that the Raman effect is of great service to thermodynamics. In order to obtain all the fundamental frequencies both Raman and infra-red spectra are needed, since usually some of these vibrations are either Raman or infra-red active, depending on the selection rules. For simplicity it is assumed that the molecule is a system of linear harmonic oscillators and the vibrational heat capacity is

$$C_{\text{vib}} = R \sum_1^r (x_i^2 \exp(x_i)) / (\exp(x_i) - 1)^2; \quad (166)$$

$$x_i = (h\nu_i) / (kT)$$

if it contains v internal oscillators or v fundamental vibrations. Expressions are of course known for the rotational contributions and they differ if the molecule is a rigid rotator, a symmetrical or asymmetrical top, or even a more complicated rotating system.

The heat capacity of a compound can be determined calorimetrically and by the third law the entropy of the substance can be obtained. It is customary to give values at 298.1°K or 25°C. There are then two types of determination of entropy which can be compared: (1) the calorimetric measurement and (2) the statistical calculation. The latter was outlined very briefly above, in order to indicate the type of thermodynamic function which was to be computed by the help of the Raman effect. In this method molecular data such as vibration frequencies, interatomic distances, valency angles, atomic masses, and moments of inertia are used. Of course, it is expected that the two methods should check. At least so far it has always been possible to find some good reason why certain comparisons did not agree. As a matter of fact investi-

gators feel so certain that the calorimetric and statistical methods must check that they do not hesitate to look far and wide for an "explanation" in case of disagreement. A typical case in point is the instance of hindered rotation (Section IV). Lack of free internal rotation would, of course, react on the thermal behavior of the substance and manifest itself in the heat capacity. Should the same quantity be calculated statistically and the internal oscillations be neglected or misinterpreted, agreement would not be expected between the two types of measurement. It is quite customary to evaluate a "potential hindering internal rotation" in case of such disagreement if the structure of the molecule warrants it.

Thermodynamic calculations and measurements as mentioned have been made extensively and have been reviewed lately by Kassel (205), Wilson (494), Pitzer (339), Aston (6), and Zeise (507). Such studies as carried out by Yost and Anderson (505) and Stevenson and Yost (435) give valuable information on the thermodynamic properties of gaseous phosphorus compounds obtained from spectrographic and equilibrium data. They found the standard free energies ($-\Delta F^0$) at 25°C to be = PH₃ (3140), PCl₃ (65,300), PCl₅ (74,800), and POCl₃ (127,300 calories/mole). A suggestion by Murphy (295) might be followed and the quantity $(F^0 - E_0^0)/T$ be calculated from spectroscopic data by fitting it to an empirical equation with five constants. He also evaluated equilibrium constants for exchange reactions involving isotopes. Cyanogen gas has had the attention of three different workers. The gas was studied by two different calorimetric methods by Burcik and Yost (52) and by Stitt (437). Measurements and calculations using spectrographic information agree quite well. Solid and liquid cyanogen was investigated in similar manner by Ruehrwein and Giauque (387) who found the entropy of (CN)₂ at 298.1°K to be 57.64 E.U. in good comparison with the determination from molecular data involving Raman frequencies. Cyanogen halides were studied by Stevenson (432).

Such researches show clearly the great need of spectrographic information. In most instances some of the fundamental frequencies are lacking and must be estimated. This discrepancy is not so bad for the higher frequencies (3000 cm⁻¹)

because their contribution is relatively small. However, the lower frequencies (100–400 cm^{-1}) should be known if any accuracy is desired. As Aston and Messerly (12) point out the energy and the free energy functions are not so very sensitive to the assignment of fundamental frequencies, but the same is not true of the heat capacity. In the case of long chain hydrocarbons, several writers (Kirkwood (217) and Thomas and Whitcomb (453)) have considered the theoretical problem of the modes of oscillation of the carbon skeleton, and Pitzer (339–341) developed some ingenious approximations for such hydrocarbon molecules and, following Kirkwood, adopted certain average values for particular sets of frequencies. The carbon skeleton is considered to possess its individual vibrations which fall into two classes for the normal paraffins: one fairly narrow band near 1000 cm^{-1} and a broader region extending from 0–460 cm^{-1} . The hydrogen atom contributions to any thermodynamic quantity are different depending on whether they come from methyl, methylene, or methine groups. A threefold hindering potential and a special steric factor complete Pitzer's picture of the frequency spectrum of paraffins.

On this basis any thermodynamic function (th.f.) is given by

$$\begin{aligned} \text{th.f.} = & F_{0(T)} + N_1[\text{C}-\text{C stretch}] \\ & + N_2[\text{C}-\text{C bend}] + N_3[\text{Int. rot.}] \\ & + F(\text{steric}) + F(\sigma) + N_4[\text{CH}_3] \\ & + N_5[\text{CH}_2] + N_6[\text{CH}], \quad (167) \end{aligned}$$

where $F_{0(T)}$ is a function of temperature not depending on the molecule, N_i the number of items of a particular kind contained in the structure of the molecule, $F(\text{steric})$ is a factor referring to steric repulsion, and $F(\sigma)$ takes care of the symmetry number of the molecule. Pitzer further assumes a barrier of 3600 calories for all hydrocarbons. The agreement between calculated and experimental values of the entropy at 298.1°K of normal paraffins is surprisingly good. For branch chain hydrocarbons the method needs to be developed further. In a semi-empirical manner Pitzer and Scott (346) have improved the matter of calculating the entropy of branch-chain hydrocarbons by making a compromise

between the approximate statistical method and the empirical procedure of Parks and Huffman (VIII). Pitzer and Scott retain the symmetry numbers for both external (σ_e) and internal (σ_i) rotation of the carbon skeleton as well as the isomer factor (I) from the statistical equations:

$$S = S_n + R \ln 2 + R \ln [I/(\sigma_e \sigma_i)] - 3.5B, \quad (168)$$

where S_n is the entropy of the corresponding normal paraffin, R is the gas constant per mole, and B is the number of chain branchings. The second term arises because of the external symmetry number (2) for the normal paraffins. Huggins (190) also considers the calculation of the entropy of long chain hydrocarbons. For the vibrational portion he takes averages of frequencies for given typical bonds as did Pitzer (340). Similar pertinent studies were carried out by El'yashevich (114–115), Stepanov (429–430), and Parodi (331).

22. Equilibrium Constants

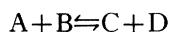
These important chemical constants can be calculated from the fundamental frequencies, as obtained from the Raman and infra-red spectra and other necessary data. The first method depends upon the fact that an equilibrium constant can be expressed as the ratio of products of partition functions for the reacting molecules and those formed during the chemical transformation (II). In the second method the energy (ΔE^0) for the chemical reaction and the entropy (ΔS^0) are used to obtain the free energy (ΔF^0) and the equilibrium constant (K) is found in the usual way from the relation

$$\Delta F^0 = -RT \ln K. \quad (169)$$

The possibility of calculating thermodynamic quantities of the simpler gaseous substances from spectroscopic data was suggested by Tolman and Badger (457) and Urey (458). Giauque (137) and his co-workers applied the method to a number of diatomic molecules. Urey and Rittenberg (459) studied the reactions of deuterium as have many other workers.

The first procedure mentioned has been applied in a comprehensive manner by Jones and Sherman (194) to the calculation of equilibrium constants and activation energies of reactions

involving various isotopic species of hydrogen, water, and hydrogen sulphide. They consider dimolecular reactions, having the same number of molecules of reactants and products. In the reaction



the symbols C and D refer to isotopic species of A and B. The equilibrium constant is

$$K = [F(C) \cdot F(D)] / [F(A) \cdot F(B)], \quad (170)$$

where the F values denote the partition function of the molecule in question. It is a product of a translational (F_{tr}), a rotational (F_r), a vibrational part (F_v), a factor (g_m) depending on the electron states, and a factor (i_m) related to the nuclear spins:

$$F = (F_{tr}) \times (F_r) \times (F_v) \times (g_m) \times (i_m).$$

For a diatomic molecule

$$\begin{aligned} F_{tr} &= [(2\pi mkT)^3 V] / h^3, \\ F_r &= (8\pi^2 I kT) / (\sigma h^2), \\ F_v &= [\exp \{E_0 - (\frac{1}{2} hc\omega_0) / (kT)\}] / \\ &\quad [1 - \exp \{(-hc\omega_0) / (kT)\}], \end{aligned} \quad (171)$$

where m = mass; V = reaction volume; I = moment of inertia; σ = symmetry number; E_0 = energy; and ω_0 = fundamental vibration frequency of the molecule. The other symbols have their usual meaning. The importance of considering the nuclear spin and the symmetry number has been discussed by Mayer, Brunauer, and Mayer (273).

From Raman or infra-red spectroscopy the fundamental vibrations of the molecule can be obtained and the exponential term can be evaluated. The base E_0 is the energy of the atoms, which is taken to be zero. The quantity $\frac{1}{2} hc\omega_0$ is the zero-point energy of the molecule.

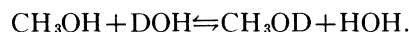
For a polyatomic molecule the rotation partition function will change to

$$F_r = [8\pi^2 (8\pi^2 ABC)^{\frac{1}{2}} (kT)^{\frac{3}{2}}] / (\sigma h^3), \quad (172)$$

where A , B , C are the three moments of inertia of the molecule. The vibration partition function is also different, because there are now several frequencies:

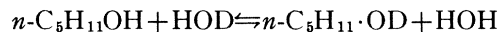
$$F_v = [\exp \{E_0 - (\frac{1}{2} \sum hc\omega_i) / (kT)\}] \cdot [\prod_i (1 - \exp \{-(hc\omega_i) / (kT)\})]^{-1}. \quad (173)$$

These concepts have lately been applied by Halford and Pecherer (179) to the reaction

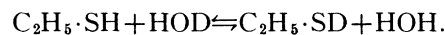


The experimentally determined equilibrium constant at 80°C is 0.481 ± 0.015 . By taking 1120 cm^{-1} for the hydroxyl deformation and estimating a torsional frequency for hindered rotation of 250 cm^{-1} the statistically calculated equilibrium constant is found to be 0.495.

Hobden *et al.* (183) determined the equilibrium constant for the hydrogen-deuterium exchange

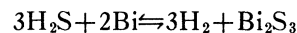


and

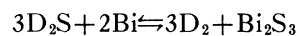


In order to apply the statistical calculation outlined above, they had to study the fundamental frequency spectrum of *n*-amyl alcohol and ethylthiol. In general where the full compliments of fundamentals are doubtful, investigators are forced to rely on reasonable estimates considering similar vibrations in analogous molecules. Hobden *et al.* find the equilibrium constant for amyl alcohol to be 0.50 by direct experiment and 0.49 from the molecular data. Similarly for ethylthiol the values are 0.21 and 0.24. Uncertainty in the frequencies produces a possible error of about 0.04.

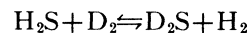
Another investigation of this kind was carried out by Grafe, Clusius, and Kruis (173). They determined the equilibrium constants for the two heterogeneous reactions



and



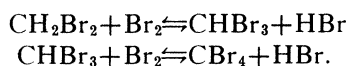
in an electric oven and analyzed the gas mixture (H_2S , H_2 or D_2S , D_2) by pressure measurements and by freezing out the gaseous sulphides. The two reactions add to



and the equilibrium constant of this reaction is the ratio of the ones for the heterogeneous

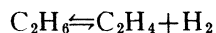
reactions. They find $[D_2] \cdot [H_2S] / [H_2] \cdot [D_2S]$ to be 0.855 (350°C), 0.889 (400), 0.919 (450), 0.949 (500), 0.963 (550), and 0.973 (600). These values correspond to an energy change for the reaction of 885 ± 45 calories. Again the spectroscopic situation is not too satisfactory but with reasonable assumptions they construct a set of acceptable frequencies. Their use permits them to evaluate the reaction energy to be 800 ± 80 calories in reasonably good agreement with experiment. They point out that the correction for anharmonicity of the fundamental vibrations is very important and cannot be neglected for molecules just because they possess a large moment of inertia as stated by Jones and Sherman (194). This factor is not of significance because the calculated energy depends on how large a fraction the anharmonicity is of the difference of the zero-point energies. The smaller this difference the more important is the effect of the anharmonicity.

Stevenson and Beach (433) determined the thermodynamic functions of several halomethanes and Strong and Pease (442) found the equilibrium constant for the reactions

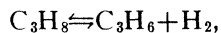


Actual measurement of this equilibrium checked the statistical calculation of the equilibrium constant $[CBr_4] \cdot [HBr] / [CHBr_3] \cdot [Br_2]$ fairly well.

The hydrogenation of ethylene and propylene,



and



were studied over an aged Cr_2O_3 catalyst by Kistiakowsky and Nickle (220). Equilibrium was approached from both sides. The reaction heats obtained from the equilibrium constants differ from directly measured values by only a few hundred calories and the experimental constants agree very well with the same quantities calculated statistically by the usual means of Raman frequencies, moments of inertia, etc. At 450°C K (exp.) = 5.16×10^{-4} and K (stat.) = 5.19×10^{-4} for the first reaction using 2750 cal. for the potential barrier for hindered rotation. For the second reaction with a hindering po-

tential of 3300 calories for propane and 2100 calories for propylene Kistiakowsky obtained K (stat.) = 5.6×10^{-4} at 375°C in comparison with 5.25×10^{-4} from direct experiment. The lower barrier for propylene of 800 calories, mentioned by Pitzer and Gwinn (343) is unsatisfactory [Section IV].

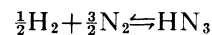
The gaseous equilibrium existing between *cis*- and *trans*-dichloroethylene was measured by Wood and Stevenson (500) at 185 to 275°C. Iodine was used as a catalyst for the isomerization. The equilibrium constant as a function of temperature is

$$\ln K = 0.364(1/T \times 10^3) - 0.247.$$

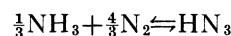
From this expression the heat of the reaction (H^0 ; *cis-trans*) is 723 cal./mole.

The Raman spectrum for these compounds is not completely known, but Wood and Stevenson combined their equilibrium measurements and existing spectrographic and electron diffraction data and calculated a value for the sum of two fundamentals of *trans*-dichloroethylene. At 0°K the *cis*-form is more stable than the *trans*-structure by about 530 cal./mole. It is interesting to note that the reverse calculation is of course also possible and values of the fundamental frequencies may be deduced from purely chemical measurements!

Eyster and Gillette (120) studied the vibration spectra of hydrazoic acid, methyl azide, and methyl isocyanate. Correlation of the spectra of these structurally similar molecules allowed the determination of all the fundamentals of hydrazoic acid and all but the torsional frequencies of the methyl derivatives. The thermodynamic functions of HN_3 were calculated and equilibrium constants for the reactions



and



were also obtained at various temperatures.

The cyclohexane-methylcyclopentane equilibrium was investigated by Mizusima *et al.* (280) by means of the Raman effect. The equilibrium is established by the use of $AlCl_3$ and H_2O and from the composition of the mixture at several temperatures, they found the entropy of isomerization:

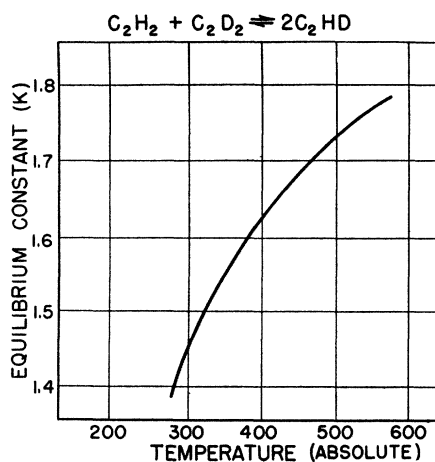
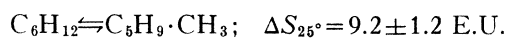
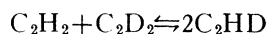


FIG. 13. Equilibrium constants for the reaction $C_2H_2 + C_2D_2 \rightleftharpoons 2C_2HD$ [Glockler and Morrell (155)].



This value agrees well with calculation from molecular data.

The second method mentioned above was applied by Glockler and Morrell (155) to the exchange reactions between light and heavy acetylene



to the rigid rotator, harmonic oscillator approximation. For room and higher temperatures the effect of the spin terms in the acetylene molecules can be approximated by adding $-RT \ln \mu$, to the free energy (F^0), where μ has the value $\frac{1}{2}(2i+1)^2$ for the symmetric molecules C_2H_2 and C_2D_2 and the value $(2i_1+1)(2i_2+1)$ for the asymmetric molecule C_2HD [Urey and Rittenberg (459)]. The numbers i_1 and i_2 represent the nuclear spin of the proton and deuteron, respectively. While the free energy values depend on the spins, the equilibrium constant is independent of them because of the general fact that nuclear spins remain unchanged during a chemical reaction at temperatures considerably removed from zero. Quantities of the type $-(F^0 - E_0^0)/T$ were determined for the various acetylene gases at a number of temperatures, where E_0^0 refers to the zero-point energy. It was calculated as the difference between the zero-point vibration energies of the product and the reactants, with probably little error on account of the great similarity of the gases concerned:

$$\Delta E_0^0 = \frac{1}{2} [2 \sum_i h\nu_i(C_2HD) - \sum_i h\nu_i(C_2H_2) - \sum_i h\nu_i(C_2D_2)] = 519.0 \text{ cal.} \quad (174)$$

The equation used is

$$\Delta F^0/T = -R \ln K = \Delta(F^0 - E_0^0)/T + \Delta E_0^0/T. \quad (175)$$

The equilibrium constant was found to be 1.37 (273.2°K), 1.43 (298.2°), 1.58 (373.2°), 1.72 (500°), 1.79 (600°) and 1.82 (700°). (See Fig. 13.)

Reyerson and Gillespie (374) have studied the various equilibria between heavy acetylene and water and have shown that exchange takes place. The spectroscopically determined constant fits into the general reaction scheme.

23. Entropy and Molecular Structure

It has been seen that disagreement between the calorimetrically determined entropy and the statistically calculated value can be resolved by the assumption of a potential barrier hindering internal rotation. The entropy obtained from thermal measurement is bound to be accurate. But besides restricted rotation lack of agreement may also be due to wrong molecular data, incomplete Raman or infra-red spectra, or incorrect assignment of fundamental frequencies. Aston, Schumann, Fink, and Doty (14) cite the interesting case of cyclopentane. They measured the heat capacities from 11.1° to 323.2°K and compared the entropies so obtained with values derived from the usual molecular constants. They based their statistical calculations on three different ring models: a planar form (D_{5h}), a non-planar structure with one atom out of the plane (C_s), and another non-planar configuration with two atoms out of the plane (C_2). The symmetry number (σ) of these structures is: 10, 1, and 5. The second model (C_s ; $\sigma=1$) seems to fit the thermal measurements best. Cyclopentane is then non-planar and the authors suggest that the forces causing the hydrogen repulsions in hindered rotation in other compounds are also operative here. The result is that either one or two carbon atoms are pushed out of the carbon plane of the others. They find that a similar study on methylcyclopentane and cyclohexane leads to the same conclusion. However, Langseth and Bak (253) [Section 30] believe cyclohexane to be planar, but Aston *et al.* consider their

evidence insufficient. Pitzer and Gwinn (344) suppose that the repulsion of the electrons in the CH bonds is the same force which keeps different molecules from approaching one another too closely. While such studies may need further refinement especially in reference to the Raman work involved, it is very gratifying that such varied measurements can find applications to structure problems which the organic chemist has been struggling with for decades.

In order to bring their calorimetric measurements for ethylene into agreement with statistical calculations Burcik, Eyster, and Yost (53) predict that there must be a fundamental frequency at 828.5 cm^{-1} . It will be interesting to see if further investigation confirms this view. Their own comparison is remarkably clear cut and the fit obtained of curves of specific heat *versus* temperature on both the thermal and statistical method is as satisfactory as can be expected.

24. Heat Capacities

Halogenated carbon compounds such as the halomethanes and ethanes have been studied by a number of investigators in reference to their thermal properties because of their importance in the refrigeration industry. Vold (466) calculated the heat capacities of CH_3Cl , CH_2Cl_2 , and CHCl_3 ; Lord and Blanchard (264) used new heat measurements on CCl_4 and found them to agree with statistical calculations; and Stevenson and Beach (433) determined the thermodynamic functions of a series of chloro- and bromomethanes. The engineering profession showed its interest in these substances by several studies of their physical properties: Plank and Seger (347) reviewed CF_2Cl_2 and Riedel (375-376) considered "freon 113" ($\text{CF}_2\text{Cl}\cdot\text{CFC}_2$). Egan and Kemp (113) compared thermal and spectroscopic data of methyl bromide, and methyl chloride was similarly considered by Messerly and Aston (276).

Ryss (389) calculated the entropy of silicon tetrafluoride from molecular constants. Some question arises in this case as to the proper value of the Si-F distance. For chlorodifluoro-, dichlorofluoro-, and trichlorofluoro-methane and 1,1,2-trichloro-1,2,2-trifluoro-ethane, Benning, McHarness, and co-workers (30-31) determined thermal properties, pressure-volume-temperature

relations, vapor pressures, and densities without, however, having recourse to spectrographic information. This latter method was employed by Justi and Langer (195) on methylene chloride and dichloro-difluoro-methane. Calorimetric measurements and spectrographic information by Osborne *et al.* (329) yielded the usual comparison of the entropy of the ideal gas at 1 atmosphere and 298.16°K : $74.07 \pm 0.1\text{ cal./deg./mole}$ from thermal data. With the use of the Raman frequencies determined by Glockler and Leader (150) the calculated value checked within 0.02 entropy unit. Some empirical relationships were found by Edgell and Glockler (109) in their research on the fundamental frequencies of the halomethanes. They discovered that a plot of the heat capacity against the logarithm of the absolute temperature ($T=298.1^\circ$ to 600°K) was very nearly a straight line for the following substances: CHX_3 , CH_2X_2 , and CH_3X ($\text{X}=\text{F}, \text{Cl}, \text{Br}$). These curves may be brought into coincidence by shifting the temperature scale of each substance, i.e., by plotting the heat capacity against $\log T/\theta$, where θ is a characteristic temperature for each substance. If $\log \theta$ is plotted against the molecular weight a straight line plot is obtained. The heat capacity of methylene bromide calculated by Stevenson and Beach (433) did not fit into these graphs because of uncertain assignment of frequencies. Edgell and Glockler believe that the Raman line 478 cm^{-1} is not a fundamental but that a rather weak line at 1183 cm^{-1} should be included as a fundamental vibration. With this new assignment the molal heat capacity fits into the empirical graphs. These curves are useful as just shown and they can be extended to include other substances. The heat capacities of several trihalomethanes (CHF_3 , CHClF_2 , and CHCl_2F) were calculated from Raman spectra by Glockler and Edgell (145).

A semi-empirical relationship for the calculation of heat capacities was obtained by Bennewitz and Rossner (29). They adopt certain increments in heat capacity for given bonds in molecules containing carbon, hydrogen, and oxygen. To each bond a deformation frequency is also assigned from Raman spectra. This type of approximation is valid whenever the bond appears only in angles of the same kind as in

those molecules treated by them. Glockler and Edgell (146-147) applied similar considerations to the halomethanes. In these molecules rotation has been excited to its full classical value before room temperature is reached and the only concern is the vibrational contribution. The fundamental vibrations of a molecule can, to a considerable extent, be ascribed to certain atoms or bonds in the molecule. For halomethanes this fact is seen in Table XV.

Thus in a molecule CXYZF, the C-F bond has very nearly the frequency 1050 cm^{-1} and in a halomethane there are four such bond stretching frequencies. The remaining five vibrations result from the deformation of the six angles and are more or less characteristic of them. The heat capacity can therefore be expressed as

$$C_p^0 = 4R + \sum_{i=1}^4 C^0(\nu_i) + \sum_{j=1}^5 C^0(\delta_j). \quad (176)$$

The term $4R$ is the contribution due to translation ($3R/2$) and rotation ($3R/2$) and R for the difference between the molar heat at constant pressure and constant volume. The quantities $C^0(\nu_i)$ and $C^0(\delta_j)$ are Einstein functions for the valency bond stretching and angle deformation frequencies.

The third term referring to the angle changes can be approximated by expanding it into a summation over the six angles, weighted according to the total number of angles. The simple method used with the valence vibrations cannot be employed because the deformations

are more nearly functions of all the angles rather than any one. The molal heat capacity then becomes

$$C_p^0 = 4R + \sum_{i=1}^4 C^0(\nu_i) + 5/6 \sum_j n_j C^0(\delta_j), \quad (177)$$

where n_j is the number of j angles and the summation is over all the different angles. This relation determines the heat capacity of any halomethane from the bonds and angles making up the molecule. The hypothetical deformation frequencies to be associated with each angle were evaluated from statistically calculated heat capacities. They are shown in Table XVI.

Thus the heat capacity of CHBrF_2 at 373.1°K is

$$\begin{aligned} C_p^0 = & 7.948 + (0.0026 + 1.284 + 2 \times 0.595) \\ & + 5/6(0.694 + 1.530 + 2 \times 0.411 \\ & + 2 \times 1.701) = 15.80 \text{ cal./}^\circ\text{K/mole.} \end{aligned} \quad (178)$$

A comparison made between the values in which constant stretching and deformation frequencies were used and those calculated by the more rigorous statistical method employing experimentally determined frequencies shows that these quantities differ on the average by only 0.6 percent. The largest deviation is 2.8 percent. It must be remembered that Vold (466) has shown that heat capacities calculated to the rigid rotator-harmonic oscillator approximation, by using Raman lines obtained from liquids, are accurate to only five percent when corrected to final pressures. The values obtained by the empirical method just outlined are probably more reliable than the meager thermal data available at present.

TABLE XVI. Contribution of angles and bonds to heat capacity [Glockler and Edgell (147)].

Angle or bond	ν or δ cm^{-1}	C_δ^0 or C_ν^0 , Small cal./ $^\circ\text{K}$ /mole		
		298.1°K	373.1°K	473.1°K
HCH	1508	0.075	0.205	0.441
HCCl	1040	0.340	0.607	0.922
CICCl	223	1.806	1.869	1.913
HCF	1219	0.196	0.411	0.710
FCF	467	1.328	1.530	1.686
HCBBr	973	0.412	0.694	1.010
BrCBr	54	1.976	1.980	1.983
FCCl	377	1.522	1.673	1.784
FCBr	359	1.559	1.701	1.802
ClCBr	166	1.884	1.920	1.945
C-H	3000	0.0002	0.0026	0.0188
C-F	1050	0.330	0.595	0.910
C-Cl	730	0.778	1.073	1.344
C-Br	610	1.017	1.284	1.507

IV. HINDERED ROTATION

25. Organic Chemistry

Chemists have recognized for many years the existence of hindered rotation in the case of the carbon-carbon double bond. They could separate isomers as, for example, the symmetrical dihaloethylenes, which differed from each other only in the relative rotational orientation of the two halves of the molecules. Table XVII gives some of the physical properties of certain isomeric ethylenes. With molecules of the type $\text{XH}_2\text{C}\cdot\text{CH}_2\text{X}$ no such isomers have ever been

isolated and hence organic chemists have considered that free rotation exists about a carbon-carbon single bond. A few quotations from recent books illustrate the opinion of chemists up to five years ago:

"It is universally recognized that groups may rotate freely about a single bond" [Watson (XIII)].

"Chemical evidence shows that two singly linked atoms can rotate (with their attached atoms or groups of atoms) round the line joining their centers, so as to take up the most stable configuration, so that a compound of such a formula as $\text{XH}_2\text{C}\cdot\text{CH}_2\text{X}$ can only occur in one form" [Sidgwick (XI)].

"Principle of free rotation. Ethane exists in only one form. This means that the two carbon atoms in ethane and its derivatives must be able to rotate with reference to each other about the single bond joining the two together" [Shriner, Adams, and Marvel (X)].

In the past few years considerable evidence has been accumulated to indicate that the principle of free rotation is not correct. Our present views on hindered rotation are based on experiments in Raman scattering, electron diffraction and dipole measurements, and on thermodynamic considerations. The rotational isomers considered here differ only by relatively small amounts in energy and other properties. During any attempt to separate them by the usual means, for example, fractional distillation, they readily change into one another at least at a sufficient rate to make their separation difficult if not impossible. Aston and Schumann (13) report hysteresis effects in the heat capacity and vapor pressure measurements which they interpret as due to the slow transfer of one isomer into the other. Evidently newer phenomena were needed in order to indicate their presence. The sum total of the evidence based on spectroscopy, electrical, and thermal measurements seems quite

conclusive and it is assumed now that a restricting potential exists between parts of molecules which hinders the free rotation of these groups about a carbon-carbon single bond. The latest studies of Raman spectra show definitely from the number of lines found and from the temperature variation of intensity that several species of molecules must be present. Detailed considerations in individual cases will doubtless have to be changed but the over-all picture speaks very clearly for the existence of rotational isomers.

26. Nature of Hindering Potential

While chemists did not consider the problem of hindered rotation around a carbon-carbon single bond, they were thoroughly familiar with the possibility of steric hinderance. They ascribed this effect to the "size" of the interfering atom or group. It might equally well be said that the force field of the disturbing atom interacts with the remainder of the molecule. Such restraint involves the notion of atomic and radical size and as Eyring (119) remarks: "Kinetic theory diameters are a convenient measure of the distance at which steric hindrance starts to be important." He attempted to study the case of the hindered rotation on the usual quantum mechanical basis of chemistry. The energy (E) of any molecular system is made up of the following parts:

Q is sum of all coulombic interactions, the mutual polarization of atomic pairs (van der Waals forces), and the interaction arising from dipoles (independent of electron spins); $\sum\alpha_p$ is the sum of the resonance attractions between the pairs of electrons forming shared bonds and $\frac{1}{2}\sum\alpha_u$ is the sum of the resonance repulsions between all electron pairs where there is no bond (the positive repulsive exchange energy). The energy of the molecule is

$$E = Q + \sum \alpha_p - \frac{1}{2} \sum \alpha_u. \quad (179)$$

Interactions *between* molecules will be dependent on the same forces. The collision energy will be of the form

$$E = q - \frac{1}{2} \sum \alpha_u \quad (180)$$

when q refers to coulombic, van der Waals, and dipole interaction between molecules and

TABLE XVII. Physical properties of ethylenes.

	$\text{C}_2\text{H}_2\text{Cl}_2$		$\text{C}_2\text{H}_2\text{BrCl}$		$\text{C}_2\text{H}_2\text{Br}_2$	
	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>
Boiling point (°C)	80.25	48.35	84.7	75.4	112	108
Melting point (°C)	-80.5	-50.0	-86.7	-41.0	-53.0	-6.5
Density	1.291	1.265	1.797	1.777	2.285	2.267

$-\frac{1}{2} \sum \alpha_u$ is the energy term of unpaired electrons of the two molecules. The same relation holds for the interaction between parts of the same molecule. Since the interchange integrals are presumably all negative, the term $-\frac{1}{2} \sum \alpha_u$ will increase as unpaired electrons approach one another. According to Eyring this last term is largely responsible for steric hindrance. This repulsion becomes appreciable at kinetic theory diameters. On this basis he calculated a restricting potential for ethane. Having considered earlier the repulsion potential of two hydrogen atoms which are attached to other groups, he was able to evaluate the nine interaction potentials between the hydrogen atoms of the two methyl radicals of ethane (Fig. 14) and obtained about 360 calories. The potential varies periodically with the angle of rotation around the C—C bond. It is largest when the hydrogen atoms of one methyl eclipse or oppose the hydrogen atom of the other one. Hence the staggered configuration is the more stable. The interaction studies by Eyring concerned the unpaired electrons of the hydrogen atoms of the two methyl groups. Kistiakowsky and Nazmi (219) state that Howard on examining the quantum-mechanical problem of ethane finds that interaction of pairs of electrons lead to only small hindering potentials of the order of magnitude found by Eyring. Since in propane the barrier is 3200–3600 calories and in propylene it is only about 800 calories, Kistiakowsky, Lacher, and Ransom (225) discard the idea of hydrogen interactions being the cause of the restriction to rotation. They propose a new postulate: interaction of electron pairs forming single bonds on adjacent polyvalent atoms. They further state that electron pairs forming double bonds do not take part in this orientation. From a study of heats of reaction such as hydrogenation of hydrocarbons, Conn, Kistiakowsky, and Smith (86) come to the conclusion that the staggered position of the methyl groups in ethane is the more stable one. They are very emphatic and are willing to take position unreservedly on this issue. In a purely formal way they ascribe this stability to the existence of repulsive forces (steric hindrance) between non-bonded atoms in polyatomic molecules. This statement is undoubtedly true but does not give any picture of the situation. They recall that the planar zigzag

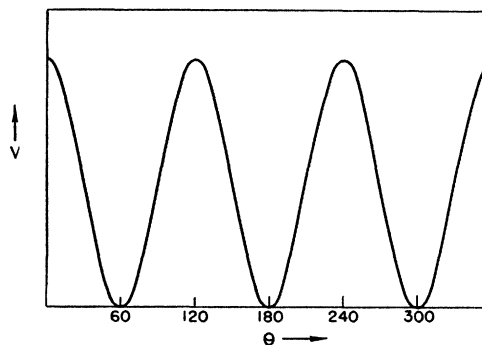


FIG. 14. Potential restricting rotation in ethane [Eyring (119)].

hydrocarbon chains in crystals also speak for the staggered configuration. There are then two possible alternatives to explain hindered rotation: (1) Steric hindrance and hindered rotation are due to entirely different mechanisms (as yet unknown), or (2) Eyring's (119) calculations on a wave mechanical basis have so far only qualitative correctness, that is hindered rotation and steric hindrance are due to interactions which must be contained in our present picture of quantum chemistry. Conn *et al.* subscribe to the second of these alternatives and they suggest in the wave mechanical treatment that the repulsive energy should be made a steeper function of distance and much larger at small distances. Other investigators expressed their ideas regarding the nature of hindered rotation along more or less the same lines. Karweil and Schäfer (204) note that the large interactions between the methyl groups of ethane cannot be accounted for by van der Waals forces alone. Actual chemical bond interaction between hydrogen atoms (not on the same carbon), i.e., exchange forces, must be considered. This remark means that the valency of hydrogen is not satisfied completely by the carbon atom to which it is attached. Resonance may exist between different structures such as in the "hydrogen-bond" or "hydrogen-bridge." Karweil and Schäfer favor the eclipsed or opposed structure for ethane (D_{3h}). Eucken and Schäfer (118) express the view that the electron distribution about the C—C bond does not have circular symmetry, but shows an enrichment whenever two hydrogen atoms belonging to two different carbon atoms are opposite each other. Furthermore inductive effects due to

the CH dipoles contribute to the hindrance to rotation.

The whole problem was re-examined by Gorin, Walter, and Eyring (166) on modern quantum-mechanical basis. They decided that any possible lack of cylindricity of the C—C bond cannot account for the magnitude of the hindering potential. They also consider an extension of the usual $s-p$ hybridization of the CH bond by including d -orbitals, making the sum of their charge distributions unsymmetrical about the C—C bond. The interactions between these hybridized C orbitals give a maximum for the barrier of 500 calories favoring the staggered configuration. Another contribution arises from this hybridization, namely a part due to the interaction of hydrogen atoms on one carbon with the carbon orbital on the other. This leads to 700 (minimum) to 1400 (maximum) calories with the opposite configuration stable. If it is recalled that the repulsion of hydrogen atoms yields 300 calories with the staggered form it is seen that the sum of these effects indicate a small barrier of about 600 calories with the opposed form stable. However, these authors discuss still other resonance effects which are of greater importance than the interactions considered so far. They find that with resonance interaction involving double bonded structures (with reasonable assumptions concerning the angular dependence of the exchange integrals between carbon orbitals) a potential of 700–1900 calories results, favoring the opposed structure of ethane. Adding the effect of the dissymmetry of the carbon atom, a potential hill of about the right order of magnitude is obtained. However, Kistiakowsky and Rice (222) believe that Gorin *et al.* will have great difficulty in explaining the fact that in dimethyl ether a barrier of 2500 calories exists while in dimethyl acetylene it is less than 500 calories. But it should be said that every molecule must be dealt with individually and an oxygen atom is after all not a $-C\equiv C-$ group. If the barrier in dimethyl acetylene is due to interaction of the methyl groups, one would expect a smaller one in this compound because of the greater separation. If, however, the restriction to rotation is due to the double bond character of the C—C bond one should expect a large hindering potential, especially since the

C—C bond in dimethyl acetylene is 0.07A shorter than the usually accepted value (1.54A). This decrease in length is interpreted as indicating considerable double bond character of this C—C bond.

On the basis of their investigations on cyclohexane and tetrachloroethane Langseth *et al.* (253–5) also consider the nature of the forces causing hindered rotation. Dipole forces are not responsible alone; they may, in fact, act in opposition to the forces which cause the restriction to rotation about the carbon-carbon bond. The interaction must stabilize eclipsed or opposed configurations. They suppose that these forces arise from the lack of rotational symmetry of the C—C bond itself (which Eyring had shown to be too small). A free carbon atom in the excited state is described by $s-p$ hybrid bond wave functions and has tetrahedral symmetry. If three hydrogen atoms are attached to the carbon atom the resulting methyl group still has one free bond. Langseth assumes that this remaining single carbon wave function now has the trigonal symmetry of the methyl group. A section of the trigonally symmetrical bond function in a plane perpendicular to the bond direction has the symmetry D_{3h} . If two such methyl groups approach each other with their free carbon bonds, the greatest overlapping of bond functions will occur for the eclipsed or opposed configuration (D_{3h}) and the least for the staggered arrangement. If it is assumed that the greatest drop in potential energy occurs for maximum overlapping of wave function, then the eclipsed form of ethane must be the more stable. The difference in amount of overlap for the two forms (D_{3d} and D_{3h}) gives the potential barrier. The general picture involves, of course, the idea of competition between the various forces: dipole-interaction and bond function interplay. For long chain hydrocarbons steric hindrance, as usually considered, may stabilize the staggered form. When the dipole effect is great the staggered configuration may also be favored over the eclipsed model. This last factor may explain why $C_2H_4Cl_2$ and $C_2H_4Br_2$ seem to have more stable *trans*-(C_{2h}) than *cis*-(C_{2v}) patterns as claimed by Mizusima and Morino (279). The difference in structure between dichloro-ethane (stable *trans*-(C_{2h}) isomer) and tetra-chlorethane (stable *cis*-(C_{2v}))

isomer) can be accounted for by supposing that the introduction of another chlorine atom caused the "overlapping effect" to become large enough to overcome the dipole action entirely. From these various efforts at explanation it is clear that no satisfactory theory of hindered rotation exists at present.

27. Thermodynamic Functions

Pitzer (337) calculated the contributions of a single rotational degree of freedom to the entropy, energy, free energy, and heat capacity, assuming a barrier of the form

$$V = \frac{1}{2} V_0 (1 - \cos n\varphi), \quad (181)$$

where V_0 = height of barrier, n = number of maxima, and φ the angle of rotation about the bond direction. These calculations and formulae were applied to various hydrocarbons. In many cases where the fundamental frequencies were not known accurately because the Raman and/or the infra-red spectra had not been completely determined, it was necessary to approximate many of the fundamental vibrations. Concerning this point Kistiakowsky and Rice (222) remark that the frequencies of isomers such as the two isomeric butenes must be significantly different, which may lead to appreciable errors in the calculated thermodynamic functions. Kistiakowsky and Wilson (224) similarly contend that many uncertainties are involved in Pitzer's calculations and the choice of values for the barrier is arbitrary. However, Pitzer and Kemp (345) state that their values of the barriers are based on experimental thermodynamic data and that the method of calculation involving the frequencies was not arbitrary but based on reasonable selection.

Another calculation to obtain the partition functions for hindered rotation was made by Crawford (91). He considered both external and internal hindered rotation of molecules consisting of a rigid frame work to which symmetric hindered rotators are attached. Using the perturbation method of Wilson (492) he obtained the partition function for this model, correct to the second order of approximation. Pitzer and Gwinn (343) showed that the formulae, originally presented by Pitzer (337) for molecules considered

to be two coaxial tops, hold for the more general case: a rigid framework with attached symmetrical top. They also outline another slightly less precise derivation based on the work of Crawford (91). The latter's analysis was extended by Price (348-349) to molecules consisting of a rigid frame with asymmetrical tops attached. The moment of inertia of the top must be small and its center of gravity must be near the axis of rotation. Molecules satisfying these conditions are structures containing $-\text{NH}_2$, $-\text{ND}_2$, $-\text{OH}$, $-\text{OD}$, or $-\text{CHD}_2$ radicals.

The vibration problem of molecules with internal torsional motions was studied by Crawford and Wilson (98). They treated molecules consisting of a framework with any number of symmetrical tops attached, such as methyl groups. The vibration part can be separated from the over-all rotation and the internal torsion, if the potential function is chosen so that the vibration frequencies do not depend on the torsion angles, i.e., all force constants involving torsion angles are taken to be zero.

28. Ethane Problem

Witt and Kemp (498) measured the heat capacity of ethane to very low temperatures (15°K) and Kemp and Pitzer (209-210) compared the entropy calculated from these measurements (49.64 ± 0.15 E.U. at 181.4°K) with the value obtained from statistical-mechanical considerations in which it is assumed that there are freely rotating methyl groups (51.21 ± 0.2 E.U.). The difference of 1.57 entropy units can be resolved if it is assumed that the methyl radicals are not freely rotating and a potential restricting rotation of about 3150 calories exists. Furthermore the heat of hydrogenation of ethylene (-32940 ± 300 cal.) determined by Kistiakowsky and co-workers (229-230) agrees with the value (-32824 ± 50 cal.) obtained from free energy calculations only when the same assumption is made. In the theoretical calculation the vibrational specific heat must be obtained from the fundamental frequencies of the molecule. In ethane one fundamental vibration cannot be obtained experimentally because of the selection rules. It was estimated earlier by Eucken and co-workers (116-117) to be 750 cm^{-1} and a restricting potential of about 315 calories was

considered by them. Kemp and Pitzer find that an unknown frequency of 1160 cm^{-1} and a hindering potential of 3150 calories also will fit the heat capacity data. This set of values was already mentioned by Eucken. Others became

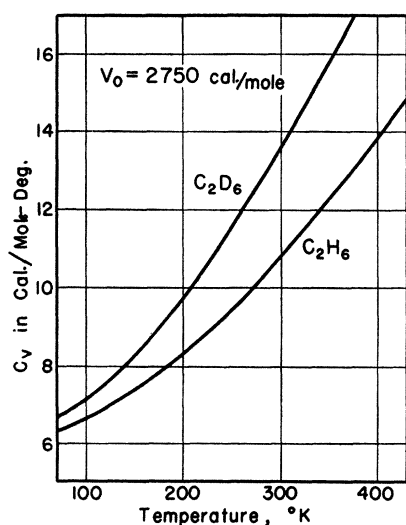


FIG. 15. Specific heat of ethanes [Kistiakowsky, Lacher, and Stitt (228)].

interested in the ethane problem and Howard *et al.* (185–189) made a dynamical study of a model of ethane to which they ascribe the symmetry D'_{3h} . The prime indicates a point group of C_2H_6 with an arbitrary position of the methyl groups in reference to the angle of possible rotation. While the point group D_{3h} describes the equilibrium configuration of the molecule, it does not fully picture it when vibrating in one of the normal modes. Using a normal coordinate treatment based on a three-constant valency type of potential function he finds that he can account satisfactorily for the Raman and infra-red frequencies of ethane, with the selection rules of the space group D'_{3h} , without knowledge of the internal hindering potential. However, if there were free rotation, the rotational details of certain perpendicular type bands in the infra-red would be quite different from the usual rigid symmetrical top. Since this difference is not observed one must assume a restricting potential of at least 2000 calories between the two forms of ethane which differ by an internal rotation of 60° . The earlier measurements of the specific heat

of gaseous ethane (of Eucken and his co-workers (116–117)) were repeated by Kistiakowsky and Nazmi (219). The important question was whether or not the specific heat values keep on decreasing or level off above the classical value at lower temperatures. Kistiakowsky and Nazmi found that the specific heat kept on decreasing while Eucken had found that the values became constant. Eucken's result would favor a small hindering potential of 300 calories which would mean that at room temperature most ethane molecules are freely rotating. On the other hand Kistiakowsky and Nazmi's results fit the higher restricting potential of Pitzer (3100 calories) with a value of 1100 cm^{-1} for the "uncertain" ethane frequency. Further studies by Bartholomé and Karweil (26) on the infra-red ethane spectrum, by Crawford, Avery, and Linnett (99) on the infra-red and Raman spectrum, by Glockler and Renfrew (156–158) and by Goubeau and Karweil (169) on the Raman effect in liquid ethane, by Karweil and Schäfer (204) on the assignment of Raman and infra-red frequencies, and by Schäfer (406–407) on statistical calculations of the rotational specific heat of ethane and its entropy, contributed to a clarification of this important problem. Wilson (490–491) refuted a suggestion by Hunsmann (191) that the observed results are due to nuclear spin quantum effects such as occur in ortho- and parahydrogen. Hunsmann remeasured the specific heat of gaseous C_2H_6 as did Kistiakowsky and Rice (221) and Kistiakowsky, Lacher, and Stitt (227–228) (see Fig. 15). These investigators also measured the specific heat of gaseous C_2H_6 to 93°K . Results on light and heavy ethane indicate a potential barrier of 2750 calories per mole. The latest attempt to assign the normal vibrations of ethane and deuterio-ethane was made by Stitt (436). The infra-red spectrum of gaseous C_2D_6 from 2 to 22μ was investigated and the Raman lines of the liquid were photographed. Stitt considered both symmetries D_{3d} and D_{3h} but concluded that at present not enough data are available to decide upon the structure, i.e., eclipsed or staggered. The "uncertain frequency" has the value 1170 cm^{-1} if the symmetry is D_{3d} and the product rule is used. A modified valency force field containing interactions between the methyl groups was employed. While the present assignment may be

changed it is the latest information on the subject. It may be said that these investigations establish the potential restricting internal rotation to be 2750 calories. This value corresponds to a torsional frequency for the hindered rotation of 275 cm^{-1} for C_2H_6 and 200 cm^{-1} for C_2D_6 . The "uncertain frequencies" are 1170 cm^{-1} and 970 cm^{-1} , respectively. The present values of the fundamental frequencies are given in Table XVIII.

Pitzer and Gwinn (344) cite further evidence that ethane must have the staggered (D_{3d}) configuration. The electron diffraction and x-ray methods have been applied to determine the structures of sym. $\text{C}_2\text{H}_4\text{Cl}_2$ [Beach and Palmer (27)], 2,3-dibromobutane [Stevenson and Shoemaker (434)], and of long chain paraffins [Bunn (51)]. All these molecules show the staggered form and they have internal rotation barriers of about 2000 to 3000 calories. Penney (335) points out that the specific heat of ethane at constant volume theoretically should be $7R/2$ but is found experimentally between 3 and $7R/2$ showing there is only approximately free rotation of the C—C bond.

29. Halogenated Ethanes

If restriction to rotation exists in the molecule $\text{YX}_2\text{C}\cdot\text{CX}_2\text{Y}$ two cases of possible potential minima can exist. Langseth and Bernstein (254) consider a potential energy curve with three minima as one (YX_2C)-group rotates relative to the other one. The two possible cases "eclipsed" or "opposed" and "staggered" are shown in Fig. 16(a). The second case proposed by them is a two-minima potential field for one complete rotation as shown in Fig. 16(b). There are 18 possible modes of vibration all allowed in the Raman spectrum. The chlorine deformation vibrations should occur below 400 cm^{-1} and there should be six such lines for the C_{2v} (*cis*)-model. Similarly the C_2 configuration should also show six lines but the C_{2h} (*trans*)-structure should only exhibit three low frequencies. Langseth and Bernstein found ten Raman lines in the spectrum of $\text{C}_2\text{H}_2\text{Cl}_4$ and $\text{C}_2\text{D}_2\text{Cl}_4$ in the low frequency range (zero to 400 cm^{-1}). There are then far too many lines for any isomer to possess the *trans*- (C_{2h}) configuration. Hence the 2-minima potential

TABLE XVIII. Fundamental frequencies of ethanes (436).

D'_{3h}	D_{3d}	D_{3h}	C_2D_6			C_2H_6		
A_1	A_{1g}	A'_1	2115	1158	825	2925	1375	993
A_2	A_{2u}	A''_2	2100	1072		2925	1380	
E	E_u	E'	2237	1102	601	2980	1465	827
\bar{E}	E_g	E''	2225	1055	970	2960	1460	1170
\bar{A}_1	A_{1u}	A''_1	200			275		

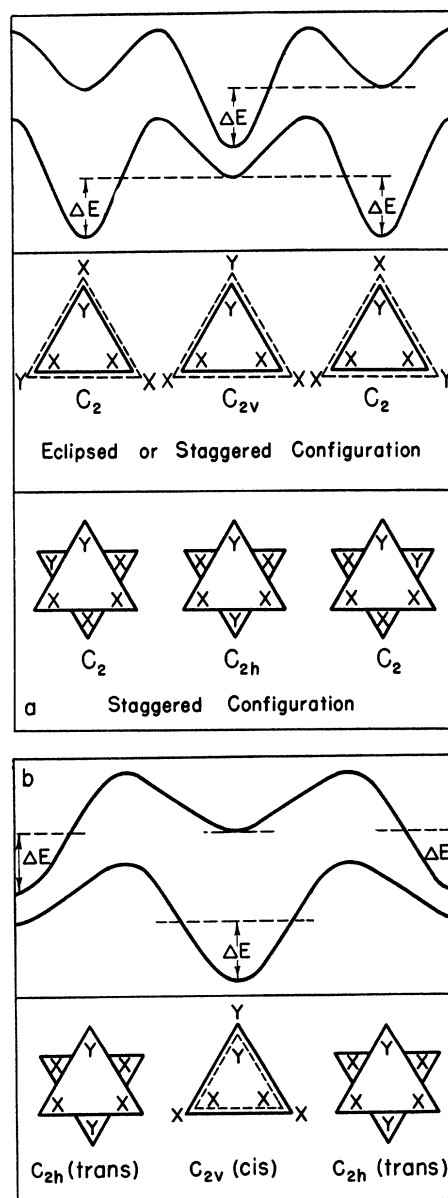


FIG. 16. Potential restricting rotation in $\text{YX}_2\text{C}\cdot\text{CX}_2\text{Y}$ molecules [Langseth and Bernstein (254)].

cannot be correct and the molecule must possess a 3-minima type of field. The only two forms to be considered then are the C_{2v} and the C_2 structures. Of these only the *cis*-(C_{2v}) isomer has a plane of symmetry and it corresponds to the minimum at 0° [Fig. 16(a)]. The question of, which one of these two isomers is the more stable has been answered by Langseth and Bernstein by studying the temperature variation of the Raman lines. The relative concentration of the two forms changes with temperature. The spectrum lines of the more stable isomer lose intensity when the temperature is raised and the lines of the less stable one increase in intensity with increase of temperature:

$$N(C_{2v})/N(C_2) = (1/S) \exp(\Delta E/RT). \quad (182)$$

$N(C_{2v})$, $N(C_2)$ = number of molecules per cc with the C_{2v} and C_2 configuration, respectively.

S = statistical weight of C_2 molecules.

ΔE = energy difference (Fig. 16).

R = gas constant per mole per degree.

T = absolute temperature.

From a study of properly chosen Raman lines in respect to their intensity changes with temperature Langseth and Bernstein conclude that the *cis*-(C_{2v}) isomer is the more stable one. The value of the potential hill (ΔE) is 1100 calories. Sym-tetra-chloroethane is therefore an equilibrium mixture of two rotational isomers. Regarding the nature of the hindering potential, it can be said that dipole-dipole interaction would make the molecules take up the *trans*-(C_{2h}) configuration, whereas the net result of the forces involved produces a stable *cis*-(C_{2v}) structure and two C_2 forms somewhat intermediate between a *cis*- and *trans*-stage. There must then be present in the molecule another set of forces acting in opposition to the dipole interaction and restricting the internal free rotation about the carbon-carbon bond, in which the atoms attached to carbon are in eclipsed or opposed positions.

$DH_2C \cdot CH_2Br$ should exist in a *cis*-form in which the deuterium atom is opposed to the bromine atom and two *trans*-forms in which the D atom is eclipsed by either of the H atoms of the CH_2Br group. Langseth, Bernstein, and Bak (255) studied the Raman spectrum of this compound and compared it with CH_3-CH_2-Br .

They find, from analogy with other *cis*- and *trans*-isomers and from calculations based on a simple potential function that a symmetrical vibration of a *cis*-form has a lower frequency than the corresponding one of the *trans*-isomer. Hence the Raman spectrum should exhibit doublets with the intensity of the bluer component about twice the intensity of the redder one of any doublet arising from a symmetrical vibration. The C-Br stretching oscillation indicates this behavior. In $CH_3 \cdot CH_2 \cdot Br$ this mode of vibration yields a single Raman line at 561.0 cm^{-1} while $CH_2 \cdot D \cdot CH_2Br$ shows a doublet (557.5 and 536.5 cm^{-1}). The intensity ratio $I(557)/I(537) = 1.6$. Since this result agrees with Langseth's ideas that opposed or eclipsed configurations exist he naturally argues that the present finding is a point in favor of the view that ethane is also of the opposed structure type (D_{3h}).

Wu (501) reviewed the earlier work on 1,2-dichloroethane and concluded that both the *trans*- and *cis*-forms must exist in the liquid at ordinary temperature. All the observed Raman and infra-red frequencies can then be assigned. A potential hindering internal rotation of about 6000 calories, making the *trans*-position the more stable, was deduced from the temperature variation of the electric moments and from electron diffraction. This large value would mean that only a negligibly small number of *cis*-molecules would exist at room temperature, as calculated from the Boltzmann factor. But Raman and infra-red spectra show both species (*trans* and *cis*) to be present. The simplest solution of the difficulty seems to be to contend that the electric moment measurements have not been interpreted correctly. Probably the restricting potential is not more than a few thousand calories. Mizusima and co-workers (281, 283-284) continued their extensive researches on the Raman effect and hindered rotation. They examined the spectrum of solid and liquid tetradeutero-1,2-dibromomethane. In the solid state most of the molecules are in the *trans*-position, while in the liquid other forms such as the *cis*-stage appear.

The Raman spectra of ethylene-chlorhydrin ($Cl \cdot CH_2 \cdot CH_2 \cdot OH$), normal propyl chloride, and butane were obtained by the last-mentioned investigators in order to compare their spectra with the ones belonging to the haloethanes. Again

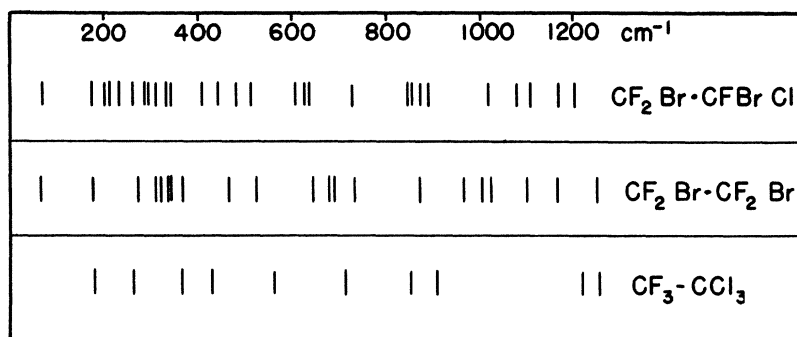


FIG. 17. Raman spectra of haloethanes [Sage (390)].

many Raman lines disappear in the solid state. In the latter phase ethylenechlorhydrin and butane assume the *trans*-form while *n*-propylchloride exists in the "gauche" (i.e., staggered) forms. Nakamura (306) similarly studied 1-chloropropane, 1-bromopropane, 1-iodopropane, 1-bromobutane, ethylene glycol, ethylene chlorhydrin, ethylene bromhydrin, and ethylene iodhydrin. Two forms exist in the liquid state while one of them vanishes on solidification. Nakamura and Kanda (307) also find that butane assumes the *trans*-form on freezing, but contains another rotational isomer in the liquid state. Di-iodoethane gives Raman spectra in the solid and dissolved state which, according to Kahovec and Kohlrausch (198), indicate the presence of one isomer in the crystalline state and several forms in the liquid.

Several of the halogenated ethanes differing in the halogens and in the number of such atoms attached to the carbon atoms have been considered by Glockler and Sage (161). These sub-

stituted ethanes have eight atoms and hence a maximum of eighteen fundamental vibrations. The number of active Raman lines depends, in any one case, on the selection rules as determined by the symmetry of the molecule. It, in turn, varies with the rotational orientation of the two halves of the molecule relative to one another. Since a number of investigations on electron diffraction and dipole moment seem to favor the staggered configuration over the eclipsed one, the present investigators assumed that the haloethanes studied by them had this configuration. By the use of Kohlrausch's tables (V) of selection rules, the number of Raman active frequencies for each isomeric structure were obtained. Since any one substance exists as a mixture of isomers the maximum number of Raman lines can be tabulated as in Table XIX.

It is seen that the number of observed lines increases with the number of possible isomers. That there is not complete correspondence may be due to three factors: (1) some observed lines may be overtones or combination frequencies; (2) the relative abundance of the isomers may be such that only the strongest lines of the one in small amount may be observed; (3) some frequencies may be the same for several isomers (Fig. 17). Glockler and Sage (160) studied symmetric difluorotetrachloroethane and found a very low frequency (81.4 cm^{-1}) which may be the torsional oscillation.

30. Cyclohexane

Organic chemists have pointed out that this hydrocarbon (C_6H_{12}) could exist in two non-planar configurations without distorting the

TABLE XIX. Selection rules for halogenated ethanes [Glockler and Sage (161)].

Compound	Isomers		Active vibrations	Lines observed
CCl_3CF_3	one form	C_{3v}	11	13
CCl_3CHFCl	one form	C_1	18	18
$\text{CF}_2\text{ClCF}_2\text{Cl}$	<i>trans</i>	C_{2h}	9	23
		C_2	18	
$\text{CF}_2\text{BrCF}_2\text{Br}$	<i>trans</i>	C_{2h}	9	22
		C_2	18	
$\text{CF}_2\text{ClCF}_2\text{H}$	<i>trans</i>	C_{1h}	18	21
		C_1	18	
$\text{CF}_2\text{ClCFCl}_2$		C_{1h}	18	24
		C_1	18	
$\text{CF}_2\text{ClCHFCl}$	three forms all	C_1	$3 \times 18 = 54$	29
$\text{CF}_2\text{BrCFClBr}$	three forms all	C_1	$3 \times 18 = 54$	28

tetrahedral angles. Four carbon atoms lie in a plane in either model. However, the other CH_2 groups lie one above and one below this plane in the "chair-structure" and both lie above this plane in the "tub-form." Langseth and Bak (253) used the Raman effect in order to decide which one of these configurations corresponds to reality. The chair-model has a high symmetry D_{3d} , but the tub-structure is flexible, because without change in the tetrahedral angle, by rotation about C—C bonds, anyone of the six carbon atoms can be brought up in the ends of the "tub." The symmetry changes between C_{2v} (tub), C_2 , and D_2 . If all configurations are possible ordinary cyclohexane should consist of a mixture in the ratio of the statistical weight 1 : 3. If it should be found experimentally that this ratio does not occur, then there must be a force opposing rotation about the C—C bond, because in the equilibrium mixture these forms must be able to change freely from one stage to the other and this change involves rotation about the C—C bond. Hence "any restriction having the required properties will be equivalent to a limitation of the internal rotation." Furthermore hindrance to rotation will tend to make the tub-form assume an intermediate configuration (between C_{2v} , C_2 , and D_2) and probably a plane model (D_{6h}) will result. Langseth and Bak studied the number of Raman lines of C_6H_{12} , $\text{C}_6\text{H}_{11}\text{D}$, and C_6D_{12} . Monodeutero-cyclohexane has only a plane of symmetry (C_s). According to the selection rules molecules having the symmetries D_2 , C_{2v} , or C_s should show 48 Raman active frequencies. The classes D_{6h} and D_{3d} have eleven and fourteen lines, respectively. For C_6H_{12} , $\text{C}_6\text{H}_{11}\text{D}$, and C_6D_{12} twenty, fifty-three, and twenty-nine Raman lines were found experimentally. Since some of the shifts must be combinations and overtones it is clear that C_6H_{12} and C_6D_{12} cannot be D_2 , C_2 , C_{2v} , or C_s . Hence these molecules have the much higher symmetry D_{6h} or D_{3d} . Langseth and Bak note that the principal difference between the two classes is the fact that in D_{6h} only two totally symmetric fundamentals below 1500 cm^{-1} are allowed, whereas in D_{3d} four such polarized frequencies should appear in the Raman spectrum. They find two strongly polarized and six depolarized lines in cyclohexane in this frequency range and hence they decide

that cyclohexane has the symmetry D_{6h} . Other more detailed considerations support this view. Hence the Raman spectrum indicates that free rotation about a carbon-carbon bond does not exist in cyclohexane. But Conn *et al.* (86) note that cyclohexane has nearly the same heat of combustion per CH_2 group as the open chain hydrocarbons. In the paraffins puckered carbon chains are usually accepted.

31. Alkyl Halides

These compounds show the expected C—X valence vibration which remains quite constant in a homologous series. The following cases illustrate this point: CH_3Br (603), $\text{C}_2\text{H}_5\text{Br}$ (566), $\text{C}_3\text{H}_7\text{Br}$ (563, 648), $\text{C}_4\text{H}_9\text{Br}$ (563, 642), and $\text{C}_6\text{H}_{11}\text{Br}$ (564, 642 cm^{-1}). The behavior of normal alkyl chlorides and iodides is quite similar. Cleveland and Murray (78) found these two frequencies in 1-bromo-dodecane ($\text{C}_{12}\text{H}_{25}\text{Br}$) at 563 and 647 cm^{-1} . They ascribe them to two isomers following Kohlrausch (233) who assigned the low frequency to the *trans*-form and the high one to the *cis*-form. However, Edgell and Glockler (108) show that $\text{C}_{12}\text{H}_{25}\text{Br}$ can be considered to be $\text{CH}_2\text{Br}\cdot\text{CH}_2\text{Y}$, where Y represents $-\text{C}_{10}\text{H}_{21}$ or the rest of the hydrocarbon chain. The haloethanes also have the above-mentioned C—Br frequencies. For example, $\text{CH}_2\text{Br}\cdot\text{CH}_2\text{Br}$ has two Raman lines at 551 and 659 cm^{-1} and $\text{CH}_2\text{Cl}\cdot\text{CH}_2\text{Br}$ at 568 and 662 cm^{-1} . Hence these compounds may well possess the same isomers. Since Mizusima and Morino (279) have shown by the Raman effect that the ethylene halides $\text{CH}_2\text{Cl}\cdot\text{CH}_2\text{Cl}$ and $\text{CH}_2\text{Br}\cdot\text{CH}_2\text{Br}$ exist only in the *trans*-form in the solid state and since these lines also persist in the liquid, one of the two must be the *trans*-configuration. The other need not necessarily be *cis*. Edgell and Glockler consider the C_2 forms which are intermediate between a *trans*- and *cis*-structure. They are obtained by rotating one-half of the molecule through 120° from the *trans*-position. The assumption that the two isomers present in the liquid state are "staggered" (*trans* and C_2) correlates much better with existing data. For example, the number of depolarized Raman lines below 1600 cm^{-1} expected from different configurations of $\text{CH}_2\text{X}\cdot\text{CH}_2\text{X}$ are as follows:

trans (2), *cis* (9), and C_2 (6). Actually eight lines were observed by Kahovec and Kohlrausch (198). Thus it would seem that the *trans* and C_2 patterns are present in the liquid state. The number of observed depolarized Raman lines of $\text{CH}_2\text{Cl}\cdot\text{CH}_2\text{Br}$ are also better accounted for if staggered models are assumed. Similar views are held by Mizusima *et al.* (285). Dipole moment data on some dihaloethanes also require a C_2 form. It is interesting to point out [Sage (390)] that Wierl's (481) data from electron diffraction measurements on 1,2-dichloroethane show two Cl-Cl distances, 4.4 and 3.2A (which are interpreted as due to the presence of *trans*- and *cis*-isomers).

The Cl-Cl distance is

$$d_{\text{Cl-Cl}}^2 = 7.65 + 5.85(1 - \cos \theta),$$

where θ is zero for the *cis*-form. This equation yields 4.4A for the *trans*-case and 2.77A for the *cis*-structure. If the experimentally found value (3.2A) is due to the *cis*-form it must be under great strain. However, if one assumes the "staggered" design (C_2) and takes $\theta = 60^\circ$, the Cl-Cl distance is calculated to be 3.1A in good agree-

ment with observation. Hence Edgell and Glockler consider the *trans* and staggered shapes to represent the isomers of dihaloethanes as well as the alkyl halides mentioned earlier.

32. Complicated Molecules

Ballus and Wagner (23) studied the Raman spectrum of isobutyl and propylene oxide derivatives and deduced the existence of several rotational isomers from the number of lines found. A similar investigation with analogous results was carried out by Radinger and Wittek (353) on *n*- and *i*-propyl derivatives. Kahovec and Kohlrausch (200) dealt with the possible rotation isomers of vinyl-, acetyl-, isopropyl-, and alkyl-derivatives. They found that at least the alkyl compounds have two isomeric forms in the liquid state. The various molecules for which a value of the hindering potential is known are given in Table XX.

33. Methyl Mercaptan

It should be of interest to give at least one example of a calculation of the barrier to internal rotation from thermal and molecular data.

TABLE XX. Potential restricting internal rotation.

Substance	Barrier volts	Reference
ethane	2750	Kistiakowsky <i>et al.</i> (228).
propane	3300	Kemp and Egan (208); Pitzer (338); Kistiakowsky <i>et al.</i> (226); Kistiakowsky and Rice (223).
propylene	2100	Pitzer (338); Kistiakowsky <i>et al.</i> (226); Kistiakowsky and Rice (223); Kistiakowsky and Nickle (220); Crawford <i>et al.</i> (100) (91); Pitzer and Gwinn (343); Telfair and Pielemeier (449); Wilson and Wells (497).
<i>n</i> -butane (CH_3)	3600	Pitzer (338) (342).
<i>n</i> -butane (C_2H_5)	large	Aston and Messerly (12).
iso-butane	3870	Aston <i>et al.</i> (11); Kennedy (211).
butene (1-; <i>cis</i> -2; <i>trans</i> -2)	<800	Pitzer (338).
isobutene	1800	Pitzer (338).
	8000	Schumann <i>et al.</i> (409).
pentane	3600	Pitzer (342); Messerly and Kennedy (277).
neopentane	4200	Pitzer (338); Aston and Meserly (12).
dimethylacetylene	<500	Crawford and Rice (97); Kistiakowsky and Rice (223); Crawford (89); Osborne <i>et al.</i> (328); Yost <i>et al.</i> (506).
tetrachlorethane	1100	Langseth <i>et al.</i> (254).
methylamine	1520	Aston and Doty (7); Aston <i>et al.</i> (15).
methylalcohol	3400	Crawford (93); Russell <i>et al.</i> (388); Koehler and Dennison (232).
methyl mercaptan	1460	Russell <i>et al.</i> (388).
nitro methane	800	Wells and Wilson (480); Pendl <i>et al.</i> (334); Pitzer and Gwinn (344).
dimethylsulfide	2000	Thompson (454); Osborne <i>et al.</i> (326-7) Fonteyne (126).
dimethylamine	3460	Aston <i>et al.</i> (8).
dimethyl ether	2500	Kennedy (211); Kistiakowsky and Rice (223); Kennedy <i>et al.</i> (212).
	3100	
silicon tetramethyl	1280	Aston and Kennedy (9); Aston <i>et al.</i> (10); Kennedy (211).
diborane	5000(?)	Stitt (439-40).
hydrazine	6-10000	Fresenius and Karweil (129).
nitric acid	7000	Forsythe and Giauque (127).

Russell, Osborne, and Yost (388) have determined the heat capacity, entropy, heats of fusion, transition, and vaporization, and the vapor pressures for methyl mercaptan. Their thermal measurements of the entropy are shown in Table XXI.

TABLE XXI. The molal entropy of methyl mercaptan.
0°C = 273.16°K; molecular weight: 48.102.

	$\Delta S(\text{cal./deg./mole})$
0–15°K Debye function, $\theta = 128^\circ$	0.274
15–137.6°K graphical	14.679
Transition (52.5/137.6)	0.350
137.6–150.16°K graphical	1.339
Fusion (1411.4/150.16)	9.399
150.16–279.12°K graphical	12.968
Vaporization (5872/279.12)	21.038
Entropy of actual gas at b.p. and 1 atmos.	60.047
Correction for gas imperfection	0.112
Entropy of ideal gas at 279.12°K and 1.atmos.	60.16 ± 0.10

The translational entropy is obtained from the Sackur-Tetrode equation and the rotational entropy was calculated from the classical partition function of an asymmetric rotator, neglecting internal rotation. The principal moments of inertia from data in the literature are: $A = 68.78$, $B = 65.94$, and $C = 8.14 \times 10^{-40} \text{ g} \times \text{cm}^2$. Thompson and Skerrett (456) have assigned all the fundamental frequencies from infra-red and Raman data: 3000(2), 2870, 2597, 1475, 1430, 1335, 1060, 975, 803, and 704 cm^{-1} . The entropy can now be calculated from molecular constants and compared with the thermal measurements as is done in Table XXII.

TABLE XXII. Statistical and thermal entropy of methyl mercaptan.

	$\Delta S(\text{cal./deg./mole})$
Translational	37.207
Rotational (without internal rotation)	20.338
Vibrational	0.592
Total (without internal rotation)	58.137 ± 0.10
Thermal entropy	60.16 ± 0.10
Entropy of torsional motion	2.02 ± 0.14
Contribution assuming free rotation	2.50
Contribution of hindered rotation with a barrier of 1460 cal./mole.	2.02

In other words if it is assumed that there exists a potential hindering the free rotation of the methyl group relative to the SH frame, amounting to 1460 calories per mole, then the thermal and statistical method of computing the entropy of methyl mercaptan agree.

V. STRUCTURAL CHEMISTRY

34. Organic Problems

Kohlrausch (234–235) has lately reviewed the accomplishments of the Raman effect in ascertaining the constitution of molecules, while Murphy (296) has discussed its use in determining molecular structures and Burgel and Pio (54) have considered especially the field of organic chemistry. It is evident that organic chemists are adopting this optical method as a supplementary tool, most useful in assisting them in determining the structure of molecules. Since chemical bonds have relatively constant characteristic frequencies, the existence of a given type can readily be established. To be sure the presence of various groups, the environment (i.e., solvent), association, and polymerization will affect the value of a bond but usually a given link can readily be recognized by its Raman line or band. Houo (184) showed the presence of ethylenic double bonds in α -substituted β -ethylene and $\alpha\gamma$ -diethylenic alcohols by observing the characteristic line of this double bond at about 1640–1670 cm^{-1} . An alcohol whose structure at times has been under discussion is pentaerythritol ($\text{C}(\text{CH}_2\text{OH})_4$) for which Ballus and Wagner (23) find indications, using the CH-valence vibrations that hydrogen bridges exist in this compound. Similar structures ($\text{C}(\text{CH}_2\text{X})_4$, $\text{X} = \text{Cl}, \text{Br}, \text{and I}$) have the space group V_d . Kohlrausch (236) notes that certain ketones (RCOX ; $\text{R} = \text{methyl or vinyl radical}$; $\text{X} = \text{OH}, \text{CH}_3, \text{Cl}, \text{or H}$) have the keto-form as against the enol-configuration. As is to be expected attachment of various groups to the carbon atom of a carbonyl group affects its characteristic frequency. Mutri and Seshadri (303–304) studied the influence of a variety of substituents such as phenyl-, methyl-, and ethyl-groups and they find that the C–O frequency is lower in aromatic than in aliphatic esters. If the phenyl-group is not directly attached to the carbon of the carbonyl-group but is connected through the oxygen atom then the C–O frequency is increased. These various effects can be discussed on the basis of electrometric polarization and resonance. A similar lowering of the ethylene double bond vibration is found by the same investigators (304). On the basis of electronic

resonance Vol'kenshtein and Syrkin (470–471) studied pyrone compounds. Halogen substitution in halogenated ethylenes also affects the characteristic value of the ethylene bond vibration according to Prilezhaeva *et al.* (350). In a study on atmospheric oxidation of 6-dodecyne, Murray and Cleveland (298) used the Raman effect and found that replacement of two hydrogen atoms by one oxygen caused three lines to merge into one. As is well known aldehydes and ketones form "addition-compounds" with sodium bisulfite and the question of the chemical bond is, of course, of great interest. In this connection Caughlin and Tartar (62) showed that a definite C–S bond exists and there is no need to write "polymolecular" formulae. Normal and isopropyl derivatives (C_3H_7X ; $X = NH_2, OH, CH_3, SH, Cl, Br, I$) were investigated by Radinger and Wittek (353). They showed that the more flexible carbon chain of the normal compounds permits these molecules to assume several spatial configurations, while the rigid carbon frame of the iso-structures allows one space form only. The substitution of deuterium for hydrogen makes possible the allocation of certain frequencies to given groups in the molecule. Edsall and Scheinberg (111) compared deuterium-substituted amines with the ordinary hydrogen-containing variety and they showed three classes of frequencies: (1) those arising from the methyl group and unchanged by D substitution in the NH_2 group; (2) the amino and NH_2 group frequencies which are higher in the H than in the D compounds by a factor of 1.33 to 1.36, and (3) other frequencies changed by a factor less than 1.3 when D replaces H, such as C–N and N–N stretching vibrations near 1000 cm^{-1} which show a decrease of 20 to 50 cm^{-1} . The Raman spectra of cholesterol and sodium cholate as determined by Sannie (402) indicate considerable analogy in the first case with the spectra of carvomenthene and carvomenthone but for the sodium salt the resemblance is much more vague. In their study of ozonides Briner *et al.* (47–48) used the Raman effect with other physical properties in order to determine the structure of these compounds. The influence of solidification on molecules can be investigated by the Raman effect as Kotera and Morino (245) have shown in the case of polyoxyphenylene compounds. The

results are consistent with the assumption that in the liquid state or in solution the end groups are rotating around almost freely while in the solid state they assume the *trans*-position by holding three benzene planes almost perpendicular to the middle benzene nucleus. The much-discussed question as to the planar or puckered structure of the carbon ring in the case of cyclohexane was attacked once more by Kohlrausch and Wittig (244) (Langseth, Section 30). The Raman spectra indicate that cyclohexane must have the form of chair or staircase and cannot be plane and that oxalyl chloride may have a planar structure but more probably is a mixture of rotation isomers. Solid ethylene dioxide exists in the *trans*-form in the solid state according to Morino and Simidu (288). On the basis of the evidence of the Raman spectra Putilova (352) studied the relation of the structures of styrene, polystyrene and other compounds to rubber and other synthetic polymers.

The problem of polymerization and association has been attacked by various workers. Increased dilution and/or rise in temperature will tend to reduce the polymerized or associated molecules because of equilibrium shifts. Some carboxylic acids were examined by Bai (19) by means of their Raman spectra and he showed that these molecules are associated, as are amides investigated similarly by Rao (359) and Sannie and Poremski (403–404). Koteswaram (246–249) finds that acetic, formic, and benzoic acids, acetone, and methyl ethyl ketone are all associated, as indicated by the behavior of certain of their Raman lines upon dilution. The solvent itself has an influence upon the association of a given compound. For example, Mutri and Seshadri (302) find that carbonyl compounds associate in chloroform but not in carbon tetrachloride, because of lowering in frequency of Raman lines in the first but not the second solvent. There is also the possibility that solidification may be accompanied by polymerization. For example, in biphenyl according to Aziz (17) new lines appear on freezing and all Raman lines are sharper in the solid state than in the liquid because of absence of rotation. Nielsen and Ward (320) explored the Raman effect of gases and liquids. Not all Raman lines show shifts and the effect varies greatly from compound to com-

TABLE XXIII. Organic compounds studied by the Raman effect.

Compounds	References
Hexanes, heptane	Grosse <i>et al.</i> (177-178); Rosenbaum <i>et al.</i> (382).
Octane, decane, cetane, eicosane	Rosenbaum (379)
Hexene, dimethyl hexane	Koch and Hilberath (231)
Substituted acetylenes	Cleveland and Murray (72, 74-76, 78, 80, 82); Murray and Cleveland (297, 299).
Ethers	Murray and Cleveland (300); Cleveland <i>et al.</i> (84, 85); Cleveland (71).
Aldehydes	Gerding and Rijnders (135); Ansidei and Carissimi (4).
Alcohols	Williamson (483); Saksena (398); Rao (358).
Ketones	Cleveland <i>et al.</i> (83).
Acids	Bonner and Kirby-Smith (45); Saksena (399); Kohlrausch and Sabathy (239).
Sugars	Spedding and Stamm (426); Spedding and Hixon (427); Leibfried (258); Rao (357); Cleveland (69).
Halogenated methanes and ethanes	Glockler <i>et al.</i> (139-141, 151-154, 164); Volkringer <i>et al.</i> (473); Wittek (499); Prilezhaeva <i>et al.</i> (350); Kowalewska (250); Venkateswarlu (462).
Ethylene sulphide	Thompson and Dupré (455).
Antimony trimethyl	Rosenbaum and Ashford (380).
Aluminum and arsenic trimethyl	Feher and Kolb (122).
Mercury organic compounds	Martin (267).
Benzene	Bapayya (24).
Deutero-benzenes	Langseth and Lord (256).
Cycli trimethylene derivatives	Rambaud (356).
Diphenyl benzene	Mukerji <i>et al.</i> (290-292).
Mono- and dichlorobenzenes	Sponer and Kirby-Smith (428).
Polyoxyphenylenes	Kotera and Morino (245).
Various benzene derivatives	Pendl and Radinger (333); Paulson (332).
Aromatic carbonyl and nitro compounds	Murray <i>et al.</i> (301).
Tetralone and indanone	Biquard (41).
Camphorone and pulegenone	Calas (58).
Coumarins and Chromones	Mookerjee and Gupta (287).
Cyclanones	Godchot and Cauquil (165).
Camphor	Amand and Narain (1).
Saturated heterocyclics	Kohlrausch and Reitz (238).
Thiophene compounds	Simon and Kirret (422).
Oximes	Biquard (42).
Guanidine, urea	Otvos and Edsall (330); Reitz and Wagner (373).
Glycine	Goubeau and Luning (170).
Thioacetamid, thiourea	Kohlrausch and Wagner (243).
Methylated benzotriazole, indazole	Kohlrausch and Seka (241).
Imines	Kirrmann and Laurent (218).
Ketimines	Cantarel (60).
Carbamic acid esters	Wagner (475).
Alkylated acetamides	Kahovec (197).
Pyrroles	Lord and Miller (265).
Aldehyde-amine condensates	Kohlrausch and Seka (240).
Plant volatile products	Naves and Perrottet (309).

pound. Alcohol in hexane solution [Brüll, Errera, and Sack (50)], formamide [Saksena (394)] and chloroacetic, formic, and acetic acids dealt with by the same author (397), all show association as indicated by their Raman spectra. The formation of chelate structures can also be decided by a study of the vibration frequencies of certain pertinent groups such as the carbonyl-group as was done by Ansidei (3).

Problems of isomerism and tautomerism can be solved by the Raman effect as was demonstrated by Gerding and Karsten (133), Nagai (305), Mathieu and Massignon (270-271), Vaidya (460), McCutcheon *et al.* (274), Kahovec and Kohlrausch (199), Kahovec and Wagner (202),

and Syrkin (447) in a variety of cases. The Raman effect of oxonium compounds gives information of their structure [Gantmacher *et al.* (132)]. As is well known Raman lines change with the surrounding medium, i.e., the solvent, and information concerning intermolecular forces is therefore obtainable from the changes in Raman frequencies in various solvents. This topic was broached by Malyshev (266) through a study on methyl alcohol and by Williamson (484) in water solution. Raman spectrum evidence for hindrance of resonance by ortho-substitution has been obtained by Saunders *et al.* (405) with nitromesitylene and mesitylenic C-O derivatives. The frequencies of the C-O and

NO₂ groups approach values found in unconjugated derivatives. This result indicates that resonance between the ring and these groups is greatly reduced. A great variety of organic compounds have been investigated as is shown in the summary in Table XXIII.

35. Analysis and Identification

Since each substance has a Raman spectrum characteristic of its own constitution it is to be hoped that this type of spectroscopy will be developed into an important branch of qualitative and even quantitative chemistry. There are no doubt possibilities which further research will make available, but at the present time only special problems are being dealt with by Raman spectrum analysis. Carvalho (61) and Chulanovskii (64) reviewed the Raman effect in relation to analytical organic chemistry. During the catalytic reaction of propene with isoolefins Ipatieff (193) produced heptenes, which upon hydrogenation to heptanes were analyzed by physical methods including the Raman effect. Most of the attempts to use these spectra for analysis center around the identification of hydrocarbons. Mizusima *et al.* (282) and Okazaki (325) showed that a sample of petroleum ether contained isopentane, pentane, isohexane, and several other cyclic hydrocarbons, and they analyzed an artificial petroleum prepared by Fischer's method. This material consists mainly of normal paraffins, contaminated with olefins and benzene. Similar studies on gasolines and liquid fuels were made by Vol'kenshtein and co-workers (467-469) who find the Raman method satisfactory for the lighter fractions. For larger molecules the existence of certain groups only can be established. A description of Raman spectroscopy applied to the qualitative and semi-quantitative determination of individual hexane, heptane, and octane isomers is given by Grosse *et al.* (178). Goubeau and Schneider (171) dealt with the identification of paraffins and olefins with straight and branched chains, and Goubeau and Thaler (172) prepared some standards of binary systems such as amylene hydrate-binary butyl alcohol, benzene-toluene, benzene-cyclohexane, and cyclohexane-methylcyclohexane, and showed that analysis on the basis of relative blackness of lines is not

satisfactory. If the relative intensity of the lines and that of the background is used, the method is satisfactory for these binary mixtures, but the results cannot be applied to ternaries. Landsberg and co-workers (252) believe they solved the application of Raman spectroscopy to complex compounds, by comparison of intensities of standard spectra taken at the same time and by the same source as the Raman spectra. Application of the method to known mixtures of cyclohexane and benzene showed satisfactory results. The strong symmetrical breathing vibration of the cyclopentane ring at about 900 cm⁻¹ can be used to recognize cyclopentane derivatives according to Rosenbaum and Jacobson (381). They studied a number of mono-alkyl derivatives but found that the minimum percentage which can be detected is relatively high because of the diffuse nature of the line. An interesting relationship, stated by Bonino (43) between Raman spectra and knock tendencies of paraffins is found to hold as more data from the literature were applied: "The square root of the sum of the squares of the intensities of all Raman lines between 600 and 1000 cm⁻¹ increases with the octane number of the fuel."

36. Inorganic Problems

Just as the organic chemist can learn a great deal about molecular structure from the Raman effect, so also is this true of inorganic compounds. There is only one-tenth the number of substances and, therefore, not as extensive investigations are known. The type of problem amenable to solution by Raman study can be illustrated by the following researches [Simon (421)]. Conn *et al.* (87) have shown that solid hydrogen and deuterium chloride have several types of association in the crystal because certain Raman lines shift with change in state (gas to solid). This conclusion is in agreement with certain x-ray investigations which revealed such a low symmetry that the crystal structure could not be determined. The exchange taking place on mixing H₂O and D₂O is reflected in the Raman spectrum of the mixture. There are certain Raman displacements created on mixing, and Rao and Rao (364, 367) explained these by the formation of HDO and depolymerization. The Raman band of water at 3400 cm⁻¹ is the same

for water activated by means of a discharge tube containing mercury and neon as for ordinary water [Frongia (130-131)]. The frequency 877 cm^{-1} appears in H_2O_2 , HDO_2 , and D_2O_2 and must therefore belong to the O-O bond, according to Feher (121) who also noted that because of resonance several lines are doubled. Ochs *et al.* (324) found that, at concentrations greater than $9N$, hydrochloric acid solutions have a band at 2630 cm^{-1} which increases in proportion to the concentration. Water bands are little affected. They did not mention any grouping or structure which might be responsible for this effect. The existence of CdBr_4^{--} ion in solution was demonstrated by Delwaulle *et al.* (104). Potassium cyanate solution suffered a change in Raman spectrum on aging [Cleveland (70)] and by taking photographs of Na_2CO_3 , NaHCO_3 , $(\text{NH}_4)_2\text{CO}_3$, and NH_4HCO_3 solutions this investigator could demonstrate that these substances are formed on standing. The work of Schäfer (408) and Fresenius and Karweil (129) indicates that hydrazine has an unsymmetrical structure in which one NH_2 group is at right angles to the other one and Goubeau (167) finds some association. Other researches in the field of inorganic chemistry involve the topics summarized in Table XXIV.

By means of the Raman effect, Taufen *et al.* (448) showed that coordination complexes of silver ion with *cis*-2-butene, cyclopentene, cyclohexene or substituted acetylenes exhibit very definite changes in characteristic frequencies. The vibrations of benzene when coordinated to silver ion in silver perchlorate solution are affected significantly, involving the stretching of carbon-carbon bonds. Another research concerned with coordination in Werner complexes was carried out by Mathieu *et al.* (268-269) on the complex cyanides, amines, or nitrites of several metals. Principal and secondary coordination links play similar roles in the Raman effect production. Pure primary valency forces are insufficient for explaining the spectra found. It must be assumed that coordinated groups act upon one another.

Rotational Raman scattering was observed by Saha (391) in liquid oxygen. An electronic Raman effect of samarium ions [Sibaya (415)] appears to rest upon a misinterpretation of the absorption spectrum [Gross *et al.* (176), Sibaya

(416)]. No satisfactory evidence has as yet been produced for an electronic Raman effect. Absorption and fluorescence bands of different solvents obtained in the presence of various substances [KMnO_4 , $\text{Er}(\text{NO}_2)_3$] show frequency differences discovered by Prosad and Bhattacharya (351), which are in good agreement with Raman frequencies of these solvents.

37. Crystalline State

Continuing earlier studies Bhagavantam and Venkatarayudu (40) discussed a theory of the normal oscillations of crystal lattices and the selection rules in relation to the Raman effect for various types. Bhagavantam (38) states that there is no special reason for assuming that the low frequency Raman lines in crystals have any different origin than the high frequency vibrations. They are all to be regarded as belonging to the various optical series into which the normal oscillations of the crystal may be divided. For convenience in description they are placed into three classes; internal, external rotation and

TABLE XXIV. Inorganic compounds studied by the Raman effect.

Compounds	References
Magnesium sulphate (hydrate)	Canals and Collet (59)
Disodium hydrogen phosphate	Canals and Collet (59)
Copper sulphate	Canals and Collet (59)
Aluminum chloride	Rosenbaum (378)
Boric acid esters	Kahovec (196)
Thiocyanates	Goubeau and Gott (168)
Nitric acid	Rao (366); Desmaroux <i>et al.</i> (106)
Fused nitrates	Moses (289)
Ammonium nitrate, sulfate	Volkringer <i>et al.</i> (472)
Ortho phosphoric acid and salts	Simon and Schulze (423)
Phosphonitrile	Ficquelmont <i>et al.</i> (124)
Arsenates	Mitra (278)
Antimony trichloride	Kurnosova and Ashkinazi (251)
Rhombic sulfur	Venkateswarlu (463)
Sulphuric acid	Rao (365); Ashkinazi and Kurnosova (5)
<i>Meta</i> -tungstic acid	Cordier <i>et al.</i> (88)
Neutral tungstates	Theodoresco (451)
<i>Meta</i> -tungstates	Theodoresco (452)
Neutral molybdates	Darmois and Theodoresco (102)
Columbates	Nikitina (322)
Tantalates	Nikitina (322)
Silicates	Nikitina (322)
Chlorates, bromates	Rolla (377)
Chloric, bromic and iodic acids	Fonteyne (125)
Perchlorates	Ansidi (3)
Binary glasses	Vuks and Ioffe (474)
Alums	Leibfried (258)

translatory type. In interpreting results three principles are of importance: Raman lines corresponding to the translatory mode have extremely low frequencies and if they occur at all will be very weak; the rotation type has relatively large frequencies and strong Raman lines if the rotating group has considerable optical anisotropy. These lines are prone to fall into a crowded region of the Raman spectra and hence are difficult to detect.

The behavior of Raman lines observed in the transverse and longitudinal scattering of polarized light in crystals of sodium nitrate with specific orientations, the origin of the Raman lines, selection rules, polarization, and symmetrical, asymmetrical, and degenerate vibrations were discussed by Saksena (395). Rao (362) observed two lattice vibrations in crystalline NaNO_3 and CaCO_3 . They correspond to the longitudinal motion of the RO_3 group in a direction transverse to the trigonal axis and to a rotatory type of motion of the same groups. Nedungadi (311, 315) and Bhagavantam (37–38) made similar observations and Bhagavantam and Rao (39) measured the intensity of the components of 1084 cm^{-1} of calcite for various orientations of the optical axis and the plane and direction of the vibration of the incident light. Saksena (400) and Rao (363) studied single crystals of gypsum and Balakrishnan (20) used incident unpolarized light on a single crystal of barite for three different orientations. The sulfate ion frequencies split into several components, but the symmetrical vibration (989 cm^{-1}) remained single. None of the three orientations gave all the Raman lines. Incident light polarized in and perpendicular to the plane of observation permits the assignment of components to symmetric and asymmetric vibrations. Rao (360) dealt with single crystals of potassium tartrate and several nitrates and sulfates. Nedungadi (312) studied quartz and Nedungadi (313) and Saksena (396) used Rochelle salt crystals to show twenty-five distinct Raman shifts along with the four water bands. These findings were compared by Nedungadi (313) with a saturated solution. The intensities of many of the Raman lines change considerably for various orientations of the crystal axes with respect to the direction of incidence and obser-

vation, even when the exciting light is unpolarized. Those lines which change conspicuously with orientation are presumably symmetrical vibrations while those which do not are asymmetrical oscillations. The Raman spectrum of a single crystal of sulphur contains the lines 50 (7), 85 (5), 115 ($\frac{1}{2}$), 153 (10), 184 (2), 216 (10), 243 (2), 434 (3), 470 (9), and 556 cm^{-1} (1). Norris (323) noted the following changes with the incident light (unpolarized or polarized parallel to the c axis) along the b axis and observing along the a axis: 50 (2), 434 (0), 470 (7). When looking along the c axis with incident light along the a axis, there was little change unless the radiation was polarized parallel to the b axis, when the intensities were 50 (10) and 85 (3). The others remained about the same. All but the two lowest lines fit into the crystal group assignment V_h^{24} but the two low frequencies 50 and 85 cm^{-1} are identified as three rotational modes of the S_8 molecule. With this assignment the calculated specific heat checks very well with the calorimetric value. From the polarizability tensor Cabannes (56) deduced expressions for the depolarization factor for uniaxial, binary, and ter-binary crystals oriented in different ways and Aynard (16) examined the orientation of water molecules in gypsum and applied Cabannes' method of classification.

Besides the inorganic crystalline materials investigated, several organic substances were also examined. A study made by Nayar (310) on the temperature variation of the single Raman line of diamond showed that this line changed from 1333.8 cm^{-1} at -180°C to 1316.4 cm^{-1} at 860°C . This variation is greater than anticipated from the thermal expansion. Low frequency vibrations were found in a single crystal of hexamethyl benzene by Gross and Raskin (174) at 53 and 95 cm^{-1} which are due to intermolecular oscillations of the crystal lattice and Gross and Korshunov (175) discovered similar low-lying Raman shifts in p -, m - and o -di-iodo-benzenes. Research by Aziz (17) on solid biphenyl revealed low frequencies which he interpreted in the above-mentioned way. The Raman shifts of the solid are much sharper than the ones observed in the liquid substance owing to absence of rotation. Crystalline naphthalene had the attention of three different

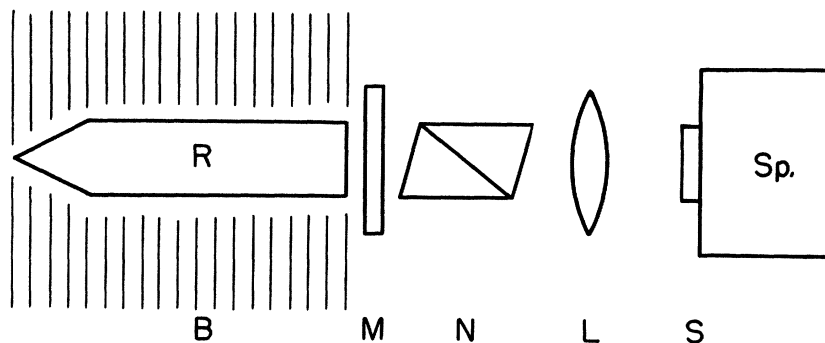


FIG. 18. Polarization measurements: B = parallel block screens; R = Raman tube; M = half-wave mica plate; N = Nicol prism; L = condensing lens; S = step weakener on slit of spectrograph; Sp = spectrograph [Stitt and Yost (441)].

investigators: Benel *et al.* (28), Kastler and Rousset (206) and Nedungadi (314). Viscosities (η) at the melting point were calculated by using the Lindemann expression by Sibaya and Rao (417). Comparison with experimental values indicates that an average correction factor $\eta(\text{obs.})/\eta(\text{calc.}) = 1.08$ must be applied. The Lindemann or maximum Debye frequency often gives rise to a Raman lattice oscillation near the scattered Rayleigh radiation.

The ratios of the intensities of the various Stokes and anti-Stokes lines in calcite and quartz at 303°K were determined by Venkateswarlu (464) and found to obey more closely the relation

$$\{(\nu - \nu_{mn})/(\nu + \nu_{mn})\}^4 \cdot \exp(h\nu_{mn}/kT)$$

than the single Boltzmann factor.

An x-ray scattering effect with frequency shift has been discussed by Raman in a series of papers (354) and dealt with experimentally by a number of Indian physicists.

VI. MISCELLANEOUS TOPICS

38. Polarization Measurements

A variety of arrangements have been proposed in order to measure the intensity of the parallel and perpendicular components of the Raman radiation (Sec. 4). Reitz (371) has discussed the problem fully, stating the experimental conditions which must be fulfilled in order to obtain acceptable results. An arrangement due to Stitt and Yost (441) shown in Fig. 18 has the disadvantage that two exposures must be made for

the two components. This inconvenience could be removed if a Wollaston prism were used in the collimator of the spectrograph in place of the half-wave plate and the Nicol prism. The apparatus has however two important advantages: (1) the step-weakener on the slit calibrates the photographic plate along the heights of each Raman line in steps of known intensity and (2) the half-wave plate eliminates correction for polarization due to the apparatus and permits each component to be photographed with the electric vector horizontally placed, thereby avoiding loss due to reflection by the prism. For photographing the parallel component for illumination in a vertical plane, the axis of the Nicol is horizontal and of the mica plate parallel to that of the Nicol. In order to obtain the other component the half-wave plate is rotated through 45°, thus rotating the electric vector of the light passing through it by 90°. A Raman tube with flat sides will minimize reflection of incident light, which was made approximately parallel by blackened screens. Stitt and Yost determined the depolarization factor ρ for Si_2Cl_6 with this apparatus.

Polaroid was used by Edsall and Wilson (112) for determining qualitatively the state of polarization of Raman lines. They wrapped a cylinder of a transparent polarizing material around the Raman tube, so that only light polarized with its electric vector parallel to the axis of the cylinder entered the scattering liquid. Four mercury arcs placed parallel to and surrounding the experimental tube furnished illumination from all sides. Two exposures were made: (1) all lamps lighted

and Polaroid in place; (2) reduced illumination and no Polaroid. All Raman lines arising from unsymmetrical vibrations should show the same decrease in intensity when the Polaroid is used, while completely symmetrical vibrations will be attenuated strongly. Another method of employing Polaroid involves the use of a disk of the material placed between arc and Raman tube (Fig. 19). Two exposures are made: (1) the incident polarized light vibrates parallel to the axis of the Raman tube and (2) the Polaroid disk is revolved through 90° (around the axis indicated in Fig. 19) to admit light polarized perpendicular to the Raman tube. The advantages of the use of Polaroid are: very strong illumination is possible in the first method described, and the technique is simple and inexpensive. However, Polaroid absorbs strongly in the spectral region employed, and two exposures must be made. Bernstein and Martin (34) also made use of Polaroid for obtaining polarization factors of Raman lines, and Cleveland and Murray (73, 77, 81) placed the Polaroid disk between the Raman tube and the slit of the spectrograph. Two exposures of equal duration were made: one with the arc below and a second one with the arc at the side of the Raman tube. Exposure times are rather short and errors due to apparatus polarization are eliminated. Cabannes and Daure (57) investigated benzene with circularly polarized light and determined the ratio $\rho/(1-\rho)$ where ρ is the depolarization factor. The Raman line 992 cm^{-1} was decomposed into ten components of which five are new. A suggestion made by Langseth and Bak (253) appears to offer a very simple way to estimate the state of polarization of Raman lines. The shape of the line is noted since its sharp or broad appearance depends on the rotational structure of the vibration-rotation transition. Raman lines are really bands and if observed with high dispersion the strongly polarized lines will be sharp lines while the depolarized ones will appear broad, approaching narrow bands with no well-defined intensity maximum. Nijveld and Gerding (321) used the method of Reitz to determine the depolarization factor of carbon tetrachloride and sulphur trioxide and Gerding and Nijveld (134) deduced the structure of the latter substance. It is a puckered ring (S_3O_9) of

three sulphur and three oxygen atoms. The same authors with Rijunders (136) studied liquid par-aldehyde and acetaldehyde. Glockler and Baker (143–144) suggested a somewhat simplified arrangement for polarization work which necessitates only a turn through 45° in order to get the two usual exposures.

39. Intensity of Raman Lines

The intensity of Raman lines depends upon the fourth power of the frequency, the change of polarizability of the substance and upon the Boltzmann factor. These relations have been described adequately [Kohlrausch (V)] as well as the relative intensity of Stokes and anti-Stokes lines. Lately Rao (361) calculated the mean polarizability and intensity of the Raman lines of carbon tetrachloride and found good agreement with experiment if a tetrahedral structure of the molecule is assumed. The degree of polarization of the first overtone of the double frequency 780 cm^{-1} was found to be large although the fundamental is completely depolarized in accordance with theoretical expectation. The overtone intensity is one-eighth that of the fundamental vibration. The intensities of the

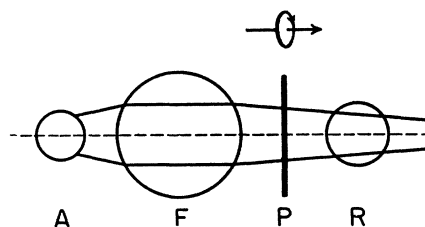


FIG. 19. *A* = mercury arc; *F* = filter solution; *P* = Polaroid; *R* = Raman tube [Edsall and Wilson (112)].

totally symmetrical Raman line and the exciting Rayleigh line are given by the expression

$$\frac{I_{\text{Raman}}}{I_{\text{Rayleigh}}} = \{h/(8\pi\nu\mu)\} \cdot \{(\partial\alpha/\partial r)^2/\alpha^2\} \quad (183)$$

where μ is one-fourth the weight of the chlorine atom; ν is the Raman frequency; α is the polarizability and r is the internuclear distance. For the lines 780 cm^{-1} and 1538 cm^{-1} the observed intensities are 7.7 and 1.0 and the depolarization factors are 0.89 and 0.41. Similarly

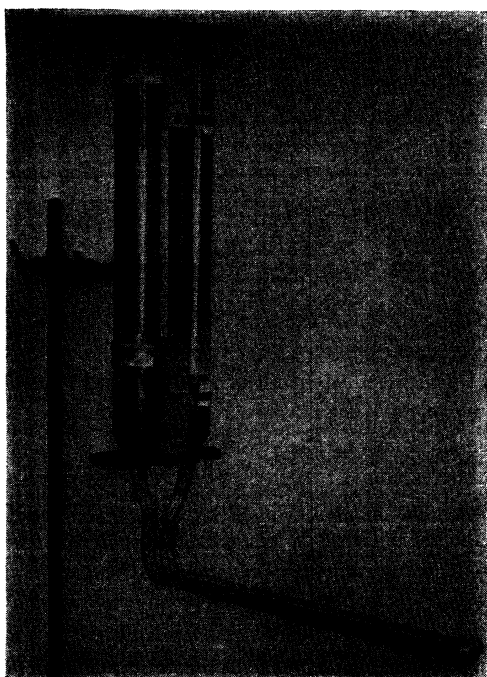


FIG. 20. Mercury-neon discharge tubes [Glockler and Morrell (155)].

the intensity ratio of the two lines of the Fermi doublet in carbon dioxide were considered by Nath and Chalam (308). They assumed that the polarizability of a molecule is the sum of the bond-polarizabilities as functions of the internuclear distances. The appearance of overtones could be accounted for by the supposition that certain of the normal coordinates are quadratic functions of some of the variations in the internuclear distances and that bond polarizabilities show only first-order changes. The calculated intensity ratio of the carbon dioxide Fermi doublet is 0.6 in good agreement with earlier experimental values.

40. Apparatus

The Raman spectrograph should have large dispersion in the visible ($\sim 8\text{\AA}/\text{mm}$) near 4358 Hg and large aperture. The mercury arc or discharge tube is the most suitable exciting radiation and 4358 and/or 4077A are the most convenient exciting lines because most of the Raman shifts will then appear between 4358 and 4916A Hg, and no other mercury lines will

usually interfere. In many cases investigators built their own spectrographs, as for example, Langseth (253) who constructed an instrument of 7A/mm dispersion and a resolving power sufficiently high to separate lines 1 cm^{-1} apart. Glockler and his co-workers (153) used a three-prism Steinheil spectrograph (8A/mm) and they employed mercury discharge tubes, Fig. 20, containing about 5 mm of neon gas for starting purposes. These tubes operate at very low temperature and if arranged cylindrically as shown in Fig. 21 give sufficient light intensity so

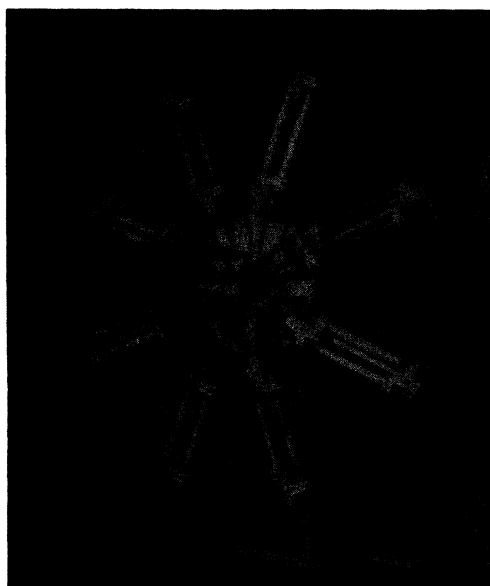


FIG. 21. Cylindrical arrangement of mercury-neon discharge tubes for Raman work [Glockler and Morrell (155)].

that the strong Raman lines of benzene could be seen with well-rested eyes. In order to keep the Raman tube containing the scattering liquid at a reasonably low temperature (30–40°C) a blower forcing air past the Raman tube is very helpful. Mercury arcs and lamps of the most varied designs have been employed. Since the exciting line (i.e., 4358A for example) is liable to be greatly overexposed in the time it takes to obtain all the Raman lines, a small mechanical absorber for the unmodified Rayleigh line is convenient. It consists of a small dihedral blackened wedge to be placed before the photographic plate. For low temperature work with liquefied gases the

arrangement adopted by Glockler and Renfrew (159) is very satisfactory. For substances which decompose photochemically it is necessary to avoid ultraviolet radiation and the mercury line 4358A is usually the most convenient source. If, however, given substances such as the alkyl iodides should be very light sensitive and show coloration during exposure a continuous distillation apparatus can be adopted as described by Kahovec and Wagner (201). Whenever possible it would be most desirable to obtain the Raman spectrum of a substance in the gaseous state, for Raman lines of liquids always differ from those obtained with the gas because of the influence of the surrounding molecular field. Kirby-Smith and Bonner (215-216) describe an apparatus enabling them to photograph spectra in 3-6 hours with the gaseous substance at low pressures (2-3 atmospheres). They used very powerful light sources consisting of sixteen high intensity mercury arcs. Since about 8 kw is dissipated in the lamps, cooling is of major importance. The technique of photographing Raman spectra of solids is especially difficult but has been accomplished by a number of investigators. Lately Reitz (372) has described more details of a previously used arrangement. The method of complimentary filters has been employed by Ansidei (2) in the case of pyrrole. After Raman spectra are obtained, the photographic plates must be read by some sort of wave-length comparator. Again different workers used their own designs and methods. These various appliances do not deviate greatly from standard

equipment. One of the procedures involves the projection of the photograph. This technique is described in the standard literature and lately has had the attention of Intonti and Milazzo (192). In order to convert the experimental datum of the photographic plate, i.e., the distance of any spectral line, into wave-lengths, the well-known Hartmann formula is employed. Mayants (272) developed a method for calculation of spectral frequencies, using tabulated values of auxiliary coefficients.

41. Addendum

A series of papers dealing with light scattering in gases, liquids, and solids was given at a symposium on fluorescence, light scattering, and the Raman effect held at Bangalore, India. These articles were published in the *Proceedings of the Indian Academy of Sciences*, pages 293 to 419 (1942). The papers on the Raman effect were:

- Analysis of the Raman Spectrum of Single Crystals of Naphthalene.** T. M. K. NEDUNGADI
- The Raman Spectra of Organic Compounds: Aniline.** Dr. C. S. VENKATESWARAN AND N. S. PANDYA
- The Raman Spectra of Organic Compounds: Diethyl Disulphide.** Dr. C. S. VENKATESWARAN AND N. S. PANDYA
- The Raman Spectra of Organic Compounds: Binary Liquid Mixtures.** Dr. C. S. VENKATESWARAN AND N. S. PANDYA
- The Scattering of Light in Emulsions.** DARABRA SINGH
- The Fluorescence of the Uranyl Compounds and Raman Spectrum of the Uranyl Ion.** B. S. SATYANARAYANA

The volume covering the papers on this symposium arrived too late to be included in this report.

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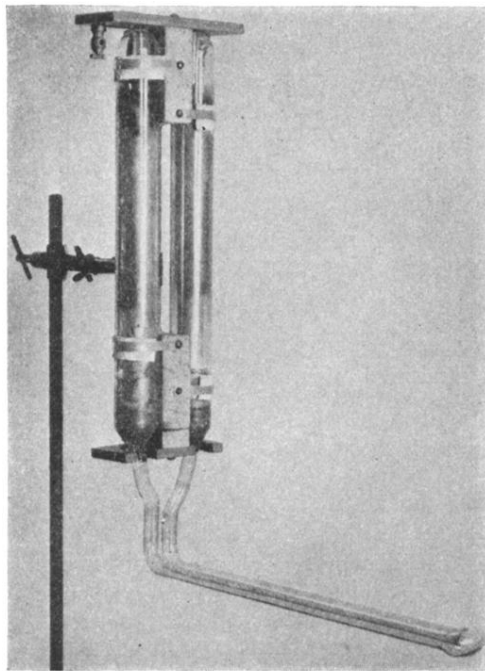


FIG. 20. Mercury-neon discharge tubes
[Glockler and Morrell (155)].

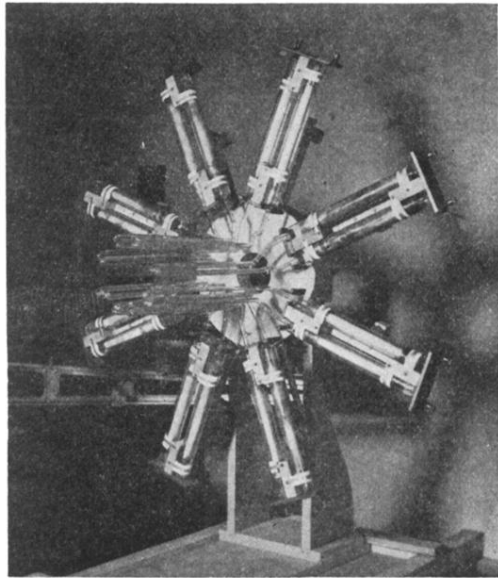


FIG. 21. Cylindrical arrangement of mercury-neon discharge tubes for Raman work [Glockler and Morrell (155)].