SOME THEORETICAL ASPECTS OF PHONON-ASSISTED RADIATIVE ELECTRONIC TRANSITIONS*,**

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The zero-phonon and the phonon-assisted optical spectra of condensed molecular and solid-state systems are analyzed theoretically in the adiabatic approximation. The separation of the radiative transition matrix into vibrational and electronic components is considered quite generally, noting the limitations of the Franck-Condon principle. An expansion approximation for the adiabatic electronic matrix element is shown to remain valid in the zero-phonon limit. The effects of dispersion in the multi-dimensional optical modes as well as of polarization from short wavelength acoustical modes are considered. The temperature dependence of the widths of phonon-assisted absorption and luminescent bands and the dependence on hydrostatic pressure of vibronic spectra are discussed.

1. Introduction

Many years ago Jabłoński [1] considered theoretically the broad band widths and spectral displacements of fluorescence compared to absorption for condensed matter, specifically for fluorescent dyes in solutions, on the basis of the Franck-Condon principle, which had been originally developed for polyatomic gases. Since then this idea has been widely used in explaining the photo-excitation and luminescent spectra of atomic or molecular dopants in solutions and in crystals. The advances in materials preparation, in spectroscopic and related measurements and in the theoretical understanding of molecular and solid-state physics now facilitate more detailed, rigorous analyses of these spectra. For example, the observation of zero-phonon and individual vibronic transitions and the effects of temperature and hydrostatic pressure on these transitions allow for more detailed understanding of the interactions of ions or molecules with local or lattice vibrations in condensed matter.

The adiabatic approximation is assumed valid, that is, the electronic states are smoothly perturbed by the motions of the nuclei and the nuclei move in an effective potential which

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includes the eigenvalue for the electronic energy with its parametric dependence on the positions of the nuclei. This effective potential is the adiabatic potential plotted as a function of the nuclear positions or configurational coordinate as shown in Fig. 1. The force constants K, equilibrium positions $R(0)$ and energy minima $E(0)$ are different for the ground and excited states because electronic eigenvalues and their parametric dependence

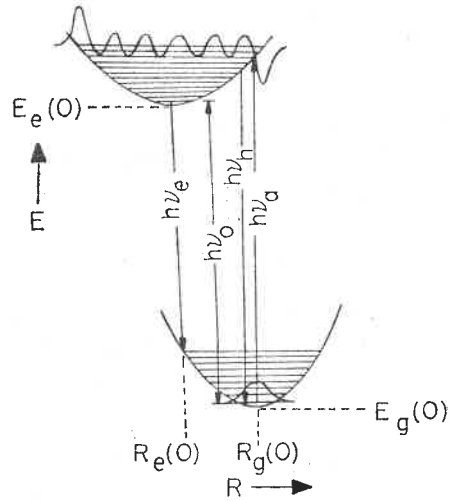

Fig. 1. Configurational coordinate model, showing representative vibrational wavefunctions, and representative transitions; $h\nu_0$ — zero-phonon transition, $h\nu_a$ — relaxed phonon-assisted absorption, $h\nu_e$ — relaxed phonon-assisted emission, and $h\nu_h$ — unrelaxed emission (hot luminescence)

on R are different for the two electronic states. For small molecular ions such as NO_2^- at anion sites in alkali halides [2] and dye molecules in solutions [1] the configuration coordinates are intramolecular vibrations modified by coupling with the matrix; for point charged dopants with effective mass states in semiconductors the configuration coordinates is describable in terms of linear combinations of optical modes of the lattice [3]. In Fig. 1 the adiabatic potential is assumed harmonic; representative vibrational levels m and n of the ground, g, and excited, e, states respectively, with vibrational wavefunctions χ_{mg} and χ_{ne} are also shown.

The Franck-Condon principle states that optical transitions take place vertically on the configurational coordinate diagram, as shown in Fig. 1. For a phonon-assisted transition with large Stokes shift, the Franck-Condon principlec an be used in combination with approximating the χ of the final state by a delta function at the classical turning point R_c. Then the optical transition matrix $M_{eg}(n, m)$ can be separated into vibrational and electronic matrix elements

$$M_{eg}(n, m) = [\int \chi^*_{ne}(R)\chi_{mg}(R)dR] \times [\int \phi^*_e(\boldsymbol{r}; R_c)\boldsymbol{r}\phi_g(\boldsymbol{r}; R_c)d\boldsymbol{r}], \tag{1}$$

which is valid if either n or m is a small integer and if the other is a large integer (the latter level has its χ approximated by the δ-function). The ϕ_e and ϕ_g are the electronic wave-

functions for excited and ground states. If we denote the overlap integral, for example for absorption

$$S_{eg}(n, m) = \int \chi^*_{ne}(R)\chi_{mg}(R)dR, \tag{2}$$

then in this case for m small and n large, within the above approximation: $S_{eg}(n, m) = \chi_m(R_c)$. In the following we consider more general approximations to $M_{eg}(n, m)$.

2. *General transition matrices for vibronic transitions*

With more detailed spectroscopic data becoming available for atomic and molecular dopants in condensed media, especially at low temperatures and for systems with vibronic structure, a better approximation to $M_{eg}(n, m)$ is needed. For harmonic adiabatic potentials $S_{eg}(n, m)$ can be calculated exactly [4], however, $M_{eg}(n, m)$ does not involve $S_{eg}(n, m)$ as a simple factor, as in Eq. (1), because the electronic matrix element is itself dependent on n and m, in the full adiabatic approximation.

Thus we consider how to approximate $M_{eg}(n, m)$ in terms of $S_{eg}(n, m)$ for more general transitions than those for which the δ-function approximation is valid. The δ-function is not valid when both n and m are small integers. A general approximation should satisfy the following limit condition

$$\lim_{m\to 0} M_{eg}(0, m) = \lim_{n\to 0} M_{eg}(n, 0), \tag{3}$$

where the functional form for $M_{eg}(n, m)$ is assumed to be unchanged in the limits. Of course, the zero-phonon transition has equal transition matrix for emission and for absorption, as is evident from detailed balance. For the phonon-assisted transitions the irreversible relaxations obviate observation of the same vibronic transition in absorption and emission, except for hot luminescence (See Fig. 1).

The general expression for the matrix element for luminescent vibronic transitions in the full adiabatic approximation is

$$M_{eg}(n, m) = \int \{\chi^*_{ne}(R)\chi_{mg}(R) [\int \phi^*_e(r; R) r \phi_g(r; R) dr]\} dR. \tag{4}$$

If we expand $\int \phi^*_e(r; R) r \phi_g(r; R)$ about some R_{nm}, we obtain

$$\int \phi^*_e(r; R) r \phi_g(r; R) dr \simeq \int \phi^*_e(r; R_{nm}) r \phi_g(r; R_{nm}) dr$$

$$+ \{(R - R_{nm}) \cdot \nabla_R + \tfrac{1}{2} [(R - R_{nm}) \cdot \nabla_R]^2\} \int \phi^*_e(r; R) r \phi_g(r; R) dr|_{R=R_{nm}} + \cdots . \tag{5}$$

The R_{nm} is chosen as follows, in order to obtain the best approximation with the fewest terms

$$R_{nm} = \int \chi^*_{ne}(R) R \chi_{mg}(R) dR [S_{eg}(n, m)]^{-1} \tag{6}$$

and thus to first order in the expansion, we have

$$M^{(1)}_{eg}(n, m) \simeq S_{eg}(n, m) \int \phi^*_e(r; R_{nm}) r \phi_g(r; R_{nm}) dr \tag{7}$$

and to second order

$$M_{eg}^{(2)}(n, m) \simeq M_{eg}^{(1)}(n, m)+\tfrac{1}{2}\{\int \chi_{ne}^{*}(R)R^2\chi_{mg}(R)dR-|R_{nm}|^2\}$$
$$\times\nabla_R^2\int \phi_e^{*}(r; R)r\phi_g(r; R)dr|_{R=R_{nm}}. \tag{8}$$

Both Eqs. (7) and (8) satisfy Eq. (3) for the zero-phonon transition. From Eq. (6) the value of R can be determined [4] for calculating the electronic matrix element in Eq. (7) or for determining $M_{eg}(n, m)$ to higher order with Eq. (8); in both cases taking account, but to different orders, of the dependence of the electronic matrix element on n and m.

3. Dispersion in multi-dimensional modes

With the increased resolution of current molecular and solid-state spectroscopy, particularly with materials of well-defined composition at low temperatures, the line shape of individual vibronic transitions can be studied. One contribution to the line widths is coupling to long wavelength acoustical phonons. We propose another contribution, consistent with the analysis of Section 2, based on the dispersion of the optical phonons responsible for the vibronic structure.

As noted earlier, in some cases the single configurational coordinate R is the coordinate of a unique local mode, for example an intramolecular impurity mode; for other cases such as effective mass dopants in crystals R is some "average coordinate" of the $6N$-normal coordinates of the lattice.[1] If we consider the $6N$-dimensional configurational coordinate diagram, then the adiabatic potential surface for motion of the atoms is

$$(E-E_0) = \sum_{s=1}^{6N}\frac{K_s}{2}[Q_s-Q_s(0)]^2, \tag{9}$$

where Q_s and $Q_s(0)$ are, respectively, the sth normal coordinate and the corresponding component of the position for the energy minimum. Phonons of different energies, $\hbar\omega_s$, can be created or annihilated in the phonon-assisted transition. Let V_s be the coupling constant between the s-mode and the electronic particle, then the interaction E_{el-ph} is

$$E_{el\text{-}ph} = \sum_s\{V_s a_s e^{-i\boldsymbol{q}_s\cdot\boldsymbol{r}}+V_s^{*}a_s^{+}e^{-i\boldsymbol{q}_s\cdot\boldsymbol{r}}\}, \tag{10}$$

where a_s and a_s^{+} are the annihilation and creation operators for phonons of the s-mode, $\boldsymbol{r}$ is the position vector of the electronic particle and $\boldsymbol{q}_s$ is the wave number vector for the phonon. We can approximate Eq. (9) by a single configurational coordinate as follows

$$(E-E_0) = \frac{K_{ave}}{2}[R-R(0)]^2, \tag{11}$$

where

$$K_{ave} = [\sum_s\sqrt{K_s}|V_s|^2]^2[\sum_s|V_s|^2]^{-2}. \tag{12}$$

[1] Here we are considering the lattice to have two atoms per unit cell and N unit cells.

The line width will be characterized by the mean square deviation in ω given by

$$(\Delta\omega)^2 = \sum_s (\omega_s - \omega_{ave})^2 |V_s|^2 [\sum_{s'} |V_{s'}|^2]^{-1}, \tag{13}$$

where

$$\omega_{ave} = \sum_s \omega_s |V_s|^2 [\sum_{s'} |V_{s'}|^2]^{-1}. \tag{14}$$

For effective mass dopant states the phonon spectrum is to a good approximation independent of electronic state of the dopant. The ω_s are obtained from the dispersion curve $f(\omega)$ for the optical phonons, thus Eq. (14) becomes

$$\omega_{ave} = \int f[\omega_{opt}(q)] \, |V_q|^2 dq [\int |V_{q'}|^2 dq']^{-1}, \tag{15}$$

where V_q can be obtained from polaron theory [5]

$$V_q = -\frac{ie}{q} \left[\frac{2\pi\hbar\omega_{opt}(q)}{v}\right] \left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}\right)^{1/2} \tag{16}$$

and ε_∞ and ε_0 are the high and low frequency dielectric constants and v is the crystal volume.

In this analysis we have shown that for effective mass dopant states in particular, the multi-dimensional configurational coordinates can be represented by a single configurational coordinate and that vibronic line width in part originates from phonon dispersion. The multi-dimensional configuration coordinate problem has been analyzed by others [6–9]. It is also to be noted that the zero-phonon and phonon-assisted transitions of effective mass dopants can be described by the adiabatic potential with the configurational coordinate represented by the lattice polarization [10, 3].

The lattice polarization is normally described in terms of the optical phonons, in fact polar modes are usually equated to the optical branch of the lattice modes. However, it can be shown, for example for a one-dimensional lattice containing two atoms per unit cell, that only in the limit of zero quasi-momentum does the acoustical branch contain no polarization and that at the zone boundary the acoustical and optical branches contribute comparably to lattice polarization. By considering two types of motion in the unit cell: one which only displaces the "center" of polarization already present; the other which only changes the magnitude and/or direction of the polarization in the cell, it can be shown that as long as the polarization effects are independent of the location of the polarization within a unit cell a single branch representation is adequate. On the other hand, if the polarization effects depend on changes over a distance small compared to a unit cell dimension then a two branch representation is necessary.

4. Temperature-dependence of broad band spectra

We consider the temperature dependence of the half-width of the broad band phonon-assisted absorption or emission spectra when a dissipative term is present. A dissipative term has been suggested for the electron-phonon interactions in organic systems [11].

Also for some inorganic materials [12] the second moment, ΔE, of the emission spectra has the form

$$\Delta E(T) = \Delta E(0) \coth^{1/2}\left[\frac{\hbar\omega}{2k}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right], \tag{17}$$

which we shall now show is explainable by including dissipation.

We use Fig. 1 with $R_e(0)$ chosen to be zero, then

$$\Delta E(T) = 2K_e[\overline{(R-\bar{R})^2}]^{1/2} R_g(0) \tag{18}$$

where $[\overline{(R-\bar{R})^2}]^{1/2}$ is the mean square deviation of configurational coordinate at T, when the system is in the excited state. In order to calculate $\overline{(R-\bar{R})^2}$, we must know dW_R, which is the probability distribution for R. The form of dW_R is

$$dW_R = \frac{C}{\sqrt{\pi}} \exp\left[-R^2C^2\right]dR, \tag{19}$$

where

$$C = \left[\frac{\omega_e}{\hbar} \tanh \frac{\hbar\omega_e}{2kT}\right]^{1/2},$$

when there is no dissipative term [13] where the following assumptions have been used

$$P_{n-1,n} = -i\omega R_{n-1,n} \qquad P_{n+1,n} = i\omega R_{n+1,n}$$

$$R_{-1,0} = 0 \qquad E_{n+1} = E_n + h\omega_e \tag{20}$$

and

$$R_{n+1,n} = R_{n,n+1},$$

where $R_{m,m}$ and $P_{m,n}$ are matrix elements for R and its conjugate momentum. If we make the assumption that there is a dissipative force acting on the oscillator, so that, detail balance does not hold, and that it is represented by replacing the last condition of Eq. (20) by

$$R_{n+1,n} = e^{-\gamma^2} R_{n,n+1}$$

then we find for C

$$C = \left[\frac{\omega_e}{\hbar} \tanh\left(\frac{\hbar\omega_e}{2kT} - \frac{\gamma^2}{2}\right)\right]^{1/2}. \tag{21}$$

If $\gamma^2 = \hbar\omega_e/kT_0 \geqslant 0$, then since $\overline{[R-\bar{R}]^2} = \dfrac{1}{2C^2}$ we get $\Delta E(T)$ given by Eq. (17).

5. *Effects of hydrostatic pressure on impurity spectra*

We next consider the application of macroscopic external forces to the microscopic system described by the configurational coordinate model. The general idea is that the macroscopic force causes a shift in the equilibrium position of the adiabatic potential energy curves for each state independently and that this shift depends only on the form of each curve for zero force plus the nature of the applied force. The equilibrium can be shifted both in position and energy. Vibronic transitions can change in energy and intensity [14].

We consider the case of the application of hydrostatic pressure in the harmonic approximation [15] as shown in Fig. 2. At the equilibrium the total force is zero and therefore for the ground electronic state

$$R_g(P) = R_g(0) - \frac{PA_g}{K_g}, \tag{22}$$

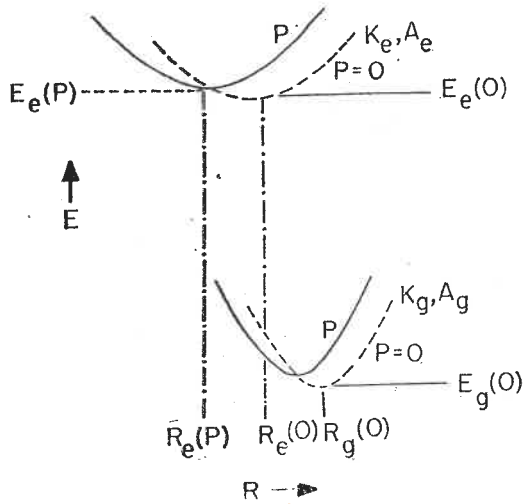

Fig. 2. Configurational coordinate model, with and without hydrostatic pressure

where A_g is the coupling constant between the system and the pressure. The energy of the new equilibrium can be determined by the work done adiabatically on the system by the force, which gives

$$E_g(P) = E_g(0) + \frac{P^2 A_g^2}{2K_g}. \tag{23}$$

The new energy curve is given by the sum of the equilibrium energy plus a position-dependent term that gives the force and is zero at $R_g(P)$. We obtain for the ground state (equations similar to (22)–(24) exist for the excited state)

$$E_g(R, P) = \frac{K_g}{2}[R - R_g(P)]^2 + \frac{P^2 A_g^2}{2K_g} + E_g(0). \tag{24}$$

From which we find the transition energy

$$E_{nm}(P) = \left(\frac{A_e^2}{K_e} - \frac{A_g^2}{K_g}\right)\frac{P^2}{2} + E_{nm}(0). \tag{25}$$

Anharmonicity introduces linear dependence on pressure [14]. Also the pressure-dependence of the vibronic transition matrix can be calculated with this model [4].

6. *Conclusions*

The general approach originally used by Professor Jabłoński to interpret broad band spectra of dyes in solutions has been extended to explain the spectra of impurity ions and molecules in condensed matter. The transition matrices have been generalized to be valid for both zero-phonon and phonon-assisted transitions; effects of the dispersion of phonons and of dissipation can be determined; and dependency of these spectra on temperature and on hydrostatic pressure calculated.

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