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Interaction in Molecules Between Rotation and Slightly Anisotropic Oscillations

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The problem of the interaction between rotation and oscillation in two dimensionally slightly anisotropic molecules is considered quantum mechanically on the basis of model rotating only about an axis normal to the plane in which the oscillations take place. The energy of the molecule in the ground state becomes $(h/2)(\nu_1 + \nu_2) + K^2 h^2 / 8\pi^2 A$ while for the upper states the energies are $E = h(\nu_1 + \nu_2) + (K^2 + \zeta^2) h^2 / 8\pi^2 A \pm ((\Delta\nu/2)^2 + (Kh/4\pi^2 A)^2 \zeta^2)^{1/2}$, where ζ is a quantity depending upon the normal coordinates which in general is not an integer. The selection rules are such as to enhance the intensities of the set of lines in the sides of the two bands adjacent to each other at the expense of the set of lines in the sides of the bands farthest away from each other. The spacings between rotational lines of the first set converge rapidly toward a limiting value of $(1 - \zeta)h/4\pi^2 A$, while for the other set the spacings approach a value $(1 + \zeta)h/4\pi^2 A$.

I. INTRODUCTION

IT has been pointed out by several writers¹ that in polyatomic molecules where the symmetries are such that oscillations, isotropic in two or three dimensions (and therefore two or threefold degenerate), may take place, the interactions between rotation and oscillation will in general give rise to anomalous spacings between the rotation lines in an absorption band. This effect is directly associated with the fact that to an isotropic oscillation may always be ascribed a certain amount of angular momentum so that the total angular momentum of the molecule must be thought of as a kind of a vector sum of the angular momentum of the molecule rotating and the angular momentum of the molecule oscillating rather than, as is usually the case, consisting just of the angular momentum of rotation. If these vectors add up in one sense the rotational spacing will be larger than the normal spacing while if these angular momentum vectors add up in the opposite sense the spacing will be smaller than the normal spacing. These vectors may be said to add up in the positive sense or the negative sense depending upon whether or not the rotating electric moment is in the same sense or the opposite sense as the oscillational angular momentum vector. This might classically be equivalent to saying that in the first case the

electric moment will rotate with a frequency in excess of the rotational frequency of the molecule while in the second case the opposite will occur.

When the isotropy is three dimensional as is the case in the methane molecule, the spacings in nearly all the bands will be affected, while if the isotropy is confined to two dimensions, as is the case in the methyl halide molecules, so that the degenerate oscillations lie in a plane normal to the axis of symmetry, only the perpendicular bands, or those arising from oscillations lying in that plane, will be affected. For molecules like the methyl halides the two identical moments of inertia are much larger than the third, so that as is well known, the perpendicular bands will consist of a series of intense and nearly equally spaced lines protruding above a background made up of lines too closely spaced to be resolved spectroscopically. These rather intense lines protruding above the general background are known to arise when the molecule executes a rotational transition where $\Delta J = 0$, $\Delta K = \pm 1$, J and K being respectively the quantum number of total angular momentum and the quantum number of angular momentum about the axis of symmetry. Now these transitions are in reality just those which a rotator rotating in two dimensions only is permitted to make and for this reason it has been possible on the basis of a model where rotation occurs only about an axis normal to the plane in which the isotropic oscillations are contained to compute and predict

¹ E. Teller and Tiza, *Zeits. f. Physik* **73**, 791 (1932); E. Teller, *Hand und Jahrbuch der Chemie Physik*, Vol. 9 (1934), p. 125; D. M. Dennison and M. Johnston, *Phys. Rev.* **48**, 868 (1935).

quite accurately what the effect upon the appearance of the absorption band will be due to the interactions of the above kind.

In polyatomic molecules of even less degree of symmetry the two dimensional isotropy will in general disappear so that the oscillational degeneracies will be removed. One might quite well expect therefore, that such interactions as those described above would vanish. An interesting case arises, however, when one considers the case where the anisotropies are small so that the now nondegenerate vibration frequencies are separated by an interval $\Delta\nu$ which is of the same order of magnitude as the rotational frequencies that may occur in the band.² We shall here consider a case where two dimensionally slightly anisotropic oscillations occur and investigate what will be the nature of the interaction between these and the rotation of the molecule, examining at the same time what may be expected to be the effect on the observed spectrum. A complication is here clearly met with, namely, that in general, such molecules may no longer be categorized as symmetric, but rather as asymmetric rotators. If, however, we confine ourselves to such molecules which are only slightly asymmetric the rotational motion may still, to a good approximation, be represented by that of a symmetric top and then we may again base our predictions upon a model where rotation occurs only about an axis normal to the plane containing the two dimensionally slightly anisotropic oscillations.

II. EIGENVALUES FOR A ROTATING ANISOTROPIC MOLECULE

The model which we shall consider is one in reality only of academic interest, but one which may be useful in interpreting certain of the bands in a coplanar XYZ_2 type of molecule of which the formaldehyde molecule is a well-known example. The X atom and the two Z atoms of such a molecule form an isosceles triangle with the Y atom located somewhere along the bisector of the vertex angle. In such a molecule, frequencies will occur which arise from oscillations of the electric moment at right angles to each other in a plane normal to the axis of symmetry of the molecule. Two such

oscillations which may frequently be expected to lie not far removed from each other are the ones which may respectively be thought of as arising from a bending at the vertex of the YZ_2 triangle, which in first approximation is to be regarded as remaining rigid, of the XY arm of the molecule in the plane of the molecule and normal to it. The nature of these is perhaps better visualized by referring to Fig. 1 where it may be seen that

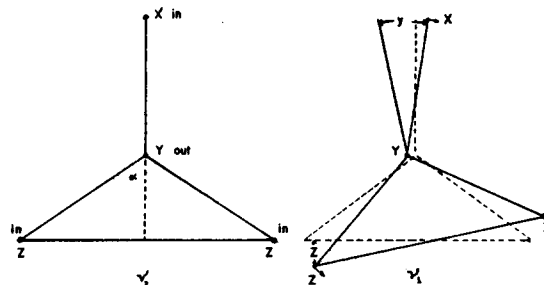


FIG. 1.

they correspond to actual deformations of the molecule. They are consequently often referred to as "deformation" frequencies. When such frequencies differ by only small amounts they will, as we shall see, when they are coupled to the rotation of the molecule, give rise to interesting interaction terms in the energy of the molecule.

The kinetic energy of the above molecule described in terms of a set of coordinates $x'y'$ and z' fixed in space will be:

$$T = \sum_{k=1}^4 (m_k/2)(\dot{x}_k'^2 + \dot{y}_k'^2 + \dot{z}_k'^2), \quad (1)$$

where m_1 , m_2 and m_3 are the masses of the particles Z , X and Y , respectively. As we have indicated earlier, we shall consider the rotation of the molecule restricted so as to be only about an axis normal to the plane containing the two anisotropic oscillations. For this purpose a set of coordinates x , y and z rotating with the molecule is more suitable. We shall consider the z axis to be the axis of symmetry of the molecule about which the rotation is to take place and for convenience it is made to coincide with the space fixed z' axis. The following simple formulations relate the two sets of coordinates to each other: $x' = x \cos \varphi - y \sin \varphi$; $y' = x \sin \varphi + y \cos \varphi$; $z' = z$. In terms of these new coordinates the rest positions of the Z , X and Y particles shall

² E. B. Wilson, Jr., J. Chem. Phys. **4**, 313 (1936).

be designated in the following manner: $x_1^0 = -a$, $y_1^0 = 0$, $z_1^0 = z_1^0$; $x_2^0 = a$, $y_2^0 = 0$, $z_2^0 = z_1^0$; $x_3^0 = 0$, $y_3^0 = 0$, $z_3^0 = z_3^0$; $x_4^0 = 0$, $y_4^0 = 0$, $z_4^0 = z_4^0$. Since the YZ_2 triangle is to be regarded as rigid we have that $x_1 = x_2$ and $y_1 = y_2$, x_1 , x_2 , y_1 and y_2 being the displacements along the x and y axes of the Z particles. By fixing the center of gravity of the molecule at the origin of the coordinate system and setting the linear and angular momenta equal to zero we have further that $x_3 = cx_1$, $x_4 = dx_1$, $y_3 = c'y_1$, $y_4 = d'y_1$, x_3 , x_4 , y_3 and y_4 being the displacements along the x and y axes of the X and Y particles. The constants c , d , c' and d' are abbreviations for the following quantities:

$$\begin{aligned} c &= -(2m_1(2m_1 + m_4)z_1^0 + 2m_1m_3z_3^0) / \\ &\quad (m_3(m_3 + m_4)z_3^0 + 2m_1m_3z_1^0), \\ d &= -2m_1(z_3^0 - z_1^0) / ((m_3 + m_4)z_3^0 + 2m_1z_1^0); \\ c' &= -(2m_1(2m_1 + m_4)z_1^0 + 2m_1m_3z_3^0 \\ &\quad + 2m_1m_4y_1^0) / (m_3(m_3 + m_4)z_3^0 + 2m_1m_3z_1^0) \text{ and} \\ d' &= -2m_1(z_3^0 - z_1^0 - y_1^0) / ((m_3 + m_4)z_3^0 + 2m_1z_1^0). \end{aligned}$$

Finally we have also that $z_1 = -z_2$ where these are the components along the z axis of the actual displacements of the Z particles in the yz plane from their positions of rest. It is convenient also to make the further substitutions:

$$\begin{aligned} x &= \frac{1}{2}((1-d)z_3^0 - (c-1)z_4^0 \\ &\quad - (2-c-d)z_1^0)x_1/(z_3^0 - z_4^0) \text{ and} \\ y &= ((1-d')z_3^0 - (1+c'-2d')z_4^0 \\ &\quad - (c'-d')z_1^0)y_1/(z_4^0 - z_1^0). \end{aligned}$$

The variables z_1 and z_2 are, however, not independent variables, but as may be seen from Fig. 1, are related to y_1 and y_4 in the following manner: $z_1 = -z_2 = (y_4 - y_1) \tan \alpha$ where α is equal to half the $Z-Y-Z$ angle. Replacing \dot{z}_1 by its equivalent $(d'-1)\dot{y}_1 \tan \alpha$, the relation (1) becomes transformed into:

$$T = (\mu/2)(\dot{x}^2 + \dot{z}^2\dot{\varphi}^2) + (\mu'/2)(\dot{y}^2 + \dot{y}^2\dot{\varphi}^2) + \mu''(x\dot{y} - \dot{x}y)\dot{\varphi} + (A/2)\dot{\varphi}^2 \quad (2)$$

μ in the above being an abbreviation for: $4(2m_1 + m_3c^2 + m_4d^2)(z_3^0 - z_4^0)^2 / ((1-d)z_3^0 - (c-1)z_4^0 - (2-c-d)z_1^0)^2$, μ' for $(2m_1 + 2m_1(d'-1)^2 \tan^2 \alpha + m_3c'^2 + m_4d'^2)(z_4^0 - z_1^0)^2 / ((1-d')z_3^0 - (1+c'+2d')z_4^0 + (c'-d')z_1^0)^2$, μ'' for $2(2m_1 + m_3cc' + m_4dd')(z_4^0 - z_1^0)(z_3^0 - z_4^0) / ((1-d)z_3^0 - (2-c-d)z_1^0 - (c-1)z_4^0)((1-d')z_3^0 - (1+c'+2d')z_4^0 - (c'-d')z_1^0)$ and A for the moment of inertia $2m_1a^2$ of the molecule.

The potential energy of the molecule ex-

pressed in these coordinates may be taken to be:

$$V = (2\pi^2\mu\nu_1^2)x^2 + (2\pi^2\mu'\nu_2^2)y^2 \quad (3)$$

so that the quantum-mechanical equation appropriate for our problem may, neglecting certain terms which will be small, be found to be:

$$\begin{aligned} \{ &(\mu'/\mu)\partial^2/\partial x^2 + \partial^2/\partial y^2 + (\mu'/A)((\mu'/\mu)y^2\partial^2/\partial x^2 \\ &- (\mu/\mu')x^2\partial^2/\partial y^2 - (\mu''/\mu\mu')(y\partial/\partial y \\ &+ 2xy\partial/\partial y\partial/\partial x + x\partial/\partial y)) + (\mu'/A)\partial^2/\partial \varphi^2 \\ &- 2(\mu'/A)(\mu''/\mu')(y\partial/\partial x - x\partial/\partial y)\partial/\partial \varphi \\ &+ (8\pi^2\mu'/h^2)(E - (2\pi^2\mu\nu_1^2)x^2 \\ &- (2\pi^2\mu'\nu_2^2)y^2)\} \Psi = 0. \end{aligned} \quad (4)$$

It is convenient to introduce the notation $\alpha = (4\pi^2\mu\nu_1/h)$ and $\beta = (4\pi^2\mu'\nu_2/h)$ in the above as well as to affect the changes of variable $\xi = \alpha^{\frac{1}{2}}x$ and $\eta = \beta^{\frac{1}{2}}y$. Noting further that φ is ignorable so that Ψ may be written $F(\xi, \eta) \exp(iK\varphi)$, K being as usual integral Eq. (4) becomes transformed into:

$$\begin{aligned} \{ &(\alpha\mu'/\mu)\partial^2/\partial \xi^2 + \beta\partial^2/\partial \eta^2 \\ &+ (\mu'/A)((\alpha\mu'/\beta\mu)\eta^2\partial^2/\partial \xi^2 \\ &+ (\beta\mu/\alpha\mu')\xi^2\partial^2/\partial \eta^2 - (\mu''/\mu\mu')(\eta\partial/\partial \eta \\ &+ 2\xi\eta\partial/\partial \xi\partial/\partial \eta + \xi\partial/\partial \xi) \\ &- (2iK\mu'/A)(\mu''/\mu')((\alpha/\beta)^{\frac{1}{2}}\eta\partial/\partial \xi \\ &- (\beta/\alpha)^{\frac{1}{2}}\xi\partial/\partial \eta) \\ &+ (\lambda - (\alpha\mu'/\mu)\xi^2 - \beta\eta^2)\} F(\xi, \eta) = 0 \end{aligned} \quad (5)$$

λ being made to replace $(8\pi^2\mu'E/h^2) - \mu'K^2/A$.

Equation (5) lends itself readily to solution only when $\alpha = (\alpha\mu'/\mu) = \beta$ in which case the problem degenerates to that of a two-dimensional isotropic oscillator rotating about an axis normal to its own plane. If, however, we confine ourselves to such molecules where the anisotropy is small so that $\langle \alpha, \rangle (\alpha\mu'/\mu)$ and β are not greatly unlike, the equation is still exactly soluble when one neglects certain terms of the order of magnitude $(\Delta\nu/\nu)(h/4\pi^2A)$ i.e., small as compared with the rotational frequencies of the molecule and which in first approximation need not be taken into account. We shall confine ourselves to the fundamental bands only so that it will be sufficient to obtain the solution and eigenvalues to Eq. (5) for the lowest and the first excited states only. Neglecting the above terms, we may take $F(\xi, \eta)$ for the ground state to be $F(\xi, \eta) = (\alpha\beta/\pi^2)^{\frac{1}{2}} \exp - (\xi^2 + \eta^2)/2$ which yields as the energy value the following:

$$E(0, K) = (h/2)(\nu_1 + \nu_2) + K^2h^2/8\pi^2A, \quad (6)$$

h being as usual Planck's constant, ν_1 and ν_2 the frequencies of the two oscillations and A the moment of inertia. For the two excited states there will be two functions $F(\xi, \eta)$ which will equally well satisfy Eq. (5), namely $\varphi_1 = 2\eta \exp -(\xi^2 + \eta^2)/2$ and $\psi_1 = 2\xi \exp -(\xi^2 + \eta^2)/2$. Substituting these into (5) one obtains respectively as the first-order terms the following:

$$\begin{aligned} & \{(\lambda - \beta - 3(\alpha\mu'/\mu) - (\mu''^2/\mu\mu'))(\mu'/A) \\ & \quad - (2iK\mu'/A)(\mu''/\mu')(\eta/\xi)(\nu_1/\nu_2)^{1/2}\}\psi_1 = 0, \\ & \{(\lambda - 3\beta - (\alpha\mu'/\mu) - (\mu''^2/\mu\mu'))(\mu'/A) \\ & \quad + (2iK\mu'/A)(\mu''/\mu')(\xi/\eta)(\nu_2/\nu_1)^{1/2}\}\varphi_1 = 0, \end{aligned}$$

which, observing that the operators ξ/η and η/ξ operating on φ_1 and ψ_1 respectively convert them into ψ_1 and φ_1 , yield at once the linear homogeneous equation:

$$\begin{aligned} & [(\lambda - \beta - 3(\alpha\mu'/\mu) - (\mu''^2/\mu\mu'))(\mu'/A)]\psi_1 \\ & \quad - (2iK\mu'/A)(\mu''/\mu')(\nu_1/\nu_2)^{1/2}\varphi_1 = 0, \quad (7) \\ & (2iK\mu'/A)(\mu''/\mu')(\nu_2/\nu_1)^{1/2}\psi_1 + [(\lambda - 3\beta \\ & \quad - (\alpha\mu'/\mu) - (\mu''^2/\mu\mu'))(\mu'/A)]\varphi_1 = 0. \end{aligned}$$

The determinant of the coefficients of φ_1 and ψ_1 , vanishing, will serve to determine the eigenvalues of the molecule for the first excited states. Diagonalizing the energy matrix, one obtains:

$$E(1, K) = h(\nu_1 + \nu_2) \pm h((\nu_1 - \nu_2)^2/4 + (K\xi h/4\pi^2 A)^2)^{1/2} + (K^2 + \xi'^2)(h^2/8\pi^2 A). \quad (8)$$

where

$$\xi = (\mu''/\mu') \quad \text{and} \quad \xi'^2 = (\mu''^2/\mu\mu').$$

The characteristic functions for these states will be linear combinations of φ_1 and ψ_1 , the coefficients in each case being given by the minors of the determinant (7) upon substitution for λ the root corresponding to that state. Designating by $\Psi(+1)$ and $\Psi(-1)$ the characteristic functions whose eigenvalues are respectively obtained by using the *plus* and the *minus* signs before the radical in Eq. (8), we obtain after normalization:

$$\begin{aligned} \Psi(+1) &= N \{ (iK\xi h^2/4\pi^2 A)(\nu_2/\nu_1)^{1/2} 2\eta \\ & \quad + h[(\nu_1 - \nu_2)/2 + ((\nu_1 - \nu_2)^2/4 \\ & \quad + (K\xi h/4\pi^2 A)^2)^{1/2}] 2\xi \} e^{-(\xi^2 + \eta^2)/2}, \\ \Psi(-1) &= N \{ -ih[(\nu_1 - \nu_2)/2 + ((\nu_1 - \nu_2)^2/4 \\ & \quad + (K\xi h/4\pi^2 A)^2)^{1/2}] 2\eta \\ & \quad + (K\xi h/4\pi^2 A)(\nu_1/\nu_2)^{1/2} 2\xi \} e^{-(\xi^2 + \eta^2)/2}, \\ N^2 &= \{ h^2[(\nu_1 - \nu_2)/2 + ((\nu_1 - \nu_2)^2/4 \\ & \quad + (K\xi h/4\pi^2 A)^2)^{1/2}]^2 \\ & \quad + (K\xi h/4\pi^2 A)^2(\nu_k/\nu_j) \}^{-1} (4\pi^2 \mu \nu_1 \nu_2/h^2)^{1/2}, \end{aligned} \quad (9)$$

k and j being respectively 1 and 2, and 2 and 1 when N is used with the first and the second functions.

Before approaching the question of what will be the selection rules for such a molecule as the above and what effect these interactions might be expected to produce on the intensities of the lines in a band it will be convenient to note how the energies and the eigenfunctions will behave in two limiting cases. In the one limiting case where $\nu_1 - \nu_2$ approaches zero so that it may be considered negligible with respect to $K\xi h/4\pi^2 A$, Eqs. (6) and (8) degenerate into $h\nu + K^2 h^2/8\pi^2 A$ and $2h\nu + (K \pm \xi)^2 h^2/8\pi^2 A$, respectively, which are just the energies of a two-dimensionally isotropic oscillator rotating in its own plane as determined by Teller and Tiza. Letting $\eta = \rho \sin \theta$ and $\xi = \rho \cos \theta$ the characteristic functions degenerate into $(\alpha/\pi)^{1/2} \exp(-\rho^2/2)$ for the ground state and into $(\alpha/2^{1/2}\pi)^{1/2} \rho \exp(-\rho^2/2) \exp(i\theta)$ and $(\alpha/2^{1/2}\pi)^{1/2} \rho \exp(-\rho^2/2) \exp(-i\theta)$, complex conjugates of each other, for the upper state.

The other limiting case arises when $\nu_1 - \nu_2$ is so large with respect to $K\xi h/4\pi^2 A$ that the latter may entirely be neglected. The energy values (6) and (8) then reduce to $(h/2)(\nu_1 + \nu_2) + K^2 h^2/8\pi^2 A$ for the ground state and for the upper state $(h/2)(3\nu_1 + \nu_2) + K^2 h^2/8\pi^2 A + \text{const.}$ and $(h/2)(\nu_1 + 3\nu_2) + K^2 h^2/8\pi^2 A + \text{const.}$ These are just the energy values which one would obtain when one assumes that the quantum mechanical equation is exactly separable in the coordinates of rotation and oscillation. The two states will now have become completely separated and the functions characterizing them will according to (9) take just the anticipated values:

$$\begin{aligned} \Psi(+1) &= (\alpha\beta/2\pi^2)^{1/2} (2\xi \exp -(\xi^2 + \eta^2)/2) \\ \text{and } \Psi(-1) &= (\alpha\beta/2\pi^2)^{1/2} (2\eta \exp -(\xi^2 + \eta^2)/2). \end{aligned}$$

We might therefore expect such a molecule as the above, for small values of the rotational quantum number K where $\Delta\nu$ could be considered large compared to $K\xi h/4\pi^2 A$ to behave very much like a molecule of the latter limiting case, but as K increases so that $K\xi h/4\pi^2 A$ becomes of the same magnitude and eventually large as compared with $\Delta\nu$, that it would approximate more nearly the first limiting case in its behavior.

III. SELECTION RULES AND THE QUESTION OF INTENSITIES

The final conclusions of the previous section may be confirmed quantitatively by a study of the selection rules and the intensity relations. The rules of transition may be arrived at by examination of the nonvanishing matrix components of the electric moment as the molecule executes a transition from the ground state to one of the two characterized either by $\Psi(+1)$ or $\Psi(-1)$. Since the method is an obvious one, we shall not here derive them, but content ourselves merely by stating what they are. When a transition from the zeroth vibration state to one of the two upper states takes place the selection rule for K will in general be $\Delta K = \pm 1$, lines in the spectrum occurring at the following corresponding frequency positions:

$$\nu = (\nu_1 + \nu_2)/2 \mp (Kh/4\pi^2A) \pm \{(\nu_1 - \nu_2)^2/4 + (K\zeta h/4\pi^2A)^2\}^{1/2}. \quad (10)$$

From this it will be seen that when $\Delta\nu$ is large compared with $K\zeta h/4\pi^2A$ the spacing between rotational lines approaches the normal value $h/4\pi^2A$, but as K increases, taking like signs in (10), the spacing approaches $(1+\zeta)h/4\pi^2A$; taking opposite signs in (10), a value approaching $(1-\zeta)h/4\pi^2A$ prevails. Examination of the matrix components verifies, moreover, that when the molecule executes an oscillational transition from the ground state to the state $+1$, the probability of the rotational transition $K=K'+1$ in the lower to $K=K'$ in the upper state increases at the expense of the transition $K=K'-1$ to

$K=K'$, as K increases. Similarly, when the molecule makes a transition from the ground state to the oscillational state -1 , the transition $K=K'-1$ to $K=K'$ increases in probability at the expense of the other.

This result is again consistent with the work of Teller and Tiza in which they showed that for a two dimensional isotropic oscillator rotating in its own plane, ζ being taken as unity, the rotational structure would collapse into a single line, i.e., the spacing between two adjacent lines would be zero. This is virtually what happens in our case as $Kh/4\pi^2A$ becomes large compared to $\Delta\nu$.

In conclusion we shall simply summarize the derived results. In certain molecules when oscillations occur which are only slightly anisotropic interactions between rotation and oscillation may occur, not wholly unlike those that take place in completely symmetric molecules. The effect upon the spectrum will be a rapid convergence of the rotational lines in the halves of the two bands adjacent to each other toward a limiting value of the spacings $(1-\zeta)h/4\pi^2A$, while on the other sides the spacings between lines rapidly approach a value $(1+\zeta)h/4\pi^2A$. The intensities of the former set of lines will at the same time be enhanced at the expense of the latter set of lines.

The author desires to express his gratefulness to Professor E. Teller and to Professor D. M. Dennison with whom he has had occasion to discuss this problem and who have made suggestions distinctly helpful in deducing the results in the present formulation.

Two Bands in the Infrared Spectrum of Formaldehyde

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Two infrared bands of the type arising from oscillations of the electric moment normal to the axis of symmetry have been measured under high dispersion and identified as the two oscillations which are at right angles to each other and which in Sutherland and Dennison's notation are ν_5 and ν_6 . Their centers are respectively at 1278 cm^{-1} and 1165 cm^{-1} . The anomalous spacing between the principal rotation lines is accounted for on the basis of an interaction between rotation and the two oscillations which are only slightly anisotropic.