

The Franck-Condon principle for nuclear gamma transitions in polyatomic molecules

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An analog of the Franck-Condon principle is formulated for nuclear gamma transitions in a polyatomic molecule, which come about through the change of state of a molecule owing to the recoil of a nucleus on the emission or absorption of a γ -ray quantum. For the case of a γ -radioactive nucleus located at the center of symmetry of a molecule, a theory of the distribution of the electronic-vibrational nuclear lines in the spectrum is constructed, taking into account the intermixing of the vibrational modes in the electronic-nuclear transition. A six-atom molecule XY_3Z_2 of symmetry type D_{3h} is analyzed in detail as an example. Some matrix elements and transition probabilities relating to vibrational-nuclear transitions are also obtained.

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1. INTRODUCTION

The description of many quantum processes is based on simulating them with a set of coupled harmonic oscillators. In this case the Hamiltonian of the quantum system is a multidimensional quadratic form in the coordinates and momenta of the oscillators. The Schrödinger equation with such a Hamiltonian has been studied by Chernikov.¹ The general theory of N -dimensional non-stationary quadratic quantum systems has been given in recent papers,² in which the coherent-state representation³ is used to obtain an exact solution, and also the Green's function and the amplitudes and probabilities of transitions are calculated.

An important concern in the study of a multidimensional quadratic system is dealing with the interaction between oscillators corresponding to different vibrational modes. For example, in the case of electronic-vibrational transitions in polyatomic molecules this sort of interaction manifests itself in a rotation of the system of normal coordinates of the final state relative to the coordinate system of the initial state (intermixing of the normal coordinates). This is known as the Dushinskii effect,⁴ which has to be taken into account in the calculation, for example, of Franck-Condon factors (FCF). A method for calculating FCF and finding the geometrical configuration of the molecule in an excited electronic state which deals exactly with the Dushinskii effect has been given in earlier papers.⁵⁻⁷ Obviously the methods for exact inclusion of correlation effects in multidimensional oscillator systems that have been developed in the theory of electronic-vibrational spectra of molecules can be reformulated for the description of other quantum phenomena which can be treated with quadratic Hamiltonians. In particular, we may mention the absorption of neutrons by nuclei in a crystal,⁸ the Mössbauer effect,⁹ and absorption by impurity centers in crystals.¹⁰

Some recent papers^{11,12} have dealt with the γ -ray spectrum of a nucleus in a molecule, as it is affected by the change of the internal state of the molecule owing to the recoil of the nucleus as it emits or absorbs a γ -ray quantum. It was shown that an emission (absorption) γ -ray line has a structure; near the line for the free nucleus there are satellites, which in the general case

correspond to electronic-vibrational-rotational-nuclear transitions in the molecule. In the case of a polyatomic molecule with a γ -radioactive nucleus located at its center of symmetry (a type of molecule which is particularly interesting experimentally) the rotational degrees of freedom can be neglected to good approximation, and the spectrum can be regarded as a spectrum of electronic-vibrational-nuclear transitions. It is shown in Refs. 11 and 12 that in the adiabatic approximation the probability of an electronic-nuclear transition is proportional to the square of the ratio of the mass of the electron to that of the molecule, $(m_e/M)^2$, and therefore the main attention was paid to transitions between the vibrational levels of the ground electronic state.

In the present paper we consider electronic-vibrational-nuclear (vibronic-nuclear) transitions in a polyatomic molecule with a γ -radioactive nucleus at its center of symmetry. By formulating an analog of the Franck-Condon principle we construct a theory of the intensity distribution of vibronic-nuclear lines in a given spectrum. The transition probabilities are calculated in the harmonic approximation by using multidimensional vibrational wave functions belonging to the interacting electronic states. A detailed investigation is made of the case of a six-atom molecule of the type XY_3Z_2 with the point symmetry group D_{3h} . Some matrix elements and probabilities relating to vibrational-nuclear transitions are also calculated.

2. THE DUSHINSKIĬ EFFECT FOR γ -TRANSITIONS OF A NUCLEUS IN A MOLECULE

The vibrations of the nuclei of a molecule with N vibrational degrees of freedom in its ground electronic state is described in the harmonic approximation by the Hamiltonian

$$H = \frac{1}{2} \sum_{i=1}^N (p_i^2 + \omega_i^2 q_i^2), \quad (1)$$

where q_i and p_i are a mass-weighted coordinate and its conjugate momentum, corresponding to the i -th vibrational mode, and ω_i is the corresponding normal frequency. The wave function for a stationary state of the Hamiltonian (1) is well known¹³ [$\mathbf{v} = (v_1, v_2, \dots, v_N)$]:

$$|v\rangle = \prod_{i=1}^N \left[N_i \exp\left(-\frac{\omega_i q_i^2}{2\hbar}\right) H_{\nu_i}\left(\sqrt{\frac{\omega_i}{\hbar}} q_i\right) \right], \quad (2)$$

$$N_i = \left[\left(\frac{\pi\hbar}{\omega_i}\right)^{1/2} 2^{\nu_i} \nu_i! \right]^{-1/2}.$$

The Hamiltonian which describes vibrations of the nuclei in an excited state is

$$H' = \frac{1}{2} \sum_{k=1}^N (p_k'^2 + \omega_k'^2 q_k'^2),$$

where the primed quantities refer to the k -th mode of the excited state.

The electronic transition results in a change of the equilibrium positions of the nuclei. Such a deformation of the equilibrium configuration of the molecule is described by the Dushinskii transformation⁴

$$q' = Sq + d, \quad (3)$$

which connects the normal coordinates of the initial and final states. Here the $N \times N$ matrix S describes a rotation of the system of coordinates, and the N -dimensional vector d gives the shift of the equilibrium positions of the nuclei. We note that the components of the vector d are different from zero only for completely symmetrical modes. The intensities of the vibronic bands are then determined, according to the Franck-Condon principle, by the squares of the overlap integrals $\langle v' | v \rangle$ between the vibrational wave functions of the two electronic states, as calculated with allowance for Eq. (3).

It is not hard to see that vibronic-nuclear transitions can also be described in the framework of the theory of ordinary vibronic transitions if a certain modification of the Franck-Condon principle is used. In fact, the amplitude for transition of the molecule from state a to state b owing to the energy of recoil of the nucleus on its emission (absorption) of a γ -ray quantum is given by the matrix element^{11,12}

$$R_{ba} = \langle b | \exp(-ik \cdot u) | a \rangle.$$

Here k_γ is the wave vector of the photon, and u is the vector displacement of the radioactive nucleus from its equilibrium position. In the Born-Oppenheimer approximation (and with the rotational degrees of freedom neglected, on which we comment later), the amplitudes for vibronic-nuclear transitions, which describe the vibrational structure of the γ -ray spectrum, are given by matrix elements of the form

$$R_{v'v} = \langle v' | \exp(-ik \cdot u) | v \rangle. \quad (4)$$

Furthermore, the recoil momentum received at the instant of emission (absorption) of the photon can be regarded as a shift in momentum space of the equilibrium positions of the operators that model the vibrations of the nuclei. In other words, the operator $\exp(-ik_\gamma \cdot u)$ is a displacement operator, and the matrix element (4) is an "overlap integral" between the wave functions of oscillators shifted relative to each other both in coordinate space and in momentum space. When the recoil momentum is taken into account an additional term appears in the Dushinskii transformation, which in this case becomes

$$q' = Sq + d + i\delta, \quad (5)$$

where the vector δ has a definite relation (which we shall

explain) to k_γ . Accordingly the desired matrix elements $R_{v'v}$ of Eq. (4) will be overlap integrals $\langle v' | v \rangle$ between vibrational wave functions of the type of Eq. (2), calculated by the use of the modified Dushinskii transformation (5). We shall hereafter be considering transitions in a molecule with a γ -radioactive nucleus located at its center of symmetry. This means that the only transitions that contribute to the shift u of this molecule will be those with vibrations that are not completely symmetrical, so that $d=0$. Accordingly, the connection between the normal coordinates of the interacting electronic states will in our case be given by the formula

$$q' = Sq + i\delta, \quad (6)$$

which describes the interaction between the various modes in the vibronic-nuclear transition and is important in our further considerations.

Let us now establish the relation between the vector δ and the wave number k_γ of the photon. For this purpose we expand the displacement vector u of the γ -active nucleus in terms of the normal coordinates of the ground electronic state¹²:

$$u = m^{-1/2} \sum_{s\sigma} b_{s\sigma} q_{s\sigma}. \quad (7)$$

Here m is the mass of the radioactive nucleus, and the components of the vector $b_{s\sigma}$ are elements of the matrix b which gives the orthogonal transformation from the normal coordinates q to the mass-weighted rectangular coordinates.¹⁴ The index s indicates the type of normal vibration, and the index σ takes care of degeneracy. We confine ourselves to the transitions between nondegenerate vibrational states in both electronic levels. Then it is not hard to show that the relation

$$\delta = (2\hbar)^{1/2} S \lambda_\omega^{-1} \kappa \quad (8)$$

holds, where the vector κ , which depends on k_γ , is

$$\kappa = \{z_s^{1/2} \cos \psi_s\}, \quad s=1, 2, \dots, N. \quad (9)$$

Here ψ_s is the angle between the vector k_γ and the direction of the displacement of the radioactive nucleus owing to the s -th normal vibration, and $\lambda_\omega = \text{diag}(\omega_1^{1/2}, \omega_2^{1/2}, \dots, \omega_N^{1/2})$. The quantity z_s is given by¹²

$$z_s = \frac{R}{\hbar\omega_s} \frac{M}{m} b_s^2 = \frac{\hbar k_\gamma^2}{2m\omega_s} b_s^2, \quad (10)$$

where $R = (E_\gamma^0)^2 / 2Mc^2$ is the recoil energy and $E_\gamma^0 = \hbar ck_\gamma$ is the energy of the nuclear transition.

3. THE TRANSITION AMPLITUDES

As has been shown above, the amplitude $R_{v'v}$ of a vibronic-nuclear transition can be regarded as the overlap integral $\langle v' | v \rangle$ between vibrational states $|v\rangle$ and $|v'\rangle$ of the interacting electronic states, calculated with connection formulas (6) of the Dushinskii type. This approach allows us to transfer many results from the theory of the vibronic spectra of molecules⁵⁻⁷ to the case under consideration.

To calculate the overlap integrals $\langle v' | v \rangle$ we shall use the coherent-state representation.³ A coherent state, which is a generating function for the states $|v\rangle$ of Eq. (2), is of the form

$$|\alpha\rangle = \frac{(\det \lambda_\omega)^{1/2}}{(\pi \hbar)^{N/4}} \exp \left[-\frac{1}{2\hbar} (\lambda_\omega \mathbf{q}, \lambda_\omega \mathbf{q}) + \left(\frac{2}{\hbar} \right)^{1/2} (\alpha, \lambda_\omega \mathbf{q}) - \frac{(\alpha, \alpha)}{2} - \frac{|\alpha|^2}{2} \right], \quad (11)$$

where $\alpha = (\alpha_1, \alpha_2, \dots, \alpha_N)$ is a set of arbitrary complex numbers, and the symbol (\dots, \dots) means the ordinary scalar product. The coherent state $|\alpha\rangle$ corresponding to the vibrations in the final electronic state is obtained from Eq. (11) by the replacements $\alpha \rightarrow \alpha'$, $\mathbf{q} \rightarrow \mathbf{q}'$, $\lambda_\omega \rightarrow \lambda_{\omega'}$.

It is obvious that the "overlap integral" between the coherent states, $\langle \alpha' | \alpha \rangle \equiv \langle \alpha' | \exp(-i\mathbf{k}\mathbf{r}, \mathbf{u}) | \alpha \rangle$ will serve as the generating function for the desired quantities $\langle \mathbf{v}' | \mathbf{v} \rangle$:

$$\langle \alpha' | \alpha \rangle = \exp \left[-\frac{1}{2} (|\alpha|^2 + |\alpha'|^2) \right] \left(\prod_{i=1}^N \sum_{v_i, v_i'=0}^{\infty} \frac{\alpha_i^{v_i} (\alpha_i')^{v_i'}}{(v_i! v_i'!)^{1/2}} \right) \langle \mathbf{v}' | \mathbf{v} \rangle.$$

Because the coherent state is expressed in the form of the exponential of a quadratic, the calculation of the overlap integral $\langle \alpha' | \alpha \rangle$ reduces to a standard Gaussian integral, and then the expansion of $\langle \alpha' | \alpha \rangle$ in a power series provides a simple way to calculate the matrix elements $R_{\mathbf{v}'\mathbf{v}}$.

The simple calculation of $\langle \alpha' | \alpha \rangle$ with the use of the explicit expressions from Eq. (11) for the coherent states and of Eq. (6) gives

$$\langle \alpha' | \alpha \rangle = (0|0) \exp \left[-\frac{1}{2} (|\alpha|^2 + |\alpha'|^2) - \frac{1}{2} (\alpha \alpha') \begin{pmatrix} L & K \\ K & M \end{pmatrix} \begin{pmatrix} \alpha \\ \alpha' \end{pmatrix} + i(\alpha \alpha') \begin{pmatrix} \mathbf{f} \\ \mathbf{g} \end{pmatrix} \right], \quad (12)$$

where

$$(0|0) = 2^{N/2} \left(\frac{\det \lambda_{\omega'}}{\det \lambda_\omega} \det \frac{1-L}{2} \right)^{1/2} \exp \left(\frac{1}{2} \delta \frac{1+M}{2} \delta \right).$$

Here the real symmetric $N \times N$ matrices L and M and the real $N \times N$ matrix K are defined as follows:

$$L = 1 - 2(1+JJ)^{-1}, \quad M = 1 - 2J(1+JJ)^{-1}J, \quad K = -2(1+JJ)^{-1}J, \quad (13)$$

where the matrix $J = \lambda_{\omega'} S \lambda_\omega^{-1}$ gives the Dushinskii rotation. The real vectors \mathbf{f} and \mathbf{g} are connected with δ by a relation of the form [cf. Eq. (8)]

$$\begin{pmatrix} \mathbf{f} \\ \mathbf{g} \end{pmatrix} = (2\hbar)^{-1/2} \begin{pmatrix} K & 0 \\ 0 & 1+M \end{pmatrix} \begin{pmatrix} \lambda_{\omega'} & 0 \\ 0 & \lambda_\omega \end{pmatrix} \begin{pmatrix} \delta \\ \delta \end{pmatrix} = \begin{pmatrix} KJ & 0 \\ 0 & (1+M)J \end{pmatrix} \begin{pmatrix} \mathbf{x} \\ \mathbf{x} \end{pmatrix}. \quad (14)$$

Expanding Eq. (12) in powers of α and α' , we find the matrix element of a vibronic-nuclear transition:

$$\langle \mathbf{v}' | \mathbf{v} \rangle = (0|0) \prod_{i=1}^N (v_i! v_i'!)^{-1/2} H_{v_i'}(\sigma_i, \tau_i) \quad (15)$$

in terms of Hermite polynomials of $2N$ variables^{15,16}; here

$$\begin{pmatrix} \sigma \\ \tau \end{pmatrix} = i \begin{pmatrix} L & K \\ K & M \end{pmatrix}^{-1} \begin{pmatrix} \mathbf{f} \\ \mathbf{g} \end{pmatrix}.$$

The calculation of the multidimensional Hermite polynomials can be carried out by means of recurrence relations which follow readily from the generating function (12). Namely, differentiating Eq. (12) with respect to α_i , expanding in power series and equating terms of equal powers of α , we find

$$\begin{aligned} & \langle \mathbf{v}' | v_i, \dots, v_i+1, \dots, v_N \rangle \\ &= \sum_{k=1}^N K_{ik} \left(\frac{v_k'}{v_i+1} \right)^{1/2} \langle \mathbf{v}' | v_i, \dots, v_k'-1, \dots, v_N' | v_i, \dots, v_i, \dots, v_N \rangle \\ & \quad - \sum_{j=1}^N L_{ij} \left(\frac{v_j}{v_i+1} \right)^{1/2} \langle \mathbf{v}' | v_i, \dots, v_j-1, \dots, v_N \rangle \\ & \quad + \frac{if_i}{(v_i+1)^{1/2}} \langle \mathbf{v}' | v_i, \dots, v_i, \dots, v_N \rangle. \end{aligned} \quad (16a)$$

Similarly,

$$\begin{aligned} & \langle \mathbf{v}' | v_i, \dots, v_k'+1, \dots, v_N' | \mathbf{v} \rangle \\ &= \sum_{k=1}^N K_{ki} \left(\frac{v_i}{v_k'+1} \right)^{1/2} \langle \mathbf{v}' | v_i, \dots, v_k', \dots, v_N' | v_i, \dots, v_i-1, \dots, v_N \rangle \\ & \quad - \sum_{k=1}^N M_{ki} \left(\frac{v_i'}{v_k'+1} \right)^{1/2} \langle \mathbf{v}' | v_i, \dots, v_i'-1, \dots, v_N' | \mathbf{v} \rangle \\ & \quad + \frac{ig_k}{(v_k'+1)^{1/2}} \langle \mathbf{v}' | v_i, \dots, v_k', \dots, v_N' | \mathbf{v} \rangle. \end{aligned} \quad (16b)$$

If certain vibrational modes are not excited through a vibronic-nuclear transition, the corresponding overlap integrals reduce to Hermite polynomials of a smaller number of variables. To obtain the overlap integral in this case, we must strike out in the matrix $(L/K \ K/M)$ the rows and columns that correspond to unexcited modes. The remaining matrix elements will form a matrix giving the arguments of the reduced Hermite polynomial. For example, if only two modes in the upper electronic term are excited, the overlap integral can be written in the following form²:

$$\begin{aligned} \langle v_k' v_i' | 0 \rangle &= (0|0) (v_k'! v_i'!)^{-1/2} H_{v_k'}(\tau_k, \tau_i), \\ \begin{pmatrix} \tau_k \\ \tau_i \end{pmatrix} &= i \begin{pmatrix} M_{kk} & M_{ki} \\ M_{ki} & M_{ii} \end{pmatrix}^{-1} \begin{pmatrix} g_k \\ g_i \end{pmatrix}. \end{aligned}$$

The overlap integrals with one nonzero vibrational quantum number can be expressed in terms of the classical Hermite polynomials³:

$$\langle v_k' | 0 \rangle = (0|0) (v_k'!)^{-1/2} (1/2 M_{kk})^{v_k'/2} H_{v_k'}(\tau_k), \quad \tau_k = i(2M_{kk})^{-1/2} g_k, \quad (17a)$$

$$(0|v_i) = (0|0) (v_i!)^{-1/2} (1/2 L_{ii})^{v_i/2} H_{v_i}(\sigma_i), \quad \sigma_i = i(2L_{ii})^{-1/2} f_i. \quad (17b)$$

Accordingly, to calculate the overlap integral $\langle \mathbf{v}' | \mathbf{v} \rangle$ with arbitrary \mathbf{v} and \mathbf{v}' one can calculate from Eq. (17) the overlap integral with one nonzero vibrational quantum number and then use the recurrence relations (16).

The problem of calculating the matrix elements $R_{\mathbf{v}'\mathbf{v}}$ thus reduces to finding the matrices K , L , and M and the vectors \mathbf{f} and \mathbf{g} . These quantities can be found from experimentally measured relative intensities of definite vibronic-nuclear transitions.

4. THE PARAMETERS OF THE DUSHINSKII TRANSFORMATION. THE MOLECULE XY_3Z_2

Let us construct a generating function

$$F(\mathbf{X}) = \sum_{\mathbf{v}, \mathbf{v}'=0}^{\infty} q(\mathbf{v}'; \mathbf{v}) \mathbf{X} \cdot \mathbf{X}' \cdot \mathbf{v}' \quad (18)$$

for the "relative Franck-Condon coefficients" $q(\mathbf{v}'; \mathbf{v}) \equiv |\mathbf{v}' | \mathbf{v} \rangle / (0|0)|^2$. Here $\mathbf{X} = (x_1, x_2, \dots, x_N)$ and $\mathbf{X}' = (x_1', x_2', \dots, x_N')$ are sets of arbitrary complex numbers. $\mathbf{X} \cdot \mathbf{X}'$ denotes the product $\prod_i x_i x_i'$. [A way to construct $F(\mathbf{X})$ explicitly, based on a knowledge of the generating function $\langle \alpha' | \alpha \rangle$ for the overlap integrals, is described in Refs. 2 and 7.] This generating function is given by

$$F(X) = [\det(1-XT)\det(1+XT)]^{-h} \exp[h(1-XT)^{-1}Xh], \quad (19)$$

where

$$X = \begin{pmatrix} X_1 & 0 \\ 0 & X_2 \end{pmatrix}, \quad X_1 = \begin{pmatrix} x_1 & 0 & \dots & 0 \\ 0 & x_2 & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & x_N \end{pmatrix},$$

$$X_2 = \begin{pmatrix} x_1' & 0 & \dots & 0 \\ 0 & x_2' & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & x_N' \end{pmatrix}, \quad T = \begin{pmatrix} L & K \\ K & M \end{pmatrix}, \quad h = \begin{pmatrix} f \\ g \end{pmatrix}.$$

Experimentally one observes intensities averaged over the angles ψ_s at which the photons are emitted. Therefore it is of interest to obtain a generating function for the averaged FCF, $q(\mathbf{v}' | \mathbf{v})$. The averaging procedure depends on the specific symmetry type of the molecule. As the subject of our further investigation we choose the six-atom molecule of the type XY_3Z_2 , with the point group D_{3h} . This choice is due to the fact that a rigorous examination of the intensities of the vibronic-nuclear transitions in a molecule of this type shows the necessity of taking the Dushinskii effect into account. Also the restriction to a specific type of molecule does not impair the generality of the considerations. The method which will be expounded retains all important features of the general theory, and affects only the details of the way the averaging is done.⁴⁾ The infrared spectra of molecules of the type XY_3Z_2 (PCl_3F_2 , SbF_3Cl_2 , PF_3Br_2 , etc.) are analyzed in some recent papers.¹⁷

The normal vibrations of the molecule XY_3Z_2 are distributed among the symmetry types in the following way: $2A_1' + 2A_2'' + 3E' + E''$. We choose a coordinate system with origin at the equilibrium position of the nucleus X , the z axis along the axis C_3 of the molecule, and the x axis passing through the equilibrium position of one of the nuclei Y . The vibrations that contribute to the displacement of the central nucleus X are ω_3 and ω_4 of the type A_2'' and ω_5 , ω_6 , and ω_7 of type E' .

We confine ourselves to the examination of transitions involving the nondegenerate vibrations of type A_2'' . The vibrations ω_3 and ω_4 will lead to displacements of the X nucleus along the z axis given by the quantities b_3^z and b_4^z . Accordingly, the matrix element $\langle v_3'v_4' | v_3v_4 \rangle$ can be written in the form

$$\langle v_3'v_4' | v_3v_4 \rangle = \langle v_3'v_4' | \exp[-ik_z \cos \psi_z (b_3^z q_3 + b_4^z q_4) m^{-h}] | v_3v_4 \rangle.$$

The Dushinskii transformation (6), which leads to an intermixing of the coordinates of type A_2'' in the vibronic-nuclear transition, will be given by one angle of rotation χ and the two-component vector δ :

$$\begin{pmatrix} q_3' \\ q_4' \end{pmatrix} = \begin{pmatrix} \cos \chi & \sin \chi \\ -\sin \chi & \cos \chi \end{pmatrix} \begin{pmatrix} q_3 \\ q_4 \end{pmatrix} + i \begin{pmatrix} \delta_3 \\ \delta_4 \end{pmatrix}. \quad (20)$$

According to Eq. (15), the matrix elements $\langle \mathbf{v}' | \mathbf{v} \rangle$ can be expressed in terms of Hermite polynomials of four variables, which depend on 2×2 matrices K , L , M and two-component vectors f and g . Using the explicit form of the matrix S , as seen in Eq. (20), and the definitions (13) for the matrices K , L , and M , we can write explicit expressions⁵:

$$L = \frac{1}{\Delta} \begin{pmatrix} -(\omega_3 - \omega_3')(\omega_4 + \omega_4') - (\omega_3 + \omega_4)(\omega_3' - \omega_4') \sin^2 \chi & (\omega_3 \omega_4)^{1/2} (\omega_3' - \omega_4') \sin 2\chi \\ (\omega_3 \omega_4)^{1/2} (\omega_3' - \omega_4') \sin 2\chi & -(\omega_3 + \omega_4)(\omega_4 - \omega_4') + (\omega_3 + \omega_4)(\omega_3' - \omega_4') \sin^2 \chi \end{pmatrix},$$

$$K = -2\Delta^{-1} \begin{pmatrix} (\omega_3 \omega_3')^{1/2} (\omega_4 + \omega_4') \cos \chi & -(\omega_3 \omega_4)^{1/2} (\omega_4 + \omega_3') \sin \chi \\ (\omega_4 \omega_3')^{1/2} (\omega_3 + \omega_4') \sin \chi & (\omega_4 \omega_4')^{1/2} (\omega_3 + \omega_3') \cos \chi \end{pmatrix},$$

$$M = \frac{1}{\Delta} \begin{pmatrix} (\omega_3 - \omega_3')(\omega_4 + \omega_4') - (\omega_3 - \omega_4)(\omega_3' + \omega_4') \sin^2 \chi & -(\omega_3' \omega_4')^{1/2} (\omega_3 - \omega_4) \sin 2\chi \\ -(\omega_3' \omega_4')^{1/2} (\omega_3 - \omega_4) \sin 2\chi & (\omega_3 + \omega_3')(\omega_4 - \omega_4') + (\omega_3 - \omega_4)(\omega_3' + \omega_4') \sin^2 \chi \end{pmatrix}, \quad (21)$$

where

$$\Delta = (\omega_3 + \omega_3')(\omega_4 + \omega_4') + (\omega_3 - \omega_4)(\omega_3' - \omega_4') \sin^2 \chi.$$

Accordingly, the elements of the matrices depend on the single parameter χ , and a knowledge of any element of one matrix enables us to calculate all the other matrix elements. The vectors f and g can be expressed according to Eq. (14) in terms of the vector κ given by

$$\kappa = \{z_3^{1/2} \cos \psi_z, z_4^{1/2} \cos \psi_z\}, \quad (22)$$

where the parameters z_3 and z_4 are related to the normalized displacements by Eq. (10). Consequently, our problem is characterized by three parameters: χ , z_3 , and z_4 .

It must be pointed out that in the general case it is always possible to obtain the quantities b_s , and from them the parameters z_s , when the constants of the secular equation of the molecule are known. As we shall show later, in dealing with vibronic-nuclear transitions in the framework of the proposed method it is not necessary to calculate the parameters b_s in explicit form.

The matrices K , L , and M and the vectors f and g are found by the method of partial analysis,^{5,6} which requires a knowledge of experimentally measured relative intensities of particular vibronic nuclear transitions. Let us consider transitions of the form $v_3'v_4' - 00$ from the ground state without vibration. The generating function for the FCF $q(v_3'v_4'; 00) \equiv q(v_3'v_4')$ follows from Eq. (19) after the replacement $X \rightarrow X_{(2)}$, $T \rightarrow M$, $h \rightarrow g$, where $X_{(2)}$ is the diagonal 2×2 matrix $(x_1'/0 \ 0/x_2')$, M is the symmetric 2×2 matrix $(M_{11}/M_{12} \ M_{12}/M_{22})$, and g is the two-component vector (g_1, g_2) . Expressing the vector g in terms of κ by Eq. (14), using κ from Eq. (22) and introducing the notation

$$g_{0i} = \sum_{j=1}^2 [(1+M)J]_{ij} z_j^{1/2}, \quad i=1,2$$

(and then also $g_1 = g_{01} \cos \psi_z$), after averaging over the angle ψ_z we get the generating function for the averaged FCF:

$$\overline{F(X_{(2)})} = \sum_{v_3', v_4'=0}^{\infty} q(v_3'v_4') (x_1')^{v_3'} (x_2')^{v_4'}$$

$$= [\det(1 - \overline{X}_{(2)} M) \det(1 + \overline{X}_{(2)} M)]^{-h} \frac{1}{a(X_{(2)})} \text{Erfi}[a(X_{(2)})], \quad (23)$$

where Erfi (x) is the probability integral,¹⁶ and $a^2(X_{(2)}) = g_0(1 - X_{(2)} M^{-1} X_{(2)} g_0)$. Expanding Eq. (23) in a power series, it is not hard to show that the following relations hold for the desired vectors and matrices:

$$g_{01} = [3q(10)]^{1/2}, \quad g_{02} = [3q(01)]^{1/2}; \quad (24)$$

$$M_{11} = -q(10) + [2q(20) - 1/3 q(10)^2]^{1/2},$$

$$M_{22} = -q(01) + [2q(02) - 1/3 q(01)^2]^{1/2},$$

$$M_{12} = [q(10)q(01)]^{1/2} - [q(11) - 1/3 q(10)q(01)]^{1/2}. \quad (25)$$

We note that the off-diagonal element M_{12} characterizes the degree of nonfactorizability of the matrix element $\langle v_3'v_4' | 00 \rangle$ into a product $\langle v_3'0 | 00 \rangle \langle 0v_4' | 00 \rangle$. The condition

for M_{12} to vanish is $\overline{q(11;00)} = (9/5)\overline{q(10;00)}\overline{q(01;00)}$, which is found when we average the factorizability condition $q(11;00) = q(10;00)q(01;00)$ over ψ_x . The relative intensities of the vibronic-nuclear transitions in the absorption spectrum are connected with the FCF in the following way:

$$\frac{I(v_3'v_4'; v_3v_4)}{I(00;00)} = \frac{\Omega(v_3'v_4'; v_3v_4)}{\Omega(00;00)} \overline{q(v_3'v_4'; v_3v_4)}, \quad (26)$$

where $\Omega(v_3'v_4'; v_3v_4)$ is the frequency of the transition $v_3'v_4' - v_3v_4$ in units cm^{-1} .

Accordingly, the finding of the parameters g and M reduces to the calculation from experimentally established relative intensities of certain definite vibronic-nuclear transitions [those whose FCF appear in Eqs. (24) and (25)] the corresponding FCF from Eq. (26), and then using Eqs. (24) and (25). It must be pointed out that the calculation of g and M from Eqs. (24) and (25) involves the problem of choosing the signs of square roots. In all of the calculations the present writers have carried out relating to the vibronic spectra of molecules, the best agreement with experiment has been achieved with the arithmetic choice of the signs, i.e., with the signs shown explicitly in Eqs. (24) and (25). Also, the ambiguity can be eliminated by comparing the relative intensities of the transitions with higher vibrational quantum numbers ($v_3', v_4' > 1$) as measured experimentally and as calculated from the recurrence relations (16). The unique choice of the diagonal elements M_{11} , $i = 1, 2$ is usually fixed by stipulating $|M_{ii}| < 1$.

The elements of the matrices K and L and the components

$$f_{0i} = \sum_{j=1}^2 (KJ)_{ij}^{2j+2}$$

are determined similarly. We have

$$\begin{aligned} f_{01} &= [3q(00;10)]^{\frac{1}{2}}, \quad f_{02} = [3q(00;01)]^{\frac{1}{2}}, \\ L_{11} &= -q(00;10) + [2q(00;20) - \sqrt{3}q(00;10)^2]^{\frac{1}{2}}, \quad |L_{11}| < 1, \\ L_{22} &= -q(00;01) + [2q(00;02) - \sqrt{3}q(00;01)^2]^{\frac{1}{2}}, \quad (27) \\ L_{12} &= [q(00;10)q(00;01)]^{\frac{1}{2}} - [q(00;11) - \sqrt{3}q(00;10)q(00;01)]^{\frac{1}{2}}, \\ K_{01} &= [q(1_{1+2}0;00)q(00;1_{1+2}0)]^{\frac{1}{2}} - [q(1_{1+2}0;1_{1+2}0) - \sqrt{3}q(1_{1+2}0;00)q(00;1_{1+2}0)]^{\frac{1}{2}}. \end{aligned}$$

As has been shown above, our problem is characterized by three parameters, which can be chosen to be g_1 , g_2 , and any one of the elements of the matrix M . This means that it is sufficient to have experimentally measured relative intensities of only three vibronic-nuclear transitions: 10-00, 01-00, and one of the following three: 11-00, 20-00, and 02-00. The first two enable us to calculate the shift parameters g_1 and g_2 , and the other one is necessary to determine an element of the matrix M . Furthermore, it follows from Eq. (21) that from any known element of the matrix M one can calculate the mixing angle χ :

$$\begin{aligned} \sin^2 \chi &= \frac{\omega_3 + \omega_4' - \omega_3 - \omega_4' - M_{11}(\omega_3 + \omega_4')}{\omega_3 - \omega_4 - \omega_3' + \omega_4' + M_{11}(\omega_3' - \omega_4')} \\ &= \frac{\omega_3 + \omega_4' - \omega_3 - \omega_4' + M_{22}(\omega_3 + \omega_4')}{\omega_3 - \omega_4 - \omega_3' + \omega_4' - M_{22}(\omega_3' - \omega_4')}, \\ \text{tg } \chi &= \frac{-\text{sign } M_{12}}{F+G} \left\{ \frac{(\omega_3' \omega_4')^{\frac{1}{2}} (\omega_3 - \omega_4)}{|M_{12}|} - \left[\frac{\omega_3' \omega_4' (\omega_3 - \omega_4)^2}{M_{12}^2} - F(F+G) \right]^{\frac{1}{2}} \right\}, \end{aligned}$$

where $F = (\omega_3 + \omega_3')(\omega_4 + \omega_4')$, $G = (\omega_3 - \omega_4)(\omega_3' - \omega_4')$, and

this makes it possible to calculate the other matrix elements from the equations (21).

Knowing the matrices M and S [from Eq. (20) with the known value of χ], we can calculate from Eqs. (13) the matrices K and L . Then it is not hard to show, starting from Eq. (14), that the vectors f_0 and g_0 are connected by the relation $f_0 = K(1+M)^{-1}g_0$. Thus from the value found for g_0 we get f_0 , which gives the vector f , since $f_i = f_{0i} \cos \psi_x$.

Accordingly, starting from the experimental values of three relative intensities of γ -transitions of a nucleus in the molecule, we can calculate completely the matrices K , L , and M and the vectors f and g . Then from recurrence relations we can find the matrix element of any transition $v_3'v_4' - v_3v_4$ and finally predict its intensity.

We note that if there were no Dushinskii effect ($S=1$) the nondiagonal elements of the matrices K , L , and M would be zero while the diagonal elements become simple functions of the normal frequencies

$$K_{ii} = \frac{2(\omega_{i+2}\omega_{i+3}')^{\frac{1}{2}}}{\omega_{i+2} + \omega_{i+3}'}, \quad M_{ii} = -L_{ii} = \frac{\omega_{i+2} - \omega_{i+3}'}{\omega_{i+2} + \omega_{i+3}'}$$

Furthermore, the matrix element $(v_3'v_4' | v_3v_4)$ breaks up into the product of two factors $(v_3' | v_3)(v_4' | v_4)$, each of which can be expressed in terms of Hermite polynomials of two variables.

5. CORRELATION EFFECTS

Let us now consider the correlations between the various vibrational modes that are excited in a vibronic-nuclear transition. We again confine ourselves to the case of a molecule XY_3Z_2 . The complete theory of correlation effects in the intensity distribution of vibronic bands in the spectra of polyatomic molecules is given earlier publications.⁷

An important characteristic of the excitation of a mode is the average number of excited vibrational quanta

$$\bar{v}_{\mu\psi_x} = \sum_{\nu_\mu=0}^{\infty} v_{\mu\psi_x}(v_3'v_4'; v_3v_4),$$

determined relative to a many-dimensional distribution function of the form

$$c(v_3'v_4'; v_3v_4) = q(v_3'v_4'; v_3v_4) / \sum_{\nu_3, \nu_4, \nu_3', \nu_4'} q(\bar{\nu}_3\bar{\nu}_4'; \bar{\nu}_3\bar{\nu}_4'). \quad (28)$$

The Greek index $\mu = 1, 2, 3, 4$ numbers the quantum numbers in the following order: v_3, v_4, v_3', v_4' . The subscript ψ_x means that the quantity is not averaged over the angle ψ_x . The use of a bar over $v_{\mu\psi_x}$ to indicate averaging over the mode must not be confused with the use of the bar in $q(v_3'v_4'; v_3v_4)$ for the average over the angle.

Let us denote by \bar{v}_μ the average of the quantity $v_{\mu\psi_x}$ over the angle ψ_x . The explicit value of \bar{v}_μ with the intermixing of the modes taken into account can be obtained from the generating function $F(X)$. In fact, the n -th order moment of the distribution function (28) can be found from

$$\bar{v}_\mu^n = [F(X)]^{-1} \left(x_\mu \frac{\partial}{\partial x_\mu} \right)^n F(X) |_{x=1}. \quad (29)$$

From this we can obtain an expression for the variance $\sigma_{\mu\mu}^2 = v_{\mu}^2 - \bar{v}_{\mu}^2$. Finally, a quantitative measure of the correlation between the μ -th and ν -th modes is the correlation coefficient $r_{\mu\nu}$:

$$r_{\mu\nu} = \text{cov}(\mu, \nu) / (\sigma_{\mu\mu}^2 \sigma_{\nu\nu}^2)^{1/2}. \quad (30)$$

Here $\text{cov}(\mu, \nu)$ is the second-order correlation moment, which is obtained by applying the operator $x_{\mu}(\partial/\partial x_{\mu})x_{\nu}(\partial/\partial x_{\nu})$ to $F(X)$.

We saw earlier that the calculation of the matrices K , L , and M and the vectors f and g can be accomplished by consideration of transitions with the excitation of not more than two vibrational modes. This is also true for finding the correlation moments. We shall give the appropriate expressions for vibronic-nuclear transitions $v_3'v_4' - 00$. The calculation of correlation effects for transitions of other types can be accomplished by an obvious modification of these relations.

In accordance with Eq. (29) the average number \bar{v}_{μ} of quanta excited in the μ -th mode ($\mu = 3, 4$) through the vibronic-nuclear transition $v_3'v_4' - 00$ is

$$\bar{v}_{i+2}' = \frac{(M^2)_{ii} - (\det M)^2}{\det(1-M^2)} + \frac{1}{3} \{[(1-M)^{-1}g_0]_i\}^2. \quad (31)$$

The dispersion $\sigma_{\mu\mu}^2$ is given by

$$\sigma_{i+2, i+2}^2 = \frac{(M^2)_{ii} + (M_{ii})^2 - 2(\det M)^2}{\det(1-M^2)} + 2 \left[\frac{(M^2)_{ii} - (\det M)^2}{\det(1-M^2)} \right]^2 + \frac{1}{3} \left(1 + 2 \frac{\det M - M_{ii}}{\det(1-M)} \right) \{[(1-M)^{-1}g_0]_i\}^2. \quad (32)$$

The correlation moment $\text{cov}(3, 4)$ can be written in the form

$$\text{cov}(3, 4) = \left[\frac{M_{12}}{\det(1-M^2)} \right]^2 [(1 + \det M)^2 + (\text{Sp } M)^2] + \frac{2}{3} \frac{M_{12}}{\det(1-M)} [(1-M)^{-1}g_0]_i [(1-M)^{-1}g_0]_j.$$

Having all the second-order moments, we can calculate the correlation coefficient (30) between the two modes. The case $r_{34} = 0$, which means that $M_{12} = 0$, corresponds to independent excitation of the modes, i.e., the absence of any Dushinskii effect.

When only one mode is excited in the final state, i.e., for transitions $v_{\mu}'0 - 00$, Eqs. (31) and (32) become simpler:

$$\bar{v}_{i+2}' = \frac{1}{1-M_{ii}} \left(M_{ii}^2 + \frac{1}{3} g_{0i}^2 \frac{1+M_{ii}}{1-M_{ii}} \right), \quad (33)$$

$$\sigma_{i+2, i+2}^2 = \frac{1}{(1-M_{ii})^2} \left[\frac{2M_{ii}^2}{(1+M_{ii})^2} + \frac{1}{3} g_{0i}^2 \frac{1+M_{ii}}{1-M_{ii}} \right]. \quad (34)$$

We note that consideration of the excitation of only one mode does not mean that the Dushinskii effect is neglected. The matrix element M_{ii} in Eqs. (33) and (34) depends on the mixing angle χ and is determined from experimental data [cf. Eq. (25)].

6. VIBRATIONAL-NUCLEAR TRANSITIONS

Let us now turn to vibrational-nuclear transitions between nondegenerate and twofold degenerate vibrational states of a molecule. With the expansion (7) the required matrix elements take the forms

$$R_{v', v} = \langle v_s' | \exp(-ik_1 b_s \cos \psi_s q_s m^{-1/2}) | v_l \rangle, \quad (35)$$

$$R_{v', v} = \langle v' l' | \exp[-ik_1 \sin \theta (b_{2x} q_{2x} \cos \varphi + b_{2y} q_{2y} \sin \varphi) m^{-1/2}] | v l \rangle. \quad (36)$$

Here θ is the angle between the direction of the vector k , and the z axis, perpendicular to the plane of the twofold degenerate vibrations, φ is the angle in the plane of vibrations, and $|v l\rangle$ is the state of a twofold degenerate oscillator characterized by the vibrational energy $E_v = \hbar\omega(v+1)$ and the vibrational angular momentum $\mathcal{L} = \hbar l$, with $l = v, v-2, \dots, 1$ or 0 . All vibrational states belong to the ground electronic term.

A. Let us first consider transitions between nondegenerate states. As before, we begin by calculating the matrix element $R_{\alpha_s' \alpha_s}$ of the transition between coherent states. The initial (one-dimensional) coherent state $|\alpha_s\rangle$ is of the form (11) with $N=1$ and $\lambda_{\omega} = \omega_s^{1/2}$, and the final state $|\alpha_s'\rangle$ is obtained from $|\alpha_s\rangle$ by the replacement $\alpha_s \rightarrow \alpha_s'$. We shall omit the index s hereafter for simplicity. It is not hard to verify that

$$R_{\alpha\alpha'} = \exp[-1/2(|\alpha|^2 + |\alpha'|^2) - 1/2 z \cos^2 \psi - iz^{1/2}(\alpha + \alpha') \cos \psi + \alpha\alpha'],$$

where [see Eq. (10)] $z \equiv z_s = (\hbar k_y^2 / 2m\omega) b_s^2$. From this, expanding $R_{\alpha\alpha'}$ in power series in α and α'^* , we get¹²

$$R_{v', v} = (-i)^{v'-v} \left(\frac{v!}{v'!} \right)^{1/2} \exp\left(-\frac{1}{2} z \cos^2 \psi\right) (z \cos^2 \psi)^{(v'-v)/2} L_v^{v'-v}(z \cos^2 \psi). \quad (37)$$

We note that the matrix element of the Weyl displacement operator $D(\alpha)$, of which $\exp(-ik \cdot u)$ is a special case, has been calculated in the basis of oscillator wave functions and expressed in terms of Laguerre polynomials in papers by Feynman¹⁸ and Schwinger¹⁹. In Ref. 12 expressions have been given, on the basis of Eq. (37), for the probabilities of vibrational-nuclear transitions for molecules of various types of symmetry.

In the case of a completely symmetrical vibration s_1 there is no displacement of the γ -active nucleus, which is at the center of symmetry of the molecule, so that the matrix element $R_{v', s_1 v s_1}$ is different from zero only for transitions without any change of the vibrational quantum number, i.e., $v_s' = v_s$.

Let us introduce a quantum number $n = v' - v$. Then the probability of a vibrational-nuclear transition is given by the formula

$$P_{v+n, v} = |R_{v+n, v}|^2 = \frac{v!}{(v+n)!} \exp(-z \cos^2 \psi) (z \cos^2 \psi)^n [L_v^n(z \cos^2 \psi)]^2.$$

By the method used earlier in deriving Eq. (19), we construct a generating function for the transition probabilities:

$$F(x, y) = \sum_{v=0}^{\infty} \sum_{n=-\infty}^{\infty} P_{v+n, v} x^v y^n = \frac{1}{1-x} \exp\left(-z \cos^2 \psi \frac{x-y-y+1}{1-x}\right).$$

It is easy to see that if we give the quantity x the meaning of the Boltzmann factor $\exp(-\hbar\omega/kT)$, we can use a simple integral transformation to obtain the probability for a transition in which the vibrational quantum number changes by n :

$$W_n = (1-x) \sum_{v=0}^{\infty} x^v P_{v+n, v} = \exp\left(-z \cos^2 \psi \frac{1+x}{1-x}\right) I_n\left(\frac{2zx^{1/2} \cos^2 \psi}{1-x}\right). \quad (38)$$

Here $I_n(x)$ is the modified Bessel function.¹⁶ An expression like (38) is well known in the theory of electronic-vibrational spectra of molecules and crystals (see a recent review article²⁰).

Let us now average the generating function $F(x, y)$

over the angles at which the photon is emitted:

$$\overline{F(x, y)} = \sum_{v=0}^{\infty} \sum_{n=-\infty}^{\infty} \overline{P_{v+n, v}} x^v y^n$$

$$= \frac{z^{-1/2}}{1-x} \left(\frac{x-x/y-y+1}{1-x} \right)^{-1/2} \text{Erf} \left[\left(z \frac{x-x/y-y+1}{1-x} \right)^{1/2} \right].$$

Using the well known expansion¹⁶ of Erf(x) in powers of x, we can obtain the probabilities averaged over the angles, $\overline{P_{v+n, v}}$.

Two limiting cases of Eq. (38) are worth pointing out. For $\hbar\omega/kT \gg 1$ transition probabilities are distributed according to the Poisson law, $W_n = n^{-n} (n!)^{-1} \exp(-\bar{n})$. In the opposite case, for $\hbar\omega/kT \ll 1$, we get a normal distribution $W_n = (2\pi\sigma^2)^{-1/2} \exp[-(n-\bar{n})^2/2\sigma^2]$, where $\bar{n} = z \cos^2\psi$, $\sigma^2 = 2z(kT/\hbar\omega)\cos^2\psi$. Here \bar{n} is the average number of vibrational quanta excited in the vibrational-nuclear transition.

B. The distribution of the intensities of the γ -ray satellites in the case of vibrational-nuclear transitions can also be described by means of an analog of the Franck-Condon principle. In fact, it follows from what has been said that the matrix element $R_{v'v}$ is the overlap integral between oscillator wave functions shifted in momentum space.

We shall consider vibrational-nuclear transitions between nondegenerate vibrational states of a molecule, as characterized by the transition amplitude (35). In the case of a system of oscillators the amounts of their shifts are determined by the distribution of the recoil momentum over the normal coordinates. We return to the idea of coherent states, and introduce into the discussion an α plane $\{\alpha = [(\omega/2\hbar)^{1/2}q + i(2\hbar\omega)^{-1/2}p]\}$. The initial and final states of the oscillators are represented in the α plane by circles of radii $v^{1/2}$ and $v'^{1/2}$, displaced relative to each other by the amount $(2z)^{1/2}\cos\psi$ along the imaginary axis (the momentum axis, see Fig. 1).

According to Landau,²¹ the character of the transition of the system from one state to another is determined by the points of intersection of the corresponding phase trajectories of the system. In other words, the points that are important for the transition are those at which it will change neither q nor p . It must be emphasized that this assertion is more general than the classical Franck-Condon principle, since the points of intersection of the phase trajectories can also lie in the complex region. The contribution of each point of intersection to the transition probability can be estimated, for example, by the method of steepest descents.²² Obviously the maximum transition probability is attained as the result of confluence of intersection points, i.e., in the case of mutual tangency of the phase trajectories. The two possible types of tangency correspond to the two branches of the Condon parabola in the (v, v') plane; the analytic expression for this curve can be found in the usual way and is

$$v' = v \pm 2(zv)^{1/2} \cos\psi + z \cos^2\psi.$$

Inside the parabola the transition probabilities as functions of v and v' oscillate, and they fall off exponentially outside the parabola. Using the well known asymptotic

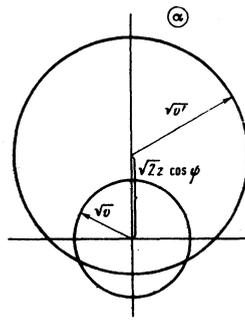


FIG. 1. Intersection of the phase trajectories of the initial and final states of an oscillator.

forms of the Laguerre polynomials,¹⁶ we can give a quantitative description of the behavior of the probabilities $P_{v'v}$ in the plane of (v, v') :

a) inside the parabola ($0 < z \cos^2\psi < 2V$, $V = v + v' + 1$)

$$P_{v'v} \sim \frac{1}{\pi} \frac{v!}{v'!} \left(\frac{1}{2} V \right)^{v'-v-1} \frac{1}{\sin 2\varepsilon}, \quad \cos \varepsilon = \left(\frac{z}{2V} \right)^{1/2} \cos\psi;$$

b) near the parabola ($z \cos^2\psi \sim 2V$)

$$P_{v'v} \sim \frac{1}{\pi^2} \frac{v!}{v'!} \left(\frac{z \cos^2\psi}{4} \right)^{v'-v} \left(\frac{3}{V} \right)^{v'} \left(\text{Ai} \left[\left(\frac{3}{V} \right)^{1/2} \left(V - \frac{1}{2} z \cos^2\psi \right) \right] \right)^2,$$

where $\text{Ai}(x)$ is the Airy function,¹⁶

c) outside the parabola ($2z \cos^2\psi > 2V$)

$$P_{v'v} \sim \frac{1}{4\pi} \frac{v!}{v'!} e^{-2\theta} \left(\frac{1}{2} V \right)^{v'-v-1} \frac{1}{\text{sh } 2\psi_1},$$

where $2\theta = V(\sinh 2\psi_1 - 2\psi_1)$, $\cosh 2\psi_1 = (z/2V)^{1/2} \cos\psi$.

C. To find the matrix element $R_{v'v}$, Eq. (36), we first calculate the matrix element of the transition between the corresponding coherent states $|\beta_1\beta_2\rangle$, which are the generating functions for the states $|v\rangle$ (see Ref. 23). Again calculating a Gaussian integral, we get $[\hbar/(4m\omega)]^{1/2} k_y \sin\theta$:

$$R_{\beta_1'\beta_2'\beta_1\beta_2} = \exp \left[-\frac{1}{2} (|\beta_1|^2 + |\beta_2|^2 + |\beta_1'|^2 + |\beta_2'|^2) \right]$$

$$\times \exp \{ -\hbar^2 (b_{2x}^2 \cos^2\varphi + b_{2y}^2 \sin^2\varphi) + \beta_1\beta_1' + \beta_2\beta_2' + \hbar [b_{2x} \sin\varphi (-\beta_1 + \beta_2 + \beta_1' - \beta_2') - i b_{2x} \cos\varphi (\beta_1 + \beta_2 + \beta_1' + \beta_2')] \}.$$
(39)

Expanding this expression in powers of $\beta_1, \beta_2, \beta_1', \beta_2'$, we find

$$R_{v'l',v'l} = \exp[-\hbar^2 (b_{2x}^2 \cos^2\varphi + b_{2y}^2 \sin^2\varphi)]$$

$$\times (-\hbar)^{l'+l} \left[\left(\frac{v-l}{2} \right)! \left(\frac{v'-l'}{2} \right)! / \left(\frac{v+l}{2} \right)! \left(\frac{v'+l'}{2} \right)! \right]^{1/2}$$

$$\times L_{(v-l)/2}^l [\hbar^2 (b_{2x}^2 \cos^2\varphi + b_{2y}^2 \sin^2\varphi)] L_{(v'-l')/2}^{l'} [\hbar^2 (b_{2x}^2 \cos^2\varphi + b_{2y}^2 \sin^2\varphi)].$$

If the symmetry properties of the molecule are such that $b_{2x} = b_{2y} = b_2$, this expression can be simplified. In this case we have for the transition probability

$$P_{v'l',v'l} = \exp(-2z_2 \sin^2\theta) (z_2 \sin^2\theta)^{l'+l} \left(\frac{v-l}{2} \right)! \left(\frac{v'-l'}{2} \right)!$$

$$\times \left[\left(\frac{v+l}{2} \right)! \left(\frac{v'+l'}{2} \right)! \right]^{-1} [L_{(v-l)/2}^l (z_2 \sin^2\theta) L_{(v'-l')/2}^{l'} (z_2 \sin^2\theta)]^2,$$

where $z_2 = (\hbar k_y^2/4m\omega) b_2^2$.

We give the first few values of the angle-averaged transition probabilities

$$\bar{P}_{00,00} = e^{-2z_2} (2z_2)^{-1/2} \operatorname{Erfi}[(2z_2)^{1/2}],$$

$$\frac{\bar{P}_{00,11}}{\bar{P}_{00,00}} = \frac{\pi}{4} z_2^{1/2}, \quad \frac{\bar{P}_{00,20}}{\bar{P}_{00,00}} = 1 - \frac{4}{3} z_2 + \frac{8}{15} z_2^2, \quad \frac{\bar{P}_{00,22}}{\bar{P}_{00,00}} = \frac{1}{3} z_2.$$

Owing to the symmetry properties

$$\frac{P_{v'l',v}}{P_{00,00}} = \frac{P_{v'l',00} P_{00,v}}{P_{00,00} P_{00,00}} \quad (40)$$

these values of the probabilities include all possible transitions with $v, v' \leq 2$.

Owing to the factorization most of the results for the nondegenerate case can be applied to these formulas. We give the formula for the probability of a transition between some state with fixed l and a state with fixed l' :

$$W_{l',l} = (1-x)^2 \sum_{v=0}^{\infty} \sum_{v'=0}^{\infty} x^{(v+l')/2} P_{v'l',v} x^{(v-l)/2}$$

$$= x^{-(l+l')/2} \exp(-2z_2 \sin^2 \theta) I_l \left(2z_2 \sin^2 \theta \frac{x^h}{1-x} \right) I_{l'} \left(2z_2 \sin^2 \theta \frac{x^h}{1-x} \right),$$

where $x = \exp(-\hbar\omega/kT)$.

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²Here and hereafter the symbol $|v_i v_j\rangle$ is used as an abbreviation for the state vector $|0, \dots, v_i, \dots, v_j, \dots, 0\rangle$ in which only two modes occur, with the frequencies ω_i and ω_j . Similarly, the symbol $|v_i\rangle$ means that there is only one excited mode with the frequency ω_i .

³We point out that whereas the many-dimensional Hermite polynomials are defined identically in Refs. 15 and 16, the definitions of the classical (one-dimensional) Hermite polynomials are different. We use the Bateman definition.¹⁶ The writers are obliged to K. Yung for this remark.

⁴We note that of the six symmetry types dealt with in Ref. 12, the molecule XY_3Z_2 is the only one in which a nontrivial Dushinskii effect is possible. For the other five types one can simply set the mixing angle χ equal to zero in the formulas which follow.

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