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A Theoretical Study of the Resonance Raman Scattering from a Molecular System. Effects of Vibronic and Nonadiabatic Couplings

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A theory of the resonance Raman scattering (RRS) from a molecular system in which the vibronic levels of the resonance state are perturbed by both the Herzberg-Teller vibronic and the nonadiabatic coupling is developed. By using the time-independent Green-function formalism, an expression for the RRS is derived in the three-electronic-state model. The RRS cross-sections obtained are classified into four types: the pure RRS cross-section, independent of the coupling mode: the vibronically induced one, the nonadiabatically induced one, and the interference term. Assuming that the molecular system consists of a totally symmetric mode characterized by a displaced harmonic oscillator, with a nontotally symmetric mode as the inducing mode, analytical expressions for the relevant RRS cross-sections of the n_s-th order vibrational transition for the totally symmetric mode are derived. Model calculations of the cross-sections indicate that, for an increasing potential displacement parameter, Δ, between the coupled states, the nonadiabatic correction to the higher-order vibrational transitions, as well as the zero-order vibrational transition, makes a significant contribution.

The mechanisms of the resonance Raman scattering (RRS) from molecules have been investigated by many authors.[1–12] It is experimentally and theoretically recognized that the intensity of the RRS is enhanced as a result of the Herzberg-Teller vibronic coupling in the resonant state and/or the nonadiabatic coupling between the resonant and other electronically excited states.[13–27] Considering a simple model for the RRS by using a nontotally symmetric vibrational mode, Mortensen[3] has shown that the excitation energy profile of the RRS derived within the conventional linear Herzberg-Teller vibronic coupling approximation consists of two identical maxima corresponding to a resonance with 0-0 and 0-1 bands, neglecting the incident-photon-frequency dependence. Zgierski[4] has investigated the effect of nonadiabatic coupling to explain the asymmetry of the 0-0 and 0-1 bands. Hassing and Mortensen[18] have claimed that the asymmetry may be explained by taking into account the interference from a displaced totally symmetric mode in the RRS of the nontotally symmetric mode. By using the third-order perturbation theory, Johnson, Nafie, and Peticolas[7] have calculated the excitation energy profile of the zero-order vibrational transition for a displaced totally symmetric mode, and have concluded that the importance of the nonadiabatic correction is minimal relative to the adiabatic contribution unless the vibronic energy level of the upper state is within a few vibrational quanta of the resonant state.

The main purpose of this paper is to develop a theory of the RRS from a molecular system in which the vibronic levels of the resonant state are perturbed by both the Herzberg-Teller vibronic and the nonadiabatic coupling, and to clarify the role of the couplings on the excitation profiles of the RRS using the adiabatic basis set. Our theory is applicable to a molecular system with any potential energy surface displacements, and includes the results obtained by Zgierski[4] and by Johnson *et al.*[7] as special cases. Their theoretical treatments are restricted to a molecular system with small potential energy surface displacements between the resonant and the ground or upper electronic states. A preliminary study of the effect of the nonadiabatic coupling on the RRS was reported in a previous paper.[28]

In theory section, on the basis of the time-independent Green-function formalism, an expression for the RRS cross-section in the weak radiation field is derived using the three-electronic-state model. The RRS cross-sections are classified in terms of its mechanisms: the pure RRS, which is irrelevant to the inducing mode; the vibronically induced RRS; the nonadiabatically induced RRS, and the RRS originating from their interference, which are further divided into three groups. The most important terms of the interference are those between the components of the RRS within the same resonant state. The interference term between the vibronically induced and nonadiabatically induced RRS contributes to the asymmetry of the vibrational transitions of the excitation profile. In displaced harmonic oscillator model section, assuming that the molecular system consists of a totally symmetric mode characterized by a displaced harmonic oscillator, with a nontotally symmetric mode as the inducing mode, analytical expressions for the relevant RRS cross-sections of the n_s-th order vibrational transition for the totally symmetric mode are derived. The RRS cross-section thus obtained is explicitly expressed as a function of two displacement parameters between the equilibrium points in the relevant state. In the final section, model calculations of the excitation-energy profiles of the RRS cross-section of the n_s-th order vibrational transitions are performed in order to compare the effects of the couplings. It is shown that, for increasing the displacement, Δ, between the two coupled states, the nonadiabatic correction to the higher-order vibrational transitions as well as the zero-order vibrational transition makes a significant contribution.

Theory

Time-independent Green-function Formalism of the RRS Cross-sections in the Three-electronic-state Model. In

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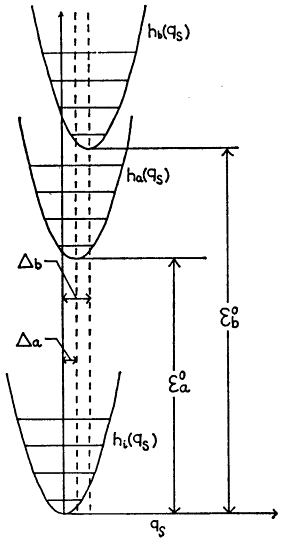

Fig. 1. Displaced harmonic potential model for three electronic state system. $h_i(q_s)$ represents the molecular Hamiltonian of a totally symmetric mode q_s in the ground state, and $h_a(q_s)$ and $h_b(q_s)$ those in the two electronic states a and b, respectively. Δ and ε^0 represent the dimensionless displacement between the equilibrium points, and the energy gap between the bottoms in the ground and relevant excited states, respectively.

a previous paper,[11] the time-independent Green-function formalism was applied to the derivation of the RRS cross-sections in the two-electronic-state model. In this section, in order to take systematically into account the effects of the vibronic and nonadiabatic couplings, we consider a typical model consisting of three electronic states. The total system of the molecular states and radiation field is assumed to be composed of an initial state, $|I\rangle = |\varepsilon_i;\ \{n_i\hbar\omega_i\}|$; two intermediate states, $|A\rangle = |\{\varepsilon_a\};\ \{n_a\hbar\omega_a\}\rangle$ and $|B\rangle = |\{\varepsilon_b\};\ \{n_b\hbar\omega_b\}\rangle$, and a final state, $|F\rangle = |\{\varepsilon_f\};\ \{n_f\hbar\omega_f\}\rangle$, where ε_i denotes the lowest state in the molecular-ground state; $\{\varepsilon_a\}$ the manifold in the a-th electronically excited state, and $n\hbar\omega$, the photon energy. The energy diagram of the molecular system is shown in Fig. 1.

The time evolution of the initial state, $|I\rangle$, is expressed by:

$$|\Psi_I(t)\rangle = \exp\left[-\mathrm{i}\hat{H}t/\hbar\right]|I\rangle \tag{1}$$

where the total Hamiltonian, $\hat{H}$, is given by:

$$\hat{H} = \hat{H}_0 + \hat{V}. \tag{2}$$

Here,

$$\hat{H}_0 = \hat{H}_m^0 + \hat{H}_r^0 \tag{2a}$$

and

$$\hat{V} = \hat{V}_{nd} + \hat{V}_{mr}, \tag{2b}$$

where $\hat{H}_m^0$ and $\hat{H}_r^0$ are the molecular Hamiltonian in the Born-Oppenheimer basis set, and the Hamiltonian for the free electromagnetic field, respectively, while $\hat{V}_{nd}$ and $\hat{V}_{mr}$ denote the nuclear kinetic energy, $\hat{T}_N$, and the molecule-radiation interaction respectively.

The transition amplitude, U_{FI}, from the initial state, I, to the final state, F, is expressed in terms of the transformation of the time-independent Green function as:

$$\begin{aligned} U_{FI}(t) &= \langle F|\Psi_I(t)\rangle \\ &= \frac{1}{2\pi\mathrm{i}}\int \exp\left(-\mathrm{i}Et/\hbar\right)G_{FI}\,\mathrm{d}E, \end{aligned} \tag{3}$$

where G_{FI} is the matrix element of the Green-function. Equations for the relevant matrix elements of the Green-function in the present model are written as:

$$G_{FI} = \sum_A G_{FF}^0 V_{FA} G_{AI} + \sum_B G_{FF}^0 V_{FB} G_{BI}, \tag{4a}$$

$$G_{AI} = G_{AA}^0 V_{AI} G_{II} + \sum_F G_{AA}^0 V_{AF} G_{FI} + \sum_B G_{AA}^0 V_{AB} G_{BI}, \tag{4b}$$

$$G_{BI} = G_{BB}^0 V_{BI} G_{II} + \sum_F G_{BB}^0 V_{BF} G_{FI} + \sum_A G_{BB}^0 V_{BA} G_{AI}, \tag{4c}$$

and:

$$G_{II} = G_{II}^0 + \sum_A G_{II}^0 V_{IA} G_{AI} + \sum_B G_{II}^0 V_{IB} G_{BI}, \tag{4d}$$

where G^0 represents the zero-order Green-function,[11] the summations in Eqs. 4 are carried out over both the molecular vibronic states and the radiation-field variables. By substituting Eqs. 4a and 4d into Eqs. 4b and 4c, we obtain:

$$\begin{aligned} (E-E_A^0-\Lambda_{AA})G_{AI} = V_{AI}G_{II}^0 &+ \sum_{A'\neq A}\Lambda_{AA'}G_{A'I} \\ &+ \sum_B (V_{AB}+\Lambda_{AB})G_{BI}, \end{aligned} \tag{5a}$$

and:

$$\begin{aligned} (E-E_B^0-\Lambda_{BB})G_{BI} = V_{BI}G_{II}^0 &+ \sum_{B'\neq B}\Lambda_{BB'}G_{B'I} \\ &+ \sum_A (V_{BA}+\Lambda_{BA})G_{AI}. \end{aligned} \tag{5b}$$

Here, $\Lambda_{AA'}$ and Λ_{AB} represent the diagonal and off-diagonal self-energy terms respectively.[11]

In order to solve the coupled equations 5a and 5b, we substitute G_{BI}, neglecting the term involving $G_{B'I}$ in Eq. 5b, into 5a:

$$(E-E_A^0-\tilde{\Lambda}_{AA})G_{AI} = \tilde{V}_{AI}G_{II}^0 + \sum_{A'\neq A}\tilde{\Lambda}_{AA'}G_{A'I}, \tag{6}$$

where:

$$\begin{aligned} \tilde{\Lambda}_{AA'} = \Lambda_{AA'} &+ \sum_B (V_{AB}+\Lambda_{AB})(E-E_B^0-\Lambda_{BB})^{-1} \\ &\times (V_{BA'}+\Lambda_{BA'}), \end{aligned} \tag{7}$$

and:

$$\tilde{V}_{AI} = V_{AI} + \sum_B (V_{AB}+\Lambda_{AB})(E-E_B^0-\Lambda_{BB})^{-1}V_{BI}. \tag{8}$$

Equation 6 can be solved by using the iterative method described in Ref. 11. By using the similar procedure described above, the decoupled equation for G_{BI} is obtained.

Substituting the decoupled equations for G_{AI} and G_{BI} into Eq. 4a, the matrix element of the Green function G_{FI} is expressed as:

$$\begin{aligned} G_{FI} = &\sum_A G_{FF}^0 V_{FA}(E-E_A^0-\tilde{\Lambda}_{AA})^{-1}\tilde{V}_{AI}G_{II}^0 \\ &+ \sum_B G_{FF}^0 V_{FB}(E-E_B^0-\tilde{\Lambda}_{BB})^{-1}\tilde{V}_{BI}G_{II}^0, \end{aligned} \tag{9}$$

where the effect of the off-diagonal terms involving $\tilde{\Lambda}_{AA'}$ and $\tilde{\Lambda}_{BB'}$ were neglected. The energy-dependent self-energy part is, at the zero-order approximation, expressed as:

$$\tilde{\Delta}_{\mathrm{AA}}=\Delta_{\mathrm{AA}}(E_{\mathrm{A}}^{0})=D_{\mathrm{A}}-\frac{\mathrm{i}\Gamma_{\mathrm{A}}}{2},\tag{10a}$$

and, in the first-order approximation, as:

$$\tilde{\Delta}_{\mathrm{AA}}=\tilde{\Delta}_{\mathrm{AA}}(E_{\mathrm{A}}^{0})=\tilde{D}_{\mathrm{A}}-\frac{\mathrm{i}\tilde{\Gamma}_{\mathrm{A}}}{2},\tag{10b}$$

where:

$$\tilde{D}_{\mathrm{A}}=D_{\mathrm{A}}+\sum_{B}\frac{(E_{\mathrm{A}}^{0}-E_{\mathrm{B}}^{0}-D_{\mathrm{B}})|V_{\mathrm{BA}}|^{2}}{(E_{\mathrm{A}}^{0}-E_{\mathrm{B}}^{0}-D_{\mathrm{B}})^{2}+(\Gamma_{\mathrm{B}}/2)^{2}},\tag{11}$$

and:

$$\tilde{\Gamma}_{\mathrm{A}}=\Gamma_{\mathrm{A}}+\sum_{B}\frac{\Gamma_{\mathrm{B}}|V_{\mathrm{AB}}|^{2}}{(E_{\mathrm{A}}^{0}-E_{\mathrm{B}}^{0}-D_{\mathrm{B}})^{2}+(\Gamma_{\mathrm{B}}/2)^{2}}.\tag{12}$$

Here, the level shift, D_{A}, and the decay width, Γ_{A}, of the A intermediate state are given in Ref. 11. In a case of weak nonadiabatic coupling, Eq. 10a can be used.

Neglecting the terms involving Δ_{AB} in $\tilde{V}_{\mathrm{AI}}$ and Δ_{BA} in $\tilde{V}_{\mathrm{BI}}$ of Eq. 9 because these terms give rise to the higher-order photon processes, and substituting Eq. 9 into Eq. 3, the transition amplitude U_{FI}, is expressed as:

$$\begin{aligned}U_{\mathrm{FI}}(t)=&\sum_{A}\Bigg(\frac{V_{\mathrm{FA}}V_{\mathrm{AI}}\exp(-\mathrm{i}E_{\mathrm{I}}^{0}t/\hbar)}{E_{\mathrm{I}}^{0}-E_{\mathrm{A}}+\mathrm{i}\tilde{\Gamma}_{\mathrm{A}}/2}\ \frac{\{1-\exp[-\mathrm{i}(E_{\mathrm{F}}^{0}-E_{\mathrm{I}}^{0})t/\hbar]\}}{E_{\mathrm{I}}^{0}-E_{\mathrm{F}}^{0}}\\&+\frac{V_{\mathrm{FA}}V_{\mathrm{AI}}\exp[-\mathrm{i}(E_{\mathrm{A}}-\mathrm{i}\tilde{\Gamma}_{\mathrm{A}}/2)t/\hbar]}{(E_{\mathrm{A}}-E_{\mathrm{F}}^{0}-\mathrm{i}\tilde{\Gamma}_{\mathrm{A}}/2)(E_{\mathrm{A}}-E_{\mathrm{I}}^{0}-\mathrm{i}\tilde{\Gamma}_{\mathrm{A}}/2)}-\frac{V_{\mathrm{FA}}V_{\mathrm{AI}}\exp(-\mathrm{i}E_{\mathrm{F}}^{0}t/\hbar)}{(E_{\mathrm{I}}^{0}-E_{\mathrm{A}}+\mathrm{i}\tilde{\Gamma}_{\mathrm{A}}/2)(E_{\mathrm{F}}^{0}-E_{\mathrm{A}}+\mathrm{i}\tilde{\Gamma}_{\mathrm{A}}/2)}\Bigg)+\sum_{B}(A\rightarrow B)\\&+\sum_{A}\sum_{B}\Bigg(\frac{V_{\mathrm{FB}}V_{\mathrm{BA}}V_{\mathrm{AI}}\exp(-\mathrm{i}E_{\mathrm{I}}^{0}t/\hbar)}{(E_{\mathrm{I}}^{0}-E_{\mathrm{A}}+\mathrm{i}\tilde{\Gamma}_{\mathrm{A}}/2)(E_{\mathrm{I}}^{0}-E_{\mathrm{B}}+\mathrm{i}\tilde{\Gamma}_{\mathrm{B}}/2)}\ \frac{\{1-\exp[-\mathrm{i}(E_{\mathrm{F}}^{0}-E_{\mathrm{I}}^{0})t/\hbar]\}}{E_{\mathrm{I}}^{0}-E_{\mathrm{F}}^{0}}\\&+\frac{V_{\mathrm{FB}}V_{\mathrm{BA}}V_{\mathrm{AI}}\exp[-\mathrm{i}(E_{\mathrm{B}}-\mathrm{i}\tilde{\Gamma}_{\mathrm{B}}/2)t/\hbar]}{(E_{\mathrm{B}}-E_{\mathrm{A}}-\mathrm{i}\tilde{\Gamma}_{\mathrm{B}}/2+\mathrm{i}\tilde{\Gamma}_{\mathrm{A}}/2)(E_{\mathrm{B}}-E_{\mathrm{I}}^{0}-\mathrm{i}\tilde{\Gamma}_{\mathrm{B}}/2)(E_{\mathrm{B}}-E_{\mathrm{F}}^{0}-\mathrm{i}\tilde{\Gamma}_{\mathrm{B}}/2)}\\&+\frac{V_{\mathrm{FB}}V_{\mathrm{BA}}V_{\mathrm{AI}}\exp[-\mathrm{i}(E_{\mathrm{A}}-\mathrm{i}\tilde{\Gamma}_{\mathrm{A}}/2)t/\hbar]}{(E_{\mathrm{A}}-E_{\mathrm{B}}-\mathrm{i}\tilde{\Gamma}_{\mathrm{A}}/2+\mathrm{i}\tilde{\Gamma}_{\mathrm{B}}/2)(E_{\mathrm{A}}-E_{\mathrm{I}}^{0}-\mathrm{i}\tilde{\Gamma}_{\mathrm{A}}/2)(E_{\mathrm{A}}-E_{\mathrm{F}}^{0}-\mathrm{i}\tilde{\Gamma}_{\mathrm{A}}/2)}\\&-\frac{V_{\mathrm{FB}}V_{\mathrm{BA}}V_{\mathrm{AI}}\exp(-\mathrm{i}E_{\mathrm{F}}^{0}t/\hbar)}{(E_{\mathrm{I}}^{0}-E_{\mathrm{A}}+\mathrm{i}\tilde{\Gamma}_{\mathrm{A}}/2)(E_{\mathrm{I}}^{0}-E_{\mathrm{B}}+\mathrm{i}\tilde{\Gamma}_{\mathrm{B}}/2)(E_{\mathrm{F}}^{0}-E_{\mathrm{B}}+\mathrm{i}\tilde{\Gamma}_{\mathrm{B}}/2)}\\&-\frac{V_{\mathrm{FB}}V_{\mathrm{BA}}V_{\mathrm{AI}}\exp(-\mathrm{i}E_{\mathrm{F}}^{0}t/\hbar)}{(E_{\mathrm{I}}^{0}-E_{\mathrm{A}}+\mathrm{i}\tilde{\Gamma}_{\mathrm{A}}/2)(E_{\mathrm{F}}^{0}-E_{\mathrm{A}}+\mathrm{i}\tilde{\Gamma}_{\mathrm{A}}/2)(E_{\mathrm{F}}^{0}-E_{\mathrm{B}}+\mathrm{i}\tilde{\Gamma}_{\mathrm{B}}/2)}\Bigg)+\sum_{A}\sum_{B}(A\rightleftarrows B),\end{aligned}\tag{13}$$

where $E_{\mathrm{A}}=E_{\mathrm{A}}^{0}+D_{\mathrm{A}}$ and $E_{\mathrm{B}}=E_{\mathrm{B}}^{0}+D_{\mathrm{B}}$. When we use the on-the-energy-shell approximation ($E_{\mathrm{I}}^{0}\rightarrow E_{\mathrm{F}}^{0}$) and the limit, $t\rightarrow\infty$, it seems that the following terms make the dominant contribution to the scattering cross-section:

$$\begin{aligned}U_{\mathrm{FI}}(t)=&\Bigg[\sum_{A}\frac{V_{\mathrm{FA}}V_{\mathrm{AI}}\exp(-E_{\mathrm{I}}^{0}t/\hbar)}{E_{\mathrm{I}}^{0}-E_{\mathrm{A}}+\mathrm{i}\tilde{\Gamma}_{\mathrm{A}}/2}+\sum_{B}(A\rightarrow B)\\&+\sum_{A}\sum_{B}\frac{V_{\mathrm{FB}}V_{\mathrm{BA}}V_{\mathrm{AI}}\exp(-\mathrm{i}E_{\mathrm{I}}^{0}t/\hbar)}{(E_{\mathrm{I}}^{0}-E_{\mathrm{A}}+\mathrm{i}\tilde{\Gamma}_{\mathrm{A}}/2)(E_{\mathrm{I}}^{0}-E_{\mathrm{B}}+\mathrm{i}\tilde{\Gamma}_{\mathrm{B}}/2)}\\&+\sum_{A}\sum_{B}(A\rightleftarrows B)\Bigg]\frac{1-\exp[-\mathrm{i}(E_{\mathrm{F}}^{0}-E_{\mathrm{I}}^{0})t/\hbar]}{E_{\mathrm{I}}^{0}-E_{\mathrm{F}}^{0}}.\end{aligned}\tag{14}$$

By using the dipole and rotating wave approximations, and after integrating over the radiation-field variables, the differential cross-section for the Raman scattering is given by:

$$\begin{aligned}\frac{\mathrm{d}\sigma(\omega_1)}{\mathrm{d}\Omega}=&\frac{\omega_1(n_2+1)}{2^4\pi^2\varepsilon_0{}^2c^4}\sum_{f}\int_0^\infty\mathrm{d}\omega_2\omega_2{}^3\\&\times\Bigg|\sum_{c}\frac{\langle f|\boldsymbol{e}_2\cdot\boldsymbol{\mu}|c\rangle\langle c|\boldsymbol{e}_1\cdot\boldsymbol{\mu}|i\rangle}{\varepsilon_{\mathrm{i}}+\hbar\omega_1-\varepsilon_{\mathrm{c}}+\mathrm{i}\tilde{\Gamma}_{\mathrm{c}}/2}\\&+\sum_{\substack{c,d\\(c\neq d)}}\frac{\langle f|\hat{\boldsymbol{e}}_2\cdot\boldsymbol{\mu}|d\rangle\langle d|\hat{T}_{\mathrm{N}}|c\rangle\langle c|\hat{\boldsymbol{e}}_1\cdot\boldsymbol{\mu}|i\rangle}{(\varepsilon_{\mathrm{i}}+\hbar\omega_1-\varepsilon_{\mathrm{c}}+\mathrm{i}\tilde{\Gamma}_{\mathrm{c}}/2)(\varepsilon_{\mathrm{i}}+\hbar\omega_1-\varepsilon_{\mathrm{d}}+\mathrm{i}\tilde{\Gamma}_{\mathrm{d}}/2)}\\&+(\text{non-resonant terms})\Bigg|^2\delta\!\left(\frac{\varepsilon_{\mathrm{i}}-\varepsilon_{\mathrm{f}}+\hbar\omega_1-\hbar\omega_2)}{\hbar}\right),\end{aligned}\tag{15}$$

where $\hbar\omega_1$ and $\hbar\omega_2$ denote the excitation and emission energies of the photon respectively, and where the summations, c and d, are taken over the vibronic states of two electronic states, a and b. Compared with the expression for the differential cross-section derived in the one-intermediate electronic state,[11] it should be noted that, in the two-intermediate-state model, the term originating from the nonadiabatic interaction appears in Eq. 15.

Mechanisms of the RRS from Randomly Oriented Molecules. We note that the complex tensor, t, for the RRS cross-section is written as the sum of symmetric and antisymmetric tensors, $\{t\}=\{S\}+\{A\}$, where $S_{12}=1/2(t_{12}+t_{21})$ and $A_{12}=1/2(t_{12}-t_{21})$. Here, the suffixes 1 and 2 specify the molecular fixed Cartesian coordinates, x, y, and z. We assume that the molecules are randomly oriented. If the incident radiation is linearly polarized, and if the polarization lies on the XY plane, the RRS cross-section, $\mathrm{d}\sigma(\omega_1)/\mathrm{d}\Omega$, along the Z axis is given by:[29]

$$\frac{\mathrm{d}\sigma(\omega_1)}{\mathrm{d}\Omega}=\frac{1}{15}\left\{7\frac{\mathrm{d}\sigma_{\mathrm{S}}(\omega_1)}{\mathrm{d}\Omega}+5\frac{\mathrm{d}\sigma_{\mathrm{A}}(\omega_1)}{\mathrm{d}\Omega}\right\},\tag{16}$$

where $\mathrm{d}\sigma_{\mathrm{S}}(\omega_1)/\mathrm{d}\Omega$ and $\mathrm{d}\sigma_{\mathrm{A}}(\omega_1)/\mathrm{d}\Omega$ represent the symmetric and antisymmetric parts of the cross-section and are given by:

$$\frac{\mathrm{d}\sigma_{\mathrm{I}}(\omega_1)}{\mathrm{d}\Omega}=\frac{\omega_1(n_2+1)}{2^6\pi^2\varepsilon_0{}^2c^4}\sum_{f}\int_0^\infty\mathrm{d}\omega_2\omega_2{}^3$$

$$
\left| \sum_{c} \left(\frac{\langle f|\mu_2|c\rangle\langle c|\mu_1|i\rangle}{\varepsilon_i+\hbar\omega_1-\varepsilon_c+i\tilde{\Gamma}_c/2} \pm \frac{\langle f|\mu_1|c\rangle\langle c|\mu_2|i\rangle}{\varepsilon_i+\hbar\omega_1-\varepsilon_c+i\tilde{\Gamma}_c/2} \right) \right.
$$

$$
+ \sum_{\substack{c,d \\ (c\neq d)}} \left(\frac{\langle f|\mu_2|d\rangle\langle d|\hat{T}_N|d\rangle\langle d|\mu_1|i\rangle}{(\varepsilon_i+\hbar\omega_1-\varepsilon_c+i\tilde{\Gamma}_c/2)(\varepsilon_i+\hbar\omega_1-\varepsilon_d+i\tilde{\Gamma}_d/2)} \right.
$$

$$
\left. \pm \frac{\langle f|\mu_1|d\rangle\langle d|\hat{T}_N|c\rangle\langle c|\mu_2|i\rangle}{(\varepsilon_i+\hbar\omega_1-\varepsilon_c+i\tilde{\Gamma}_c/2)(\varepsilon_i+\hbar\omega_1-\varepsilon_d+i\tilde{\Gamma}_d/2)} \right|^2
$$

$$
\times \delta\left(\frac{\varepsilon_i-\varepsilon_f+\hbar\omega_1-\hbar\omega_2}{\hbar} \right), \tag{17}
$$

where the + and — signs correspond to the symmetric (I=S) and antisymmetric (I=A) cross-sections respectively. In the above expression, the non-resonant terms were disregarded.

To classify the RRS into the pure RRS irrelevant to the couplings, vibronically induced, and nonadiabatically induced types, we expand the matrix element of the transition dipole and the nonadiabatic coupling matrix element as:

$$
\langle f|\mu_2|a\rangle = \langle \chi_f|M_{fa}(2)|\chi_a\rangle + \langle \chi_f|(\mathrm{M}_{fb}(2)V_{ba}-V_{fb}M_{ba}(2))q|\chi_a\rangle + \cdots, \tag{18}
$$

and:

$$
\langle a|\hat{T}_N|b\rangle = \left\langle \chi_a \left| \left(\Phi_a \left| -\frac{\hbar\omega}{2}\frac{\partial^2}{\partial q^2} \right| \Phi_b \right) \right| \chi_b \right\rangle
$$

$$
\simeq -\hbar\omega \left\langle \chi_a \left| V_{ab}\frac{\partial}{\partial q} \right| \chi_b \right\rangle, \tag{19}
$$

respectively, where $M_{fa}(2)=\langle\Phi_f|\mu_2|\Phi_a\rangle_{q=q_0}$ and where $V_{ba}=\left[\frac{\langle\Phi_b|\partial V/\partial q|\Phi_a\rangle}{\varepsilon_a-\varepsilon_b}\right]_{q=q_0}$. Here, Φ, χ, and V denote the BO electronic wave function, the nuclear wave function, and the electrostatic interaction between electron and nucleus respectively. The above matrix elements are evaluated at the equilibrium nuclear configuration (q_0) in the ground state. Restricting ourselves to the first-order variation of the nuclear coordinate, q, and disregarding the vibronic coupling between the ground (final or initial) and intermediate states because of $|\varepsilon_a(q_0)-\varepsilon_b(q_0)|<|\varepsilon_b(q_0)-\varepsilon_f(q_0)|$, the symmetric and antisymmetric cross-section of the spontaneous RRS can be written as:

$$
\frac{d\sigma_I(\omega_1)}{d\Omega} = \frac{\omega_1}{2^6\pi^2\varepsilon_0^2c^4}\sum_f\int_0^\infty d\omega_2\omega_2^3\delta\left(\frac{\varepsilon_i-\varepsilon_f+\hbar\omega_1-\hbar\omega_2}{\hbar}\right)
$$

$$
\left| \sum_c \left(\frac{\langle\chi_f|M_{fc}(2)|\chi_c\rangle\langle\chi_c|M_{ci}(1)|\chi_i\rangle}{\varepsilon_i+\hbar\omega_1-\varepsilon_c+i\tilde{\Gamma}_c/2} \pm \frac{\langle\chi_f|M_{fc}(1)|\chi_c\rangle\langle\chi_c|M_{ci}(2)|\chi_i\rangle}{\varepsilon_i+\hbar\omega_1-\varepsilon_c+i\tilde{\Gamma}_c/2} \right) \right.
$$

$$
+ \sum_{\substack{c \\ (c\neq d)}} \overset{(\mathrm{elec})}{\sum_{d}} \left[\left\{ -\frac{\langle\chi_f|M_{fc}(2)|\chi_c\rangle\langle\chi_c|V_{cd}M_{di}(1)q|\chi_i\rangle}{\varepsilon_i+\hbar\omega_1-\varepsilon_c+i\tilde{\Gamma}_c/2} + \frac{\langle\chi_f|M_{fd}(2)V_{dc}q|\chi_c\rangle\langle\chi_c|M_{ci}(1)|\chi_i\rangle}{\varepsilon_i+\hbar\omega_1-\varepsilon_c+i\tilde{\Gamma}_c/2} \right\} \right.
$$

$$
\left. \pm \left\{ -\frac{\langle\chi_f|M_{fc}(1)|\chi_c\rangle\langle\chi_c|V_{cd}M_{di}(2)q|\chi_i\rangle}{\varepsilon_i+\hbar\omega_1-\varepsilon_c+i\tilde{\Gamma}_d/2} + \frac{\langle\chi_f|M_{fd}(1)V_{dc}q|\chi_c\rangle\langle\chi_c|M_{ci}(2)|\chi_i\rangle}{\varepsilon_i+\hbar\omega_1-\varepsilon_c+i\tilde{\Gamma}_c/2} \right\} \right]
$$

$$
- \sum_{\substack{c \\ (c\neq d)}} \sum_{d} \left\{ \hbar\omega \frac{\langle\chi_f|M_{fd}(2)|\chi_d\rangle\langle\chi_d|V_{dc}\partial/\partial q|\chi_c\rangle\langle\chi_c|M_{ci}(1)|\chi_i\rangle}{(\varepsilon_i+\hbar\omega_1-\varepsilon_c+i\tilde{\Gamma}_c/2)(\varepsilon_i+\hbar\omega_1-\varepsilon_d+i\tilde{\Gamma}_d/2)} \right.
$$

$$
\left. \left. \pm \hbar\omega \frac{\langle\chi_f|M_{fd}(1)|\chi_d\rangle\langle\chi_d|V_{dc}\partial/\partial q|\chi_c\rangle\langle\chi_c|M_{ci}(2)|\chi_i\rangle}{(\varepsilon_i+\hbar\omega_1-\varepsilon_c+i\tilde{\Gamma}_c/2)(\varepsilon_i+\hbar\omega_1-\varepsilon_d+i\tilde{\Gamma}_d/2)} \right\} \right|^2, \tag{20}
$$

where $\overset{(\mathrm{elec})}{\sum_{d}}$ means the summation over the electronic states, a and b. Here, the first and second terms independent of q and $\partial/\partial q$ express the pure RRS; the terms involving q the vibronically induced RRS, and the terms involving $\partial/\partial q$, the nonadiabatically induced RRS.

In this paper, since we are interested in the RRS originating from the couplings between a and b electronic states, we will consider the special case in which the irreducible representations of the point group of the electronic states, Φ_a and Φ_b, at the equilibrium configuration in the ground state are different from each other: $M_{fa}(2)=0$ and $M_{bi}(1)=0$, which also means that $M_{ia}(2)=0$ and $M_{fb}(1)=0$, while the inducing mode, q, belongs to a nontotally symmetric mode. In this case, the pure RRS terms vanish and Eq. 20 is reduced to:

$$
\frac{d\sigma_I(\omega_1)}{d\Omega} = \frac{\omega_1}{2^6\pi^2\varepsilon_0^2c^4}\sum_f\int_0^\infty d\omega_2\omega_2^3\delta\left(\frac{\varepsilon_i-\varepsilon_f+\hbar\omega_1-\hbar\omega_2}{\hbar}\right)
$$

$$
\left| \overset{(\mathrm{vibro})}{\sum_{a}} \frac{\langle\chi_f|M_{fb}(2)V_{ba}q|\chi_a\rangle\langle\chi_a|M_{ai}(1)|\chi_i\rangle}{\varepsilon_i+\hbar\omega_1-\varepsilon_a+i\tilde{\Gamma}_a/2} - \overset{(\mathrm{vibro})}{\sum_{b}} \frac{\langle\chi_f|M_{fb}(2)|\chi_b\rangle\langle\chi_b|V_{ba}qM_{ai}(1)|\chi_i\rangle}{\varepsilon_i+\hbar\omega_1-\varepsilon_b+i\tilde{\Gamma}_b/2} \right.
$$

$$
\pm \overset{(\mathrm{vibro})}{\sum_{b}} \frac{\langle\chi_f|M_{fa}(1)V_{ab}q|\chi_b\rangle\langle\chi_b|M_{bi}(2)|\chi_i\rangle}{\varepsilon_i+\hbar\omega_1-\varepsilon_b+i\tilde{\Gamma}_b/2} \mp \overset{(\mathrm{vibro})}{\sum_{a}} \frac{\langle\chi_f|M_{fa}(1)|\chi_a\rangle\langle\chi_a|V_{ab}qM_{bi}(2)|\chi_i\rangle}{\varepsilon_i+\hbar\omega_1-\varepsilon_a+i\tilde{\Gamma}_a/2}
$$

$$
- \overset{(\mathrm{vibro})}{\sum_{\substack{a,b \\ (a\neq b)}}} \hbar\omega \left\{ \frac{\langle\chi_f|M_{fb}(2)|\chi_b\rangle\langle\chi_b|V_{ba}\partial/\partial q|\chi_a\rangle\langle\chi_a|M_{ai}(1)|\chi_i\rangle}{(\varepsilon_i+\hbar\omega_1-\varepsilon_a+i\tilde{\Gamma}_a/2)(\varepsilon_i+\hbar\omega_1-\varepsilon_b+i\tilde{\Gamma}_b/2)} \right.
$$

$$
\left. \left. \pm \frac{\langle\chi_f|M_{fa}(1)|\chi_a\rangle\langle\chi_a|V_{ab}\partial/\partial q|\chi_b\rangle\langle\chi_b|M_{bi}(2)|\chi_i\rangle}{(\varepsilon_i+\hbar\omega_1-\varepsilon_a+i\tilde{\Gamma}_a/2)(\varepsilon_i+\hbar\omega_1-\varepsilon_b+i\tilde{\Gamma}_b/2)} \right\} \right|^2. \tag{21}
$$

Utilizing the Fourier transformations, and carrying out the summations over the vibronic states in Eq. 21 by using the closure property of the states,[11] we obtain:

$$\frac{\mathrm{d}\sigma_{\mathrm{I}}(\omega_1)}{\mathrm{d}\Omega}=\frac{\mathrm{d}\sigma_{\mathrm{I}}^{\mathrm{VI}}(\omega_{\mathrm{I}})}{\mathrm{d}\Omega}+\frac{\mathrm{d}\sigma_{\mathrm{I}}^{\mathrm{NA}}(\omega_1)}{\mathrm{d}\Omega}+\frac{\mathrm{d}\sigma_{\mathrm{I}}^{\mathrm{INT(VI)}}(\omega_1)}{\mathrm{d}\Omega}$$
$$+\frac{\mathrm{d}\sigma_{\mathrm{I}}^{\mathrm{INT(NA)}}(\omega_1)}{\mathrm{d}\Omega}+\frac{\mathrm{d}\sigma_{\mathrm{I}}^{\mathrm{INT(VI-NA)}}(\omega_1)}{\mathrm{d}\Omega}, \tag{22}$$

where $\mathrm{d}\sigma_{\mathrm{I}}^{\mathrm{VI}}(\omega_1)/\mathrm{d}\Omega$ and $\mathrm{d}\sigma_{\mathrm{I}}^{\mathrm{NA}}(\omega_1)/\mathrm{d}\Omega$ represent the vibronically induced and nonadiabatically induced RRS cross-sections respectively; $\mathrm{d}\sigma_{\mathrm{I}}^{\mathrm{INT(VI)}}(\omega_1)/\mathrm{d}\Omega$ and $\mathrm{d}\sigma_{\mathrm{I}}^{\mathrm{INT(NA)}}(\omega_1)/\mathrm{d}\Omega$, the interference term between the vibronically induced RRS and that between the nonadiatically induced RRS respectively, and $\mathrm{d}\sigma_{\mathrm{I}}^{\mathrm{INT(VI-NA)}}(\omega_1)/\mathrm{d}\Omega$, the interference term between the vibronically induced and the nonadiabatically induced RRS. It should be noted that the signs specifying the symmetric and antisymmetric cross-sections are involved in the interference terms.

The vibronically induced and nonadiabatically induced cross sections are expressed as:

$$\frac{\mathrm{d}\sigma_{\mathrm{I}}^{\mathrm{VI}}(\omega_1)}{\mathrm{d}\Omega}=\frac{\omega_1}{2^7\pi^3\varepsilon_0{}^2c^4\hbar^2}|M_{\mathrm{gb}}(2)V_{\mathrm{ba}}M_{\mathrm{ag}}(1)|^2$$
$$\sum_{ca,\,b}\int_0^\infty \mathrm{d}\omega_2\omega_2{}^3\int_0^\infty \mathrm{d}\tau'\int_0^\infty \mathrm{d}\tau\int_{-\infty}^\infty \mathrm{d}t$$
$$\exp\,[-\mathrm{i}(t-\tau+\tau')\omega_1+\mathrm{i}t\omega_2]$$
$$\times\{\langle\chi_{\mathrm{i}}|\exp\,[(\mathrm{i}\hat{H}_{\mathrm{c}}^0-\tilde{\Gamma}_{\mathrm{c}}/2)\tau'/\hbar]q_{\mathrm{n}}\exp\,(\mathrm{i}\hat{H}_{\mathrm{i}}^0t/\hbar)q_{\mathrm{n}}$$
$$\exp\,[-(\mathrm{i}\hat{H}_{\mathrm{c}}^0+\tilde{\Gamma}_{\mathrm{c}}/2)\tau/\hbar]\exp\,[-\mathrm{i}\hat{H}_{\mathrm{i}}^0(t-\tau+\tau')/\hbar]|\chi_{\mathrm{i}}\rangle$$
$$+\langle\chi_{\mathrm{i}}|q_{\mathrm{n}}\exp\,[(\mathrm{i}\hat{H}_{\mathrm{c}}^0-\tilde{\Gamma}_{\mathrm{c}}/2)\tau'/\hbar]$$
$$\exp\,(\mathrm{i}\hat{H}_{\mathrm{i}}^0t/\hbar)\exp\,[-(\mathrm{i}\hat{H}_{\mathrm{c}}^0+\tilde{\Gamma}_{\mathrm{c}}/2)\tau/\hbar]q_{\mathrm{n}}$$
$$\exp[-\mathrm{i}\hat{H}_{\mathrm{i}}^0(t-\tau+\tau')/\hbar]|\chi_{\mathrm{i}}\rangle\}, \tag{23}$$

and:

$$\frac{\mathrm{d}\sigma_{\mathrm{I}}^{\mathrm{NA}}(\omega_1)}{\mathrm{d}\Omega}=\frac{\omega_1\omega_{\mathrm{n}}^2}{2^7\pi^3\varepsilon_0{}^2c^4\hbar^2}|M_{\mathrm{gb}}(2)V_{\mathrm{ba}}M_{\mathrm{ag}}(1)|^2$$
$$\sum_{c}\sum_{\substack{d\\(c\neq d)}}\int_0^\infty \mathrm{d}\omega_2\omega_2{}^3\int_0^\infty \mathrm{d}\tau'\int_0^\infty \mathrm{d}\xi'\int_0^\infty \mathrm{d}\tau\int_0^\infty \mathrm{d}\xi\int_{-\infty}^\infty \mathrm{d}t$$
$$\exp\,[-\mathrm{i}(t-\tau-\xi+\tau'+\xi')\omega_1+\mathrm{i}t\omega_2]$$
$$\times\langle\chi_{\mathrm{i}}|\exp\,[(-\mathrm{i}\hat{H}_{\mathrm{c}}^0-\tilde{\Gamma}_{\mathrm{c}}/2)\tau'/\hbar](\partial/\partial q_{\mathrm{n}})^\dagger$$
$$\exp\,[(\mathrm{i}\hat{H}_{\mathrm{d}}^0-\tilde{\Gamma}_{\mathrm{d}}/2)\xi'/\hbar]\exp\,(\mathrm{i}\hat{H}_{\mathrm{i}}^0t/\hbar)$$
$$\exp\,[-(\mathrm{i}\hat{H}_{\mathrm{d}}^0+\tilde{\Gamma}_{\mathrm{d}}/2)\xi/\hbar]\partial/\partial q_{\mathrm{n}}\exp\,[-(\mathrm{i}\hat{H}_{\mathrm{c}}^0+\tilde{\Gamma}_{\mathrm{c}}/2)\tau/\hbar]$$
$$\exp\,[-\mathrm{i}\hat{H}_{\mathrm{i}}^0(t-\tau-\xi+\tau'+\xi')/\hbar]\chi_{\mathrm{i}}\rangle, \tag{24}$$

respectively, where n denotes a nontotally symmetric mode and $\hat{H}^0$, the relevant vibronic Hamiltonian, while the vibronic-level dependence of the decay width, $\tilde{\Gamma}$, is disregarded. Because Eqs. 23 and 24 are expressed in terms of the vibronic Hamiltonians and are independent of the summation over the intermediate vibronic levels, these equations are suitable for the investigation of the coupling effects of the RRS from a molecular system consisting of any potential energy surfaces. They can thus be used as a basis for studying the frequency change[30] and anharmonic effects of the RRS. The expressions for the interference RRS cross-sections are given in Appendix A.

Displaced Harmonic Oscillator Model

In this section, we are concerned with the derivation of analytical expressions for the vibronically induced RRS, the nonadiabatically induced RRS, and their interference RRS in the displaced harmonic oscillator model. The molecular Hamiltonians of the ground and two excited states, *a* and *b* consist of a totally symmetric mode (q_{s}) with a nontotally symmetric mode (q_{n}) as the inducing mode. These potential surfaces are assumed to be harmonic and to be displaced for the totally symmetric mode. The frequency change in the vibrationsl modes were disregarded. In terms of the Boson annihilation and creation operators, $\hat{b}$ and $\hat{b}^\dagger$, which satisfy $[\hat{b},\hat{b}^\dagger]=1$, these Hamiltonians are expressed as:

$$\hat{H}_{\mathrm{i}}^0=\hat{h}_{\mathrm{i}}(q_{\mathrm{s}})+\hat{h}_{\mathrm{i}}(q_{\mathrm{n}}), \tag{25a}$$

$$\hat{h}_{\mathrm{i}}(q_{\mathrm{s}})=\frac{\hbar\omega_{\mathrm{s}}}{2}(p_{\mathrm{s}}^2+q_{\mathrm{s}}^2)=\hbar\omega_{\mathrm{s}}\left(\hat{b}_{\mathrm{s}}^\dagger\hat{b}_{\mathrm{s}}+\frac{1}{2}\right), \tag{25b}$$

$$\hat{h}_{\mathrm{i}}(q_{\mathrm{n}})=\frac{\hbar\omega_{\mathrm{n}}}{2}(p_{\mathrm{n}}^2+q_{\mathrm{n}}^2)=\hbar\omega_{\mathrm{n}}\left(\hat{b}_{\mathrm{n}}^\dagger\hat{b}_{\mathrm{n}}+\frac{1}{2}\right), \tag{25c}$$

$$\hat{H}_{\mathrm{a}}^0=\hat{h}_{\mathrm{i}}(q_{\mathrm{s}}-\Delta_{\mathrm{a}})+\hat{h}_{\mathrm{i}}(q_{\mathrm{n}})+\varepsilon_{\mathrm{a}}^0$$
$$=\hbar\omega_{\mathrm{s}}\left(\hat{b}_{\mathrm{s}}^\dagger\hat{b}_{\mathrm{s}}+\frac{1}{2}\right)-\frac{\hbar\omega_{\mathrm{s}}\Delta_{\mathrm{a}}}{\sqrt{2}}(\hat{b}_{\mathrm{s}}+\hat{b}_{\mathrm{s}}^\dagger)$$
$$+\frac{\hbar\omega_{\mathrm{s}}\Delta_{\mathrm{a}}^2}{2}+\hbar\omega_{\mathrm{n}}\left(\hat{b}_{\mathrm{n}}^\dagger\hat{b}_{\mathrm{n}}+\frac{1}{2}\right)+\varepsilon_{\mathrm{a}}^0, \tag{25d}$$

and

$$\hat{H}_{\mathrm{b}}^0=\hat{h}_{\mathrm{i}}(q_{\mathrm{s}}-\Delta_{\mathrm{b}})+\hat{h}_{\mathrm{i}}(q_{\mathrm{n}})+\varepsilon_{\mathrm{b}}^0, \tag{25e}$$

where we have taken into account the potential displacement between the potential energy surfaces of the two intermediate excited states; Δ_{a} and Δ_{b} represent the dimensionless displacements between the equilibrium points in the ground and excited states, *a* and *b* respectively, and ε^0, the electronic energy gap between the bottoms in the ground and excited states.

Nonadiabatically Induced RRS. The nonadiabatically induced RRS cross-section, $\mathrm{d}\sigma_{\mathrm{I}}^{\mathrm{NA}}(\omega_1)/\mathrm{d}\Omega$, Eq. 24 is written as:

$$\frac{\mathrm{d}\sigma_{\mathrm{I}}^{\mathrm{NA}}(\omega_1)}{\mathrm{d}\Omega}=\omega_{\mathrm{n}}^2k(\omega_1)\sum_{c}\sum_{\substack{d\\(c\neq d)}}\int_0^\infty \mathrm{d}\omega_2\omega_2{}^3$$
$$\int_0^\infty \mathrm{d}\tau'\int_0^\infty \mathrm{d}\xi'\int_0^\infty \mathrm{d}\tau\int_0^\infty \mathrm{d}\xi\int_{-\infty}^\infty \mathrm{d}t$$
$$\exp\left[-\mathrm{i}(t-\tau-\xi+\tau'+\xi')\omega_1+\mathrm{i}t\omega_2-\frac{\tilde{\Gamma}_{\mathrm{c}}}{2\hbar}(\tau+\tau')\right.$$
$$\left.-\frac{\tilde{\Gamma}_{\mathrm{d}}}{2\hbar}(\xi+\xi')+\frac{\mathrm{i}\varepsilon_{\mathrm{c}}^0}{\hbar}(\tau'-\tau)+\frac{\mathrm{i}\varepsilon_{\mathrm{d}}^0}{\hbar}(\xi'-\xi)\right]$$
$$f_{\mathrm{n}}(\tau',\xi',\tau,\xi,t)g_{\mathrm{s}}(\tau',\xi',\tau,\xi,t), \tag{26}$$

where $k(\omega_1)=\dfrac{\omega_1}{2^7\pi^3\varepsilon_0^2\mathrm{c}^4\hbar^2}|M_{\mathrm{gb}}(2)V_{\mathrm{ba}}M_{\mathrm{ag}}(1)|^2$,

$$f_{\mathrm{n}}(\tau',\xi',\tau,\xi,t)=\left\langle 0_{\mathrm{n}}\right|\exp\left[\frac{\mathrm{i}\hat{h}_{\mathrm{i}}(q_{\mathrm{n}})\tau'}{\hbar}\right]\left(\frac{\partial}{\partial q_{\mathrm{n}}}\right)^\dagger$$

$$\exp\left[\frac{\mathrm{i}\hat{h}_1(q_\mathrm{n})\xi'}{\hbar}\right]\exp\left[\frac{\mathrm{i}\hat{h}_1(q_\mathrm{n})t}{\hbar}\right]$$
$$\exp\left[-\frac{\mathrm{i}\hat{h}_1(q_\mathrm{n})\xi}{\hbar}\right]\frac{\partial}{\partial q_\mathrm{n}}\exp\left[-\frac{\mathrm{i}\hat{h}_1(q_\mathrm{n})\tau}{\hbar}\right]$$
$$\exp\left[-\frac{\mathrm{i}\hat{h}_1(q_\mathrm{n})(t-\tau-\xi+\tau'+\xi')}{\hbar}\right]\Big|0_\mathrm{n}\Big\rangle, \tag{27a}$$

and

$$g_\mathrm{s}(\tau',\xi',\tau,\xi,t) = \Big\langle 0_\mathrm{s}\Big|\exp\left[\frac{\mathrm{i}\hat{h}_1(q_\mathrm{s}-\Delta_\mathrm{c})\tau'}{\hbar}\right]$$
$$\exp\left[\frac{\mathrm{i}\hat{h}_1(q_\mathrm{s}-\Delta_\mathrm{d})\xi'}{\hbar}\right]\exp\left[\frac{\mathrm{i}\hat{h}_1(q_\mathrm{s})t}{\hbar}\right]$$
$$\exp\left[-\frac{\mathrm{i}\hat{h}_1(q_\mathrm{s}-\Delta_\mathrm{d})\xi'}{\hbar}\right]\exp\left[-\frac{\mathrm{i}\hat{h}_1(q_\mathrm{s}-\Delta_\mathrm{c})\tau}{\hbar}\right]$$
$$\exp\left[-\frac{\mathrm{i}\hat{h}_1(q_\mathrm{s})}{\hbar}(t-\tau-\xi+\tau'+\xi')\right]\Big|0_\mathrm{s}\Big\rangle. \tag{27}$$

By using the Feynman-disentangle and Boson-operator techniques, the generating functions for the nontotally symmetric and totally symmetric modes, $f_\mathrm{n}(\tau', \xi', \tau, \xi, t)$ and $g_\mathrm{s}(\tau', \xi', \tau, \xi, t)$, can be evaluated as:

$$f_\mathrm{n}(\tau',\xi',\tau,\xi,t) = \frac{1}{2}\exp\left[\mathrm{i}\omega_\mathrm{n}(\xi'-\xi+t)\right], \tag{28}$$

and:

$$g_\mathrm{s}(\tau',\xi',\tau,\xi,t) = \exp\left[\frac{\Delta_\mathrm{c}^2}{2}\{\exp(\mathrm{i}\omega_\mathrm{s}\tau')-1\}\right.$$
$$+\frac{\Delta_\mathrm{c}^2}{2}\{\exp(-\mathrm{i}\omega_\mathrm{s}\tau)-1\}+\frac{\Delta_\mathrm{d}^2}{2}\{\exp(\mathrm{i}\omega_\mathrm{s}\xi')-1\}$$
$$\left.+\frac{\Delta_\mathrm{d}^2}{2}\{\exp(-\mathrm{i}\omega_\mathrm{s}\xi)-1\}\right]\exp\left[\lambda_\mathrm{c}^*(\tau')\lambda_\mathrm{c}^*(\xi')\right.$$
$$+\lambda_\mathrm{c}(\tau)\lambda_\mathrm{c}(\xi)+\exp(\mathrm{i}\omega_\mathrm{s}t)\{\lambda_\mathrm{c}^*(\tau')\exp(\mathrm{i}\omega_\mathrm{s}\xi')+\lambda_\mathrm{d}^*(\xi')\}$$
$$\left.\{\lambda_\mathrm{c}(\tau)\exp(-\mathrm{i}\omega_\mathrm{s}\xi)+\lambda_\mathrm{d}(\xi)\}\right], \tag{28}$$

where

$$\lambda_\mathrm{c}(\tau) = \frac{\Delta_\mathrm{c}}{\sqrt{2}}\{1-\exp(-\mathrm{i}\omega_\mathrm{s}\tau)\}. \tag{29}$$

The $\frac{\partial}{\partial q_\mathrm{n}}=\frac{1}{2}(\hat{b}_\mathrm{n}-\hat{b}_\mathrm{n}^\dagger)$ relation was used. A derivation of Eq. 28 is given in detail in Appendix B. Expanding the last term in Eq. 28, the generating function for the totally symmetric mode, $g_\mathrm{s}(\tau', \xi', \tau, \xi, t)$, is written as:

$$g_\mathrm{s}(\tau',\xi',\tau,\xi,t) = \sum_{n_\mathrm{s}=0}^{\infty}\frac{1}{n_\mathrm{s}!}\{\lambda_\mathrm{c}^*(\tau')\exp(\mathrm{i}\omega_\mathrm{s}\xi')+\lambda_\mathrm{d}^*(\xi')\}^{n_\mathrm{s}}$$
$$\{\lambda_\mathrm{c}(\tau)\exp(-\mathrm{i}\omega_\mathrm{s}\xi)+\lambda_\mathrm{d}(\xi)\}^{n_\mathrm{s}}\exp\left[\frac{\Delta_\mathrm{c}^2}{2}\{\exp(\mathrm{i}\omega_\mathrm{s}\tau')-1\}\right.$$
$$+\frac{\Delta_\mathrm{c}^2}{2}\{\exp(-\mathrm{i}\omega_\mathrm{s}\tau)-1\}+\frac{\Delta_\mathrm{d}^2}{2}\{\exp(-\mathrm{i}\omega_\mathrm{s}\xi)-1\}$$
$$\left.+\lambda_\mathrm{c}^*(\tau')\lambda_\mathrm{d}^*(\xi')+\lambda_\mathrm{c}(\tau)\lambda_\mathrm{d}(\xi)+\mathrm{i}n_\mathrm{s}\omega_\mathrm{s}t\right]. \tag{30}$$

By substituting Eqs. 28 and 30 into Eq. 26 and by integrating over t, we obtain:

$$\frac{\mathrm{d}\sigma_\mathrm{I}^\mathrm{NA}(\omega_1)}{\mathrm{d}\Omega} = k(\omega_1)\sum_{\substack{c\\(c\neq d)}}\sum_{d}\sum_{n_\mathrm{s}=0}^{\infty}\frac{\pi\omega_\mathrm{n}^2}{n_\mathrm{s}!}\int_0^\infty \mathrm{d}\omega_2\omega_2{}^3$$
$$\left|\int_0^\infty\mathrm{d}\tau\int_0^\infty\mathrm{d}\xi\{\lambda_\mathrm{c}(\tau)\exp(-\mathrm{i}\omega_\mathrm{s}\xi)+\lambda_\mathrm{c}(\xi)\}^{n_\mathrm{s}}\right.$$
$$\exp\left[\mathrm{i}\tau\left(\omega_1-\frac{\varepsilon_\mathrm{c}^0}{\hbar}+\frac{\mathrm{i}\tilde{\Gamma}_\mathrm{c}}{2\hbar}\right)+\frac{\Delta_\mathrm{c}^2}{2}\{\exp(-\mathrm{i}\omega_\mathrm{s}\tau)-1\}\right.$$
$$+\mathrm{i}\xi\left(\omega_1-\frac{\varepsilon_\mathrm{d}^0}{\hbar}-\omega_\mathrm{n}+\frac{\mathrm{i}\tilde{\Gamma}_\mathrm{d}}{2\hbar}\right)+\frac{\Delta_\mathrm{d}^2}{2}\{\exp(-\mathrm{i}\omega_\mathrm{s}\xi)-1\}$$
$$\left.\left.+\lambda_\mathrm{c}(\tau)\lambda_\mathrm{d}(\xi)\right]\right|^2\delta(\omega_1-\omega_2-\omega_\mathrm{n}-n_\mathrm{s}\omega_\mathrm{s}). \tag{31}$$

Integrating over ω_2, using the binomial and Taylor expansions, and finally integrating over τ and ξ, we obtain an analytical expression for the nonadiabatically induced RRS cross-section as:

$$\frac{\mathrm{d}\sigma_\mathrm{I}^\mathrm{NA}(\omega_1)}{\mathrm{d}\Omega} = \pi\omega_\mathrm{m}^2k(\omega_1)\sum_{\substack{c\\(c\neq d)}}\sum_{d}\sum_{n_\mathrm{s}=0}^{\infty}\frac{(\omega_1-\omega_\mathrm{n}-n_\mathrm{s}\omega_\mathrm{s})^3}{n_\mathrm{s}!}$$
$$\left|\sum_{l=0}^{n_\mathrm{s}}\binom{n_\mathrm{s}}{l}\left(\frac{\Delta_\mathrm{c}}{\sqrt{2}}\right)\left(\frac{\Delta_\mathrm{d}}{\sqrt{2}}\right)^{n_\mathrm{s}-l}\sum_{m=0}^{\infty}\frac{1}{m!}\left(\frac{\Delta_\mathrm{c}\Delta_\mathrm{d}}{2}\right)^m\right.$$
$$\sum_{p=0}^{l}\binom{l}{p}(-1)^p\sum_{r=0}^{m}\binom{m}{r}(-1)^r$$
$$\sum_{t=0}^{\infty}\frac{S_{\mathrm{i0,ct}}}{\omega_1-\varepsilon_\mathrm{c}^0/\hbar-(p+r+t)\omega_\mathrm{s}+\mathrm{i}\tilde{\Gamma}_\mathrm{c}/(2\hbar)}$$
$$\sum_{q=0}^{n_\mathrm{s}-l}\binom{n_\mathrm{s}-l}{q}(-1)^q\sum_{s=0}^{m}\binom{m}{s}(-1)^s$$
$$\left.\sum_{u=0}^{\infty}\frac{S_{\mathrm{i0,du}}}{\omega_1-\varepsilon_\mathrm{d}^0/\hbar-\omega_\mathrm{n}-(l+q+s+u)\omega_\mathrm{s}+\mathrm{i}\tilde{\Gamma}_\mathrm{d}/2\hbar}\right|^2, \tag{32}$$

where $S_{\mathrm{i0,ct}}$ is the optical Franck-Condon factor between the lowest level in the ground state and the t-th vibrational level in the excited state c; it is given by $S_{\mathrm{i0,ct}}=\left(\frac{\Delta_\mathrm{c}^2}{2}\right)^t\mathrm{e}^{-\frac{\Delta_\mathrm{c}^2}{2}}/t!$. Eq. 32 is the desired analytical expression for the RRS cross-section originating from the nonadiabatic coupling between the two excited states a and b; it consists of the n_s-th order vibrational transition for a totally symmetric mode. In Ref. 28, the results have been given without a detailed derivation.

Vibronically Induced RRS. An analytical expression for the RRS cross-section originating from the vibronic coupling has been derived in Ref. 26.

Interference Terms. In Theory section, the interference RRS cross-sections have been classified into three groups. Because the significant terms are those between the components of the RRS within the same resonant state, and because the interference between the components of the resonant and other excited states can be safely disregarded, the expressions for the RRS cross-section due to the interference are written as:

a): Interference between the components of the vibronically induced RRS:

$$\frac{\mathrm{d}\sigma_\mathrm{I}^\mathrm{INT(VI)}(w_1)}{\mathrm{d}\Omega} \simeq \pm 2\pi k(\omega_1)$$
$$\sum_{c}\sum_{n_\mathrm{s}=0}^{\infty}\frac{(\omega_1-\omega_\mathrm{n}-n_\mathrm{s}\omega_\mathrm{s})^3}{n_\mathrm{s}!}(\Delta_\mathrm{c}^2/2)^{n_\mathrm{s}}$$
$$\mathrm{Re}\left\{\sum_{j=0}^{n_\mathrm{s}}\sum_{j'=0}^{n_\mathrm{s}}\binom{n_\mathrm{s}}{j}\binom{n_\mathrm{s}}{j'}(-1)^{j+j'}\right.$$

$$\sum_{k=0}^{\infty}\sum_{k'=0}^{\infty}\frac{S_{\mathrm{i0,ck}}}{\omega_1-\varepsilon_{\mathrm{c}}^{0}/\hbar-(j+k)\omega_{\mathrm{s}}-\mathrm{i}\tilde{\Gamma}_{\mathrm{c}}/2\hbar}$$

$$\left.\frac{S_{\mathrm{i0,ck'}}}{\omega_1-\varepsilon_{\mathrm{c}}^{0}/\hbar-\omega_{\mathrm{n}}-(j'+k')\omega_{\mathrm{s}}+\mathrm{i}\tilde{\Gamma}_{\mathrm{c}}/2\hbar}\right\}, \tag{33}$$

and:

b): Interference between the components of the vibronically and the nonadiabatically induced RRS:

$$\frac{\mathrm{d}\sigma_{\mathrm{I}}^{\mathrm{INT(VI\text{-}NA)}}(\omega_1)}{\mathrm{d}\Omega}=2\pi\omega_{\mathrm{n}}k(\omega_1)\sum_{\substack{c\\(c\neq d)}}\sum_{d}\sum_{n_{\mathrm{s}}=0}^{\infty}\frac{(\omega_1-\omega_{\mathrm{n}}-n_{\mathrm{s}}\omega_{\mathrm{s}})^3}{n_{\mathrm{s}}!}$$

$$\left(\frac{\Delta_{\mathrm{c}}}{\sqrt{2}}\right)^{n_{\mathrm{s}}}\mathrm{Re}\left\{\sum_{j=0}^{n_{\mathrm{s}}}\binom{n_{\mathrm{s}}}{j}(-1)^j\right.$$

$$\sum_{k=0}^{\infty}\frac{S_{\mathrm{i0,ck}}}{\omega_1-\varepsilon_{\mathrm{c}}^{0}/\hbar-(j+k)\omega_{\mathrm{s}}-\mathrm{i}\tilde{\Gamma}_{\mathrm{c}}/2\hbar}$$

$$\sum_{l=0}^{n_{\mathrm{s}}}\binom{n_{\mathrm{s}}}{l}\left(\frac{\Delta_{\mathrm{c}}}{\sqrt{2}}\right)\left(\frac{\Delta_{\mathrm{d}}}{\sqrt{2}}\right)^{n_{\mathrm{s}}-l}$$

$$\sum_{m=0}^{\infty}\frac{1}{m!}\left(\frac{\Delta_{\mathrm{c}}\Delta_{\mathrm{d}}}{2}\right)^m\sum_{p=0}^{l}\binom{l}{p}(-1)^p\sum_{r=0}^{m}\binom{m}{r}(-1)^r$$

$$\sum_{t=0}^{\infty}\frac{S_{\mathrm{i0,ct}}}{\omega_1-\varepsilon_{\mathrm{c}}^{0}/\hbar-(p+r+t)\omega_{\mathrm{s}}+\mathrm{i}\tilde{\Gamma}_{\mathrm{c}}/2\hbar}$$

$$\sum_{q=0}^{n_{\mathrm{s}}-l}\binom{n_{\mathrm{s}}-l}{q}(-1)^q\sum_{s=0}^{m}\binom{m}{s}(-1)^s$$

$$\sum_{u=0}^{\infty}\frac{S_{\mathrm{i0,du}}}{\omega_1-\varepsilon_{\mathrm{d}}^{0}/\hbar-\omega_{\mathrm{n}}-(l+q+s+u)\omega_{\mathrm{s}}+\mathrm{i}\tilde{\Gamma}_{\mathrm{d}}/2\hbar}$$

$$-\sum_{j=0}^{n_{\mathrm{s}}}\binom{n_{\mathrm{s}}}{j}(-1)^j\sum_{k=0}^{\infty}\frac{S_{\mathrm{i0,ck}}}{\omega_1-\varepsilon_{\mathrm{c}}^{0}/\hbar-\omega_{\mathrm{n}}-(j+k)\omega_{\mathrm{s}}-\mathrm{i}\tilde{\Gamma}_{\mathrm{c}}/2\hbar}$$

$$\sum_{l=0}^{ns}\binom{n_{\mathrm{s}}}{l}\left(\frac{\Delta_{\mathrm{d}}}{\sqrt{2}}\right)\left(\frac{\Delta_{\mathrm{c}}}{\sqrt{2}}\right)^{n_{\mathrm{s}}-l}$$

$$\sum_{m=0}^{\infty}\frac{1}{m!}\left(\frac{\Delta_{\mathrm{c}}\Delta_{\mathrm{d}}}{2}\right)^m\sum_{q=0}^{n_{\mathrm{s}}-l}\binom{n_{\mathrm{s}}-l}{q}(-1)^q\sum_{s=0}^{m}\binom{m}{s}(-1)^s$$

$$\sum_{u=0}^{\infty}\frac{S_{\mathrm{i0,cu}}}{\omega_1-\varepsilon_{\mathrm{c}}^{0}/\hbar-\omega_{\mathrm{n}}-(l+q+s+u)\omega_{\mathrm{s}}+\mathrm{i}\tilde{\Gamma}_{\mathrm{c}}/2\hbar}$$

$$\sum_{p=0}^{l}\binom{l}{p}(-1)^p\sum_{r=0}^{m}\binom{m}{r}(-1)^r$$

$$\left.\sum_{t=0}^{\infty}\frac{S_{\mathrm{i0,dt}}}{\omega_1-\varepsilon_{\mathrm{d}}^{0}/\hbar-(p+r+t)\omega_{\mathrm{s}}+\mathrm{i}\tilde{\Gamma}_{\mathrm{d}}/2\hbar}\right\}. \tag{34}$$

Discussion

In Theory Section, using the Born-Oppenheimer basis set, the RRS cross-section has been formulated. It is shown that the cross-section can be classified into four terms. In this paper, one is called pure RRS, while the others are the vibronically induced and the nonadiabatically induced RRS, and their interferences. The pure RRS, independent of the inducing mode, corresponds to Albrecht's A term,[31] and the vibronically induced RRS, to the B term. The RRS cross-section corresponding to the C term was disregarded because this term makes a negligibly small contribution to the Raman scattering in the resonance region.

In Fig. 2, the excitation profiles of the RRS within the weak coupling limits are analyzed. The spectra on the low- and high-frequency sides reflect the RRS from the a and b electronic states respectively, and they have a mirror symmetry with respect to the plane intersecting the center because the same potential energy surfaces and the same decay widths in the two excited states are assumed. The molecular parameters used are $\varepsilon_{\mathrm{a}}^{0}=21000\ \mathrm{cm}^{-1}$, $\varepsilon_{\mathrm{b}}^{0}=23000\ \mathrm{cm}^{-1}$, $\omega_{\mathrm{n}}=800\ \mathrm{cm}^{-1}$, $\tilde{\Gamma}_{\mathrm{a}}=\tilde{\Gamma}_{\mathrm{b}}=200\ \mathrm{cm}^{-1}$, and $\Delta_{\mathrm{a}}=\Delta_{\mathrm{b}}=0$. The dotted, broken, and solid lines represent the excitation profile of the vibronically induced RRS, that of the nonadiabatically induced RRS, and that of the RRS with both the vibronic and nonadiabatic couplings, including the interference terms respectively.

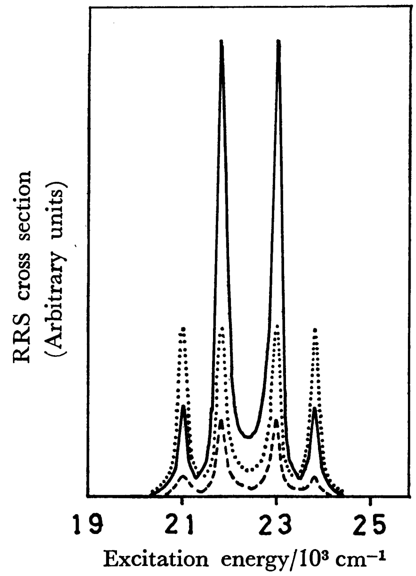

Fig. 2. Excitation profiles of the RRS in the case of $\Delta_{\mathrm{a}}=0$ and $\Delta_{\mathrm{b}}=0$. The dotted, broken, and solid lines represent the excitation profile of the vibronically induced RRS, that of the nonadiabatically induced RRS, and that of the RRS with both the vibronic and nonadiabatic couplings including the interference terms, respectively. The molecular parameters used are $\varepsilon_0^{\mathrm{a}}=21000\ \mathrm{cm}^{-1}$, $\varepsilon_0^{\mathrm{b}}=23000\ \mathrm{cm}^{-1}$, $\omega_{\mathrm{n}}=800\ \mathrm{cm}^{-1}$, and $\tilde{\Gamma}_{\mathrm{a}}=\tilde{\Gamma}_{\mathrm{b}}=200\ \mathrm{cm}^{-1}$. The profiles were plotted neglecting the constants involving the transition moments.

For the vibronically induced RRS, two bands, 0-0 and 0-1, sometimes called Mortensen's doublet, appear on the low- and high-frequency sides of the excitation profile. It is recognized that the RRS from the molecular system with small potential displacements is expressed by the succession of absorption from the ground to the resonance state and emission from the resonance state to the ground state.[11] For the 0-0 and 0-1 bands, the inducing mode operates in the course of the emission and absorption processes respectively. It can easily be seen that the intensities of the two bands are equal, for they have the same energy-denominator dependence of the polarizability.

As a result of the nonadiabatic coupling between the resonant and other excited states, two bands, 0-0 and 0-1, appear in the excitation profile as well. The band intensity of the nonadiabatically induced RRS is inversely proportional to the square of the energy difference between the relevant states; from Eq. 32, the intensities of the 0-0 and 0-1 bands in the case of the resonance with the lower excited state, *a* denoted by $I_{0\text{-}0}^{\mathrm{NA(a)}}$ and $I_{0\text{-}1}^{\mathrm{NA(a)}}$, are given by:

$$I_{0\text{-}0}^{\mathrm{NA(a)}} \propto \left| \frac{\tilde{\Gamma}_{\mathrm{a}}}{2}(\varepsilon_{\mathrm{a}}^{0} - \varepsilon_{\mathrm{b}}^{0} - \hbar\omega_{\mathrm{n}} + \mathrm{i}\tilde{\Gamma}_{\mathrm{b}}/2) \right|^{-2}, \tag{35a}$$

and:

$$I_{0\text{-}1}^{\mathrm{NA(a)}} \propto \left| \frac{\tilde{\Gamma}_{\mathrm{a}}}{2}(\varepsilon_{\mathrm{a}}^{0} - \varepsilon_{\mathrm{b}}^{0} + \hbar\omega_{\mathrm{n}} + \mathrm{i}\tilde{\Gamma}_{\mathrm{b}}/2) \right|^{-2}, \tag{35b}$$

respectively, from which we obtain the relation:

$$I_{0\text{-}0}^{\mathrm{NA(a)}} < I_{0\text{-}1}^{\mathrm{NA(a)}}. \tag{36}$$

Similarly, for the case of the resonance with the upper state *b*, we obtain:

$$I_{0\text{-}0}^{\mathrm{NA(b)}} \propto \left| \frac{\tilde{\Gamma}_{\mathrm{b}}}{2}(\varepsilon_{\mathrm{b}}^{0} - \varepsilon_{\mathrm{a}}^{0} - \hbar\omega_{\mathrm{n}} + \mathrm{i}\tilde{\Gamma}_{\mathrm{a}}/2) \right|^{-2}, \tag{37a}$$

$$I_{0\text{-}1}^{\mathrm{NA(b)}} \propto \left| \frac{\Gamma_{\mathrm{b}}}{2}(\varepsilon_{\mathrm{b}}^{0} - \varepsilon_{\mathrm{a}}^{0} + \hbar\omega_{\mathrm{n}} + \mathrm{i}\tilde{\Gamma}_{\mathrm{a}}/2) \right|^{-2}, \tag{37b}$$

and then:

$$I_{0\text{-}0}^{\mathrm{NA(b)}} > I_{0\text{-}1}^{\mathrm{NA(b)}}$$

As is shown in Fig. 2, the asymmetry of the 0-0 and 0-1 bands originates from the interference between the vibronically induced RRS and nonadiabatically induced one. The main contribution of the interference comes from Eq. 34. In the cases of the small displacement, Eq. 34 can be expressed as:

$$\frac{\mathrm{d}\sigma_{\mathrm{I}}^{\mathrm{INT(VI-NA)}}(\omega_1)}{\mathrm{d}\Omega} \simeq 2\pi\omega_{\mathrm{n}}(\omega_1 - \omega_{\mathrm{n}})^3 \sum_{c} \sum_{\substack{d \\ (c \neq d)}} \left\{ \frac{\omega_1 - \varepsilon_{\mathrm{d}}^{0}/\hbar - \omega_{\mathrm{n}}}{[(\omega_1 - \varepsilon_{\mathrm{c}}^{0}/\hbar)^2 + (\tilde{\Gamma}_{\mathrm{c}}/2\hbar)^2][(\omega_1 - \varepsilon_{\mathrm{d}}^{0}/\hbar - \omega_{\mathrm{n}})^2 + (\tilde{\Gamma}_{\mathrm{d}}/2\hbar)^2]} - \frac{\omega_1 - \varepsilon_{\mathrm{d}}^{0}/\hbar}{[(\omega_1 - \varepsilon_{\mathrm{c}}^{0}/\hbar)^2 + (\tilde{\Gamma}_{\mathrm{c}}/2\hbar)^2][(\omega_1 - \varepsilon_{\mathrm{d}}^{0}/\hbar)^2 + (\tilde{\Gamma}_{\mathrm{d}}/2\hbar)^2]} \right\}. \tag{38}$$

This expression indicates that, for the resonance with the lower excited state, *a*, the interference term between the vibronically induced RRS and the nonadiabatically induced one decreases the 0-0 band intensity and increases the 0-1 band intensity. On the other hand, for the resonance with the higher excited state, *b*, this term interferes, constructively near the 0-0 band and destructively near the 0-1 band. Eq. 33, representing the interference between the vibronically induced RRS, does not contribute to the asymmetry of the excitation profile, but makes an important contribution to the depolarization ratio.[26]

Let us now focus our attention on the effects of the RRS on the molecular parameters. In the displaced harmonic oscillator model, analytical expressions for the n_s-th order vibrational transitions of the RRS cross-sections have been derived; these cross-sections are expressed in terms of the molecular parameters, such as the dimensionless potential displacements, the molecular vibrational frequencies, the decay widths, and the electronic energy gaps. Using the analytical expressions, we have performed model calculations of the excitation profiles of the n_s-th order vibrational transitions.

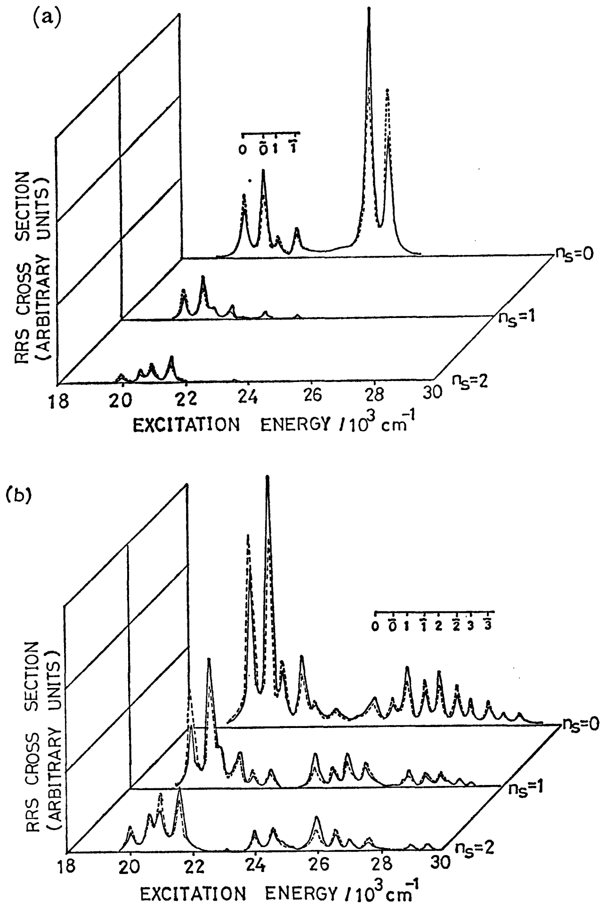

Fig. 3. The dimensionless displacements Δ_{a} and Δ_{b} dependence of the excitation profiles of the n_s-th order vibrational transition. The progressions of the totally symmetric vibration built upon one quantum of the coupling mode are monitored. The following parameters are used: $\varepsilon_{\mathrm{a}}^{0}=20000\ \mathrm{cm}^{-1}$; $\varepsilon_{\mathrm{b}}^{0}=24000\ \mathrm{cm}^{-1}$; $\omega_{\mathrm{n}}=600\ \mathrm{cm}^{-1}$ and $\omega_{\mathrm{s}}=1000\ \mathrm{cm}^{-1}$; $\tilde{\Gamma}_{\mathrm{a}}=\tilde{\Gamma}_{\mathrm{b}}=200\ \mathrm{cm}^{-1}$; $\Delta_{\mathrm{b}}=0.1$, and 1.0 in Figs. 3a and 3b, respectively, and $\Delta_{\mathrm{a}}=1.0$. The ordinate is shown without $k(\omega_1)$. The broken line represents the excitation profile without the nonadiabatic coupling, and the solid line the whole excitation profile with both the nonadiabatic and vibronic couplings including the interference terms. The band peaks which appear in the zero order vibrational transition ($n_s=0$) of the excited state, *a* in Fig. 3a and those of the excited state, *b* in Fig. 3b are indicated by the vibrational quantum number of the displaced oscillator excited in the resonant states. The band peaks with the wavy line above the number represent the one quantum excitation of the inducing mode in addition to the excitation of the displaced oscillator.

It should be noted that the expressions derived in this paper are applicable to the RRS of the molecular system with any displacement. In Figs. 3, the effects of the dimensionless displacements, Δ_{a} and Δ_{b}, are shown. The excitation profiles of the first order, $n_s=1$ and the second order, $n_s=2$, vibrational transitions, in addition to the zero-order transition, are plotted. The progressions of the totally symmetric vibrational mode built upon one quantum of the inducing mode were monitored. The broken line represents the

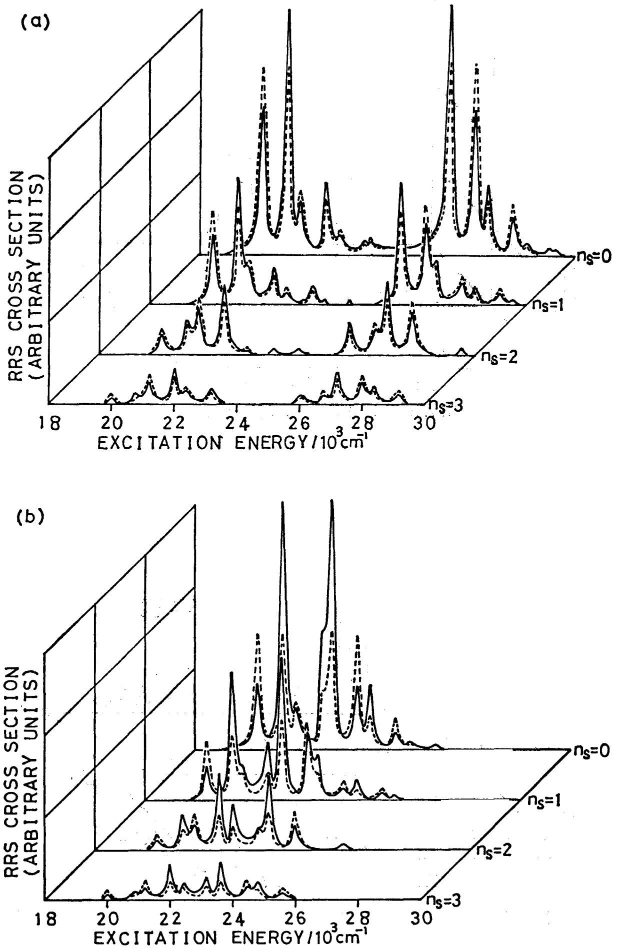

Fig. 4. The electronic gap dependence of the excitation profiles of the n_s-th order vibrational transition. The following molecular parameters are used: $\omega_n=800$ cm^{-1} and $\omega_s=1200$ cm^{-1}; $\Delta_a=\Delta_b=1.0$; $\varepsilon_b^0=26000$ cm^{-1}, and 22400 cm^{-1} in Figs. 4a and 4b, respectively. The others are the same as those in Fig. 3.

excitation profile without the nonadiabatic coupling, and the solid line, that with both the nonadiabatic and vibronic couplings. The displacements used are $\Delta_a=1.0$, and $\Delta_b=0.1$ and 2.0 in Figs. 3a and 3b respectively. The other parameters are $\varepsilon_a^0=20000$ cm^{-1}, $\varepsilon_b^0=24000$ cm^{-1}, $\omega_n=600$ cm^{-1}, $\omega_s=1000$ cm^{-1}, and $\tilde{\Gamma}_a=\tilde{\Gamma}_b=200$ cm^{-1}. In Figs. 3a and 3b, the band peaks which appear in the zero-order vibrational transitions of the excited states, *a* and *b*, are indicated by the vibrational quantum number of the respective displaced oscillator excited in the resonant states. The band peaks with the wavy line above the number represent the one-quantum excitation of the inducing mode in addition to the excitation of the displaced oscillator. It can be seen that, as the displacements increase, the first- and second-order vibrational transitions, as well as the zero-order transition, appear in the excitation profiles. The nonadiabatic coupling makes significant contributions not only to the latter transition, but also to the former transitions.

In Figs. 4, the electronic-energy-gap dependence of the RRS is shown as a function of the incident photon frequency, ω_1. The progressions for the totally symmetric vibration of $\omega_s=1200$ cm^{-1}, built upon one quantum of the inducing mode of $\omega_n=800$ cm^{-1}, are monitored. In these figures, $\Delta_a=\Delta_b=1.0$ was assumed. The electronic-energy-gaps, ε_b^0 are taken to be 26000 cm^{-1} and 22400 cm^{-1} in Figs. 4a, and 4b respectively. The others are the same as those in Figs. 3. The Figures 4 indicate that the nonadiabatic coupling plays an important role, as the two excited states exist close to each other. The nonadiabatic coupling effect on the higher-order vibrational transitions is qualitively similar that on the zero-order transition.

In the model calculations shown in Figs. 3 and 4, the effects of the potential displacements and those of the electronic-energy gap between two excited states are examined, the other parameters being fixed. In order to apply the theoretical results developed in this paper to analyzing the observed excitation profiles of the RRS, such molecular parameters as the decay widths, $\tilde{\Gamma}_a$ and $\tilde{\Gamma}_b$, should be properly chosen.[32]

In summary, in this paper, we have developed a theory of the RRS from two electronically excited states coupled by a nontotally symmetric mode. The vibronic and nonadiabatic coupling effects on the RRS cross-sections have been examined. The RRS cross-sections have been classified into four groups according to the mechanisms: one is the RRS independent of the inducing mode, while the others are the vibronically induced and the nonadiabatically induced RRS, and their interference terms. Assuming a model system with two vibrational modes, the inducing mode, and a totally symmetric mode characterized by a displaced harmonic oscillator, analytical expressions for the RRS cross-sections have been derived. The expressions consisting of the n_s-th order vibrational transition of the totally symmetric mode are explicitly formulated as a function of the two displacement parameters between the equilibrium points in the ground state and in the two excited states, and are applicable to the system with any potential displacement.

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Appendix A: Expressions for the Interference RRS Cross-sections

The interference term between the vibronically induced RRS is given by:

$$\frac{\mathrm{d}\sigma_{\mathrm{I}}^{\mathrm{INT(VI)}}(\omega_1)}{\mathrm{d}\Omega} = k(\omega_1)\int_0^\infty \mathrm{d}\omega_2\omega_2^3\int_0^\infty \mathrm{d}\tau'\int_0^\infty \mathrm{d}\tau\int_0^\infty \mathrm{d}t$$
$$\exp\,[-\mathrm{i}(t-\tau+\tau')\omega_1+\mathrm{i}t\omega_2]$$
$$\{\sum_c\,[\pm\langle\chi_{\mathrm{i}}|\alpha_{\mathrm{c}}^*(\tau')q_{\mathrm{n}}\beta_{\mathrm{i}}(t)\alpha_{\mathrm{c}}(\tau)q_{\mathrm{n}}\beta_{\mathrm{i}}(t-\tau+\tau')|\chi_{\mathrm{i}}\rangle$$
$$\pm\langle\chi_{\mathrm{i}}|q_{\mathrm{n}}\alpha_{\mathrm{c}}^*(\tau')\beta_{\mathrm{i}}^*(t)q_{\mathrm{n}}\alpha_{\mathrm{d}}(\tau)\beta_{\mathrm{i}}(t-\tau+\tau')|\chi_{\mathrm{i}}\rangle$$
$$+\sum_{c}\sum_{\substack{d\\(c\neq d)}}[\mp\langle\chi_{\mathrm{i}}|\alpha_{\mathrm{c}}^*(\tau')q_{\mathrm{n}}\beta_{\mathrm{i}}^*(t)q_{\mathrm{n}}\alpha_{\mathrm{d}}(\tau)\beta_{\mathrm{i}}(t-\tau+\tau')|\chi_{\mathrm{i}}\rangle$$
$$-\langle\chi_{\mathrm{i}}|\alpha_{\mathrm{c}}^*(\tau')q_{\mathrm{n}}\beta_{\mathrm{i}}^*(t)\alpha_{\mathrm{d}}(\tau)q_{\mathrm{n}}\beta_{\mathrm{i}}(t-\tau+\tau')|\chi_{\mathrm{i}}\rangle$$
$$-\langle\chi_{\mathrm{i}}|q_{\mathrm{n}}\alpha_{\mathrm{d}}^*(\tau')\beta_{\mathrm{i}}^*(t)q_{\mathrm{n}}\alpha_{\mathrm{i}}(\tau)\beta_{\mathrm{i}}(t-\tau+\tau')|\chi_{\mathrm{i}}\rangle$$
$$\mp\langle\chi_{\mathrm{i}}|q_{\mathrm{n}}\alpha_{\mathrm{c}}^*(\tau')\beta_{\mathrm{i}}^*(t)\alpha_{\mathrm{d}}(\tau)q_{\mathrm{n}}\beta_{\mathrm{i}}(t-\tau+\tau')|\chi_{\mathrm{i}}\rangle]\},\qquad(\mathrm{A.1})$$

where

$$k(\omega_1)=\omega_1|M_{\mathrm{gb}}(2)V_{\mathrm{ba}}M_{\mathrm{ag}}(1)|^2/(2^7\pi^3\varepsilon_0{}^2c^4\hbar^2),$$
$$\alpha_{\mathrm{c}}(\tau)=\exp\,[-(\mathrm{i}\hat{H}_{\mathrm{c}}^0-\tilde{\Gamma}_{\mathrm{c}}/2)\tau/\hbar],$$

and

$$\beta_{\mathrm{i}}(t)=\exp\,[-\mathrm{i}\hat{H}_{\mathrm{i}}^0t/\hbar].$$

The interference term between the nonadiabatically induced RRS is given by:

$$\frac{\mathrm{d}\sigma_{\mathrm{I}}^{\mathrm{INT(NA)}}(\omega_1)}{\mathrm{d}\Omega}=\mp\omega_{\mathrm{n}}^2k(\omega_1)\sum_{c}\sum_{\substack{d\\(c\neq d)}}$$
$$\int_0^\infty \mathrm{d}\omega_2\omega_2^3\int_0^\infty \mathrm{d}\tau'\int_0^\infty \mathrm{d}\xi'\int_0^\infty \mathrm{d}\tau\int_0^\infty \mathrm{d}\xi\int_{-\infty}^\infty \mathrm{d}t$$
$$\exp\,[-i(t-\tau-\xi+\tau'+\xi')\omega_1+\mathrm{i}t\omega_2]$$
$$\langle\chi_{\mathrm{i}}|\alpha_{\mathrm{c}}^*(\tau')(\partial/\partial q_{\mathrm{n}})^\dagger\alpha_{\mathrm{c}}^*(\xi')\beta_{\mathrm{i}}^*(t)\alpha_{\mathrm{c}}(\tau)$$
$$(\partial/\partial q_{\mathrm{n}})\alpha_{\mathrm{d}}(\xi)\beta_{\mathrm{i}}(t-\tau-\xi+\tau'+\xi')|\chi_{\mathrm{i}}\rangle.\qquad(\mathrm{A.2})$$

The interference term between the vibronically induced and the nonadiabatically induced RRS is given by:

$$\frac{\mathrm{d}\sigma_{\mathrm{I}}^{\mathrm{INT(VI\text{-}NA)}}(\omega_1)}{\mathrm{d}\Omega}=\omega_{\mathrm{n}}k(\omega_1)\sum_{c}\sum_{\substack{d\\(c\neq d)}}$$
$$\int_0^\infty \mathrm{d}\omega_2\omega_2^3\int_0^\infty \mathrm{d}\tau'\int_0^\infty \mathrm{d}\tau\int_0^\infty \mathrm{d}\xi\int_{-\infty}^\infty \mathrm{d}t$$
$$\{\exp[-\mathrm{i}(t-\tau-\xi+\tau')\omega_1+\mathrm{i}t\omega_2]$$
$$[\langle\chi_{\mathrm{i}}|\alpha_{\mathrm{c}}^*(\tau')q_{\mathrm{n}}\beta_{\mathrm{i}}(t)\alpha_{\mathrm{d}}(\xi)(\mathrm{i}\partial/\partial q_{\mathrm{n}})\alpha_{\mathrm{c}}(\tau)$$
$$\beta_{\mathrm{i}}(t-\tau-\xi+\tau')|\chi_{\mathrm{i}}\rangle$$
$$\mp\langle\chi_{\mathrm{i}}|\alpha_{\mathrm{c}}^*(\tau')q_{\mathrm{n}}\beta_{\mathrm{i}}^*(t)\alpha_{\mathrm{c}}(\tau)(\mathrm{i}\partial/\partial q_{\mathrm{n}})\alpha_{\mathrm{d}}(\xi)\beta_{\mathrm{i}}(t-\tau-\xi+\tau')$$
$$|\chi_{\mathrm{i}}\rangle\pm\langle\chi_{\mathrm{i}}|q_{\mathrm{n}}\alpha_{\mathrm{c}}^*(\tau')\beta_{\mathrm{i}}^*(t)\alpha_{\mathrm{d}}(\xi)(\mathrm{i}\partial/\partial q_{\mathrm{n}})\alpha_{\mathrm{c}}(\tau)$$
$$\beta_{\mathrm{i}}(t-\tau-\xi+\tau')|\chi_{\mathrm{i}}\rangle-\langle\chi_{\mathrm{i}}|q_{\mathrm{n}}\alpha_{\mathrm{c}}^*(\tau')\beta_{\mathrm{i}}^*(t)\alpha_{\mathrm{c}}(\tau)(\mathrm{i}\partial/\partial q_{\mathrm{n}})$$
$$\alpha_{\mathrm{d}}(\xi)\beta_{\mathrm{i}}(t-\tau-\xi+\tau')|\chi_{\mathrm{i}}\rangle]+$$
$$\exp[-\mathrm{i}(t-\tau+\tau'+\xi)\omega_1+\mathrm{i}t\omega_2][\langle\chi_{\mathrm{i}}|\alpha_{\mathrm{c}}^*(\tau')(\mathrm{i}\partial/\partial q_{\mathrm{n}})^\dagger$$
$$\alpha_{\mathrm{d}}^*(\xi')\beta_{\mathrm{i}}^*(t)q_{\mathrm{n}}\alpha_{\mathrm{c}}(\tau)\beta_{\mathrm{i}}(t-\tau+\tau'+\xi)|\chi_{\mathrm{i}}\rangle$$
$$\mp\langle\chi_{\mathrm{i}}|\alpha_{\mathrm{d}}^*(\xi)(\mathrm{i}\partial/\partial q_{\mathrm{n}})^\dagger\alpha_{\mathrm{c}}^*(\tau')\beta_{\mathrm{i}}^*(t)q_{\mathrm{n}}\alpha_{\mathrm{c}}(\tau)\beta_{\mathrm{i}}(t-\tau+\tau'+\xi)$$
$$|\chi_{\mathrm{i}}\rangle\pm\langle\chi_{\mathrm{i}}|\alpha_{\mathrm{c}}^*(\tau')(\mathrm{i}\partial/\partial q_{\mathrm{n}})^\dagger\alpha_{\mathrm{d}}^*(\xi)\beta_{\mathrm{i}}^*(t)\alpha_{\mathrm{c}}(\tau)q_{\mathrm{n}}\beta_{\mathrm{i}}$$
$$(t-\tau+\tau'+\xi)|\chi_{\mathrm{i}}\rangle-\langle\chi_{\mathrm{i}}|\alpha_{\mathrm{d}}^*(\xi)(\mathrm{i}\partial/\partial q_{\mathrm{n}})^\dagger$$
$$\alpha_{\mathrm{c}}^*(\tau')\beta_{\mathrm{i}}^*(t)\alpha_{\mathrm{c}}(\tau)q_{\mathrm{n}}\beta_{\mathrm{i}}(t-\tau+\tau'+\xi)|\chi_{\mathrm{i}}\rangle]\}.\qquad(\mathrm{A.3})$$

Appendix B: Derivation of Eq. 28

In this appendix, we will present a brief derivation of Eq. 28 by utilizing the Boson operator algebra. By using this relation:[11]

$$\exp\left[\frac{\mathrm{i}\hat{h}_{\mathrm{i}}(q_{\mathrm{s}}-\Delta_{\mathrm{c}})\tau'}{\hbar}\right]=\exp\left[\frac{\Delta_{\mathrm{c}}^2}{2}\{\exp\,(\mathrm{i}\omega_{\mathrm{s}}\tau')-1\}\right]$$
$$\exp\left(\frac{\mathrm{i}\hat{h}_{\mathrm{i}}\tau'}{\hbar}\right)\exp\,[-\lambda_{\mathrm{c}}(\tau')\hat{b}_{\mathrm{s}}^\dagger]\,\exp\,[\lambda_{\mathrm{c}}^*(\tau')\hat{b}_{\mathrm{s}}],\qquad(\mathrm{B.1})$$

where $\lambda_{\mathrm{c}}(\tau')=\dfrac{\Delta_{\mathrm{c}}}{\sqrt{2}}[1-\exp(-\mathrm{i}\omega_{\mathrm{s}}\tau')]$, Eq. 27 is expressed as:

$$g_{\mathrm{s}}(\tau',\xi',\tau,\xi,t)=\exp\left[\frac{\Delta_{\mathrm{c}}^2}{2}\{\exp\,(\mathrm{i}\omega_{\mathrm{s}}\tau')-1\}\right.$$
$$+\frac{\Delta_{\mathrm{c}}^2}{2}\{\exp\,(-\mathrm{i}\omega_{\mathrm{s}}\tau)-1\}+\frac{\Delta_{\mathrm{d}}^2}{2}\{\exp\,(\mathrm{i}\omega_{\mathrm{s}}\xi')-1\}$$
$$\left.+\frac{\Delta_{\mathrm{d}}^2}{2}\{\exp\,(-\mathrm{i}\omega_{\mathrm{s}}\xi)-1\}\right]\langle 0_{\mathrm{s}}|\exp(\mathrm{i}\omega_{\mathrm{s}}\tau\hat{b}_{\mathrm{s}}^\dagger\hat{b}_{\mathrm{s}})$$

$$
\begin{aligned}
&\exp[-\lambda_c(\tau')\hat{b}_s^\dagger]\exp[\lambda_c^*(\tau')\hat{b}_s]\exp[i\omega_s\xi\hat{b}_s^\dagger\hat{b}_s]\\
&\exp[-\lambda_d(\xi')\hat{b}_s^\dagger]\exp[\lambda_d^*(\xi')\hat{b}_s]\exp[i\omega_s t\hat{b}_s^\dagger\hat{b}_s]\\
&\exp[\lambda_d(\xi)\hat{b}_s^\dagger]\exp[-\lambda_d^*(\xi)\hat{b}_s]\exp[-i\omega_s\xi\hat{b}_s^\dagger\hat{b}_s]\\
&\exp[\lambda_c(\tau)\hat{b}_s^\dagger]\exp[-\lambda_c^*(\tau)\hat{b}_s]\exp[-i\omega_s\tau\hat{b}_s^\dagger\hat{b}_s]\\
&\exp[-i\omega_s(t-\tau-\xi+\tau'+\xi')\hat{b}_s^\dagger\hat{b}_s]\,|0\rangle. \qquad (\mathrm{B}.2)
\end{aligned}
$$

By using the Boson operator algebra,[11] Eq. (B.2) is expressed as:

$$
\begin{aligned}
g_s(\tau',\xi',\tau,\xi,t) = \exp\Big[&\frac{\Delta_c^2}{2}\{\exp(i\omega_s\lambda')-1\}\\
&+\frac{\Delta_c^2}{2}\{\exp(-i\omega_s\tau)-1\}+\frac{\Delta_d^2}{2}\{\exp(i\omega_s\xi')-1\}\\
&+\frac{\Delta_d^2}{2}\{\exp(-i\omega_s\xi)-1\}+\lambda_c^*(\tau')\lambda_d^*(\xi')\\
&+\lambda_c(\tau)\lambda_d(\xi)+\lambda_d^*(\xi')\lambda_d(\xi)\exp(i\omega_s t)\\
&+\lambda_c(\tau)\lambda_d^*(\xi')\exp(-i\omega_s\xi+i\omega_s t)\\
&+\lambda_c^*(\tau')\lambda_d(\xi)\exp(i\omega_s\xi+i\omega_s t)\\
&+\lambda_c^*(\tau')\lambda_c(\tau)\exp(i\omega_s\xi'-i\omega_s\xi+i\omega_s t)\Big]. \qquad (\mathrm{B}.3)
\end{aligned}
$$

This expression is equivalent to Eq. 28.