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The implication of some of the foregoing observations and conclusions will be developed in another paper. It seems, however, from the present results, that transparent polycrystalline pellets of alkali halides which can be colored by x-rays and by chemical addition (at room temperature) exhibit a variety of phenomena the study

of which complements as well as highlights similar studies with single crystals.

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Effect of Change in Moment of Inertia on the Intensity Distribution in P and R branches of $C_{\infty v}$ Molecules

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The effect of the change in moment of inertia part of the interaction between vibration and rotation on the intensities of parallel bands of linear polyatomic molecules has been determined to the first order. The results are quite similar to those of Herman and Wallis for diatomic molecules. The interaction term depends on among others a quantity, ξ_k , different in general for each band. Perpendicular bands do not show a first-order correction. A "sum rule" for the ξ_k has been determined.

INTRODUCTION

THE effect of the interaction between vibration and rotation on the intensity of individual rotation lines of diatomic molecules has recently been investigated by Herman and Wallis.¹ These authors give references to previous work and results. An analogous treatment of vibration-rotation interaction in polyatomic molecules is possible; the simplest cases being linear.

The equations derived by Herman and Wallis show a line intensity dependence on a quantity they call θ , which equals $\mu_0/\mu_1 r_e$, where μ_0 is the static dipole moment of the molecule, r_e is the equilibrium separation of the two atoms, and μ_1 is $d\mu/dr$ evaluated at $r=r_e$. A similar quantity arises in the case of linear polyatomic molecules with, in general, a different value of each band.

THEORY

The first-order corrections to the intensities of the single rotation lines due to moment of inertia change in linear polyatomic molecules may be obtained by using a Hamiltonian with the harmonic oscillator approximation and retaining the dependence of the instantaneous moment of inertia on the first power of the normal coordinates. The only normal coordinates showing up in the first power and also giving rise to active fundamentals are in the symmetry class, Σ^+ , of $C_{\infty v}$ molecules. The Hamiltonian for these coordinates alone may be

written,

$$H \cong M^2/2I_e + \frac{1}{2} \sum_{\Sigma^+} [P_k^2 + \omega_k^2 Q_k^2 - 2(M^2/2I_e)\xi_k Q_k], \quad (1)$$

where M , P_k , and ω_k have their usual significance, I_e is the equilibrium moment of inertia, and ξ_k is a quantity which will be discussed later. A standard perturbation treatment will give a matrix correct to the first order which will diagonalize H , and if this same matrix is used to transform the components of dipole moment the final result will have the intensities correct to the first order.

The matrix elements for the above Hamiltonian are

$$(jmn_k | H | jmn_k) = B_e j(j+1) + \hbar \sum_{\Sigma^+} \omega_k (n_k + \frac{1}{2})$$

$$(jmn_k | H | jmn_{k+1}) = -2B_e j(j+1) [(n_k+1)/2\gamma_k]^{\frac{1}{2}} \xi_k,$$

where $\gamma_k = \omega_k/\hbar$. If U is the unitary matrix correct to the first order which diagonalizes H , we may write $U = E + V$, where E is the unit matrix,

$$(jmn_k | V | jmn_{k+1}) = -(jmn_{k+1} | V | jmn_k) \\ = -\delta_k \xi_k j(j+1) [(n_k+1)/2\gamma_k]^{\frac{1}{2}}$$

and $\delta_k = 4\pi B_e/\omega_k$. The dipole moment as is customary may be expanded in a Taylor's series in the normal coordinates. The component of the moment along the figure axis is

$$\mu = \mu_0 + \sum_{\Sigma^+} \mu_{1,k} Q_k + \dots$$

¹ R. Herman and R. F. Wallis, *J. Chem. Phys.* **23**, 637 (1955).

Retaining terms to the first power of Q_k the matrices of

the moment referred to space fixed axes are,

$$\begin{aligned} (j+1mn_k | \mu_z | jmn_k) &= (jmn_k | \mu_z | j+1mn_k) = [(j+m+1)(j-m+1)G(j)]^{\frac{1}{2}} \mu_0 \\ (j+1mn_k+1 | \mu_z | jmn_k) &= (jmn_k+1 | \mu_z | j+1mn_k) = (j+1mn_k | \mu_z | jmn_k+1) \\ &= (jmn_k | \mu_z | j+1mn_k+1) = [(j+m+1)(j-m+1)(n_k+1)G(j)]^{\frac{1}{2}} [\mu_{1,k}/(2\gamma_k)]^{\frac{1}{2}} \\ (j+1m+1n_k | \mu_x+i\mu_y | jmn_k) &= (jmn_k | \mu_x-i\mu_y | j+1m+1n_k) = -[(j+m+1)(j+m+2)G(j)]^{\frac{1}{2}} \mu_0 \\ (j+1mn_k | \mu_x+i\mu_y | jm+1n_k) &= (jm+1n_k | \mu_x-i\mu_y | j+1mn_k) = [(j-m)(j-m+1)G(j)]^{\frac{1}{2}} \mu_0 \\ (j+1m+1n_k+1 | \mu_x+i\mu_y | jmn_k) &= (jmn_k | \mu_x-i\mu_y | j+1m+1n_k+1) \\ &= -[(j+m+1)(j+m+2)(n_k+1)G(j)]^{\frac{1}{2}} [\mu_{1,k}/(2\gamma_k)]^{\frac{1}{2}} \\ (j+1mn_k+1 | \mu_x+i\mu_y | jm+1n_k) &= (jm+1n_k | \mu_x-i\mu_y | j+1mn_k+1) \\ &= [(j-m)(j-m+1)(n_k+1)G(j)]^{\frac{1}{2}} [\mu_{1,k}/(2\gamma_k)]^{\frac{1}{2}}, \end{aligned}$$

where $G(j) = [(2j+1)(2j+3)]^{-1}$. If μ_x , μ_y , and μ_z are subjected to a unitary transformation by U , we have

$$U^{\dagger} \mu_x U \cong \mu_x + \mu_x V - V \mu_x, \text{ etc.},$$

correct to the first order. When the elements of $U^{\dagger} \mu_x U$, etc., corresponding to the fundamental transitions are squared, added together, and summed over m , the transition moment for the R branch is

$$F_k^R \cong (j+1) \mu_{1,k}^2 [1 - 4\delta_k \theta_k (j+1)] / \gamma_k,$$

where $\theta_k = \mu_0 \xi_k / \mu_{1,k}$. The P-branch expression is

$$F_k^P \cong j \mu_{1,k}^2 [1 + 4\delta_k \theta_k j] / \gamma_k.$$

With these expressions for F_k^R and F_k^P , the intensity of a single line is found to be proportional to

$$\begin{aligned} \omega_j^R (\mu_{1,k}^2 / \gamma_k) (j+1) [1 - 4\delta_k \theta_k (j+1)] \\ \times \exp[-\sigma j(j+1)], \quad R \text{ branch,} \end{aligned}$$

and

$$\omega_j^P (\mu_{1,k}^2 / \gamma_k) j [1 + 4\delta_k \theta_k j] \exp[-\sigma j(j+1)] \quad P \text{ branch,}$$

where ω_j^R and ω_j^P are the frequencies of the individual lines and $\sigma = B_e / kT$. When the explicit forms of the line frequencies in terms of B_e and the band origin are substituted, the complete intensity formulas become

$$I_k^R \cong C \mu_{1,k}^2 (j+1) [1 + \delta_k (1 - 4\theta_k) (j+1)] \times \exp[-\sigma j(j+1)]$$

and,

$$I_k^P \cong C \mu_{1,k}^2 j [1 - \delta_k (1 - 4\theta_k) j] \exp[-\sigma j(j+1)].$$

$C = N\pi/3cZ$ where N is the number of absorbing molecules per unit volume and

$$Z \sum_j (2j+1) \exp[-\sigma j(j+1)].$$

The ratio of the total intensity in the R branch, A_k^R , to that in the P branch, A_k^P , due to this perturbation alone is

$$\frac{A_k^R}{A_k^P} \cong \frac{T_1 + T_0 + \delta_k (1 - 4\theta_k) (T_2 + 2T_1 + T_0)}{T_1 - \delta_k (1 - 4\theta_k) T_2},$$

where $T_n = \sum_j j^n \exp[-\sigma j(j+1)]$. The total intensity

in the band is found to be

$$A_k = A_k^P + A_k^R \cong (N\pi/3c) \mu_{1,k}^2 [1 + \delta_k (1 - 4\theta_k)].$$

These expressions are analogous to those for diatomic molecules given by Herman and Wallis. These authors also give the T_n in terms of known functions using the Euler-MacLaurin approximation,

$$\begin{aligned} T_0 &\cong \frac{1}{2} \exp(\sigma/4) (\pi/\sigma)^{\frac{1}{2}} [1 - \text{erf}(\sqrt{\sigma/2})] \\ T_1 &\cong 1/(2\sigma) - T_0/2 \\ T_2 &\cong [1/(2\sigma); +\frac{1}{4}] T_0 - 1/(4\sigma) \end{aligned}$$

for small values of σ .

FORM OF ξ_k

The moment of inertia of a linear molecule may be written

$$I = \sum_{\alpha} m_{\alpha} (\eta_{\alpha} + \rho_{\alpha})^2,$$

where η_{α} is the equilibrium position of the α th atom and ρ_{α} is the displacement it undergoes during vibration. The vectors ρ_{α} may be written in terms of the normal coordinates

$$\rho_{\alpha} = \sum_k \mu_{\alpha} \sigma_{k\alpha} Q_k,$$

where μ_{α} is the reciprocal of the mass of the α th atom and $\sigma_{k\alpha}$ is the "s vector" for that atom and the k th normal coordinate. With this I becomes

$$I = I_e + 2 \sum_{\Sigma^+} \sum_{\alpha} \eta_{\alpha} \cdot \sigma_{k\alpha} Q_k + \sum_k Q_k^2$$

since the $\sigma_{k\alpha}$ for Σ^+ coordinates span the subspace containing the η_{α} and coordinates of other symmetry types are orthogonal to this subspace. The reciprocal of I is approximately

$$1/I \cong 1/I_e - 2(1/I_e) \sum_{\Sigma^+} \xi_k Q_k + O(Q^2),$$

where $\xi_k = (1/I_e) \sum_{\alpha} \eta_{\alpha} \cdot \sigma_{k\alpha}$. When this expression for $1/I$ is substituted into the Hamiltonian, Eq. (1) is obtained. If the terms of order Q^2 are retained they do not affect the first-order correction to the intensities but only the energy levels.

DISCUSSION

The results of this calculation are essentially the same as those of Herman and Wallis for diatomic molecules. The main difference is the inclusion of the factor ξ_k in the θ_k , which takes the place of $1/r_e$.

The dependence of the intensity relationships on θ_k has been attributed to a difference in the actual equilibrium position of the atoms for different values of j . The above perturbation treatment would seem to lend itself to a somewhat different qualitative description of what happens. The presence of the linear Q terms in the Hamiltonian tends to mix the vibrational levels. The form of the linear terms is such that the quantity of mixing is dependent on j . A fundamental transition such as $n_k=0 \rightarrow 1$ involves the states $\psi(0) + a\psi(1) \rightarrow a'\psi(0) + \psi(1) + a''\psi(2)$ where the wave functions are not normalized. The main contribution to the intensity is from $\psi(0) \rightarrow \psi(1)$, however, there is a contribution in the first order from components of the perturbed states of the type $\psi(0) \rightarrow \psi(0)$ and $\psi(1) \rightarrow \psi(1)$. In these there is no change in the unperturbed vibrational quantum number, while there is a change in j . This is just the situation in pure rotational spectra, and, of course, this contribution to the intensity depends on μ_0 not $\mu_{1,k}$. The perturbation can therefore be said to cause the total intensity of a line to have a contribution both from the unperturbed vibration-rotation spectrum and from the pure rotation spectrum. The mixing of states is such that the contributions are out of phase in the R branch and in phase in the P branch of θ_k and vice versa if θ_k is negative.

The ξ_k are not all independent. In the appendix it is shown that for any linear unsymmetrical molecule

$$\sum_{\Sigma^+} \xi_k^2 = 1/I_e.$$

This may be put in a different form as

$$\sum_{\Sigma^+} \mu_{1,k}^2 \theta_k^2 = \mu_0^2 / I_e.$$

In principle if other perturbations such as the Coriolis corrections are very small, a measurement of the ratio of R -branch to P -branch intensities yields a value for θ_k if B_e is known. In practice the sign of θ_k may be all that is obtainable, particularly if δ_k is quite small as it is likely to be for heavy molecules.

It is interesting to note also under the same conditions that in principle a determination of the ξ_k gives sufficient data when combined with the frequencies of vibration to completely determine the block of the force constant matrix associated with the Σ^+ vibrations when there are two frequencies in this symmetry class, i.e., for triatomic molecules. Quantities analogous to the ξ_k can be determined for symmetry coordinates, say, x_k . Knowing both ξ_k and x_k , the transformation matrix taking symmetry coordinates to normal coordinates can be calculated for the triatomic case. The same transformation takes the force constant matrix to the frequencies (squared). Reversal of this latter process would produce the force constants from the frequencies.

APPENDIX

The definition of the ξ_k is

$$\xi_k = (1/I_e) \sum_{\alpha} \eta_{\alpha} \cdot \sigma_{k\alpha}.$$

These quantities apply to the Σ^+ vibrational coordinates. A similar quantity may be defined for the Σ^+ translational normal coordinate:

$$\xi_T = (1/I_e) \sum_{\alpha} \eta_{\alpha} \cdot \sigma_{T\alpha} = 0.$$

The sum of the squares of all of the ξ_k then becomes

$$\sum_{\Sigma^+} \xi_k^2 = (1/I_e^2) \sum_{\Sigma^+\alpha\beta} \eta_{\alpha} \cdot \sigma_{k\alpha} \eta_{\beta} \cdot \sigma_{k\beta}$$

(including translational coordinate). Now

$$\sum_{\Sigma^+} \sigma_{k\alpha} \sigma_{k\beta} = m_{\alpha} \delta_{\alpha\beta}.$$

Therefore,

$$\sum_{\Sigma^+} \xi_k^2 = (1/I_e^2) \sum_{\alpha} m_{\alpha} \eta_{\alpha}^2 = 1/I_e.$$