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Theory of Time-resolved Photon Absorption by Molecules after Radiationless Transition. Application to Benzene after $S_2 \rightsquigarrow S_0$.

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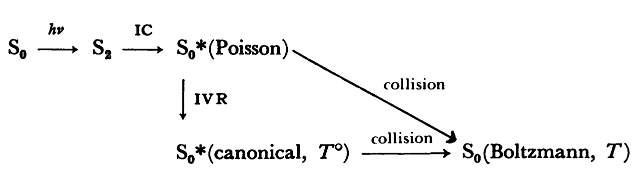
Expressions for the intensity of the time-resolved absorption (TRA) by molecules after radiationless transition have been derived. It is assumed that a non-equilibrium vibronic distribution is realized after the radiationless transition and relaxes to the equilibrium one. Two types of non-equilibrium distributions, Poisson distribution and canonical distribution with temperature higher than that of the heat bath are taken into account. The theory developed is applied to the TRA spectra ($S_3 \leftarrow S_0$) of benzene after the internal conversion $S_2 \rightsquigarrow S_0$ (N. Nakashima and K. Yoshihara, *J. Chem. Phys.* **79**, 2727, (1983)). It is shown that the expression for the intensity in the Sulzer-Wieland model is involved in the expression derived using the canonical distribution.

Recently Nakashima and Yoshihara[1] have observed the time-resolved absorption (TRA) spectra of gaseous benzenes after excitation to the $S_2(^1B_{1u})$ state. It has been shown that the transient spectra consist of the $S_3(^1E_{1u}) \leftarrow S_0(^1A_{1g})$ transition at high temperatures. The spectra reflect the vibronic energy distribution after the internal conversion from the S_2 state to the ground state. The spectral changes with time are mainly brought about by collisional deactivation processes of the hot benzene by inert gas and unexcited benzene. The transient spectrum at $t=0$ was explained by using the Sulzer-Wieland model[2] originally applied to absorption spectra of diatomic molecules with a large potential displacement at high temperatures. This model has been applied to analysis of the high temperature ultraviolet absorption spectra of polyatomic molecules in shock waves by Astholz *et al.*[3] and by Hippler *et al.*[4] as well. To our knowledge, however, there exists no any sufficient theoretical explanation for the applicability of the Sulzer-Wieland model to the polyatomic molecules in the highly excited vibronic states. The purpose of this paper is to develop a theory of the time-resolved absorption spectra of hot molecules produced by radiationless transition, and to apply the theory to the time-resolved absorption spectra of benzene observed previously.[1]

The TRA spectra of molecules strongly depend on the initial non-equilibrium vibronic energy distribution which is realized in a time scale of observation. The following scheme can account for the observed TRA spectra.



Two types of the vibronic energy distributions different from the thermal equilibrium distribution can be expected after radiationless transitions. One is a Poisson (intramolecular) vibronic energy distribution,[5,6] and the other is a canonical distribution characterized by a higher temperature $T°$ than that of the heat bath T. The former distribution is formed just after internal conversion (IC) following laser excitation. One of the evidences for the intramolecular vibronic energy distribution is seen in the TRA spectra ($^3B_{1g} \leftarrow {}^3B_{2u}$) after excitation to the S_1 state of naphthalene in vapor.[7] A vibronic structure associated with the triplet-triplet absorption appears in the TRA spectra just after the intersystem crossing takes place. A canonical vibronic energy distribution with $T°>T$, on the other hand, is expected to be realized when an intramolecular vibrational redistribution takes place following the radiationless transition. Taking into account the two types of the initial distributions we derive expressions for the absorption intensity of the TRA spectra of polyatomic molecules. In deriving the expressions for the intensity, it is assumed that the initial distributions relax to the Boltzmann distribution due to collisional deactivations and that the collision rates vary linearly with respect to the vibrational quantum number.[8] It is shown that the expression for the time-resolved absorption intensity of the molecular system with a canonical distribution as the initial distribution involves the expression derived by Sulzer and Wieland as a special case. A model calculation of the TRA spectra using the derived expressions supports the conclusion given in the previous paper:[1] the initial vibronic distribution is of the canonical one with a high temperature.

Theory

Let us consider a time-resolved absorption process from the vibrationally hot ground electronic state *a* to an electronically excited state *b*. The initial, vibrational state in the non-equilibrium condition is produced by internal conversion $S_2 \rightsquigarrow S_0^*$. The intensity per unit length, $D_{ab}(\omega_R, t)$, as a function of time, t, and the laser frequency, ω_R is expressed in the form,[5]

$$D_{ab}(\omega_R, t) = \sum_{\{v\}} k_{a\{v\}}(\omega_R)\chi_{\{v\}}(t), \tag{1}$$

where $k_{a\{v\}}(\omega_R)$ represents the absorption coefficient from a single vibronic level $\{v\}$ in the ground state *a*, and $\chi_{\{v\}}(t)=\prod_j^N \chi_{v_j}(t)$ in which $\chi_{v_j}(t)$ denotes the vibronic energy distribution of the optical vibrational mode *j* per unit volume at time t, and N is the number of the optical modes whose potential forms between a and b states are different. The distribution $\chi_{\{v\}}(t)$ depends on the dynamical behavior and the initial distribution. In this paper we consider Poisson and canonical distributions. First we treat the time-evolution of molecules characterized by a Poisson distribution which relaxes to the equilibrium distribution with T. In a previous paper,[6] a theoretical treatment of the TRA spectroscopy was presented in the case of the relaxation of the Poisson distribution to the lowest vibronic state in the low temperature limit.

Poisson Vibronic Energy Distribution. We assume that at $t=0$ a non-equilibrium state originating from an intramolecular radiationless transition has been prepared. It has been shown that the distribution of the vibrational mode j with frequency ω_j after the radiationless transition from the lowest vibronic level is expressed as[5,6]

$$\chi_{v_j}(0) = S_{0_j'v_j} \exp\left[-v_j\bar{\beta}\hbar\omega_j + \frac{\bar{\Delta}_j^{\,2}}{2}\{1-\exp(-\bar{\beta}\hbar\omega_j)\}\right], \quad (2)$$

where the displaced harmonic oscillator model has been used. $S_{0_j'v_j}$ is the optical Franck-Condon factor between $0_j'$ and v_j states, and given by $S_{0_j'v_j}=(\bar{\Delta}_j/\sqrt{2})^{2v_j}$ $\exp(-\bar{\Delta}_j^2/2)/v_j!$. $\bar{\Delta}_j$ is the displacement of the mode j in the equilibrium points between the relevant two electronic states. $\bar{\beta}$ in Eq. (2) is a parameter which is determined from the condition of the energy conservation for the radiationless transition. Equation (2) satisfies $\sum_{v_j}\chi_{v_j}(0)=1$. Equation (2) can be rewritten in the form of a Poisson distribution,

$$\chi_{v_j}(0) = \frac{\alpha_j^{\,v_j}}{v_j!}\exp(-\alpha_j), \quad (3)$$

with the average vibrational quantum number[5] given by

$$\alpha_j = \frac{\bar{\Delta}_j^{\,2}}{2}\exp(-\bar{\beta}_j\hbar\omega_j). \quad (4)$$

In the case of the radiationless transition from v_j' level, the expression for the distribution can approximately be represented by Eq. (2) in which $S_{0_j'v_j}$ is replaced by $S_{v_j'v_j}$.

If we assume that the molecular system undergoes only a collisional vibrational energy exchange between the system and the heat bath, and interactions between the vibrational modes of the system are neglected, *i.e.* each vibrational mode relaxes to its equilibrium distribution, then the time-dependent distribution χ_{v_j} satisfies the master equation,[8]

$$\begin{aligned}\frac{\mathrm{d}\chi_{v_j}(t)}{\mathrm{d}t} = {} & \kappa_j\{1-\exp(-\theta_j)\}^{-1}[v_j\exp(-\theta_j)\chi_{v_j-1}(t) \\ & - \{v_j+(v_j+1)\exp(-\theta_j)\}\chi_{v_j}(t) \\ & + (v_j+1)\chi_{v_j+1}(t)],\end{aligned} \quad (5)$$

where κ_j is the transition probability per unit time between levels $v_j=1$ and 0 of mode j, and $\theta_j=\hbar\omega_j/kT$. T denotes temperature of the heat bath consisting of unexcited benzenes. The master equation with the initial condition as given by Eq. (3) is solved as[8]

$$\begin{aligned}\chi_{v_j}(\tau_j) = {} & \left\{\frac{1-\exp(\theta_j)}{\exp(-\tau_j)-\exp(\theta_j)}\right\} \\ & \times \exp\left[\frac{\alpha_j\exp(-\tau_j)\{\exp(\theta_j)-1\}}{\exp(-\tau_j)-\exp(\theta_j)}\right] \\ & \times \left\{\frac{1-\exp(-\tau_j)}{\exp(\theta_j)-\exp(-\tau_j)}\right\}^{v_j}\mathrm{L}_{v_j}(y_j),\end{aligned} \quad (6)$$

in which $\mathrm{L}_{v_j}(y_j)$ is the Laguerre polynomials,

$$y_j = \frac{\alpha_j\exp(-\tau_j)\{\exp(\theta_j)-1\}^2}{\{1-\exp(-\tau_j)\}\{\exp(-\tau_j)-\exp(\theta_j)\}}, \quad (7)$$

and

$$\tau_j = \kappa_j t\{1-\exp(-\theta_j)\}. \quad (8)$$

In the case in which the vibronic band is characterized by a Lorentzian envelope, the absorption coefficient $k_{a\{v\}}$ in Eq. (1) is given by

$$k_{a\{v\}}(\omega_R) = \frac{4\pi\omega_R}{3\hbar c}\mathrm{Re}\sum_{\{v''\}}\frac{|R_{bv'',av}|^2}{\mathrm{i}(\omega_{bv'',av}-\omega_R)+\Gamma_{ba}}, \quad (9)$$

where $\omega_{bv'',av}$ is the frequency difference between two vibronic levels, bv'' and av, $R_{bv'',av}$, the matrix element of the electric transition dipole moment, and Γ_{ba}, the damping constant associated with the interactions between the optical and other vibrational modes. We invoke the adiabatic and Condon approximations since we are interested in the allowed electronic transition $S_3(\mathrm{E_{1u}})\leftarrow S_0(\mathrm{A_{1g}})$ of benzene. In these approximations, Eq. (9) can be expressed as

$$k_{a\{v\}}(\omega_R) = C\sum_{\{v''\}}\frac{\Gamma_{ba}|\langle\eta_{bv''}|\eta_{av}\rangle|^2}{(\omega_{bv'',av}-\omega_R)^2+\Gamma_{ba}^2}, \quad (10)$$

where $C=4\pi\omega_R|R^0_{ab}|^2/(3\hbar c)$, and η denote the vibrational wavefunctions. We adopt a displaced harmonic oscillator model for the optical modes.

Carrying out the summation over the vibronic states in Eq. (1), we express the absorption coefficient, Eq. (10), as:

$$\begin{aligned}k_{a\{v\}}(\omega_R) = {} & \frac{C}{2}\exp(-S)\int_{-\infty}^{\infty}\mathrm{d}\xi\exp[\mathrm{i}\xi(\omega_{ba}-\omega_R)-\Gamma_{ba}|\xi| \\ & + \sum_{j=1}^{N}\frac{\Delta_j^{\,2}}{2}\exp(\mathrm{i}\omega_j\xi)]\sum_{n_1=0}^{v_1}\cdots\sum_{n_j=0}^{v_j}\cdots\sum_{n_N=0}^{v_N}\prod_j \\ & \times\frac{v_j!\,\Delta_j^{\,2n_j}}{(v_j-n_j)!\,(n_j!)^2}(\cos\omega_j\xi-1)^{n_j},\end{aligned} \quad (11)$$

where S $(=\sum_{j=1}^{N}\bar{\Delta}_j^2/2)$ is the coupling strength in the low temperature limit. Substituting Eqs. (6) and (11) into Eq. (1), we can derive an analytical expression for the time-dependent intensity:

$$\begin{aligned}D_{ab}(\omega_R,\tau) = {} & C\exp[-S-\sum_{j=1}^{N}a(\tau_j)]\sum_{n_1=0}^{\infty}\cdots\sum_{n_j=0}^{\infty}\cdots\sum_{n_N=0}^{\infty} \\ & \times\sum_{l_1=0}^{\infty}\cdots\sum_{l_j=0}^{\infty}\cdots\sum_{l_N=0}^{\infty}\ \sum_{m_1=0}^{l_1}\cdots\sum_{m_j=0}^{l_j}\cdots\sum_{m_N=0}^{l_N}\ \sum_{k_1=0}^{l_1-m_1}\cdots\sum_{k_j=0}^{l_j-m_j}\cdots\sum_{k_N=0}^{l_N-m_N}\end{aligned}$$

$$\times \sum_{p_1=0}^{2(m_1+k_1)} \cdots \sum_{p_j=0}^{2(m_j+k_j)} \cdots \sum_{p_N=0}^{2(m_N+k_N)} \Bigg[\prod_{j=1}^{N} \binom{l_j}{m_j} \binom{l_j-m_j}{k_j} \binom{2m_j+2k_j}{p_j}$$

$$\times \frac{(-1)^{p_j}}{n_j!\,(m_j+k_j)!\,(l_j-m_j)!} \left(\frac{\Delta_j{}^2}{2}\right)^{n_j+m_j+k_j}$$

$$\times a(\tau_j)^{l_j-m_j} \left\{ \frac{1-\exp(-\tau_j)}{\exp(\theta_j)-1} \right\}^{m_j} \Bigg]$$

$$\times \frac{\Gamma_{ba}}{\{\omega_{ba}+\sum_{j=1}^{N}\omega_j(n_j+k_j+m_j-p_j)-\omega_R\}^2+\Gamma_{ba}^2}, \tag{12}$$

where $\tau\equiv\{\tau_j\}$, $j=1, 2, \cdots, N$, and

$$a(\tau_j) = \frac{\alpha_j \exp(-\tau_j)\{\exp(\theta_j)-1\}}{\exp(\theta_j)-\exp(-\tau_j)}. \tag{13}$$

A detailed derivation of Eq. (12) is presented in Appendix A.

In the case in which $a(\tau_j)>1$ is satisfied, it is appropriate to use the following approximate expression for the intensity:

$$D_{ab}(\omega_R, \tau) = C \exp[-S] \sum_{n_1=0}^{\infty} \cdots \sum_{n_j=0}^{\infty} \cdots \sum_{n_N=0}^{\infty} \; \sum_{l_1=0}^{\infty} \cdots \sum_{l_j=0}^{\infty} \cdots \sum_{l_N=0}^{\infty}$$

$$\times \sum_{m_1=0}^{l_1} \cdots \sum_{m_j=0}^{l_j} \cdots \sum_{m_N=0}^{l_N} \; \sum_{k_1=0}^{l_1-m_1} \cdots \sum_{k_j=0}^{l_j-m_j} \cdots \sum_{k_N=0}^{l_N-m_N} \; \sum_{p_1=0}^{m_1+k_1} \cdots \sum_{p_j=0}^{m_j+k_j} \cdots \sum_{p_N=0}^{m_N+k_N}$$

$$\times \sum_{q_1=0}^{p_1} \cdots \sum_{q_j=0}^{p_j} \cdots \sum_{q_N=0}^{p_N} \; \sum_{r_1=0}^{m_1+k_1-p_1} \cdots \sum_{r_j=0}^{m_j+k_j-p_j} \cdots \sum_{r_N=0}^{m_N+k_N-p_N}$$

$$\times \Bigg\{ \prod_{j=1}^{N} \frac{(-1)^{p_j-q_j+r_j}}{n_j!\,(m_j+k_j)!} \left(\frac{\Delta_j{}^2}{2}\right)^{n_j+m_j+k_j}$$

$$\times \binom{l_j}{m_j} \binom{l_j-m_j}{k_j} \binom{m_j+k_j}{p_j} \binom{p_j}{q_j} \binom{m_j+k_j-p_j}{r_j}$$

$$\times \left[\frac{1-\exp(-\tau_j)}{\exp(\tau_j)-1} \right]^{m_j} \exp\left[-\frac{\{l_j-m_j-a(\tau_j)\}^2}{2a(\tau_j)} \right] \Bigg\}$$

$$\times \frac{\Gamma_{ba}}{\{\omega_{ba}+\sum_{j=1}^{N}\omega_j(n_j+k_j+m_j-p_j)-\omega_R\}^2+\Gamma_{ba}^2}. \tag{14}$$

Canonical Vibronic Energy Distribution. It is assumed that at $t=0$, a local equilibrium characterized by a canonical distribution with $T°$ ($>T$) has been prepared. The solution of the master equation Eq. (5) in this case is given[8] by

$$\chi_{v_j}(\tau_j) = \{1-\exp[-u(\tau_j)]\} \exp[-v_j u(\tau_j)], \tag{15}$$

with

$$u(\tau_j) = \log\left[\frac{\exp(-\tau_j)\{1-\exp(\theta_j-\theta_j{}^0)\}-\exp(\theta_j)\{1-\exp(-\theta_j{}^0)\}}{\exp(-\tau_j)\{1-\exp(\theta_j-\theta_j{}^0)\}-\{1-\exp(-\theta_j{}^0)\}} \right]. \tag{16}$$

The expression for the intensity of the TRA spectra can be written as

$$D_{ab}(\omega_R, \tau) = \frac{C}{2} \exp[-S(\tau)] \int_{-\infty}^{\infty} d\xi \exp\Bigg[i\xi(\omega_{ba}-\omega_R) - \Gamma_{ba}|\xi| + \sum_{j=1}^{N} \frac{\Delta_j{}^2\{n(\tau_j)+1\}}{2} \exp(i\omega_j\xi) + \sum_{j=1}^{N} \frac{\Delta_j{}^2 n(\tau_j)}{2} \exp(-i\omega_j\xi) \Bigg], \tag{17}$$

where $S(\tau)$, time dependent coupling strength, is defined as

$$S(\tau) = \sum_{j=1}^{N} \{2n(\tau_j)+1\} \frac{\Delta_j{}^2}{2}. \tag{18}$$

Equation (17) has the same structure as that of the absorption band shape in the equilibrium condition. In Eq. (17), $n(\tau_j)$, the time-dependent occupation number of the optical mode j, is given as

$$n(\tau_j) = [\exp\{u(\tau_j)\}-1]^{-1}. \tag{19}$$

From Eqs. (16) and (19), we obtain $n(0)=[\exp(\theta^0)-1]^{-1}$ and $n(\infty)=[\exp(\theta)-1]^{-1}$ which are the occupation numbers at the initial time and in the equilibrium state, respectively.

Applying the Tayler expansions to Eq. (17), and carrying out the integration of the resulting expression over ξ, we can derive an analytical expression for the intensity as

$$D_{ab}(\omega_R, \tau) = C \exp[-S(\tau)] \sum_{k_1=0}^{\infty} \cdots \sum_{k_j=0}^{\infty} \cdots \sum_{k_N=0}^{\infty} \; \sum_{l_1=0}^{\infty} \cdots \sum_{l_j=0}^{\infty} \cdots \sum_{l_N=0}^{\infty}$$

$$\times \left[\prod_{j=1}^{N} \frac{\left[\{n(\tau_j)+1\}\frac{\Delta_j{}^2}{2}\right]^{k_j} \left\{n(\tau_j)\frac{\Delta_j{}^2}{2}\right\}^{l_j}}{k_j!\; l_j!} \right]$$

$$\times \frac{\Gamma_{ba}}{\{\omega_{ba}+\sum_{j=1}^{N}\omega_j(k_j-l_j)-\omega_R\}^2+\Gamma_{ba}^2}. \tag{20}$$

Equation (20) can be applied to both weak and strong coupling cases in principle. A fast convergence for the summations over k_j and l_j in Eq. (20) can be expected for the weak coupling case in which $S(\tau)\leq 1$. In the strong coupling case in which $S(\tau)>1$, on the other hand, we cannot expect the fast convergence. The classification for these coupling cases depend on time, as well as temperature, the frequency of the mode and the potential displacement. In the time domain in which the strong coupling case is satisfied and further $\Gamma_{ba}^2<\sum_j \omega_j^2\Delta_j^2\{2n(\tau_j)+1\}$, it is better to use an approximate expression for the absorbance rather than Eq. (20). Neglecting Γ_{ba}, expanding $\exp(\pm i\omega_j\xi)$ to the second order of ξ in Eq. (17), and carrying out the integration of the equation over ξ we obtain

$$D_{ab}(\omega_R, \tau) = \frac{\sqrt{2\pi}C}{\sigma(\tau)} \exp\left[-\frac{\left(\omega_{ba}+\sum_{j=1}^{N}\frac{\omega_j\Delta_j{}^2}{2}-\omega_R\right)^2}{2\sigma^2(\tau)} \right], \tag{21}$$

where $\sigma(\tau)$, the time-dependent half-width of the TRA spectrum, is given as

$$\sigma(\tau) = \left[\sum_{j=1}^{N} \frac{\omega_j{}^2\Delta_j{}^2}{2} \{2n(\tau_j)+1\} \right]^{1/2}, \tag{22}$$

or

$$\sigma(\tau) = \left[\sum_{j=1}^{N} \frac{\omega_j{}^2\Delta_j{}^2}{2} \coth\frac{u(\tau_j)}{2} \right]^{1/2}. \tag{23}$$

It should be noted that the expression for the intensity in the Sulzer-Wieland model is involved in Eq. (21), that is, by setting $\tau=0$ in Eq. (21) we can obtain the expression given by Sulzer and Wieland[2] for one vibrational mode case:

$$D_{ab}(\omega_R, 0) \propto \left\{\tanh\frac{\hbar\omega}{2kT}\right\}^{1/2} \times \exp\left[-\tanh\frac{\hbar\omega}{2kT}\left\{\frac{\omega_{ba}+\omega\varDelta^2/2-\omega_R}{\omega\varDelta}\right\}^2\right]. \tag{24}$$

For the multimode case we can obtain the intensity expression simillar to that given by Asholz *et al.*[3]

Discussion

In order to clarify the initial vibronic distribution reflected in the TRA spectra we apply the derived expressions for the absorbance to benzene S_0^* produced by internal conversion after the $S_2 \leftarrow S_0$ excitation.[1] We shall first calculate the TRA spectra assuming that Poisson distribution is realized and relaxes to the equilibrium one. It is necessary to estimate the parameter set for constructing vibronic distribu tion given by Eq. (3) after the internal conversion ($^1B_{1u} \rightsquigarrow {}^1A_{1g}$). Though it is recognized that benzene in the $^1B_{1u}$ state is subjected to the pseudo Jahn-Teller effect and the geometry of the $^1B_{1u}$ state may belong to D_{2h} symmetry, we neglect the geometry reduction. We simply adopt a model in which there are two displaced optical modes, one is a carbon–carbon stretching mode with frequency $\omega_{\text{C-C}}=1000\,\text{cm}^{-1}$, and the other is a carbon-hydrogen stretching mode with $\omega_{\text{C-H}}=3000\,\text{cm}^{-1}$. It was tentatively assumed that $\varDelta_{\text{C-C}}=1.5$ and $\varDelta_{\text{C-H}}=0.3$ for the dimensionless displacements.[9,10] Using these parameters we obtained $\alpha_{\text{C-C}}=6.8$ and $\alpha_{\text{C-H}}=12.5$ in Eq. (3) from the constraint of the energy conservation of the internal conversion with the electronic energy gap of 6.43 eV. Figure 1 shows the TRA spectra ($S_3 \leftarrow S_0$) calculated by using Eq. (12). Here the same molecular parameters of the S_3 state as those of the S_2 state were assumed.[11] The TRA spectra for the case of $\tau=0$, 0.5 (which corresponds to $t \simeq 0.5\times10^{-6}$ s) and 1 are indicated by solid, broken and dotted-broken lines, respectively. The remaining parameters have been assumed as follows: $\kappa_{\text{C-C}}=10^6\,\text{s}^{-1}$, $\kappa_{\text{C-H}}=2\times10^4\,\text{s}^{-1}$, $\Gamma_{ba}=500\,\text{cm}^{-1}$, and $T=300$ K. In Fig. 1 we can see the vibronic structure originating from the C–C stretching mode in the wavelength region of 180~200 nm even at early times. The carbon–hydrogen mode is, on the other hand, almost inactive in the TRA spectra because of its small magnitude of the displacement though this mode acts as the effective accepting mode for the internal conversion.[12] The TRA spectrum calculated at $\tau=0$ is different from the structureless spectrum which has been observed by Nakashima and Yoshihara.[1]

Assuming that the canonical distribution with temperature higher than that of the heat bath is produced and relaxes to the equilibrium one, we now calculate the TRA spectra of benzene by using Eq. (21). Figure 2 shows the calculated spectra. The solid, broken and dotted-broken lines denote the TRA spectra at $\tau=0$, 0.5 ($t \simeq 0.14\times10^{-6}$ s) and 1, respectively. Here we, for simplicity, adopt an approximate expression for the half-width given by Eq. (23): $\sigma(0) \approx (\overline{\omega\varDelta})^2 kT^\circ/\hbar\bar{\omega}$ at $\tau=0$, where the bars indicate magnitudes of the quantities averaged over the vibrational modes: we use $\overline{\omega\varDelta}=2600\,\text{cm}^{-1}$, $\bar{\omega}=200\,\text{cm}^{-1}$, $T^\circ=3400$ K and $T=300$ K which were estimated in a previous paper.[1] The collisional vibrational transition probability κ is taken as $6\times10^6\,\text{s}^{-1}$. The closed circles in Fig. 2 denote experimental values for 2 Torr benzene at $\tau=0$.[1] In order to compare the experimental values with the calculated ones at $\tau=0$ the calculated molar extinction coefficient at 230 nm was taken to be equal to the experimental one. From Fig. 2 we can see that the initial vibronic distribution is of the canonical one rather than the Poisson one. In other words, lifetime of the vibronic states just after the internal conversion

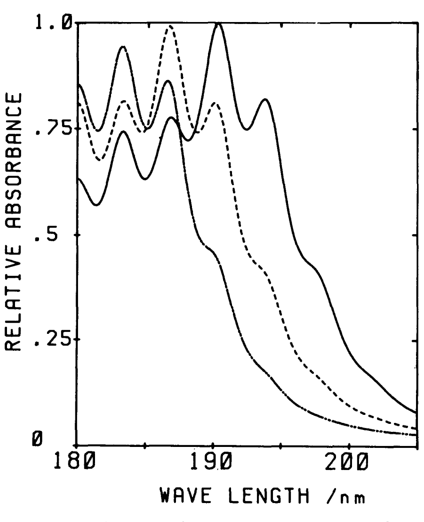


Fig. 1. The calculated TRA spectra ($S_3 \leftarrow S_0$) of benzene. Poisson distribution is adopted as the initial vibronic distribution. The calculation has been carried out by using Eq. (12). The solid, broken and dotted-broken lines denote TRA spectra at $\tau=0$, 0.5 and 1, respectively. See text for the parameter set.

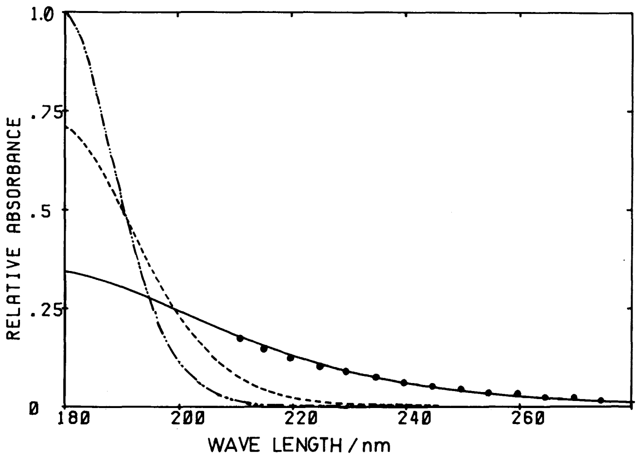


Fig. 2. The calculated TRA spectra of benzene when a canonical distribution is adopted as the initial distribution. The calculation has been carried out by using Eq. (21). The solid, broken and dotted-broken lines denote TRA spectra at $\tau=0$, 0.5, and 1, respectively. The closed circles represent experimental values for 2 Torr benzene at $\tau=0$.

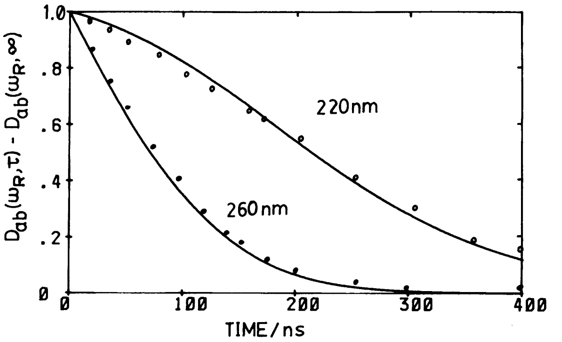


Fig. 3. The calculated decay curves, $D_{ab}(\omega_R, \tau)-D_{ab}(\omega_R, \infty)$ at 220 and 260 nm. The measured values of the absorbances of the 2 Torr (1 Torr≈133.322 Pa) benzene and 10 Torr propane are denoted at 220 nm (○) and 260 nm (●). See text for detail.

$S_2 \rightsquigarrow S_0$ is too short to observe the Poisson distribution because of a fast vibrational redistribution in the high vibronic state of S_0. The vibrational redistribution is caused by intramolecular couplings such as the ones caused by anharmonicities and mode mixings. This explains why the low vibrational frequency and the large potential displacement within the harmonic approximation has to be included in simulating the TRA spectra of benzene with the canonical distribution.

In Fig. 3 are shown decay curves, $D_{ab}(\omega_R,\tau)-D_{ab}(\omega_R,\infty)$ at 220 and 260 nm calculated by using Eq. (21). The same parameters as those in Fig. 2 are adopted except for $\kappa=9\times10^6\,\mathrm{s}^{-1}$. The measured absorbances of the 2 Torr benzene and 10 Torr propane are plotted at 220 nm (○) and 260 nm (●).[13] The calculated decay curves are in fairly good agreement with the observed values. This suggests the validity of the linear collisional deactivation mechanism for the vibrationally hot benzene. In the previous paper, an energy-dependent energy transfer model has been adopted in order to explain the decay curves.

In summary we have developed a theory of the TRA spectra of molecules after radiationless transition. Two types of the initial vibronic distribution, Poisson and canonical ones are taken into account. The theory developed has been applied to the TRA spectra ($S_3 \leftarrow S_0$) of benzene produced by the internal conversion $S_2 \rightsquigarrow S_0$. It has been shown that the canonical distribution can explain the transient behavior of benzene after the internal conversion. Finally it should be noted that we can semi-quantitatively explain both time-resolved spectra and decay curves of benzenes in a foreign gas by using the derived expressions for the time-dependent absorption intensity. These expressions can be applied to the investigation of the relaxation processes in hot molecules, such as hexafluorobenzene[14] and other polyatomic molecules as well.

Appendix

A. Time-resolved absorption intensity for a Poisson distribution.

In this appendix, analytical expressions for the intensity $D_{ab}(\omega_R,\tau)$ are derived for the molecular system characterized by a Poisson distribution. Two cases depending on the magnitudes of the coupling strength $\sum_j \Delta_j^2/2 \gtrless 1$ will be considered.

Substituting Eqs. (6) and (11) into Eq. (1) yields

$$
\begin{aligned}
D_{ab}(\omega_R, \tau) &= \frac{C}{2}\sum_{v_1=0}^{\infty}\cdots\sum_{v_j=0}^{\infty}\cdots\sum_{v_N=0}^{\infty} \\
&\times \exp(-S)\int_{-\infty}^{\infty}\mathrm{d}\xi \exp\Big[\mathrm{i}\xi(\omega_{ba}-\omega_R)-\Gamma_{ba}|\xi| \\
&+\sum_{j=1}^{N}\frac{\Delta_j^2}{2}\exp(\mathrm{i}\omega_j\xi)\Big]\Bigg[\prod_{j=1}^{N}\mathrm{L}_{v_j}\{\Delta_j^2(1-\cos\omega_j\xi)\} \\
&\times \frac{1-\exp(\theta_j)}{\exp(-\tau_j)-\exp(\theta_j)}\exp\left[-\frac{\alpha_j\exp(-\tau_j)\{\exp(\theta_j)-1\}}{\exp(\theta_j)-\exp(-\tau_j)}\right] \\
&\times \left\{\frac{1-\exp(-\tau_j)}{\exp(\theta_j)-\exp(-\tau_j)}\right\}^{v_j}\mathrm{L}_{v_j}(y_j)\Bigg],
\end{aligned}
\tag{A.1}
$$

or

$$
\begin{aligned}
D_{ab}(\omega_R, \tau) &= \frac{C}{2}\exp(-S) \\
&\times \left\{\prod_{j=1}^{N}\exp\left[-\frac{\alpha_j\exp(-\tau_j)\{\exp(\theta_j)-1\}}{\exp(\theta_j)-\exp(-\tau_j)}\right]\right\} \\
&\times \int_{-\infty}^{\infty}\mathrm{d}\xi\exp\Big[\mathrm{i}\xi(\omega_{ba}-\omega_R)-\Gamma_{ba}|\xi|+\prod_{j=1}^{N}\frac{\Delta_j^2}{2}\exp(\mathrm{i}\omega_j\xi)\Big] \\
&\times \prod_{j=1}^{N}\frac{1-\exp(\theta_j)}{\exp(-\tau_j)-\exp(\theta_j)}\sum_{v_j=0}^{\infty}\sum_{n_j=0}^{v_j}\frac{v_j!\,x_j^{n_j}(\xi)}{(v_j-n_j)!\,(n_j!)^2} \\
&\times \sum_{m_j=0}^{v_j}\frac{v_j!\,(-y_j)^{m_j}}{(v_j-m_j)!\,(m_j!)^2}\left\{\frac{1-\exp(-\tau_j)}{\exp(\theta_j)-\exp(-\tau_j)}\right\}^{v_j},
\end{aligned}
\tag{A.2}
$$

where $x_j(\xi)=\Delta_j^2(\cos\omega_j\xi-1)$, $y_j=\alpha_j\exp(-\tau_j)\{\exp(\theta_j)-1\}^2/[\{1-\exp(-\tau_j)\}\{\exp(-\tau_j)-\exp(\theta_j)\}]$, and the following expression for the Laguerre polynomials has been used,

$$
\mathrm{L}_v(y)=\sum_{m=0}^{v}\frac{v!\,(-y)^m}{(v-m)!\,(m!)^2}. \tag{A.3}
$$

Applying the identity

$$
\frac{1}{n!}=\frac{1}{2\pi\mathrm{i}}\oint\frac{\exp(z)}{z^{n+1}}\mathrm{d}z \tag{A.4}
$$

to Eq. (A. 2) and after taking summations over m_j and n_j, one obtains

$$
\begin{aligned}
D_{ab}(\omega_R, \tau) &= \frac{C}{2}\exp(-S) \\
&\times \left\{\prod_{j=1}^{N}\exp\left[-\frac{\alpha_j\exp(-\tau_j)\{\exp(\theta_j)-1\}}{\exp(\theta_j)-\exp(-\tau_j)}\right]\right\} \\
&\times \int_{-\infty}^{\infty}\mathrm{d}\xi\exp\Big[\mathrm{i}t(\omega_{ba}-\omega_R)-\Gamma_{ba}|\xi|+\prod_{j=1}^{N}\frac{\Delta_j^2}{2}\exp(\mathrm{i}\omega_j\xi)\Big] \\
&\times \prod_{j=1}^{N}\frac{1-\exp(\theta_j)}{\exp(-\tau_j)-\exp(\theta_j)}A_j(\xi),
\end{aligned}
\tag{A.5}
$$

where

$$
\begin{aligned}
A_j(\xi) &= \left(\frac{1}{2\pi\mathrm{i}}\right)^2\oint\mathrm{d}z_1\oint\mathrm{d}z_2\frac{\exp(z_1+z_2)}{z_1z_2}\sum_{v_j=0}^{\infty}\left\{1+\frac{x_j(\xi)}{z_1}\right\}^{v_j} \\
&\times \left(1-\frac{y_j}{z_2}\right)^{v_j}\left\{\frac{1-\exp(-\tau_j)}{\exp(\theta_j)-\exp(-\tau_j)}\right\}^{v_j}.
\end{aligned}
\tag{A.6}
$$

Assuming convergence of the summation over v_j in Eq. (A. 6), one can express Eq. (A. 6) as

$$\Lambda_j(\xi) = \left(\frac{1}{2\pi \mathrm{i}}\right)^2 \oint \mathrm{d}z_1 \oint \mathrm{d}z_2 \frac{\exp(z_1+z_2)}{z_1 z_2(1-A_j)} \times \left\{1-\frac{A_j x_j(\xi)}{(1-A_j)z_1}+\frac{A_j y_j}{(1-A_j)z_2}+\frac{A_j x_j(\xi) y_j}{(1-A_j)z_1 z_2}\right\}^{-1}, \tag{A.7}$$

where

$$A_j = \{1-\exp(-\tau_j)\}/\{\exp(\theta_j)-\exp(-\tau_j)\}. \tag{A.8}$$

Equation (A. 7) can be expanded as

$$\Lambda_j(\xi) = \left(\frac{1}{2\pi \mathrm{i}}\right)^2 \oint \mathrm{d}z_1 \oint \mathrm{d}z_2 \frac{\exp(z_1+z_2)}{z_1 z_2(1-A_j)} \times \sum_{l_j=0}^{\infty}\left\{\frac{A_j x_j(\xi)}{(1-A_j)z_1}-\frac{A_j y_j}{(1-A_j)z_2}-\frac{A_j x_j(\xi) y_j}{(1-A_j)z_1 z_2}\right\}^{l_j}. \tag{A.9}$$

In order to obtain the correct values of the intensity for the limiting cases, $\tau\rightarrow 0$ and $\tau\rightarrow\infty$, it is necessary to define

$$B_j = -A_j y_j = \frac{\alpha_j \exp(-\tau_j)\{\exp(\theta_j)-1\}^2}{\{\exp(\theta_j)-\exp(-\tau_j)\}^2}. \tag{A.10}$$

Utilizing the binomial expansion and Eq. (A. 4) one can rewrite Eq. (A. 9) as

$$\Lambda_j(\xi) = \frac{\exp(-\tau_j)-\exp(\theta_j)}{1-\exp(\theta_j)} \sum_{l_j=0}^{\infty} \sum_{m_j=0}^{l_j} \sum_{k_j=0}^{l_j-m_j} \binom{l_j}{m_j}\binom{l_j-m_j}{k_j} \times \left(\frac{A_j}{1-A_j}\right)^{m_j}\left(\frac{B_j}{1-A_j}\right)^{l_j-m_j} \frac{\{x_j(\xi)\}^{m_j+k_j}}{(m_j+k_j)!\,(l_j-m_j)!}. \tag{A.11}$$

Here it should be noted that one has $m_j=0$ for $\tau_j\rightarrow 0$ that is, $A_j=0$, and $k_j=0$ and $l_j=m_j$ for $\tau_j\rightarrow\infty$, that is, $B_j=0$.

One uses the following expansions,

$$\{x_j(\xi)\}^{m_j+k_j} = \left(\frac{\Delta_j^2}{2}\right)^{m_j+k_j} \sum_{p_j=0}^{m_j+k_j} \sum_{q_j=0}^{p_j} \sum_{r_j=0}^{m_j+k_j-p_j} \binom{m_j+k_j}{p_j}\binom{p_j}{q_j} \times \binom{m_j+k_j-p_j}{r_j}(-1)^{m_j+k_j-q_j-r_j} \exp[\mathrm{i}\omega_j(q_j-r_j)\xi], \tag{A.12a}$$

or

$$\{x_j(\xi)\}^{m_j+k_j} = \left(\frac{\Delta_j^2}{2}\right)^{m_j+k_j} \sum_{p_j=0}^{2(m_j+k_j)} (-1)^{p_j}\binom{2(m_j+k_j)}{p_j} \times \exp\{\mathrm{i}\omega_j(k_j+m_j-p_j)\xi\}, \tag{A.12b}$$

Substituting Eq. (A. 11) with Eq. (A. 12b) into Eq. (A. 5) yields

$$\begin{aligned} D_{ab}(\omega_R, \tau) = {} & \frac{C}{2}\exp\left[-S-\sum_{j=1}^{N}\frac{\alpha_j \exp(-\tau_j)\{\exp(\theta_j)-1\}}{\exp(\theta_j)-\exp(-\tau_j)}\right] \\ & \times \sum_{l_1=0}^{\infty}\cdots\sum_{l_j=0}^{\infty}\cdots\sum_{l_N=0}^{\infty} \sum_{m_1=0}^{l_1}\cdots\sum_{m_j=0}^{l_j}\cdots\sum_{m_N=0}^{l_N} \sum_{k_1=0}^{l_1-m_1}\cdots\sum_{k_j=0}^{l_j-m_j}\cdots\sum_{k_N=0}^{l_N-m_N} \\ & \times \sum_{p_1=0}^{2(m_1+k_1)}\cdots\sum_{p_j=0}^{2(m_j+k_j)}\cdots\sum_{p_N=0}^{2(m_N+k_N)} \left[\prod_{j=1}^{N}\left(\frac{\Delta_j^2}{2}\right)^{m_j+k_j}\binom{l_j}{m_j}\binom{l_j-m_j}{k_j}\right. \\ & \times \left\{\frac{1-\exp(-\tau_j)}{\exp(\theta_j)-1}\right\}^{m_j}\left\{\frac{\alpha_j\exp(-\tau_j)[\exp(\theta_j)-1]}{\exp(\theta_j)-\exp(-\tau_j)}\right\}^{l_j-m_j} \\ & \left.\times \frac{(-1)^{p_j}\binom{2m_j+2k_j}{p_j}}{(m_j+k_j)!\,(l_j-m_j)!}\right]\int_{-\infty}^{\infty}\mathrm{d}\xi \exp[\mathrm{i}\xi\{\omega_{ba} \\ & +\sum_{j=1}^{N}\omega_j(k_j+m_j-p_j)-\omega_R\}+\sum_{j=1}^{N}\frac{\Delta_j^2}{2}\exp(\mathrm{i}\omega_j\xi)-\Gamma_{ba}|\xi|]. \end{aligned} \tag{A.13}$$

Integration over ξ in Eq. (A. 13) will be carried out in the weak coupling case, $S\leq 1$ and the strong coupling case, $S>1$, separately.

i. Weak Coupling Case. In this case, utilizing the Tayler expansion and integrating the expression over ξ, one can obtain the analytical expression for the absorption intensity,

$$\begin{aligned} D_{ab}(\omega_R, \tau) = {} & C\exp\left[-S-\sum_{j=1}^{N}\frac{\alpha_j \exp(-\tau_j)\{\exp(\theta_j)-1\}}{\exp(\theta_j)-\exp(-\tau_j)}\right] \\ & \times \sum_{n_1=0}^{\infty}\cdots\sum_{n_j=0}^{\infty}\cdots\sum_{n_N=0}^{\infty} \sum_{l_1=0}^{\infty}\cdots\sum_{l_j=0}^{\infty}\cdots\sum_{l_N=0}^{\infty} \sum_{m_1=0}^{l_1}\cdots\sum_{m_j=0}^{l_j}\cdots\sum_{m_N=0}^{l_N} \\ & \times \sum_{k_1=0}^{l_1-m_1}\cdots\sum_{k_j=0}^{l_j-m_j}\cdots\sum_{k_N=0}^{l_N-m_N} \sum_{p_1=0}^{2(m_1+k_1)}\cdots\sum_{p_j=0}^{2(m_j+k_j)}\cdots\sum_{p_N=0}^{2(m_N+k_N)} \\ & \times \left[\prod_{j=1}^{N}\left(\frac{\Delta_j^2}{2}\right)^{n_j+m_j+k_j}\binom{l_j}{m_j}\binom{l_j-m_j}{k_j}\frac{(-1)^{p_j}\binom{2m_j+2k_j}{p_j}}{n_j!\,(m_j+k_j)!\,(l_j-m_j)!}\right. \\ & \left.\times \left\{\frac{\alpha_j\exp(-\tau_j)[\exp(\theta_j)-1]}{\exp(\theta_j)-\exp(-\tau_j)}\right\}^{l_j-m_j}\left\{\frac{1-\exp(-\tau_j)}{\exp(\theta_j)-1}\right\}^{m_j}\right] \\ & \times \frac{\Gamma_{ba}}{\{\omega_{ba}+\sum_{j=1}^{N}\omega_j(n_j+k_j+m_j-p_j)-\omega_R\}^2+\Gamma_{ba}^2}. \end{aligned} \tag{A.14}$$

ii. Strong Coupling Case. In this case, one can use the expansion of $\exp(\mathrm{i}\omega_j\xi)$ to the second order,

$$\exp(\mathrm{i}\omega_j\xi) \fallingdotseq 1 + \mathrm{i}\omega_j\xi - \frac{\omega_j^2\xi^2}{2}. \tag{A.15}$$

In the strong coupling case the following relation is satisfied for the optical transition between two electronic states of molecules,

$$\sum_{j=1}^{N}\frac{\omega_j^2\Delta_j^2}{4} > \Gamma_{ba}^2, \tag{A.16}$$

that is, effect of the damping on the spectrum can be neglected.

Substituting Eq. (A. 15) into Eq. (A. 13) and integrating the expression over ξ yield

$$\begin{aligned} D_{ab}(\omega_R, \tau) = {} & D_{ab}(\omega_{\max}, \infty)_{T=0} \\ & \times \exp\left[-\sum_{j=1}^{N}\frac{\alpha_j \exp(-\tau_j)\{\exp(\theta_j)-1\}}{\exp(\theta_j)-\exp(-\tau_j)}\right] \sum_{l_1=0}^{\infty}\cdots\sum_{l_j=0}^{\infty}\cdots\sum_{l_N=0}^{\infty} \\ & \times \sum_{m_1=0}^{l_1}\cdots\sum_{m_j=0}^{l_j}\cdots\sum_{m_N=0}^{l_N} \sum_{k_1=0}^{l_1-m_1}\cdots\sum_{k_j=0}^{l_j-m_j}\cdots\sum_{k_N=0}^{l_N-m_N} \sum_{p_1=0}^{2(m_1+k_1)}\cdots\sum_{p_j=0}^{2(m_j+k_j)}\cdots\sum_{p_N=0}^{2(m_N+k_N)} \\ & \times \left[\prod_{j=1}^{N}\left(\frac{\Delta_j^2}{2}\right)^{m_j+k_j}\binom{l_j}{m_j}\binom{l_j-m_j}{k_j}\frac{(-1)^{p_j}\binom{2m_j+2k_j}{p_j}}{(m_j+k_j)!\;(l_j-m_j)!}\right. \\ & \left.\times \left\{\frac{\alpha_j\exp(-\tau_j)[\exp(\theta_j)-1]}{\exp(\theta_j)-\exp(-\tau_j)}\right\}^{l_j-m_j}\left\{\frac{1-\exp(-\tau_j)}{\exp(\theta_j)-1}\right\}^{m_j}\right] \\ & \times \exp\left[-\frac{\left\{\omega_{ba}+\sum_{j=1}^{N}\omega_j\left(\frac{\Delta_j^2}{2}+k_j+m_j-p_j\right)-\omega_R\right\}^2}{2\sum_{j=1}^{N}\frac{\omega_j^2\Delta_j^2}{2}}\right] \end{aligned} \tag{A.17}$$

where $D_{ab}(\omega_{\max}, \infty)_{T=0}=\sqrt{2\pi}C/\{\sum_{j=1}^{N}\omega_i^2\Delta_j^2/2\}^{1/2}$ is the maximum absorption intensity at 0 K in the equilibrium state.

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