A Displaced Harmonic Oscillator Model for the Time-resolved Emission Spectra

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(Received March 30, 1981)

In a displaced harmonic oscillator model for an energy-accepting mode, analytical expressions for the time-resolved emission intensity distribution are derived for both the allowed and vibronically induced electronic transitions. In the case of the vibronically induced transition, the inducing mode as well as the accepting mode is assumed to undergo a collisional vibrational relaxation. A linear vibrational quantum-number-dependence of the electronic and collisional vibrational relaxation constants is assumed. Model calculations of the time-resolved emission-intensity distribution for a molecular system are performed using the expressions derived. The calculated time-resolved emission spectra of benzene in the vapor phase after an excitation to a single vibronic level semi-quantitatively account for the experimental results.

It is well known that time-resolved spectroscopy plays an important role in elucidating the dynamics as well as the static behavior of vibronically excited molecules. The time-resolved emission spectra have been reported by several authors. Hochstrasser and Wessel¹⁾ have observed the time-resolved fluorescence of anthracene in mixed crystals of low temperatures. Werkhoven *et al.*²⁾ have investigated the vibrational redistribution effects by analyzing the time-resolved emission spectrum of the isolated pyrene molecule. Swords and Phillips³⁾ have observed the nano-second time-resolved emission of benzene in order to study the collisional processes.

The purpose of this paper is to develop a theory for the time-resolved emission of a molecular system. The time-resolved emission intensity distribution is expressed as the emission intensity weighted by the time-dependent population of the single vibronic level in the excited state. In other words, the observed intensity distribution is governed by both the Franck-Condon factor and the kinetics of the excited state. The time-dependence of the population is determined by solving the kinetic equation in the excited state in which the vibronic level undergoes the electronic relaxation, the collisional vibrational relaxation, and/or the vibrational redistribution among the vibrational modes.

A similar time-dependent theory has been proposed for analyzing the time-resolved absorption spectra of electronically excited molecules.⁴⁻⁶⁾ Fleming *et al.*⁷⁾ have developed a theory for the time-resolved emission spectra of molecules in which the single vibronic emission-intensity distribution of the δ-function form is adopted. A master-equation approach to the time-dependent luminescence during the vibrational relaxation has been used by Seshadri and Kenkre.⁸⁾

In Theory section, analytical expressions for the time-resolved emission-intensity distribution are given for both the allowed and vibronically induced electronic transitions in the displaced harmonic oscillator model for an accepting mode. Both Lorentzian and Gaussian single vibronic level intensity distributions are assumed. It is assumed that the electronic and vibrational relaxation constants are linear functions of the vibrational quantum number. This assumption is valid for a molecular system with low excited vibronic levels. In the case of the vibronically induced transition, the inducing mode as well as the accepting mode is assumed to undergo a collisional deactivation. In discussion, model calculations of the time-resolved emission intensity distribution are performed. A nonexponential fluorescence decay can be predicted if the rate of vibrational relaxation is fast compared with those of the radiation and electronic relaxations. For the vibronically induced transition, a fast fluorescence decay can be expected upon the excitation to the vibronic level of the inducing mode.

Theory

We will consider an electronic transition, $a \leftarrow b$, of a molecular system. The time-resolved emission-intensity distribution, $P_{ab}(\nu, t)$, as a function of the optical frequency, ν, and time, t, is given by:⁷⁾

$$P_{ab}(\nu, t) = \sum_{\{v\}}\sum_{\{v'\}} I_{a\{v\},b\{v'\}}(\nu)\chi_{b\{v'\}}(t), \tag{1}$$

where $I_{a\{v\},v\{b'\}}(\nu)$ represents the intensity of the emission from a single vibronic level of the b electronic state, $b\{v'\}$, to that of the ground state $a\{v\}$, and $\chi_{b\{v'\}}(t) = \prod_j \chi_{bv'_j}(t)$, the population of the molecule in the single vibronic level, $b\{v'\}$, at time t.

The $\chi_{bv'}(t)$ population, depends on the dynamical behavior in the electronic state, such as the electronic and/or vibrational relaxations. χ satisfies the following equation for the molecular system undergoing the electronic and vibrational relaxations after the optical transition:

$$\frac{\mathrm{d}\chi_{bv'}(t)}{\mathrm{d}t} = C_{bv'}(t) - K_{bv',bv'}\chi_{bv'}(t) - \sum_{v''} R_{bv'bv''}\chi_{bv''}(t), \tag{2}$$

where K is a diagonal matrix element involving the radiative and nonradiative decay constants; R represents the vibrational relaxation matrix in the electronic state b, and $C_{bv}(t)$ is a function related to the optical excitation. Equation 2 can be solved by using i) the diagonalization method of the matrix⁹⁾ or ii) the generating-function method.¹⁰⁾ In this paper, we use the generating-function method. Assuming, for the rates of vibrational and nonradiative relaxations, linear dependences on the vibrational quantum num-

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bers of the vibronic levels, *i.e.* $k_{\mathrm{v}}^{\mathrm{c}}{}'=v'k^{\mathrm{c}}$ and $k_{\mathrm{v}}^{\mathrm{n}}{}'=k+v'k^{\mathrm{n}}$ respectively, with the effect of the radiative decay being included as the k parameter, the solution of Eq. 2 is given by:4,5)

$$\chi_{bv'}(t) = \frac{v_0'!}{v'!(v_0'-v')!}\left\{\frac{k^{\mathrm{c}}}{k^{\mathrm{c}}+k^{\mathrm{n}}}[1-\exp\{-(k^{\mathrm{c}}+k^{\mathrm{n}})t\}]\right\}^{v_0'-v'}$$
$$\exp[-kt-v'(k^{\mathrm{c}}+k^{\mathrm{n}})t], \tag{3}$$

where an optical exitation to a single vibronic level, bv_0', at $t=0$ has been assumed.

Two types of emission, dipole-allowed transitions and vibronically induced transitions, are taken into account of in this paper.

Dipole-allowed Transition. In the case of the Lorentzian single-vibronic-level-intensity distribution, the intensity from the vibronic level, bv', to av is given by:

$$I_{av,bv'}(\nu) = \frac{4\pi\nu^3}{3\hbar c^3}|M_{ab}^0|^2|\langle\theta_{av}|\theta_{bv'}\rangle|^2\frac{\Gamma_{av,bv'}}{(\omega_{bv',av}-\nu)^2+\Gamma_{av,bv'}^2}, \tag{4}$$

where M_{ab}^0, θ, $\Gamma_{ab,bv'}$, and $\omega_{bv',av}$ represent the electronic transition moment evaluated at the equilibrium nuclear configuration in the initial electronic state, the nuclear wave function, the damping constant, and the energy gap between two single-vibronic levels, bv' and av, respectively. Using the transformation:

$$\frac{a}{x^2+a^2} = \frac{1}{2}\int_{-\infty}^{\infty}\mathrm{d}\tau\exp[-\mathrm{i}x\tau-a|\tau|], \tag{5}$$

and summing over the vibronic level, v, in the electronic state, a, Eq. 4 can be expressed as:

$$I_{a,bv'}(\nu) = \sum_v I_{av,bv'}(\nu)$$
$$= \frac{2\pi\nu^3}{3\hbar c^3}|M_{ab}^0|^2\int_{-\infty}^{\infty}\mathrm{d}\tau\exp[\mathrm{i}\nu\tau-\Gamma_{ab}|\tau|]$$
$$\langle\theta_{bv'}|\exp[-\mathrm{i}\hat{H}_b\tau/\hbar]\exp[\mathrm{i}\hat{H}_a\tau/\hbar]|\theta_{bv'}\rangle, \tag{6}$$

where $\hat{H}_{\mathrm{a}}$ and $\hat{H}_{\mathrm{b}}$ represent the nuclear Hamiltonian in the electronic states, a and b, respectively; the vibronic-level dependence of the damping constant is neglected *i.e.*, $\Gamma_{ab}\simeq\Gamma_{av,bv'}$.

In the displaced-harmonic-oscillator model (the other modes are assumed to be common in the electronic states a and b),

$$\hat{H}_b = \frac{\hbar\omega}{2}\{p^2+(q-\Delta)^2\} + \omega_{ba}, \tag{7a}$$

and

$$\hat{H}_a = \frac{\hbar\omega}{2}(p^2+q^2), \tag{7b}$$

where ω and Δ are the frequency and the displacement of the vibrational mode respectively, with ω_{ba} the electronic energy difference between two states, b and a. Equation 6 can be expressed as:

$$I_{a,bv'}(\nu) = \frac{2\pi\nu^3}{3\hbar c^3}|M_{ab}^0|^2\exp\left(-\frac{\Delta^2}{2}\right)\int_{-\infty}^{\infty}\mathrm{d}\tau$$
$$\exp\left[\mathrm{i}\tau(\nu-\omega_{ba})-\Gamma_{ab}|\tau|+\frac{\Delta^2}{2}\mathrm{e}^{\mathrm{i}\omega\tau}\right]$$
$$\sum_{n=0}^{v'}\frac{v'!(\Delta^2/2)^n}{(v'-n)!(n!)^2}(\cos\omega\tau-1)^n. \tag{8}$$

Substituting Eqs. 3 and 8 into Eq. 1, and summing over v', the time-resolved emission intensity for the allowed transition can be expressed as:

$$P_{ab}(\nu,t) = \frac{4\pi\nu^3}{3\hbar c^3}|M_{ab}^0|^2\exp\left(-\frac{\Delta^2}{2}\right)\exp(-kt)$$
$$\sum_{l=0}^{\infty}\sum_{n=0}^{v_0'}\sum_{r=0}^{2n}\frac{v_0'!(2n)!\left(\frac{\Delta^2}{2}\right)^{l+n}}{l!(n!)^2(v_0'-n)!(2n-r)!r!}$$
$$\exp[-n(k^{\mathrm{c}}+k^{\mathrm{n}})t]\left\{\frac{k^{\mathrm{c}}}{k^{\mathrm{c}}+k^{\mathrm{n}}}+\frac{k^{\mathrm{n}}}{k^{\mathrm{c}}+k^{\mathrm{n}}}\right.$$
$$\left.\exp[-(k^{\mathrm{c}}+k^{\mathrm{n}})t]\right\}^{v_0'-n}\frac{\Gamma_{ab}}{\{\nu-\omega_{ba}+\omega(l+n-r)\}^2+\Gamma_{ab}^2}. \tag{9}$$

By assuming the homogeneous broadening, the Lorentzian band shape has so far been used. In the case of an inhomogeneous broadening, the band shape is usually expressed by a Gaussian form. After the Fourier transformation, the band-shape function, $A(x)$, is given by:

$$A(x) = \frac{1}{2\sqrt{\pi a}}\int_{-\infty}^{\infty}\exp\left[-\mathrm{i}x\tau-\frac{\tau^2}{4a}\right]\mathrm{d}\tau, \tag{10}$$

where $a=\ln 2/\tilde{\Gamma}^2$, in which $\tilde{\Gamma}$ is the half width at the half-maximum. In this case, the time-resolved emission-intensity distribution can be formulated by using a method similar to that described above. The result is written as:

$$P_{ab}(\nu,t) = \frac{4\pi\nu^3}{3\hbar c^3}|M_{ab}^0|^2\exp\left(-\frac{\Delta^2}{2}\right)\exp(-kt)$$
$$\sum_{l=0}^{\infty}\sum_{n=0}^{v_0'}\sum_{r=0}^{2n}\frac{v_0'!(2n)!\left(\frac{\Delta^2}{2}\right)^{l+n}}{l!(n!)^2(v_0'-n)!(2n-r)!r!}\exp[-n(k^{\mathrm{c}}+k^{\mathrm{n}})t]$$
$$\left\{\frac{k^{\mathrm{c}}}{k^{\mathrm{c}}+k^{\mathrm{n}}}+\frac{k^{\mathrm{n}}}{k^{\mathrm{c}}+k^{\mathrm{n}}}\exp[-(k^{\mathrm{c}}+k^{\mathrm{n}})t]\right\}^{v_0'-n}$$
$$\exp[-a\{\nu-\omega_{ba}+\omega(l+n-r)\}^2]. \tag{11}$$

Vibronically Induced Transition. The emission intensity from the single vibronic level, $bv_{\mathrm{d}}'v_{\mathrm{i}}'$, to $av_{\mathrm{d}}v_{\mathrm{i}}$ is given by:

$$I_{bv_d'v_i',av_dv_i}(\nu) = \frac{4\pi\nu^3}{3\hbar c^3}\left(\frac{\partial M_{ab}}{\partial q_i}\right)_{q_i=0}|\langle\theta_{av_i}|q_i|\theta_{bv_i'}\rangle|^2$$
$$|\langle\theta_{av_d}|\theta_{bv_d'}\rangle|^2\frac{\Gamma_{ab}}{(\omega_{bv_d'v_i',av_dv_i}-\nu)^2+\Gamma_{av}^2}, \tag{12}$$

where i and d specify the inducing and accepting modes respectively; the Lorentzian band shape has been assumed. In Eq. 12, one inducing mode and one accepting mode were assumed (*i.e.*, the other modes are disregarded), and the v_i-dependence of the damping constant was neglected.

We will consider a model system in which the accepting and inducing modes consist of a displaced harmonic oscillator and a harmonic oscillator with no frequency change and no displacement respectively. After summing over the vibronic levels, v_i and v_d, Eq. 12 can be expressed as:

$$I_{a,bv_d'v_i'}(\nu) = C(\nu)\exp\left(-\frac{\Delta^2}{2}\right)\int_{-\infty}^{\infty}\mathrm{d}\tau$$
$$\exp\left[-\mathrm{i}(\nu-\omega_{ba})\tau-\Gamma_{ab}|\tau|+\frac{\Delta^2}{2}\exp(\mathrm{i}\omega\tau)\right]$$

$$\{(1+v_i')\exp(-\mathrm{i}\omega_i\tau)+v_i'\exp(\mathrm{i}\omega_i\tau)\}$$

$$\sum_{n=0}^{v_d'}\frac{v_d'!\Delta^{2n}}{(v_d'-n)!(n!)^2}(\cos\omega\tau-1)^n, \tag{13}$$

where ω_i represents the frequency of the inducing mode; the constant, $C(\nu)$, is given by:

$$C(\nu)=\nu^3\left(\frac{\partial M_{ab}}{\partial q_i}\right)_{q_i=0}\Big/3\hbar c^3\beta_i \text{ in which } \beta_i=(\omega_i/\hbar)^{1/2}.$$

The time-resolved emission intensity in a case in which the molecular system is excited to a singlet vibronic level $bv_{d0}'v_{i0}'$ at $t=0$ can be expressed as:

$$P_{ab}(\nu,t)=C(\nu)\exp\left(-\frac{\Delta^2}{2}\right)\exp(-kt)$$

$$\sum_{l=0}^{\infty}\sum_{n_d=0}^{v'_{d0}}\sum_{n_i=0}^{v'_{i0}}\sum_{r=0}^{n_d2}\frac{v'_{i0}}{n_i!(v'_{i0}-n_i)!}$$

$$\left[\frac{k_i^c}{k_i^c+k_i^n}\{1-\exp[-(k_i^c+k_i^n)t]\}\right]^{v'_{i0}-n}$$

$$\exp[-n_i(k_i^c+k_i^n)t-n_d(k^n+k^c)t]$$

$$\frac{(-1)^r v'_{i0}!(2n_d)!\left(\frac{\Delta^2}{2}\right)^{l+n_i}}{l!(n_d!)^2(v'_{d0}-n_i)!(2n_d-r)!r!}$$

$$\left\{\frac{k^c}{k^c+k^n}+\frac{k^n}{k^c+k^n}\exp[-(k^c+k^n)t]\right\}^{v'_{d0}-n_d}$$

$$\left[(n_i+1)\frac{\Gamma_{ab}}{\{\nu-\omega_{ba}+\omega(l+n_d-r)+\omega_i\}^2+\Gamma_{ab}^2}\right.$$

$$\left.+n_i\frac{\Gamma_{ab}}{\{\nu-\omega_{ba}+\omega(l+n_d-r)-\omega_i\}^2+\Gamma_{ab}^2}\right], \tag{14}$$

where a linear dependence of the relaxation constants on the vibrational quantum number of the inducing mode as well as the accepting mode has been assumed; $k^c_{v_i'}=v_i'k_i^c$, $k^n_{v_i'}=k_i^0+v_i'k_i^n$; and $k\equiv k+k_i^0$. The time-resolved emission-intensity distribution in which the vibronic band shape is expressed by the Gaussian form can easily be derived.

Model Calculations and Discussion

Figures 1 and 2 show the time-dependence of the emission spectra calculated by using Eq. 9 in the case of $\nu=\omega_{ba}$. The ordinate expresses the emission intensity relative to that at $t=0$. The excitation to the first vibronic level, $v_0'=1$, from the lowest level in the ground state is assumed. Figures 1 and 2 correspond to the slow and fast vibrational-relaxation cases respectively. The parameters used for Figs. 1 and 2 are $k=10^8\,\mathrm{s}^{-1}$, $k^c=2\times10^7\,\mathrm{s}^{-1}$. $k^n=4\times10^7\,\mathrm{s}^{-1}$, and $\Delta=0.14$, and $k=2\times10^7\,\mathrm{s}^{-1}$, $k^c=10^8\,\mathrm{s}^{-1}$, $k^n=4\times10^7\,\mathrm{s}^{-1}$, and $\Delta=0.14$, respectively. In Fig. 1, a single exponential decay is shown, while in Fig. 2, a nonexponential time-dependence is seen. The appearance of the nonexponential decay can be qualitatively explained by examining Eq. 9. For simplicity, we consider the weak coupling limit to be where $\Delta\to0$. Then, in the case of ν near ω_{ba}, Eq. 9 for $v_0'=1$ can be expressed as:

$$P(\nu,t)\propto\left\{\frac{k^c}{k^c+k^n}\exp(-kt)+\frac{k^n}{k^c+k^n}\right.$$

$$\left.\exp[-(k+k^n+k^c)t]\right\}\frac{\Gamma}{(\nu-\omega_{ba})^2+\Gamma^2}. \tag{15}$$

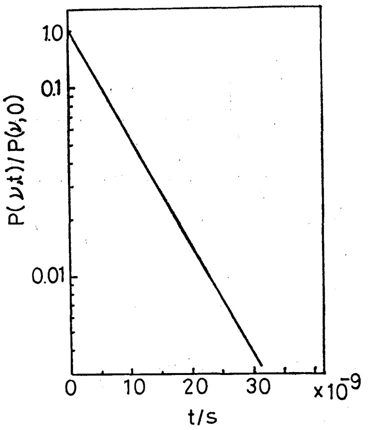

Fig. 1. Time-dependence of the emission intensity in the case of the slow collisional vibrational relaxation. The intensity relative to that at $t=0$ is plotted by using Eq. 9 for $\nu=\omega_{ba}$. The excitation to the first vibronic level $v_0'=1$ from the lowest level in the ground state is assumed. The parameters used are $k=10^8\,\mathrm{s}^{-1}$, $k^c=2\times10^7\,\mathrm{s}^{-1}$, $k^n=4\times10^7\,\mathrm{s}^{-1}$, and $\Delta=0.14$.

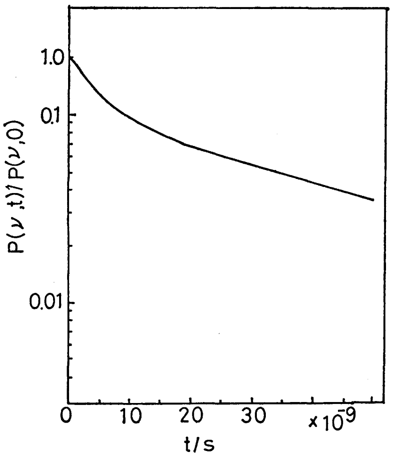

Fig. 2. Time-dependence of the emission intensity in the case of the fast collisional vibrational relaxation. The excitation and emission monitoring conditions are the same in Fig. 1. The parameters used are $k=2\times10^7\,\mathrm{s}^{-1}$ and $k^c=10^8\,\mathrm{s}^{-1}$, and the other parameters are the same in Fig. 1. When $k<k^c$ and $k^n\approx k^c$, the bi-exponential decay of fluorescence may be observed as shown in this figure.

Equation 15 indicates that, when $k\gg k^c+k^n$ (or $k^c\gtrless k^n$), $P(\nu,t)$ obeys a single exponential decay, while when $k\ll k^c+k^n$ and $k^n\approx k^c$, a bi-exponential fluorescence decay can be expected.

Figures 3 and 4 show model calculations of the time-resolved emission-intensity distribution as a function of the frequency for a model system corresponding to a vibronically induced optical transition such as ${}^1\mathrm{A}_{1g}\leftarrow{}^1\mathrm{B}_{2u}$ of benzene. The emission intensity distribution relative to its maximum value, $\tilde{P}(\omega_0,t)$, is plotted by using Eq. 14. In Figs. 3 and 4, the intensity distribution is plotted in the case of the excitation to a vibronic level with $v'_{d0}=1$ and $v'_{i0}=0$, and with $v'_{d0}=v'_{i0}=1$, respectively. The parameters used are $\omega=993\,\mathrm{cm}^{-1}$, $k^n=3.67\times10^6\,\mathrm{s}^{-1}$, and $\Delta=$

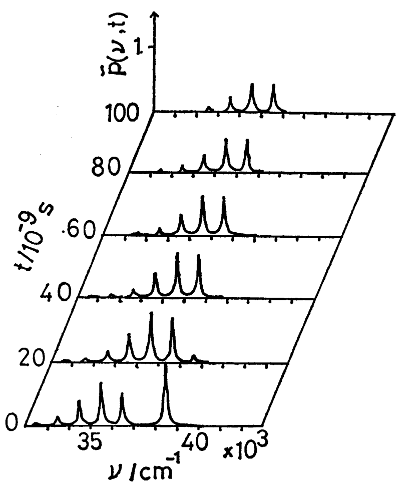

Fig. 3. Calculated time-resolved emission intensity distribution for a model system corresponding to a vibronically induced optical transition. The emission intensity distribution relative to its maximum value, $\tilde{P}(\nu,t)=P(\nu,t)/P(\nu,t)_{\max}$ is plotted by using Eq. 12. The excitation to the vibronic level $v'_{d0}=1$ and $v'_{i0}=0$ is assumed. The parameters used are $\omega_{ab}=38090$ cm^{-1}, $\omega=993$ cm^{-1}, $\omega_i=522$ cm^{-1}, $\Delta=1.43$, $k^n=3.67\times10^6$ s^{-1}, $k_i^n=1.35\times10^6$ s^{-1}, $k=7.8\times10^6$ s^{-1}, and $\Gamma_{ab}=75$ cm^{-1}.

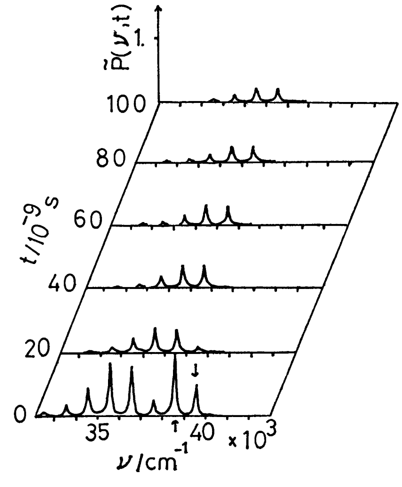

Fig. 4. Calculated time-resolved emission intensity distribution. The excitation to the vibronic level with $v'_{d0}=1$ and $v'_{i0}=1$ is assumed. The parameters used are the same in Fig. 3. The downward and upward arrows indicate the origins of the progressions, $6^1_0 1^1_n$ and $6^1_2 1^1_n$, respectively.

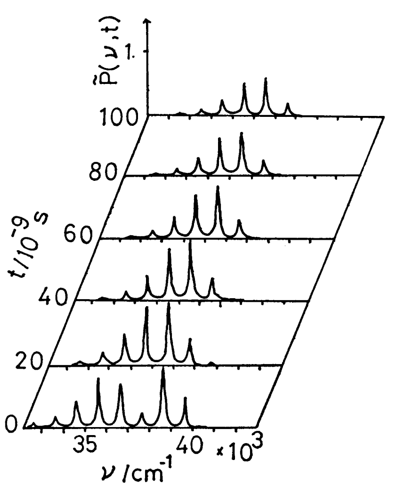

Fig. 5. Calculated time-resolved emission intensity distribution in the case of no collisional vibrational and electronic relaxations relevant to the inducing mode. The excitation to the vibronic level with $v'_{d0}=1$ and $v'_{i0}=1$ is assumed. The parameters used are the same in Fig. 3 except for $k_i^c=k_i^n=0$.

1.43[11] for the accepting mode (ν_1); $\omega_i=522$ cm^{-1} [12] and $k_i^n=1.35\times10^6$ s^{-1} for the inducing mode (ν_6), and $k=7.8\times10^6$ s^{-1},[13] $\omega_{ab}=38090$ cm^{-1}, and $\Gamma_{ab}=75$ cm^{-1}. These parameters are taken from the calculated and experimental data for the $^1A_{1g}\leftarrow{}^1B_{2u}$ transition of benzene. The collisional vibrational-relaxation constants, which depend on pressure, are assumed to be $k^c=0.1\times10^9$ s^{-1} and $k_i^c=0\,2\times10^9$ s^{-1}. In Fig. 3, the diffuse spectrum as a function of the emission frequency at $t=0$ is shown, and we can see no band peak corresponding to the 1←1 vibronic transition for the accepting mode near 37600 cm^{-1}. This can be explained by the vanishingly small Franck-Condon overlap for $\Delta^2/2\simeq1$. It is shown that the intensity decay in Fig. 4 is faster than that in Fig. 3. This is qualitatively due to the fact that, in the case of the one-vibrational quantum excitation of the inducing mode, not only are there two emission-decay paths, but also there are a collisional vibrational relaxation and a nonradiative decay path involving the inducing mode compared with the case of the zero-quantum excitation.

It is shown in Fig. 4 that the emission spectrum at $t=0$ consists of two progressions, $6^1_0 1^1_n$ and $6^1_2 1^1_n$, where n=0, 1,⋯(their origins are indicated by downward and upward arrows respectively), while after time enough to reach the steady state, the emission-intensity distribution consists of one progression, $6^0_1 1^0_n$. These spectral features have been observed by Blondeau and Stockburger[15] and by Swords and Phillips.[3] Blondeau and Stockburger have also studied the resonance flourescence spectra of benzene in the vapor phase, and have compared them with the fluorescence spectra from a Boltzmann distributed vibrational levels in the first excited state; the resonance fluorescence from the $6^1 1^1$ level consists of two progressions, $6^1_0 1^1_n$ and $6^1_2 1^1_n$; the main progression in the equilibrated fluorescence by the 253.7 nm excitation is $6^0_1 1^1_n$. The time-resolved fluorescence spectra of benzene in the gas phase have been reported by Swords and Phillips.[3] In the time-resolved fluorescence spectra observed at $t=70$ ns after the excitation at 257.25 nm in which two major transitions, $6^0_1 1^1_0 16^2_0$ and $6^1_0 16^3_1$, are involved, the bands related to the inducing mode decrease, while those belonging to the $6^0_1 1^0_n$ progression increase, in intensity compared with those observed at $t=20$ ns.

In Fig. 5, the relative emission-intensity distribution in the case of no collisional vibrational and electronic relaxations related to the inducing mode, $k_i^c=k_i^n=0$, is shown. The emission-intensity distribution is plotted by using Eq. 14. The other parameters used are the same as in Fig. 4. We can see that the vibronic-intensity distribution in Fig. 5 after a long time is different from that in Fig. 4. In Fig. 5, the band peak at about 38600 cm^{-1}, which corresponds to the 0←1 transition for the inducing mode, still remains because of the absence of any relaxation for the mode.

Finally, we should mention the value of the damping constant. The damping constant is expressed by a sum of two terms: $\Gamma_{ab}=1/2(\Gamma_{aa}+\Gamma_{bb})+\Gamma^{(d)}_{ab,at}$,16) where Γ_{aa} and Γ_{bb} are the population-decay constants of the a and b states respectively, and where $\Gamma^{(d)}_{ab,ab}$ denotes the pure dephasing constant originating from elastic interaction processes between molecules and heat bath. A value of Γ_{ab} close to that observed in nanosecond time-resolved emission spectroscopy3) has been used in this paper. In other words, the value does not always represent the real damping constant, for there are no corrections for the optical detection or for the inhomogeneous broadening.

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