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Spectral Band Shape of Absorption and Emission of Molecules in Dense Media*

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A quantitative theory of the shape of absorption and emission curves for solute molecules dissolved in crystalline solvents based on the Franck-Condon principle is given. The relation between the radiationless transition and absorption or emission is discussed.

Eine auf dem Franck-Condon-Prinzip basierende, quantitative Theorie für die Form von Absorptions- und Emissionslinien von Molekülen in kristallinen Lösungsmitteln wird entwickelt und die Beziehung zwischen strahlungslosen Übergängen und Absorption bzw. Emission diskutiert.

Théorie quantitative de la forme des courbes d'absorption et d'émission, pour des molécules dissoutes dans des solvants cristallins, basée sur le principe de Franck-Condon. Discussion de la relation entre la transition non radiative et l'absorption ou l'émission.

1. Introduction

Although the basic mechanism underlying the absorption and emission of light is clear, there has been little discussion of the shape of absorption and emission bands for an electronic transition of molecules in dense media. In this paper, we shall make quantitative investigation of the absorption coefficient and rate of spontaneous emission for all temperatures and frequencies on the basis of the Franck-Condon principle [1] applied to the solute plus solvent molecules. The line broadening due to the resonance interactions [2] among the solute moledules and due to the damping effect [3] will be neglected in this investigation, but they can easily be included by generalizing the argument given in this discussion. We restrict our discussion to the system consisting of solute molecules of one species embedded in a crystalline solvent of another species. If, as with Moffit and Moscowitz [4], we consider each solute molecule in a liquid solvent to occupy a site within a locally rigid matrix of solvent molecules and its translation and rotational degrees of freedom to appear as librations, then our discussion can be applied to the case of light absorption or emission of molecules dissolved in a liquid solvent.

In our previous investigations [5, 6], we discussed the radiationless transitions from the viewpoint of the non-stationary character of the Born-Oppenheimer approximation, and found that the radiationless transition probability depends very much on the modifications of the normal coordinates and frequencies of the two electronic states, and because of the lack of knowledge of normal coordinates and frequencies of local modes between the two electronic states in which the non-radiative transition occurs, it is difficult to carry out the calculations of the

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radiationless transition probability accurately. In this investigation, it will be shown that the main difficulties involved in the calculation of the radiationless transition probability will be resolved if one carries out and analyzes the measurement of the light absorption or emission of the solute molecules dissolved in the crystalline solvent. It will also be shown that when there is an overlap of two or more absorption bands one can determine the absorption coefficient for each electronic transition as a function of frequency and by plotting the absorption coefficient against frequency one can obtain the oscillator strength for each electronic transition.

It is to be noticed that the band-shape function (see Eq. (5), next section) based on the Franck-Condon principle consists of a number of delta functions centered at various frequencies. As more vibrational modes of various frequencies are added, the average spacing between adjacent delta functions decrease, until ultimately the spacing becomes less than the band width of the spectrophotometer and the observed spectrum becomes continuous.

2. General Formulation

We consider a system consisting of a solute molecule embedded in the solvent molecular lattice. From time-dependent perturbation theory, the transition probability from the state (bv') to a final state (av'') due to absorption of light of frequency ν is [7, 8, 9]

$$P(bv' \to av'') = \frac{2\pi}{3\hbar^2}\,\varrho(\nu)\,|\langle av''|e\vec{R}|bv'\rangle|^2\,\delta(\nu_{av'',bv'} - \nu) \tag{1}$$

where $\varrho(\nu)$ represents the radiation density per unit frequency range and $\delta(x)$ is the delta function. The single and double primes designate the quantities belonging to the initial and final electronic states, respectively. a and b signify the electronic states, and v, the overall vibrational state. $\nu_{av'',bv'}$ is the frequency for the transition between the state (av'') and (bv'). The corresponding rate of light absorption is given by

$$R(bv' \to av'') = \frac{4\pi^2\nu}{3\hbar}\,\varrho(\nu)\,|\langle av''|e\vec{R}|bv'\rangle|^2\,\delta(\nu_{av'',bv'} - \nu) \tag{2}$$

For $T > 0$, we have to include a Boltzmann factor to take care of the distribution of the population in the various vibrational levels. The absorption band is thus a series of bands that merge into a single broad one. Hence the total rate of light absorption is obtained by summing Eq. (2) over all initial vibrational states v' weighted by their Boltzmann factor $P_{bv'}$ and then summing over all final vibrational states v'' consistent with the conservation of energy:

$$R(b \to a) = \frac{4\pi^2\nu}{3\hbar}\,\varrho(\nu)\sum_{v'v''} P_{bv'}\,|\langle av''|e\vec{R}|bv'\rangle|^2\,\delta(\nu_{av'',bv'} - \nu) \tag{3}$$

where $P_{bv'}$ is given by [10]

$$P_{bv'} = \prod_i^N \left(2\sinh\frac{\hbar\omega_i'}{2kT}\right)\exp\left[-\frac{(v_i'+\frac{1}{2})\hbar\omega_i'}{kT}\right]. \tag{4}$$

Using the relation between the radiation density and the radiation intensity $I(\nu) = ac\varrho(\nu)$, we obtain the molecular absorption coefficient $k_{b\to a}(\nu)$:

$$k_{b\to a}(\nu) = \frac{4\pi^2\nu}{3\hbar ac}\sum_{v'v''} P_{bv'}\,|\langle av''|e\vec{R}|bv'\rangle|^2\,\delta(\nu_{av'',bv'} - \nu) \tag{5}$$

a is a function of refractive index n and is a correction due to the change in the volocity of light in the medium and due to an inhomogeneity of electric field in the solid. For example, if we use the Lorentz field [11], then $a = \frac{9n}{(2+n^2)^2}$. In the adiabatic approximation, the state of the system is described by the product of the wave functions,

$$\Psi_{av''} = \Phi_a \Theta_{av''} \quad \text{and} \quad \Psi_{bv'} = \Phi_b \Theta_{bv'} \tag{6}$$

where Φ_a and Φ_b are the wave functions for the electrons of the system as though the nuclei were fixed in their instantaneous positions and $\Theta_{av''}$ and $\Theta_{bv'}$ designate the wavefunctions of both intra- and intermolecular vibrations of the system. Substitution of Eq. (6) into Eq. (5) gives:

$$k_{b\to a}(\nu) = \frac{4\pi^2 \nu}{3\hbar a c} |\vec{R}_{ab}|^2 \sum_{v'v''} P_{bv'} |\langle \Theta_{av''} | \Theta_{bv'} \rangle|^2 \, \delta(\nu_{av'',bv'} - \nu) \tag{7}$$

Here the Franck-Condon principle has been used. $\vec{R}_{ab}$ denotes the transition moment between the two electronic states:

$$\vec{R}_{ab} = \langle \Phi_a | e\vec{R} | \Phi_b \rangle \,. \tag{8}$$

To evaluate the molecular absorption coefficient $k_{b\to a}(\nu)$, we approximate the vibrational wavefunctions by a product of harmonic-oscillator wavefunctions:

$$\Theta_{av''} = \prod_i^N X_{av_i''}(Q_i'') \,, \qquad \Theta_{bv'} = \prod_i^N X_{bv_i'}(Q_i') \tag{9}$$

where $X_{av_i''}$ are the wavefunctions of harmonic oscillators and Q_i denote the normal coordinates.To take into account the modifications of both normal coordinates and frequencies between the two electronic states, we can express them in general as follows [12]

$$Q_i' = Q_i - d_i' \,, \qquad Q_i'' = Q_i - d_i'' \tag{10}$$

and

$$\omega_i'' = \omega_i'(1 - \varrho_i) \tag{11}$$

if the modifications are not very large. It should be noted that the anharmonicity in the potential curve is neglected here. This may cause some changes in the Franck-Condon factor in the cases where there are modifications of normal coordinates and frequencies, but the effect is higher order, so long as the modifications of normal coordinates and frequencies exist, so it will not be considered here. In certain cases where the modifications of normal coordinates and frequencies are extremely small or negligible, the anharmonicity may then become very important. We do not treat these cases in the present investigation.

To simplify Eq. (7), it is convenient to introduce the integral expression for the delta function [9]

$$\delta(\nu_{av'',bv'} - \nu) = \int_{-\infty}^{\infty} \mathrm{d}t \exp(it\Delta\omega) \prod_i^N \exp\{it[(v_i'' + \tfrac{1}{2})\omega_i'' - (v_i' + \tfrac{1}{2})\omega_i']\} \tag{12}$$

where $\Delta\omega = \omega_{ab} - \omega$. $\hbar\omega_{ab}$ is the energy difference between the two electronic states and for the cases of light absorption, it is positive. Substituting Eq. (9) to Eq. (12) into Eq. (7), we find,

$$k_{b\to a}(\nu) = \frac{4\pi^2 \nu}{3\hbar a c} |\vec{R}_{ab}|^2 \int_{-\infty}^{\infty} dt \exp(it\Delta\omega) \prod_i^N L_i(t) \tag{13}$$

where

$$L_i(t)=\sum_{v_i''v_i'}\left(\sinh\frac{\hbar\omega_i'}{2kT}\right)|\langle X_{av_i''}|X_{bv_i'}\rangle|^2\exp\left[it(v_i''+\tfrac{1}{2})\omega_i''-(v_i'+\tfrac{1}{2})\left(it\omega_i'+\frac{\hbar\omega_i'}{kT}\right)\right] \quad (14)$$

By using the Mehler's formula [13].

$$\sum_v \exp[-(v+\tfrac{1}{2})t]\,X_v(Q)\,X_v(Q')$$
$$=\beta(2\pi\sinh t)^{-\frac{1}{2}}\exp\left\{-\frac{\beta^2}{4}\left[(Q+Q')^2\tanh\frac{t}{2}+(Q-Q')^2\coth\frac{t}{2}\right]\right\} \quad (15)$$

where $\beta=(\omega/\hbar)^{\frac{1}{2}}$ Eq. (14) can be written as:

$$L_i(t)=\frac{2\beta_i'\beta_i''\sinh\frac{\hbar\omega_i'}{2kT}}{(4\pi^2\sinh\lambda_i'\sinh\mu_i'')^{\frac{1}{2}}}\iint\limits_{-\infty}^{\infty}dQ_i\,d\bar{Q}_i\exp\left\{-\frac{\beta_i''^2}{4}\left[(Q_i''+\bar{Q}_i'')^2\tanh\frac{\mu_i''}{2}\right.\right.$$
$$\left.\left.+(Q_i''-\bar{Q}_i'')^2\coth\frac{\mu_i''}{2}\right]-\frac{\beta_i'^2}{4}\left[(Q_i'+\bar{Q}_i')^2\tanh\frac{\lambda_i'}{2}+(Q_i'-\bar{Q}_i')^2\coth\frac{\lambda_i'}{2}\right]\right\} \quad (16)$$

where $\lambda_i'=it\omega_i'+\frac{\hbar\omega_i'}{\mathrm{kT}}$, and $\mu_i''=-it\omega_i''$. The integral in Eq. (16) is elementary and has been carried out [5, 14]. The result is:

$$L_i(t)=\frac{2\beta_i'\beta_i''\sinh\frac{\hbar\omega_i'}{2kT}}{(\sinh\lambda_i'\sinh\mu_i'')^{\frac{1}{2}}}\cdot\frac{\left(\beta_i'^2\tanh\frac{\lambda_i'}{2}+\beta_i''^2\tanh\frac{\mu_i''}{2}\right)^{-\frac{1}{2}}}{\left(\beta_i'^2\coth\frac{\lambda_i'}{2}+\beta_i''^2\coth\frac{\mu_i''}{2}\right)^{\frac{1}{2}}}$$
$$\exp\left[-\frac{\beta_i'^2\beta_i''^2(d_i''^2-d_i')^2}{\left(\beta_i'^2\coth\frac{\mu_i''}{2}+\beta_i''^2\coth\frac{\lambda_i'}{2}\right)}\right]. \quad (17)$$

Substitution of Eq. (17) into Eq. (13) gives:

$$k_{b\to a}(v)=\frac{4\pi^2 v}{3\hbar ac}|\vec{R}_{ab}|^2\int\limits_{-\infty}^{\infty}\exp(it\,\Delta\omega)\prod_i^N\frac{\left(\beta_i'^2\tanh\frac{\lambda_i'}{2}+\beta_i''^2\tanh\frac{\mu_i''}{2}\right)^{-\frac{1}{2}}}{\left(\beta_i'^2\coth\frac{\lambda_i''}{2}+\beta_i''^2\coth\frac{\mu_i''}{2}\right)^{\frac{1}{2}}}$$
$$\frac{2\beta_i'\beta_i''\sinh\frac{\hbar\omega_i'}{2kT}}{(\sinh\lambda_i'\sinh\mu_i'')^{\frac{1}{2}}}\exp\left[-\frac{\beta_i'^2\beta_i''^2(d_i''-d_i')^2}{\left(\beta_i'^2\coth\frac{\mu_i''}{2}+\beta_i''^2\coth\frac{\lambda_i''}{2}\right)}\right]. \quad (18)$$

Except for the assumption of Eq. (10) that the same classification for normal coordinates can be applied to the two different electronic states, Eq. (18) is a general result.

One useful relation [15] can be obtained by integrating Eq. (7) over frequency v:

$$\int k_{b\to a}(v)\,dv=\frac{4\pi^2}{3\hbar ac}|\vec{R}_{ab}|^2\sum_{v'v''}v_{av'',bv'}\,P_{bv'}|\langle\Theta_{av''}|\Theta_{bv'}\rangle|^2. \quad (19)$$

Replacing $\nu_{av'' , bv'}$ by an average $\nu_{a,b}$ and using the relation, $\sum_{v' v''} P_{bv'} |\langle \Theta_{av''} | \Theta_{bv'} \rangle|^2 = 1$ (Appendix), we find

$$\int k_{b\to a}(\nu)\, d\nu = \frac{4\pi^2}{3\hbar a c} |\vec{R}_{ab}|^2 \, \nu_{a,b} \tag{20}$$

Introducing the oscillator strength, $f = \frac{4\pi \nu m}{3\hbar} |\langle \Psi_2 | \vec{r} | \Psi_1 \rangle|^2$, *Eq.* (20) *becomes*

$$\int k_{b\to a}(\nu)\, d\nu = \frac{\pi e^2}{m a c} f_{ab} \tag{21}$$

The integration in Eq. (18) can not be carried out without introducing approximations. We assume that the modifications of normal frequencies and coordinates between the two electronic states are small, i.e., ϱ_i and $\beta_i'^2(d_i'' - d_i')^2$ are small and have the same order of magnitude. To this approximation, we have [5],

$$\begin{aligned} &\frac{\beta_i'^2 \beta_i''^2 (d_i'' - d_i')^2}{\left(\beta_i' 2 \coth \frac{\mu_i''}{2} + \beta_i''^2 \coth \frac{\lambda_i'}{2}\right)} \\ &\qquad = \tfrac{1}{2} \beta_i'^2 (d_i'' - d_i')^2 \left[\coth \frac{\hbar\omega_i'}{2kT} - \operatorname{csch} \frac{\hbar\omega_i'}{2kT} \cosh\left(i t \omega_i' + \frac{\hbar\omega_i'}{2kT}\right)\right] \end{aligned} \tag{22}$$

$$\begin{aligned} &\left(\beta_i''^2 \coth \frac{\mu_i''}{2} + \beta_i'^2 \coth \frac{\lambda_i'}{2}\right) \left(\beta_i'^2 \tanh \frac{\lambda_i'}{2} + \beta_i''^2 \tanh \frac{\mu_i''}{2}\right) \\ &\qquad = \frac{4 \beta_i'^2 \beta_i''^2 \sin^2\mathrm{h}\, \frac{1}{2}(\lambda_i' + \mu_i'')}{\sinh \mu_i'' \sinh \lambda_i'} \end{aligned} \tag{23}$$

and

$$\frac{\sinh \frac{\hbar\omega_i'}{2kT}}{\sinh\left(\frac{\hbar\omega_i'}{2kT} + \frac{1}{2} i t \varrho_i \omega_i'\right)} = \exp\left(-\tfrac{1}{2} i t \varrho_i \omega_i' \coth \frac{\hbar\omega_i'}{2kT}\right). \tag{24}$$

Combining Eq. (22)–(24) with Eq. (18), we obtain the molecular absorption coefficient as:

$$\begin{aligned} k_{b\to a}(\nu) = \frac{4\pi^2 \nu}{3\hbar a c} |\vec{R}_{ab}|^2 \int_{-\infty}^{\infty} dt \exp\Bigg\{ & i \Delta\omega t - \frac{it}{2} \sum_i^N \varrho_i \omega_i' \coth \frac{\hbar\omega_i'}{2kT} - \tfrac{1}{2} \sum_i^N \beta_i'^2 \\ & (d_i'' - d_i')^2 \left[\coth \frac{\hbar\omega_i'}{2kT} - \operatorname{csch} \frac{\hbar\omega_i'}{2kT} \cosh\left(i t \omega_i' + \frac{\hbar\omega_i'}{2kT}\right)\right]\Bigg\} \end{aligned} \tag{25}$$

Next we define $\bar{\omega}'$ and $\bar{\phi}'$ by the following equation:

$$\sum_i^N \tfrac{1}{2} \beta_i'^2 (d_i'' - d_i')^2 \operatorname{csch} \frac{\hbar\omega_i'}{2kT} \cos\left(\omega_i' t - \frac{i\hbar\omega_i'}{2kT}\right) = S \operatorname{csch} \frac{\hbar\bar{\omega}'}{2kT} \cos(\bar{\omega}' t - \bar{\phi}') \tag{26}$$

where $S = \frac{1}{2} \sum_i^N \beta_i'^2 (d_i'' - d_i')^2$ and let $z = \bar{\omega}' t - \bar{\phi}'$ and $y = S \operatorname{csch} \frac{\hbar\bar{\omega}'}{2kT}$. Using these relations, the molecular absorption coefficient can be expressed as:

$$\begin{aligned} k_{b\to a}(\nu) = \frac{4\pi^2 \nu}{3\hbar a c \bar{\omega}'} |\vec{R}_{ab}|^2 \exp & \left[- i P \bar{\phi}' - \tfrac{1}{2} \sum_i^N \beta_i'^2 (d_i'' - d_i')^2 \coth \frac{\hbar\omega_i'}{2kT}\right] \\ & \int_{-\infty}^{\infty} dz \exp(y \cos z - i P z) \end{aligned} \tag{27}$$

where P is defined by the equation,

$$P=\frac{1}{\overline{\omega}'}\left[\Delta\omega-\tfrac{1}{2}\sum_{i}^{N}\varrho_i\omega_i'\coth\frac{\hbar\omega_i'}{2kT}\right]. \tag{28}$$

The integral in Eq. (25) has been evaluated by Lax [16]. Using his result, we obtain:

$$k_{b\to a}(v)=\frac{8\pi^3 v}{3\hbar a c\overline{\omega}'}|\vec{R}_{ab}|^2\exp\left[-iP\overline{\phi}'-\tfrac{1}{2}\sum_{i}^{N}\beta_i'^2(d_i''-d_i')^2\coth\frac{\hbar\omega_i'}{2kT}\right]I_P(y) \tag{29}$$

where $I_P(y)$ is the Bessel functions of imaginary argument [17];

$$I_P(y)=\frac{1}{2\pi}\int_{0}^{2\pi}dx\exp(iPx+y\cos x). \tag{30}$$

Eq. (29) gives the molecular absorption coefficient of molecules dissolved in a crystalline medium as a function of radiation frequency v, and thus will give the shape of the absorption curve for a particular electronic transition. Although the above derivation is for the molecular absorption coefficient of molecules dissolved in crystalline media, it can be applied to the calculation of the absorption coefficient of solute molecules dissolved in liquid media, if we consider the solute molecules to librate [4] in a site formed by solvent molecules. Eq. (29) has been applied to the systems of Br_2 and I_2 dissolved in various solvents [18].

If we are interested in the shape of absorption curves for an electronic transition accompanied by a particular intra-molecular vibrational transition, say $(b, v_k')\to(a, v_k'')$, by repeating the above processes, we obtain:

$$\begin{aligned}k_{bv_k'\to av_k''}(v)=\frac{4\pi^2 v}{3\hbar a c}|\vec{R}_{ab}|^2 P_{bv_k'}|\langle\Theta_{av_k''}|\Theta_{bv_k'}\rangle|^2\int_{-\infty}^{\infty}dt\exp(it\Delta\omega')\prod_{i}^{N}{}'\\ \frac{2\beta_i'\beta_i''\sinh\frac{\hbar\omega_i'}{2kT}}{(\sinh\lambda_i'\sinh\mu_i'')^{\frac{1}{2}}}\cdot\frac{\left(\beta_i'^2\tanh\frac{\lambda_i'}{2}+\beta_i''^2\tanh\frac{\mu_i''}{2}\right)^{-\frac{1}{2}}}{\left(\beta_i'^2\coth\frac{\lambda_i'}{2}+\beta_i''^2\coth\frac{\mu_i''}{2}\right)^{\frac{1}{2}}}\\ \cdot\exp\left[-\frac{\beta_i'^2\beta_i''^2(d_i''-d_i')^2}{\left(\beta_i'^2\coth\frac{\mu_i''}{2}+\beta_i''^2\coth\frac{\lambda_i'}{2}\right)}\right]\end{aligned} \tag{31}$$

corresponding to Eq. (18), and

$$\begin{aligned}k_{bv_k'\to av_k''}(v)=\frac{8\pi^3 v}{3\hbar a c\overline{\omega}'}|\vec{R}_{ab}|^2 P_{bv_k'}|\langle\Theta_{av_k''}|\Theta_{bv_k'}\rangle|^2 I_{P'}\left(S'\operatorname{csch}\frac{\hbar\overline{\omega}'}{2kT}\right)\\ \exp\left[-P'\overline{\phi}'-\tfrac{1}{2}\sum_{i}^{N}{}'\beta_i'^2(d_i''-d_i')^2\coth\frac{\hbar\omega_i'}{2kT}\right]\end{aligned} \tag{32}$$

corresponding to Eq. (29), where $S'=\tfrac{1}{2}\sum_{i}^{N}{}'\beta_i'^2(\mathrm{d}_i''-\mathrm{d}_i')^2$,

$P'=\frac{1}{\overline{\omega}'}\left[\Delta\omega'-\tfrac{1}{2}\sum_{i}^{N}{}'\varrho_i\omega_i'\coth\frac{\hbar\omega_i'}{2kT}\right]$ and $\Delta\omega'=\Delta\omega+\sum_{k}[(v_k''+\tfrac{1}{2})\omega_k''-(v_k+\tfrac{1}{2})\omega_k']$.

$|\langle\Theta_{av_k''}|\Theta_{bv_k'}\rangle|^2$ represents the Franck-Condon factor of the intramolecular vibration.

The shape of emission curves can be discussed in a similar manner and to save the space, its discussion will not be produced here.

3. Discussion

In our previous investigation [5], an expression has been derived for the radiationless transition probability based on the non-stationary character of the Born-Oppenheimer approximation, and at low temperatures it can be expressed as:

$$W_a = \sum_i^N \frac{\pi\omega_i''}{\overline{\omega}''\hbar^3} |R_i(ab)|^2 \exp\left[-\tfrac{1}{2}\sum_j \beta_j'^2 (d_j''-d_j')^2 \coth\frac{\hbar\omega_j'}{2kT}\right] \left[\frac{S^{P_i^+}}{\Gamma(1+P_i^+)} + \frac{S^{P_i^-}}{\Gamma(1+P_i^-)}\exp\left(-\frac{\hbar\omega_i''}{kT}\right)\right] \tag{33}$$

where

$$R_i(ab) = -\hbar^2 \left\langle \Phi_a \left| \frac{\partial}{\partial Q_i} \right| \Phi_b \right\rangle \tag{34}$$

and

$$P_i^{\pm} = -\frac{1}{\overline{\omega}''}\left[\omega_{ba} \pm \omega_i'' - \sum_j \tfrac{1}{2}\varrho_j\omega_j' \coth\frac{\hbar\omega_j'}{2kT}\right]. \tag{35}$$

$\Gamma(x)$ in Eq. (33) respresents the gamma function. From Eq. (33) we can see that the radiationless transition probability depends very much on S which in turn is related to the modifications of normal coordinates between the two electronic states. In view of our lack of knowledge of normal coordinates and frequencies of local modes between the two electronic states in which the transition occurs, it is difficult to carry out the calculation of the radiationless transition probability accurately. From the present investigation, we can see that by measuring the absorption coefficient as a function of radiation frequencies ν, one can determine the transition moment $\vec{R}_{ab}$ from the area of the absorption curve $k_{b\to a}(\nu)$ vs ν, by the relation of Eq. (20), and one can determine S from Eq. (29) or from Eq. (37) and Eq. (40) given below. Once the modification of normal coordinates has been determined, one can calculate the radiationless transition probability rather accurately from Eq. (33).

At low temperatures where $S \operatorname{csch}\frac{\hbar\overline{\omega}'}{2kT}$ in Eq. (29) is very small, we can use the following expansion to approximate the Bessel functions [17]:

$$I_p(y) = \frac{\left(\frac{y}{2}\right)^p}{\Gamma(p+1)}\left[1 + \frac{\left(\frac{y}{2}\right)^2}{(1+p)} + \frac{\left(\frac{y}{2}\right)^4}{(1+p)(2+p)} + \cdots\right]. \tag{36}$$

To the first order approximation for the Bessel functions, Eq. (29) becomes:

$$k_{b\to a}(\nu) = \frac{8\pi^3\nu}{3\hbar a c\overline{\omega}'} |\vec{R}_{ab}|^2 \exp\left[-\tfrac{1}{2}\sum_i^N \beta_i'^2 (d_i''-d_i')^2 \coth\frac{\hbar\omega_i'}{2kT}\right]\frac{S^P}{\Gamma(P+1)}. \tag{37}$$

In this case the absorption maximum occurs at

$$\omega_{\max} = \omega_{ab} + S\overline{\omega}' - \tfrac{1}{2}\sum_i^N \varrho_i\omega_i' \coth\frac{\hbar\omega_i'}{2kT}.$$

At high temperatures where csch $\frac{\hbar\overline{\omega}'}{2\mathrm{kT}}$ is not small and y is larger than unity, we can use the assymptotic expansion for the Bessel functions [17].

$$I_p(y)=\frac{e^y}{(2\pi y)^{\frac{1}{2}}}\left\{1+\sum_{n=1}^{\infty}\frac{(-1)^n\,[4p^2-1]\,[4p^2-3^2]\cdots[4p^2-(2n-1)^2]}{n!\,(8y)^n}\right\} \tag{38}$$

If P values are not very small, to a very good approximation, we can replace Eq. (38) by [17]:

$$I_p(y)=\frac{1}{(2\pi y)}\exp\left(y-\frac{p^2}{2y}\right). \tag{39}$$

Substituting Eq. (39) into Eq. (40), we obtain:

$$\begin{aligned}k_{b\to a}(v)=&\frac{8\pi^3 v}{3\hbar a c\overline{\omega}'}|\vec{R}_{ab}|^2\frac{1}{(2\pi y)^{\frac{1}{2}}}\\ &\cdot\exp\left[y-\frac{P^2}{2y}+\frac{P\hbar\overline{\omega}'}{2kT}-\tfrac{1}{2}\sum_i^N\beta_i'^2\,(d_i''-d_i')^2\coth\frac{\hbar\omega_i'}{2kT}\right].\end{aligned} \tag{40}$$

In this case the absorption maximum occurs at $\omega_{\max}=\omega_{ab}-\frac{1}{2}\sum_i^N \varrho_i\omega_i'\coth\frac{\hbar\omega_i'}{2kT}$ $+S\overline{\omega}'\frac{\hbar\overline{\omega}'}{2kT}\operatorname{csch}\frac{\hbar\overline{\omega}'}{2kT}$ and Eq. (40) can be expressed in a Gaussian form.

From the above discussion, one can notice that the broadening is mainly caused by a change in normal coordinates of solute molecules plus local environment between the two electronic states and that the modification of normal frequencies between the two electronic states can at most shift the absorption or emission maximum. One can also see that when there is an overlap of two or more absorption bands, one can determine S and $\overline{\omega}'$ for each electronic transition from the absorption curve and hence the absorption coefficient for each electronic transition as a function of frequency. In this way the oscillator strength

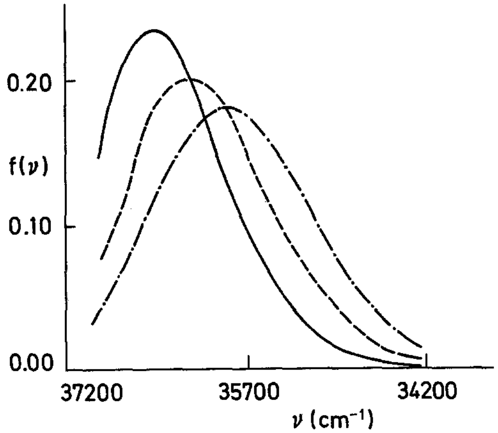

Fig. 1. $f(v)=\frac{3\hbar a c\overline{\omega}' k_{bv'\to av''}(v)}{8\pi^2 v|\vec{R}_{ab}|^2\,|\langle X_{av''}|X_{bv''}\rangle|^2}$ vs v at $\overline{\omega}'=300\,\mathrm{cm}^{-1}$. ——— $S=3$. - - - - - - - - $S=4$. — · — · — $S=5$.

for each electronic transition can be obtained by plotting the absorption coefficient of that electronic transition against frequency. To show an application of the above derivation, we choose as solute molecules, diatomic molecules with $\omega_{ab} = 38000\,\mathrm{cm}^{-1}$, $\omega' = 1900\,\mathrm{cm}^{-1}$, and $\omega'' = 1020\,\mathrm{cm}^{-1}$. In Fig. 1, we plot $\dfrac{3\hbar a c \bar{\omega}' k_{bv' \to av''}(\nu)}{8\pi^2 \nu\, |\vec{R}_{ab}|^2\, |\langle X_{av''} | X_{bv'} \rangle|^2}$ against frequency at very low temperatures and at various S values for $\bar{\omega}' = 300\,\mathrm{cm}^{-1}$. It can be seen that both the band width and the absorption maximum depends on S. As S increases, the band width increases and the absorption maximum shifts toward the longer wavelength.

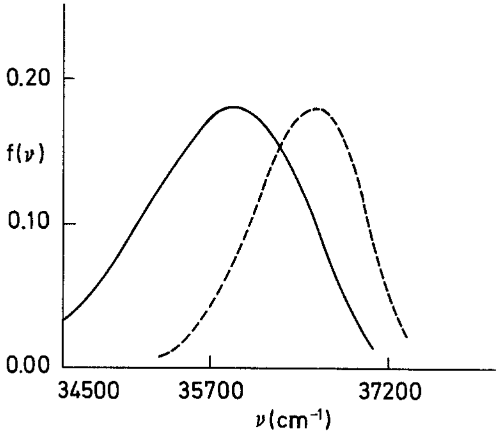

Fig. 2. $f(\nu) = \dfrac{3\hbar a c \bar{\omega}' k_{bv' \to av''}(\nu)}{8\pi^2 \nu |\vec{R}_{ab}|^2\, |\langle X_{av''} | X_{bv'} \rangle|^2}$ vs ν at $S = 5$. ——— $\bar{\omega}' = 300\,\mathrm{cm}^{-1}$. --------- $\bar{\omega}' = 200\,\mathrm{cm}^{-1}$

Appendix

To prove that $\sum\limits_{v'v''} P_{bv'}\, |\langle \Theta_{av''} | \Theta_{bv'} \rangle|^2 = 1$, we observe

$$\sum_{v'v''} P_{bv'}\, |\langle \Theta_{av''} | \Theta_{bv'} \rangle|^2 = \sum_{v'v''} \prod_i^N \left(\sinh \frac{\hbar\omega_i'}{2kT}\right) \exp\left[-(v_i' + \tfrac{1}{2})\,\frac{\hbar\omega_i'}{kT}\right] \cdot \iint_{-\infty}^{\infty} dQ_i\, d\bar{Q}_i\, X^*_{av_i''}(Q_i'')\, X^*_{av_i''}(\bar{Q}_i'')\, X_{bv_i'}(Q_i')\, X_{bv_i'}(\bar{Q}_i')\,. \tag{A-1}$$

Making use of the Mehler's formula, we find

$$\sum_{v'v''} P_{bv'} |\langle \Theta_{av''} | \Theta_{bv'} \rangle|^2 = \operatorname*{Lim}_{t\to 0} \prod_i^N \frac{2\beta_i'\beta_i'' \sinh \dfrac{\hbar\omega_i'}{2kT}}{\left(4\pi^2 \sinh t \sinh \dfrac{\hbar\omega_i'}{kT}\right)^{\frac{1}{2}}} \iint_{-\infty}^{\infty} dQ_i\, d\bar{Q}_i \cdot \exp\left\{-\frac{\beta_i''^2}{4}\left[(Q_i'' + \bar{Q}_i'')^2 \tanh\frac{t}{2} + (Q_i'' - \bar{Q}_i'')^2 \coth\frac{t}{2}\right] - \frac{\beta_i'^2}{4}\left[(Q_i' + \bar{Q}_i')^2 \tanh\frac{\hbar\omega_i'}{2kT} + (Q_i' - \bar{Q}_i')^2 \coth\frac{\hbar\omega_i'}{2kT}\right]\right\}. \tag{A-2}$$

Integration of Eq. (A-2) gives

$$\sum_{v'v''} P'_{bv'}\,|\langle\Theta_{av''}|\Theta_{bv'}\rangle|^2 = \operatorname*{Lim}_{t\to 0}\prod_{i}^{N} \frac{2\beta'_i\beta''_i \sinh\dfrac{\hbar\omega'_i}{2kT}}{\left(\sinh\dfrac{t}{2}\sinh\dfrac{\hbar\omega'_i}{kT}\right)^{\frac{1}{2}}} \tag{A-3}$$

$$\cdot\frac{\left(\beta_i'^2\coth\dfrac{\hbar\omega'_i}{2kT}+\beta_i''^2\coth\dfrac{t}{2}\right)^{-\frac{1}{2}}}{\left(\beta_i'^2\tanh\dfrac{\hbar\omega'_i}{2kT}+\beta_i''^2\tanh\dfrac{t}{2}\right)^{\frac{1}{2}}}\cdot\exp\left[-\frac{\beta_i'^2\beta_i''^2(d''_i-d'_i)^2}{\left(\beta_i'^2\coth\dfrac{t}{2}+\beta_i''^2\coth\dfrac{\hbar\omega'_i}{2kT}\right)}\right].$$

By setting $t\to 0$, it can easily be shown that

$$\sum_{v'v''} P_{bv'}\,|\langle\Theta_{av''}|\Theta_{bv'}\rangle|^2 = 1\,.$$

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