The Duschinsky Effect and Optical Spectra

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Dedicated to Professor G. O. Schenck on the occasion of his 70th birthday

The influence of the normal mode rotation (i.e. the Duschinsky mixing) on the molecular electronic spectra in polyatomic molecules is treated by means of multidimensional intramolecular distributions (MID). It is shown that symmetry properties of the two-dimensional MID which relate emission and absorption spectra or pertain to the exchange of modes do not exist if the number of non-separable modes exceeds 2. Specific examples of emission band shapes are calculated for weakly (linear) coupled electronic states for both, zero and finite temperatures. The strength of the mixed quadratic interaction parameter is shown to influence the shape considerably.

I. Introduction

Electronic transitions within polyatomic molecules (and impurities in solids) are quite strongly affected by the molecular (lattice) vibrations. In addition to the sharp absorption and emission lines due to the purely electronic (zero-phonon) transitions, there are a number of vibronic induced lines which produce the so-called vibrational side band near the $0-0'$ line and which arise principally from a linear vibrational-electronic coupling mechanism (of the Herzberg-Teller type). If highly resolved spectra are observed, these vibronic induced transitions are assigned to the ground-state normal coordinates (the so-called intensity "promoting" modes) because the electronic transition is in this case accompanied by the single excitation of one or more promoting modes.

There are far-reaching consequences if one or more "accepting" modes are involved in the transition: These modes have not only shifted origins and different frequencies, in the excited electronic state, but they may also be rotated relative to the normal modes of the ground-electronic state (i.e., the Duschinsky effect [4]). Consequently, such modes are not separable[1] (or parallel), and the multidimensional vibrational overlap, which is required for the qualitative and quantitative unravelling of molecular electronic spectra (absorption and emission) must be expressed by a single but rather complicated quantity instead of a convolution of relatively simple one-dimensional overlap factors as in the case of parallel modes. From the physical point of view, it is the rotation of the normal coordinates in the excited state vs. ground state that makes the spectral line-shape unusually broad and complicated to interpret. In the normal case, the rotation causes an irregularly structured and shaped band which becomes regularly structured and well shaped only at certain values of the rotation angle.

It is convenient do discuss some of the important problems in these areas by reference to recent papers [1, 2], where a theoretical rate expression for radiative and nonradiative transitions is derived. The transition rate is expressed in terms of a weighted sum (the weighting parameters being the interstate coupling coefficients) of line-shape functions, which in turn are written as a density-of-states weighted intramolecular distribution (ID). The ID's are introduced by the aid of multidimensional generating functions of complex variables and incorporate all spectroscopic parameters resulting from both linear and quadratic (pure and mixed) coupling terms. The explicit expression for the generating function in [1] was derived for the case of two ($N=2$) nonseparable modes. The case $N=2$ warrants special treatment as it exhibits special symmetries; these symmetries are important in establishing general relations between transitions in both absorption and emission, which are quite important in practical applications.

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[1] The term "separable" implies that the equilibrium positions and frequencies of the normal modes in the excited state (s) are simply shifted from their values in the ground electronic state (l).

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In Sect. II of this paper the case $N=2$ is recapitulated from the standpoint of symmetry and the general expression for the corresponding case $N=3$ is presented; it is shown that the abovementioned symmetry properties are lost if the number of nonseparable modes becomes greater than two. The final section is devoted to calculations of spectra in which the Duschinsky rotation becomes relevant.

II. The Generating Function

In considering the general structure and relative intensity distribution within the emission (and absorption) bands associated with symmetry-allowed as well as vibronic induced electronic transitions in polyatomic molecules, it is convenient to start with the expression,

$$f(\omega)=\prod_{\mu} Z_{\mu}^{-1} \int_{-\infty}^{\infty} \exp\left[i t(\omega-\Omega)-\gamma|t|\right] G(t)\, \mathrm{d} t\,, \quad (1)$$

which constitutes a line shape function for a symmetry-allowed electronic transition, satisfying the normalization condition $\frac{1}{\pi} \int_{0}^{\infty} f(\omega)\, \mathrm{d}\omega=1$. In the case of vibronic induced transition, we need several line-shape function of the type (1), each of which is centered at $\Omega \pm \omega_{\varkappa}$, where $\hbar\, \omega_{\varkappa}$ is the energy of the $\varkappa$-th promoting mode [1]. The quantity $Z_{\mu}=[1-\exp(-\hbar\, \omega_{\mu}^{(i)}/k T)]^{-1}$, where $\omega_{\mu}^{(i)}$ denotes the vibrational frequency of an accepting mode in the initial electronic state (i), is the partition function and $\gamma=\gamma_{0} \coth(\hbar\langle\omega\rangle/2 k T)$ is a temperature-dependent width which incorporates both the radiative and nonradiative decay of the states under consideration. In our treatment, γ_{0} will be assumed to be constant over the whole spectral range. Mathematically, the damping factor $\exp(-\gamma|t|)$ insures that the pseudo Fourier transform (F.T.) (1) converges. The time-dependent generating function [2] $G(t)$ (G.F.) contains the time variable t in terms of exponentials $z_{\mu}=\exp(i t\, \omega_{\mu}^{(l)})$ and

$$w_{\mu}=\exp(-i t\, \omega_{\mu}^{(s)}-\hbar\, \omega_{\mu}^{(s)}/k T)\ {}^{3}, \quad \mu=1,2, \ldots, N),$$

where ω_{μ} are molecular frequencies and (s) and (l) denote excited and ground electronic state, respectively. Thus we can treat this function as a multidimensional analytical function of $2N$ complex variables in the polycylinder

$$C_{N}(0,1)\left[|z_{i}| \leqq 1,\ |w_{i}|<1, \quad i=1,2, \ldots, N\right]$$

$$G_{N}(w_{1}, w_{2}, \ldots, w_{N}, z_{1}, \ldots, z_{N} \mid \{\varDelta_{j_{1} j_{2} \ldots j_{q}}^{i_{1} \ldots i_{p}}\} ; \{\beta_{i}, \beta_{ij}\})$$
$$=\frac{1}{2N} \prod_{i=1}^{N} \beta_{i}^{1/2}(1+\bar{w}_{i})(1+\bar{z}_{i}) \quad (2)$$
$$\times \frac{\exp\left[-\dfrac{A(\bar{w}_{1}, \ldots, \bar{w}_{N}, \bar{z}_{1}, \ldots, \bar{z}_{N})}{B_{1}(\bar{w}_{1}, \ldots, \bar{w}_{N}, \bar{z}_{1}, \ldots, \bar{z}_{N})}\right]}{\left[B_{1}(\bar{w}_{1}, \ldots, \bar{w}_{N}, \bar{z}_{1}, \ldots, \bar{z}_{N})\, B_{2}(\bar{w}_{1}, \ldots, \bar{w}_{N}, \bar{z}_{1}, \ldots, \bar{z}_{N})\right]^{1/2}}\,,$$

where the complex variables $\bar{w}_{i}$ and $\bar{z}_{i}$ are homographic transformations of the form

$$\bar{w}_{i}=(1-w_{i})/(1+w_{i}) \quad \text{and} \quad \bar{z}_{i}=(1-z_{i})/(1+z_{i})\,,$$

respectively. Here, N is the total number of the coupled (nonseparable) normal modes and $\{\varDelta_{j_{1} \ldots j_{q}}^{i_{1} \ldots i_{p}}\}$ and $\{\beta_{i}, \beta_{ij}\}$ which appear on the l.h.s. of (2) indicate two sets of spectroscopic parameters. The first refers to the geometry change (see Appendix) and the second one to the frequency change associated with the $s \leftrightarrows l$ transition. The expressions A and $B_{1}(B_{2})$ are homogeneous polynomials of degree $N+1$ and N in $\bar{w}_{1}, \ldots, \bar{w}_{N}, \bar{z}_{1}, \ldots, \bar{z}_{N}$, respectively, which additionally depend on the spectroscopic parameters as well as on the normal coordinate rotations.

We now proceed to summarize our previous results [1] for these functions for the case of $N=2$, and to present new results for the case of $N=3$, recasting them in an alternative form which emphasizes symmetry and facilitates generalization.

A) $N=2$

In this case we have

$$A(\bar{w}_{1}, \bar{w}_{2}, \bar{z}_{1}, \bar{z}_{2})=\beta_{1} \varDelta_{12}^{(1)^{2}} \bar{w}_{1} \bar{z}_{1} \bar{z}_{2}+\beta_{2} \varDelta_{12}^{(2)^{2}} \bar{w}_{2} \bar{z}_{1} \bar{z}_{2}$$
$$+\beta_{2} \varDelta_{1}^{(12)^{2}} \bar{w}_{1} \bar{w}_{2} \bar{z}_{1}+\beta_{1} \varDelta_{2}^{(12)^{2}} \bar{w}_{1} \bar{w}_{2} \bar{z}_{2}\,, \quad (3\mathrm{a})$$

$$B_{1}(\bar{w}_{1}, \bar{w}_{2}, \bar{z}_{1}, \bar{z}_{2})=\beta_{1} \beta_{2} \bar{w}_{1} \bar{w}_{2}+(\bar{w}_{1}, \bar{w}_{2}) \quad (3\mathrm{b})$$
$$\cdot\begin{pmatrix} W\binom{1}{2}^{2} \beta_{12}, & W\binom{1}{1}^{2} \beta_{1} \\ W\binom{2}{2}^{2} \beta_{2}, & W\binom{2}{1}^{2} \beta_{21} \end{pmatrix}\begin{pmatrix} \bar{z}_{1} \\ \bar{z}_{2} \end{pmatrix}+\bar{z}_{1} \bar{z}_{2}\,,$$

$$B_{2}(\bar{w}_{1}, \bar{w}_{2}, \bar{z}_{1}, \bar{z}_{2})=\bar{w}_{1} \bar{w}_{2} \bar{z}_{1} \bar{z}_{2}$$
$$\cdot B_{1}(\bar{w}_{1}^{-1}, \bar{w}_{2}^{-1}, \bar{z}_{1}^{-1}, \bar{z}_{2}^{-1})\,.$$

[2] The exact definition and role of this generating function will be given in Section III.

[3] Or, alternatively, $z_{\mu}=\exp(-i t\, \omega_{\mu}^{(s)})$ and $w_{\mu}=\exp(i t\, \omega_{\mu}^{(l)}-\hbar\, \omega_{\mu}^{(l)}/k T)$ if the transition occurs in absorption.

Here $W(^i_j)$ are minors of the rotation matrix $\mathbf{W}$ with the determinant

$$W(^{12}_{12}) = \begin{vmatrix} \cos\Phi\,, & -\sin\Phi \\ \sin\Phi\,, & \cos\Phi \end{vmatrix}\,. \tag{4}$$

The super index i refers to the row and the sub index j to the column of the matrix $\mathbf{W}$.

The matrix $\mathbf{W}$ is chosen to diagonalize the potential energy of the vibrational Hamiltonian in the excited state (s). This can be accomplished, as derived in the Appendix by a linear transformation

$$\mathbf{q}^s = \mathbf{W}\,\mathbf{q}^l + \mathbf{k}_{12} \tag{5}$$

requiring

$$\mathbf{W}\,\mathbf{U}^{(s)}\,\mathbf{W}^{-1} = \mathbf{D}^s\,, \tag{6}$$

where $\mathbf{U}^{(s)}$ is the 2×2 matrix of the potential energy (see Appendix) and $\mathbf{W}^{-1}$ is the inverse matrix of $\mathbf{W}$.

This requirement is easily satisfied by imposing that

$$2\,\Phi = \operatorname{arctg}\left[\frac{2\,U^{(s)}_{12}}{U^{(s)}_{11} - U^{(s)}_{22}}\right]. \tag{7}$$

Because of the interaction $U^{(s)}_{12}$, there is a tendency for the motion of the oscillators to be correlated and this leads to a change of the frequencies of the system (relative to the ground electronic state) and to a rotation in the configuration space spaned by the normal coordinates, q^l_1 and q^l_2. The translation vector in (5), $\mathbf{k}_{12} = \mathrm{col}\,(k^{(1)}_{12}, k^{(2)}_{12})$, is chosen to remove the linear terms $\mathbf{f}^+\,\mathbf{q}^l$ in the potential energy of the vibrational Hamiltonian h^s. These linear terms arise, as outlined in the Appendix, from the excited state distortion, $(\mathbf{R}^l_0 - \mathbf{R}^s_0)$, relative to the ground state equilibrium positions $\mathbf{R}^l_0$. The essential thing to be noted here is that owing to the normal coordinate rotations, two additional displacement parameters are generated. These are

$$\mathbf{k}^{(12)} = \mathbf{W}^{-1}\,\mathbf{k}_{12} \tag{8}$$

where $\mathbf{k}^{(12)} = \mathrm{col}\,(k^{(12)}_1, k^{(12)}_2)$. Both $\mathbf{k}_{12}$ and $\mathbf{k}^{(12)}$ are directly related to the dimensionless displacement parameters appearing in (3a), namely

$$\Delta^{(i)}_{12} = (\omega^{(l)}_i/\hbar)^{1/2}\,k^{(i)}_{12}\,, \tag{9a}$$

$$(i = 1, 2)$$

$$\Delta^{(12)}_i = (\omega^{(s)}_i/\hbar)^{1/2}\,k^{(12)}_i\,. \tag{9b}$$

($\Delta^{(i)}_{12}$ are the usual Franck-Condon displacements appearing in the parallel mode approximation.) The frequency changes associated with the transition $s \to l$ are comprised in the β-factors appearing in (3a–c). They are defined by the ratio of frequencies in the s-th and l-th electronic manifolds as follows: $\beta_i = \omega^{(s)}_i/\omega^{(l)}_i$ and $\beta_{ij} = \omega^{(s)}_i/\omega^{(l)}_j$.

If the off-diagonal term $U^{(s)}_{12}$ is neglected, the normal coordinates q^s and q^l are treated as parallel, because now $\Phi = 0$ and the oscillators vibrate independently of one another. Furthermore, in this case, it is easily seen from (3) and (9) that

$$\frac{A}{B_1} = \frac{\beta_1\,\Delta^{(1)^2}_{12}\,\bar{w}_1\,\bar{z}_1}{\beta_1\,\bar{w}_1 + \bar{z}_1} + \frac{\beta_2\,\Delta^{(2)^2}_{12}\,\bar{w}_2\,\bar{z}_1}{\beta_2\,\bar{w}_2 + \bar{z}_2}\,, \tag{10}$$

$$B_1 = (\beta_1\,\bar{w}_1 + \bar{z}_1)\,(\beta_2\,\bar{w}_2 + \bar{z}_2)\,, \tag{11}$$

$$B_2 = (\bar{w}_1 + \beta_1\,\bar{z}_1)\,(\bar{w}_2 + \beta_2\,\bar{z}_2)\,, \tag{12}$$

and, therefore the G.F. (2) for $N = 2$ is a product of two single-mode generating functions, each of which has the form

$$G_1(w, z, \Delta, \beta) = \frac{1}{2}\,\beta^{1/2}(1 + \bar{w})\,(1 + \bar{z})\,\frac{\exp\left[-\dfrac{\beta\,\Delta^2\,\bar{w}\,\bar{z}}{\beta\,\bar{w} + \bar{z}}\right]}{[(\beta\,\bar{w} + \bar{z})\,(\bar{w} + \beta\,\bar{z})]^{1/2}}\,, \tag{13}$$

where $\beta = \omega^{(s)}/\omega^{(l)}$ and $\Delta^2 = (\omega^{(l)}/\hbar)\,(q^l_0 - q^s_0)^2$.

We have remarked before that the G.F. (2), with A, B_1, and B_2 given by (3), has certain symmetry properties that are of interest. In order to discuss these properties, it is convenient to rewrite the two-mode generating function in the following form which explicitly reveals the dependence of G_2 upon the molecular parameters:

$$G_2\left(w_1, w_2, z_1, z_2 \,\middle|\, \begin{matrix} \Delta^{(1)}_{12}, & \Delta^{(2)}_{12} \\ \Delta^{(12)}_1, & \Delta^{(12)}_2 \end{matrix}\,;\, \begin{matrix} \beta_1, \beta_2 \\ \beta_{12}, \beta_{21} \end{matrix}\right) = \frac{1}{4}\,\beta^{1/2}_1\,\beta^{1/2}_2\,(1 + \bar{w}_1)\,(1 + \bar{w}_2)\,(1 + \bar{z}_1)\,(1 + \bar{z}_2)$$

$$\times\,\frac{\exp\left[-\dfrac{A\,(\bar{w}_1, \bar{w}_2, \bar{z}_1, \bar{z}_2)}{B_1\,(\bar{w}_1, \bar{w}_2, \bar{z}_1, \bar{z}_2)}\right]}{[B_1\,(\bar{w}_1, \bar{w}_2, \bar{z}_1, \bar{z}_2)\,B_2\,(\bar{w}_1, \bar{w}_2, \bar{z}_1, \bar{w}_2)]^{1/2}}\,. \tag{14}$$

Adopting this notation and taking into account that $W\binom{1}{1} = W\binom{2}{2} = \cos\varPhi$, we have the relation

$$G_2\left(w_1, w_2, z_1, z_2 \,\middle|\, \begin{matrix} \varDelta_{12}^{(1)}\ \varDelta_{12}^{(2)} \\ \varDelta_1^{(12)}\varDelta_2^{(12)} \end{matrix};\ \begin{matrix} \beta_1, \beta_2 \\ \beta_{12}, \beta_{21} \end{matrix}\right) = G_2\left(z_1, z_2, w_1, w_2 \,\middle|\, \begin{matrix} \varDelta_1^{(12)}, \varDelta_2^{(12)} \\ \varDelta_{12}^{(1)}, \varDelta_{12}^{(2)} \end{matrix};\ \begin{matrix} \beta_1^{-1}, \beta_2^{-1} \\ \beta_{21}^{-1}, \beta_{12}^{-1} \end{matrix}\right), \tag{15}$$

which follows directly from (3), (4) and (14). Thus, the G.F. has a very simple symmetry with respect to the interchange of $\bar{w}_i$ and $\bar{z}_i$ which may be formulated as follows: The G.F. (14) is invariant under the interchange $\bar{w}_i \rightleftarrows \bar{z}_i$ (and also $w_i \rightleftarrows z_i$) if, simultaneously, the shift parameters $\varDelta_{12}^{(i)}$ are interchanged with the $\varDelta_i^{(12)}$ and the frequency factor β_i and β_{ij} are replaced by the reciprocals β_i^{-1} and β_{ji}^{-1}, respectively. The physical significance of this will be apparent when we later introduce the intramolecular distribution (ID).

Another useful relation, which is still easier to derive, is the invariance of G_2 under the operation flip $1 \rightleftarrows 2$, symbolized by the equation

$$G_2\left(w_1, w_2, z_1, z_2 \,\middle|\, \begin{matrix} \varDelta_{12}^{(1)}, \varDelta_{12}^{(2)} \\ \varDelta_1^{(12)}, \varDelta_2^{(12)} \end{matrix};\ \begin{matrix} \beta_1, \beta_2 \\ \beta_{12}, \beta_{21} \end{matrix}\right) = G_2\left(w_2, w_1, z_2, z_1 \,\middle|\, \begin{matrix} \varDelta_{12}^{(2)}, \varDelta_{12}^{(1)} \\ \varDelta_2^{(12)}, \varDelta_1^{(12)} \end{matrix};\ \begin{matrix} \beta_2, \beta_1 \\ \beta_{21}, \beta_{12} \end{matrix}\right). \tag{16}$$

This characteristic follows directly from the fact that $W\binom{1}{2}^2 = W\binom{2}{1}^2 = \sin^2\varPhi$ and $W\binom{1}{1} = W\binom{2}{2} = \cos\varPhi$, i.e. from the symmetry of the 1st compound matrix of **W** [7] which appears in (3b). An important application of these expressions (which will be postponed to the next section), is in the discussion of the relation between emission and absorption. Both (15) and (16) are quite useful in practical application.

B) $N = 3$

We have seen that in the special example of two nonseparable oscillators, the G.F. for the vibrational overlap exhibits two symmetry properties formulated in (15) and (16) which follow from the symmetry of the 1st compound matrix **W** appearing in (3b). For the three-oscillator problem, the homogeneous polynomials in $\bar{w}_1, \bar{w}_2, \bar{w}_3, \bar{z}_1, \bar{z}_2$ and $\bar{z}_3$ appearing in (2) become

$$\begin{aligned} A(\bar{w}_1, \bar{w}_2, \bar{w}_3, \bar{z}_1, \bar{z}_2, \bar{z}_3) &= \beta_1 \varDelta_{123}^{(1)^2} \bar{w}_1 \bar{z}_1 \bar{z}_2 \bar{z}_3 + \beta_2 \varDelta_{123}^{(2)^2} \bar{w}_2 \bar{z}_1 \bar{z}_2 \bar{z}_3 + \beta_3 \varDelta_{123}^{(3)^2} \bar{w}_3 \bar{z}_1 \bar{z}_2 \bar{z}_3 \\ &+ (\bar{w}_1 \bar{w}_2, \bar{w}_1 \bar{w}_3, \bar{w}_2 \bar{w}_3) \begin{pmatrix} \beta_1^{1/2}\beta_{23} \varDelta_{12}^{(12)^2} & \beta_1 \beta_2 \varDelta_{13}^{(12)^2} & \beta_1 \beta_2 \varDelta_{23}^{(12)^2} \\ \beta_3 \varDelta_{12}^{(13)^2} & \beta_3^{1/2}\beta_{12} \varDelta_{13}^{(13)^2} & \beta_1 \beta_3 \varDelta_{23}^{(13)^2} \\ \beta_3 \varDelta_{12}^{(23)^2} & \beta_2 \varDelta_{13}^{(23)^2} & \beta_2^{1/2}\beta_{31} \varDelta_{23}^{(23)^2} \end{pmatrix} \begin{pmatrix} \bar{z}_1 \bar{z}_2 \\ \bar{z}_1 \bar{z}_3 \\ \bar{z}_2 \bar{z}_3 \end{pmatrix} \\ &+ \beta_2 \beta_3 \varDelta_1^{(123)^2} \bar{w}_1 \bar{w}_2 \bar{w}_3 \bar{z}_1 + \beta_1 \beta_3 \varDelta_2^{(123)^2} \bar{w}_1 \bar{w}_2 \bar{w}_3 \bar{z}_2 + \beta_1 \beta_2 \varDelta_3^{(123)^2} \bar{w}_1 \bar{w}_2 \bar{w}_3 \bar{z}_3, \end{aligned} \tag{17a}$$

$$\begin{aligned} B_1(\bar{w}_1, \bar{w}_2, \bar{w}_3, \bar{z}_1, \bar{z}_2, \bar{z}_3) &= \beta_1 \beta_2 \beta_3 \bar{w}_1 \bar{w}_2 \bar{w}_3 \\ &+ (\bar{w}_1 \bar{w}_2, \bar{w}_1 \bar{w}_3, \bar{w}_2 \bar{w}_3) \begin{pmatrix} W\binom{12}{23}^2 \beta_{12} \beta_{23} & W\binom{12}{13}^2 \beta_1 \beta_{23} & W\binom{12}{12}^2 \beta_1 \beta_2 \\ W\binom{13}{23}^2 \beta_{12} \beta_3 & W\binom{13}{13}^2 \beta_1 \beta_3 & W\binom{13}{12}^2 \beta_1 \beta_{32} \\ W\binom{23}{23}^2 \beta_2 \beta_3 & W\binom{23}{13}^2 \beta_{21} \beta_3 & W\binom{23}{12}^2 \beta_{21} \beta_{32} \end{pmatrix} \begin{pmatrix} \bar{z}_1 \\ \bar{z}_2 \\ \bar{z}_3 \end{pmatrix} \\ &+ (\bar{z}_1 \bar{z}_2, \bar{z}_1 \bar{z}_3, \bar{z}_2 \bar{z}_3) \begin{pmatrix} W\binom{1}{3}^2 \beta_{13} & W\binom{2}{3}^2 \beta_{23} & W\binom{3}{3}^2 \beta_3 \\ W\binom{1}{2}^2 \beta_{12} & W\binom{2}{2}^2 \beta_2 & W\binom{3}{2}^2 \beta_{32} \\ W\binom{1}{1}^2 \beta_1 & W\binom{2}{1}^2 \beta_{21} & W\binom{3}{1}^2 \beta_{31} \end{pmatrix} \begin{pmatrix} \bar{w}_1 \\ \bar{w}_2 \\ \bar{w}_3 \end{pmatrix} + \bar{z}_1 \bar{z}_2 \bar{z}_3, \end{aligned} \tag{17b}$$

and

$$B_2(\bar{w}_1, \bar{w}_2, \bar{w}_3, \bar{z}_1, \bar{z}_2, \bar{z}_3) = \bar{w}_1 \bar{w}_2 \bar{w}_3 \bar{z}_1 \bar{z}_2 \bar{z}_3 B_1(\bar{w}_1^{-1}, \bar{w}_2^{-1}, \bar{w}_3^{-1}, \bar{z}_1^{-1}, \bar{z}_2^{-1}, \bar{z}_3^{-1}). \tag{17c}$$

In analogy with (9) the dimensionless shift parameters on the r.h.s. of (17a) are defined as follows:

$$\varDelta_{123}^{(i)} = \beta_{il}^{1/2} k_{123}^{(i)} \qquad (i = 1, 2, 3) \tag{18a}$$

$$\varDelta_i^{(123)} = \beta_{is}^{1/2} k_i^{(123)} \tag{18b}$$

and

$$\begin{aligned} &\varDelta_{13}^{(12)} = \beta_{1l}^{1/2} k_{13}^{(12)}, \quad \varDelta_{12}^{(13)} = \beta_{1s}^{1/2} k_{12}^{(13)}, \quad \varDelta_{23}^{(12)} = \beta_{2l}^{1/2} k_{23}^{(12)}, \quad \varDelta_{12}^{(23)} = \beta_{2s}^{1/2} k_{12}^{(23)}, \quad \varDelta_{23}^{(13)} = \beta_{3l}^{1/2} k_{23}^{(13)}, \\ &\varDelta_{13}^{(23)} = \beta_{3s}^{1/2} k_{13}^{(23)}, \quad \varDelta_{12}^{(12)} = \beta_{1l}^{1/4} \beta_{1s}^{1/4} k_{12}^{(12)}, \quad \varDelta_{13}^{(13)} = \beta_{3l}^{1/4} \beta_{3s}^{1/4} k_{13}^{(13)}, \quad \varDelta_{23}^{(23)} = \beta_{2l}^{1/4} \beta_{2s}^{1/4} k_{23}^{(23)} \end{aligned} \tag{18c}$$

with

$$\beta_{il} = (\omega_i^{(l)}/\hbar)\,, \qquad \beta_{is} = (\omega_i^{(s)}\hbar)\,.$$

Apart from a phase factor ± 1, the dimensioned shift parameters are given by

$$\mathbf{k}^{(123)} = \mathbf{W}^{-1}\,\mathbf{k}_{123}\,, \tag{19a}$$

$$k_{12}^{(12)} = W\binom{2}{3}\,k_{123}^{(1)} - W\binom{1}{3}\,k_{123}^{(2)}\,, \quad k_{13}^{(12)} = -\,W\binom{2}{2}\,k_{123}^{(1)} + W\binom{1}{2}\,k_{123}^{(2)}\,, \quad k_{23}^{(12)} = W\binom{2}{1}\,k_{123}^{(1)} - W\binom{1}{1}\,k_{123}^{(2)}\,, \tag{19b}$$

$$k_{12}^{(13)} = W\binom{3}{3}\,k_{123}^{(1)} - W\binom{1}{3}\,k_{123}^{(3)}\,, \quad k_{13}^{(13)} = -\,W\binom{3}{2}\,k_{123}^{(1)} + W\binom{1}{2}\,k_{123}^{(3)}\,, \quad k_{23}^{(13)} = W\binom{3}{1}\,k_{123}^{(1)} - W\binom{1}{1}\,k_{123}^{(3)}\,, \tag{19c}$$

$$k_{12}^{(23)} = W\binom{3}{3}\,k_{123}^{(2)} - W\binom{2}{3}\,k_{123}^{(3)}\,, \quad k_{13}^{(23)} = -\,W\binom{3}{2}\,k_{123}^{(2)} + W\binom{2}{2}\,k_{123}^{(3)}\,, \quad k_{23}^{(23)} = W\binom{3}{1}\,k_{123}^{(2)} - W\binom{2}{1}\,k_{123}^{(3)}\,. \tag{19d}$$

Here $W\binom{ij}{kl}$ and $W\binom{i}{j}$ are, as before, minors of the orders 2 and 1 of the rotation matrix $\mathbf{W}$. In terms of the three Eulerian angles Φ, θ, ψ, the corresponding determinant is [3]

$$W\binom{123}{123} = \begin{vmatrix} \cos\Phi\cos\theta\cos\psi - \sin\Phi\sin\psi & \sin\Phi\cos\theta\cos\psi + \cos\Phi\sin\psi & -\sin\theta\cos\psi \\ -\cos\Phi\cos\theta\sin\psi - \sin\Phi\cos\psi & -\sin\Phi\cos\theta\sin\psi + \cos\Phi\cos\psi & \sin\theta\sin\psi \\ \cos\Phi\sin\theta & \sin\theta\sin\Phi & \cos\theta \end{vmatrix}\,, \tag{20}$$

where $0 \leqq \Phi \leqq 2\pi$, $0 \leqq \psi \leqq 2\pi$ and $0 \leqq \theta \leqq \pi$. Equation (19a) evidently defines a set of displacements exactly analogous to (8) for the case $N = 2$, while (19b – 19d) have no parallels in the $N = 2$ case. As before, the normal coordinate rotation $\mathbf{W}$ generates from the usual (dimensioned) Franck-Condon shifts $k_{123} = \mathrm{col}\,(k_{123}^{(1)}, k_{123}^{(2)}, k_{123}^{(3)})$, appropriate for the parallel mode approximation, additional sets of shifts parameters, the number of which increases with increasing N.

With the aid of (17) we now consider the question of the symmetry of the G.F., (2), for $N = 3$. Firstly, we note that if a symmetry associated with an interchange of w_i and z_i like that symbolised by (15) should exist, the squared matrix elements of the 2nd compound matrix in (17b) must be equal to the corresponding squared matrix elements of the 1st compound matrix. This implies (cf. (17)) for example that

$$W\binom{12}{23} = \pm\,W\binom{1}{3}\,, \qquad W\binom{12}{13} = \pm\,W\binom{2}{3}$$

etc.

However, with the help of the determinant (20), we have

$$W\binom{12}{23} = W\binom{3}{1} = \cos\Phi\sin\theta \mp W\binom{1}{3} = -\sin\theta\cos\psi\,,$$

$$W\binom{12}{13} = W\binom{3}{2} = -\sin\Phi\sin\theta \mp W\binom{2}{3} = \sin\theta\sin\psi$$

from which it follows directly that an equation similar to (15) which holds for $N = 2$ cannot be realized in the case $N = 3$. It is further obvious from the relations above that the $N = 2$ symmetry property of (16) does also not exist in the case $N = 3$. This is a direct consequence of the properties of the matrices appearing in (17) which are constructed from the 2nd and 1st compound matrices of the 3-dimensional rotation matrix $\mathbf{W}$[4]. The same holds also for $N = 4$ with obvious generalizations to higher N. For example, for four nonseparable modes ($N = 4$) the invariance of the G.F. (2) with respect to the interchange $w_i \rightleftarrows z_i$ implies that

$$W\binom{i}{j} = \pm\,W\binom{j}{i} \quad \text{for all} \quad i, j = 1, 2, 3, 4\,. \tag{21}$$

Furthermore, the 2th compound matrix of W must be either symmetric or must possess certain properties of an antisymmetric matrix. Since all these conditions are not satisfied, we conclude that the special symmetry properties of the G.F. for $N = 2$ are lost in the general case of $N \geqq 3$.

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[4] The homogeneous polynomials $A\,(\bar{w}_1, \ldots, \bar{w}_3, \bar{z}_1, \ldots, \bar{z}_3)$ can always be chosen symmetric with respect to the interchanges $\bar{w}_i \rightleftarrows \bar{z}_i$ by a proper normalization of the dimensionless shift parameters $\Delta_{123}^{(i)}$, $\Delta_{pq}^{(ij)}$ and $\Delta_i^{(123)}$ and the interchanges $\Delta_{123}^{(i)} \rightleftarrows \Delta_i^{(123)}$ and $\Delta_{pq}^{(ij)} \rightleftarrows \Delta_{ij}^{(pq)}$.

III. The Line Shape Function

The theory presented in the previous section [culminating in (2)] is directly applicable to the calculation of the spectral band shape of the electronic transitions in polyatomic molecules. In doing this, we begin by expanding the G.F. in a multiple-power series in the polycylinder $C_N(0,1)$ $[|z_i| \leqq 1,\ |w_i| < 1,\ i = 1, 2, \ldots, N]$[5]

$$G_N(w_1, \ldots, w_N, z_1 \ldots, z_N \,|\, \{\Delta^{i_1 \ldots i_p}_{j_1 \ldots j_q}\}; \{\beta_i, \beta_{ij}\}) = \sum_{m_1, \ldots, m_N = 0}^{\infty} \sum_{n_1, \ldots, n_N = 0}^{\infty} I_N \left(\begin{smallmatrix} m_1, \ldots, m_N \\ n_1, \ldots, n_N \end{smallmatrix} \,\middle|\, \{\Delta^{i_1 \ldots i_p}_{j_1 \ldots j_q}\}; \{\beta_i, \beta_{ij}\}\right) w_1^{m_1} \ldots w_N^{m_N} z_1^{n_1} \ldots z_N^{n_N}. \qquad (22)$$

The quantity I_N, which will be used below to express the intensity distribution associated with electronic transitions in polyatomic molecules, is the intramolecular distribution (ID) of the dimensionality N. It expresses the relative transition probability of going from a single vibronic component $|s m_1 m_2, \ldots, m_N\rangle$, into the ground state manifold $|l n_1, \ldots, n_N\rangle$ and, vice versa, in absorption. For $N = 2$, the relation between these transitions is governed by the following equation,

$$I_2 \left(\begin{matrix} n_1, n_2 \\ m_1, m_2 \end{matrix} \,\middle|\, \begin{matrix} \Delta^{(1)}_{12}, \Delta^{(2)}_{12} & \beta_1, \beta_2 \\ \Delta^{(12)}_1, \Delta^{(12)}_2; & \beta_{12}, \beta_{21} \end{matrix}\right) = I_2 \left(\begin{matrix} m_1, m_2 \\ n_1, n_2 \end{matrix} \,\middle|\, \begin{matrix} \Delta^{(12)}_1, \Delta^{(12)}_2 & \beta_1^{-1}, \beta_2^{-1} \\ \Delta^{(1)}_{12}, \Delta^{(2)}_{12}; & \beta_{21}^{-1}, \beta_{12}^{-1} \end{matrix}\right), \qquad (23)$$

which follows directly from the symmetry of (15) by applying (22). (23) allows us to predict the spectral band shape in absorption, if the spectrum in emission is known and vice versa. Particularly, (23) shows that the conditions for the occurrence of mirror symmetry of absorption and emission spectra are $\Phi = 0$ $(\Delta^{(i)}_{12} = \Delta^{(12)}_i)$ and $\beta_i = 1$ $(i = 1, 2)$. This can be fulfilled only in purely linearly interacting systems. For system with $N \geqq 3$, which contain quadratic interaction terms, a symmetry of the type (23) does not exist (as pointed out in the previous section), and consequently there is no relationship between absorption and emission.

Returning now to (22), we have

$$I_N \left(\begin{smallmatrix} m_1, \ldots, m_N \\ n_1, \ldots, n_N \end{smallmatrix} \,\middle|\, \{\Delta^{i_1 \ldots i_p}_{j_1 \ldots j_q}\}; \{\beta_i, \beta_{ij}\}\right) = \frac{1}{\prod_{i=1}^{N} m_i!\, n_i!} \left(\frac{\partial^{m+n} G_N}{\partial w_1^{m_1} \ldots \partial w_N^{m_N} \partial z_1^{n_1} \ldots \partial z_N^{n_N}}\right)_0$$

which, in principle, is mathematically simple but, in practice, tedious to perform. Therefore, in [2] four-term recurrence equations have been derived which enable us to calculate the values of I_N for arbitrary numbers m_i and n_i. As an illustration of such calculations, we consider the I_2 distribution for

$$m_1 = m_2 = 0$$

(Figure 1). The linear shift parameters $k^{(i)}_{12}$ are chosen appropriatly for strongly coupled states (strong linearly interacting system). The curves in Fig. 1 are loci of equal values of I_2. As the angle Φ of rotation varies, the curves move in the n_1, n_2 plane running for special values of Φ close to the n_1 axis or close to the n_2 axis. Note that the Φ-dependence of I_2 arises from inclusion of the mixed quadratic interaction term $U^{(s)}_{12}$, as previously mentioned in Section II.

If one or both of the m_i numbers differ from zero the surface of I_2 is still more complicated; it then possesses two maxima for $m_1 = 1$, $m_2 = 0$ $(m_1 = 0,\ m_2 = 1)$, four maxima for $m_1 = m_2 = 1$, three maxima for $m_1 = 2$, $m_2 = 0$ $(m_1 = 0,\ m_2 = 2)$, etc.

For smaller linear displacements $k^{(i)}_{12}$ (weakly linear interacting system), it is difficult to present the I_2-surface graphically. In this case, the intramolecular distributions have appreciable values only near the $0-0'$ line reflecting the increased overlap of the wavefunctions in the vicinity of $n_1 = n_2 = 0$. In order to investigate this behaviour, we prefer a presentation of I_2 by means of the spectral line shape function given by (1). By

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[5] This is possible, since the G.F. represents an analytic function in $C_N(0.1)$.

substituting (22) in (1), and returning to the time dependent representation of G_N, we easily find that

$$f(\omega) = (1 - \exp(\hbar\,\omega_1^{(s)}/kT))\,(1 - \exp(\hbar\,\omega_2^{(s)}/kT)) \times \sum_{m_1, m_2 = 0}^{\infty} \sum_{n_1, n_2 = 0}^{\infty} \frac{2\gamma \exp[-\hbar\,(m_1\,\omega_1^{(s)} + m_2\,\omega_2^{(s)})/kT]}{(\omega - \Omega - m_1\,\omega_1^{(s)} - m_2\,\omega_2^{(s)} + n_1\,\omega_1^{(l)} + n_2\,\omega_2^{(l)})^2 + \gamma^2}\, I_2\left(\begin{matrix} m_1\, m_2 \\ n_1\, n_2 \end{matrix} \,\middle|\, \begin{matrix} \Delta_{12}^{(1)},\ \Delta_{12}^{(2)} \\ \Delta_1^{(12)}, \Delta_2^{(12)} \end{matrix};\ \begin{matrix} \beta_1, \beta_2 \\ \beta_{12}, \beta_{21} \end{matrix}\right), \tag{24}$$

where we have restricted ourselves to the case $N = 2$ in the calculation presented below. In writing (24), we have tacitly assumed that the initial state is the electronically excited state. The line shape in absorption analogously can be calculated replacing $\omega_i^{(s)}$ with $\omega_i^{(l)}$ in the Boltzmann factors in (24) and invoking the symmetry property of I_2 (see (23)).

In order to get a visual idea of what complicated situations arise when mode mixing takes place, we illustrate in Fig. 2, via (24) the line shape $f(\omega)$ for several angles of rotation Φ. The spectra are calculated for weakly linear ($\Delta_{12}^{(1)} = 1.0$, $\Delta_{12}^{(2)} = 0.5$) and quadratic interactions, of moderate strength ($\beta_1 = 0.9$, $\beta_2 = 1.25$, $\beta_{12} = 0.36$, $\beta_{21} = 3.0$) where the mixed quadratic interaction term is varied by changing the angle of rotation Φ (cf. (7)). As may be seen in Fig. 2a, the spectrum is dominated by the $0-0'$ line and by progressions in the two accepting modes. The intensity distribution within the progressions is governed by the ID. Apart from these lines, a large number of combination-lines can be assigned. In contrast to the parallel mode approximation (at $\Phi = 0$), there are two extreme situations with predominantly single mode progressions. Thus, at $\Phi = 15°$, the progression in $\omega_1^{(l)} = 100\ \text{cm}^{-1}$ of the first accepting mode dominates, while the second mode with the frequency $\omega_1^{(l)} = 240\ \text{cm}^{-1}$ is suppressed. At $\Phi = 110°$ $(-70°)$, the reversed situation is observed. This allows us to conclude that in these situations, the 2-dimensional ID behaves as an ID of the dimensionality one being distributed first mainly along the n_1 axis and then along the n_2 axis; this is an effect which we have already portrayed for strongly coupled states (large linear interaction terms $\Delta_{12}^{(i)}$ in Figure 1. For other angles of rotation (for example $\Phi = 60°$), the lines (peaks) in the spectrum are more or less scrambled.

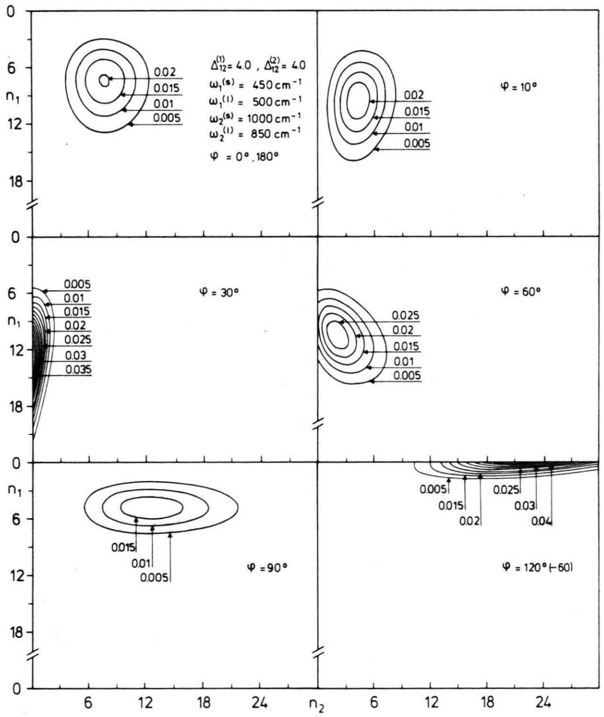

Fig. 1. Contour map of $I_2\left(\begin{matrix} m_1, m_2 \\ n_1, n_2 \end{matrix} \,\middle|\, \begin{matrix} \Delta_{12}^{(1)},\ \Delta_{12}^{(2)} \\ \Delta_1^{(12)}, \Delta_2^{(12)} \end{matrix};\ \begin{matrix} \beta_1, \beta_2 \\ \beta_{12}, \beta_{21} \end{matrix}\right)$ for strongly coupled electronic states (large Franck-Condon displacements $\Delta_{12}^{(i)}$). The mixed quadratic interaction term is varied by changing the angle of rotation Φ (taken in counterclockwise direction). Other spectroscopic parameters are indicated in the figure.

As a further striking aspect of mode mixing, we note an appreciable spread or broadening of the over-all spectral band-shape (on the low-energy side) as the angle Φ increases. This is illustrated by a considerable enhancement of the number of members in the single mode progression from 3 for $\Phi = 15°$ to about 8 for $\Phi = 110°$ $(-70°)$; this effect has already been observed for strongly coupled states [2].

As the temperature is raised, the individual lines in the spectrum broaden, the peak intensity decreases and the low-energy side of the spectral band becomes uniformly smoothed. Simultaneoulsy, the thermal population of the initial (excited) levels contribute to the transitions, localised on the high-energy side of the spectral band. The structural

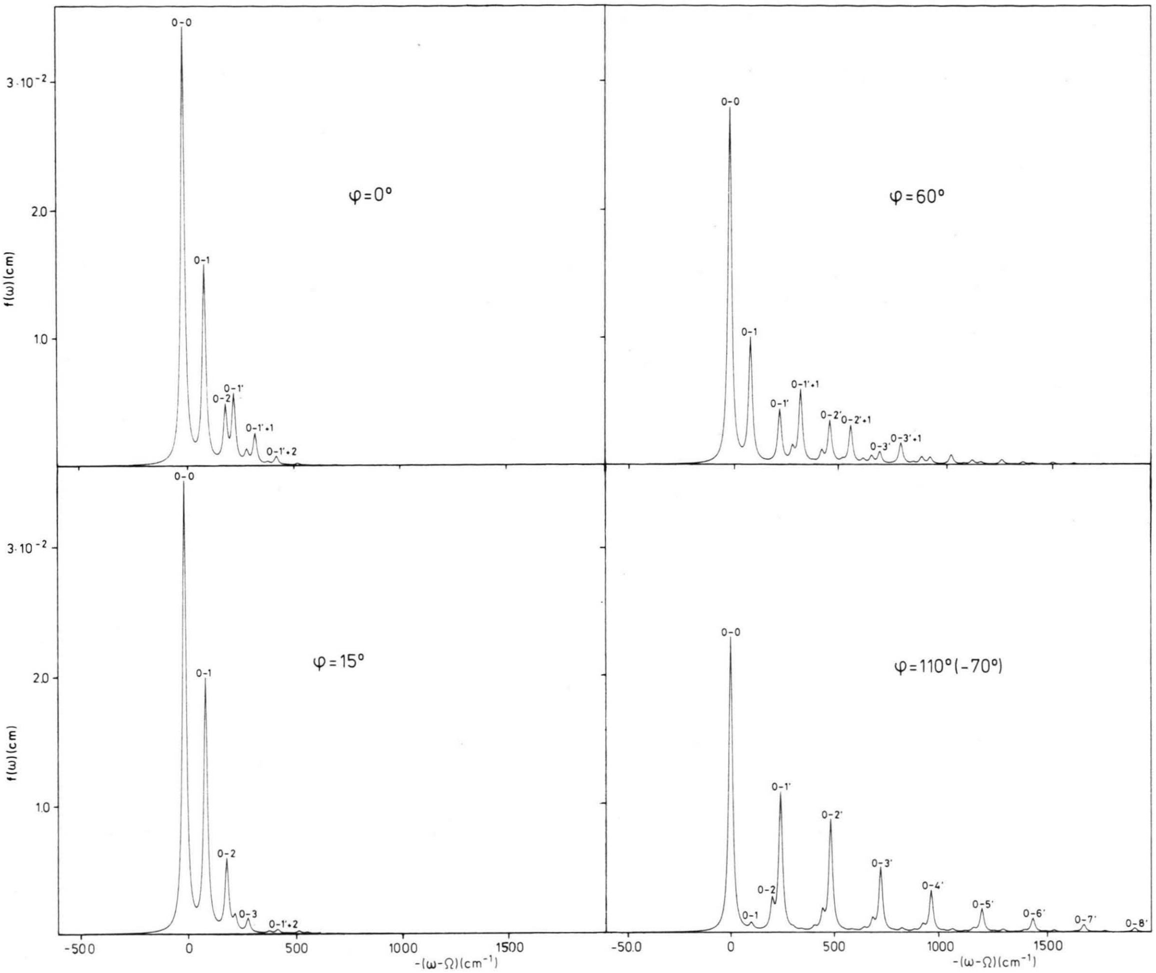

Fig. 2a. Highly resolved ($\gamma = 10\ \mathrm{cm}^{-1}$) zero-temperature spectral band shape calculated for weakly coupled states ($\Delta_{12}^{(1)} = 1.0$, $\Delta_{12}^{(2)} = 0.5$). The strength of the mixed quadratic interaction parameter (expressed in terms of the angle of rotation Φ) is shown to influence the shape considerably. Some of the vibronic components have been assigned.

nature of the spectrum is, however, essentially unchanged (see Figure 2b).

The examples presented above should provide some idea of how the ID technique may be useful in interpreting the complexities observed in real molecular spectra.

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Appendix

In polyatomic molecules, the normal coordinates of one molecular (electronic) state are expressed in terms of those of the other states as pointed out by Duschinsky [4]. In particular, we have

$$\mathbf{q}^s = \mathbf{W}\,\mathbf{q}^l + \mathbf{k}_{12\ldots N}\,, \tag{A1}$$

where (s) and (l) denote excited and ground electronic states, respectively and N is the number of nonseparable modes. This can be carried out by the matrix method of Wilson et al. [5]. In this approach, the relationship between the mass-weighted Carte-

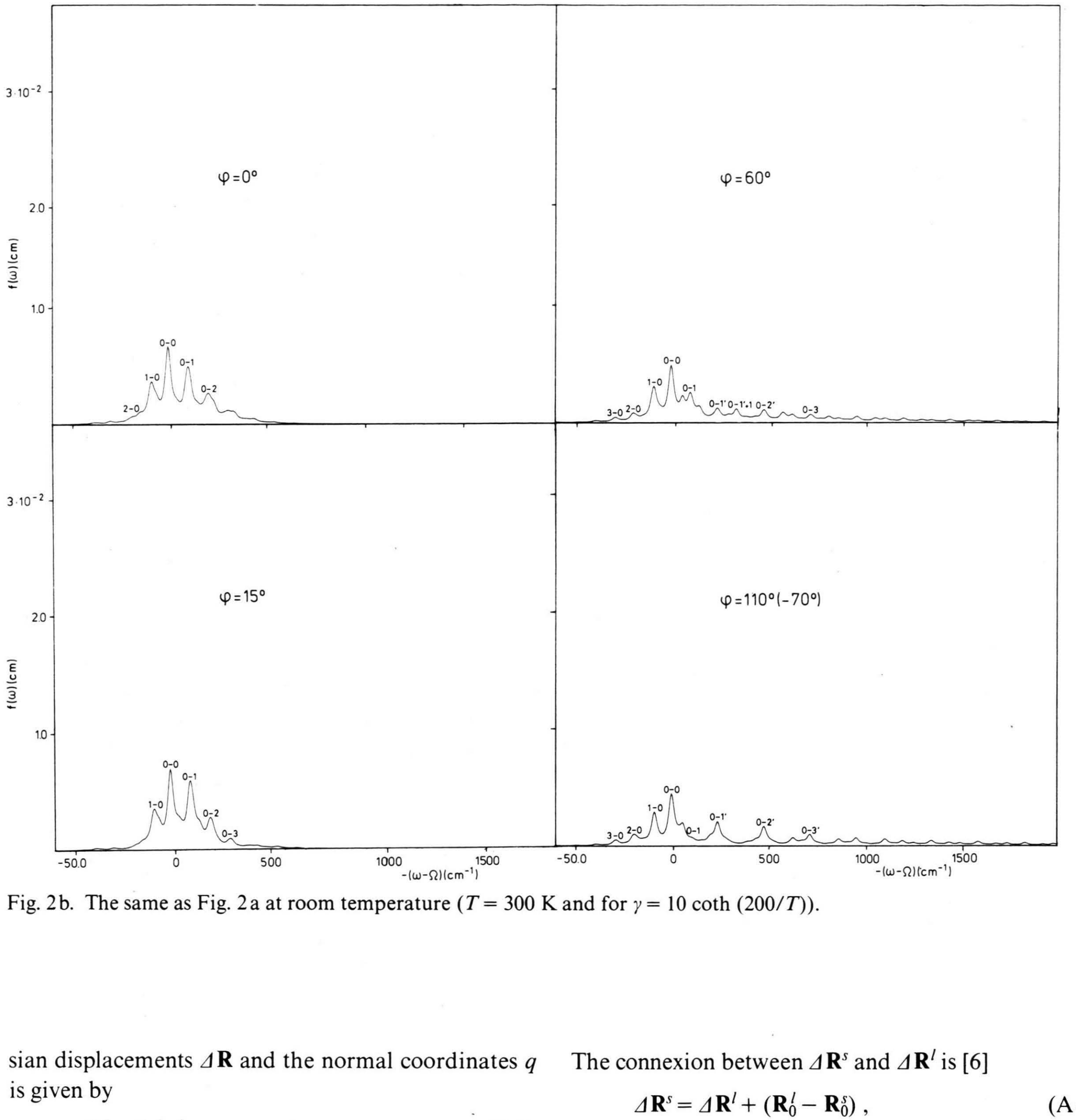

Fig. 2b. The same as Fig. 2a at room temperature ($T = 300$ K and for $\gamma = 10 \coth(200/T)$).

sian displacements $\Delta\mathbf{R}$ and the normal coordinates q is given by

$$\Delta\mathbf{R}^l = \mathbf{L}'^l\,\mathbf{q}^l\,, \tag{A2}$$

where $\mathbf{L}'$ is the orthogonal transformation[5] that diagonalizes the force constant matrix in terms of mass-adjusted Cartesian coordinates. The analogous expression for the excited electronic state (s) is

$$\Delta\mathbf{R}^s = \mathbf{L}'^s\,\mathbf{q}^s\,. \tag{A3}$$

The connexion between $\Delta\mathbf{R}^s$ and $\Delta\mathbf{R}^l$ is [6]

$$\Delta\mathbf{R}^s = \Delta\mathbf{R}^l + (\mathbf{R}_0^l - \mathbf{R}_0^s)\,, \tag{A4}$$

where $\mathbf{R}_0^l$ ($\mathbf{R}_0^s$) denotes the equilibrium position of the molecule in the ground (excited) electronic state. Note that in (A1–A4), as in the following equations, boldface letters are column vectors, or square matrices. From (A2–A4), we have

$$\mathbf{q}^s = (\mathbf{L}'^s)^+\,\mathbf{L}'^l\,\mathbf{q}^l + (\mathbf{L}'^s)^+\,(\mathbf{R}_0^l - R_0^s) \tag{A5}$$

because of the orthogonality of $\mathbf{L}^s$ ($\mathbf{L}^l$).

On setting $\mathbf{W} = (\mathbf{L}'^s)^+\,\mathbf{L}'^l$ and

$$\mathbf{k}_{12\ldots N} = (\mathbf{L}'^s)^+\,(\mathbf{R}_0^l - \mathbf{R}_0^s)$$

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[6] The $\mathbf{L}'$ matrix corresponds to the $(l')_{ij}$ matrix in the Wilson-Decius-Cross notation (see [5], Chapter 2). Faulkner and Richardson use the notation $\mathbf{U}$ for $\mathbf{L}'$.

(A5) is reduced to (A1). In (A5), $\mathbf{L}'^{+}$ is the transpose of $\mathbf{L}'$.

In the normal coordinates $\mathbf{q}^l$, the vibrational Hamiltonian is

$$h^l = \tfrac{1}{2}\,\mathbf{p}^{l^2} + \tfrac{1}{2}\,\mathbf{q}^{l^+}\mathbf{D}^l\,\mathbf{q}^l\,, \tag{A6}$$

where $\mathbf{p}^l$ is the momenta conjugate to the normal coordinates $\mathbf{q}^l$ ($p^l_\mu = -\,i\,\hbar\,\partial/\partial q^l_\mu$) and $\mathbf{D}^l$ is the diagonal matrix of vibrational eigenvalues obtained by diagonalizing the mass-weighted Cartesian force constant matrix for the ground electronic state $\mathbf{F}^l$

$$\mathbf{D}^l = (\mathbf{L}'^l)^+\,\mathbf{F}^l\,\mathbf{L}'^l = \mathrm{diag}\,(\omega_1^{(l)^2}, \ldots, \omega_N^{(l)^2})\,. \tag{A7}$$

Analogously, we have for the excited (electronic) state

$$h^s = \tfrac{1}{2}\,\mathbf{p}^{s^2} + \tfrac{1}{2}\,\mathbf{q}^{s^+}\mathbf{D}^s\,\mathbf{q}^s \tag{A8}$$

with

$$\mathbf{D}^s = (\mathbf{L}'^s)^+\,\mathbf{F}^s\,\mathbf{L}'^s = \mathrm{diag}\,(\omega_1^{(s)^2}, \ldots, \omega_N^{(s)^2})\,. \tag{A9}$$

On returning to the transformation (A5), we easily see that

$$\mathbf{p}^s = (\mathbf{L}'^s)^+\,\mathbf{L}'^l\,\mathbf{p}^l\,. \tag{A10}$$

Squaring the operator, we obtain,

$$\tfrac{1}{2}\,\mathbf{p}^{s^2} = \tfrac{1}{2}\,\mathbf{p}^{l^2}\,, \tag{A11}$$

i.e., the kinetic energy remains invariant under the transformation (A1). Insertion of (A5) into the potential energy operator of h^s yields

$$\begin{aligned}\mathbf{q}^{s^+}\mathbf{D}^s\,\mathbf{q}^s = {} & (\mathbf{R}_0^l - \mathbf{R}_0^s)^+\,\mathbf{L}'^s\,\mathbf{D}^s\,(\mathbf{L}'^s)^+\,(\mathbf{R}_0^l - \mathbf{R}_0^s)\\ & + 2\,(\mathbf{R}_0^l - \mathbf{R}_0^s)^+\,\mathbf{F}^s\,\mathbf{L}'^l\,\mathbf{q}^l\\ & + \mathbf{q}^{l^+}(\mathbf{L}'^l)^+\,\mathbf{F}^s\,\mathbf{L}'^l\,\mathbf{q}^l\,,\end{aligned} \tag{A12}$$

where in the second and third term of (A12), use has been made of (A9). After inserting (A11) and (A12) into (A8), the vibrational Hamiltonian for the electronic excited state (expressed in terms of the ground normal coordinates) may be written in the form

$$h^s = \tfrac{1}{2}\,\mathbf{p}^{l^2} + \tfrac{1}{2}\,\mathbf{q}^{l^+}\mathbf{U}^s\,\mathbf{q}^l + \mathbf{f}^+\,\mathbf{q}^l + h_0\,, \tag{A13}$$

where we have set

$$\mathbf{U}^s = (\mathbf{L}'^l)^+\,\mathbf{F}^s\,\mathbf{L}'^l \quad \text{and} \quad \mathbf{f} = (\mathbf{L}'^l)^+\,\mathbf{F}^s\,(\mathbf{R}_0^l - \mathbf{R}_0^s)\,.$$

and h_0 is the constant factor in (A12).

Since generally $\mathbf{F}^s \neq \mathbf{F}^l$, the matrix $\mathbf{U}^s$ has off-diagonal elements and, therefore, the diagonal nature of the quadratic form in h is not retained when going from the ground to the excited state.

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