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Theory of Time-resolved Resonance Raman Scattering from Vibrationally Hot Molecules

Yuichi Fujimura,* Yukiyoshi Ohtsuki, and Takeshi Nakajima
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980

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A theory of time-resolved resonance Raman scattering (RRS) from molecules is developed. The time-resolved RRS cross section is defined as a product of the time-dependent vibronic energy distribution and the scattering cross section from the single vibronic level. The theory is applied to the time-resolved RRS from vibrationally hot molecules whose vibronic distribution characterized by a canonical distribution with temperature higher than that of the heat bath relaxes to the equilibrium one in the presence of a collisional vibrational relaxation. Analytical expressions for the time-resolved RRS cross section are derived within a displaced harmonic oscillator model. It is shown that in the strong coupling case the intensities of the Stokes and anti-Stokes Raman bands in the rigorous resonance case vary inversely as the time-dependent average vibrational occupation number. Some model calculations are performed to illustrate the time-dependent intensity changes of the Raman bands.

Time-resolved Raman spectroscopy is one of the attractive methods for studying relaxation dynamics taking place in highly non-equilibrium ground or electronically excited states of molecules. There have been a considerable number of experimental results on the application of the time-resolved Raman spectroscopy to vibronically excited molecules, photochemical and biological intermediates and so on.[1,2]

Let us consider vibrationally hot molecules characterized by a canonical distribution with temperature T^0 higher than that of the heat bath T. This distribution relaxes to the equilibrium distribution with T after collisional vibrational relaxations. The vibrational energy distribution in the v vibrational state at time t is given as[3]

$$\rho_v(t) = \{1 - \exp[-u(t)]\}\exp[-vu(t)], \tag{1}$$

where

$$u(t) = \log\left[\frac{\exp[-z(t)]\{1-\exp(\theta-\theta^0)\}-\exp(\theta)\{1-\exp(-\theta^0)\}}{\exp[-z(t)]\{1-\exp(\theta-\theta^0)\}-\{1-\exp(-\theta^0)\}}\right], \tag{2}$$

with $z(t)=\kappa t\{1-\exp(-\theta)\}$, $\theta=\hbar\omega/kT$ and $\theta^0=\hbar\omega/kT^0$ in which κ is the collisional vibrational relaxation constant, and ω is the frequency of the vibrational mode of the molecule. The canonically hot molecules are produced by a shock wave method[4] or by a radiationless transition following an optical excitation[5] *etc.* The collisional vibrational relaxation of the hot molecules in the presence of heat bath molecules has mainly been investigated by using the time-resolved one-photon absorption technique so far.[5] The typical relaxation times are in micro to nanoseconds region, depending on the pressure of the perturber molecules. Application of the time-resolved Raman spectroscopy to the investigation of the relaxation mechanism has not been reported. It is interesting to mention the difference in the band structure between the time-resolved one-photon absorption spectra and the time-resolved Raman spectra to be observed. The former consists of a structureless, broad bands,[5] and on the other hand, the latter should consist of vibrational Stokes and anti-Stokes band structures in a highly non-equilibrium condition. The broad band structure in the absorption spectra originates mainly from electronic relaxations taking place in the optically excited electronic state. Compared with the time-resolved absorption method, the time-resolved Raman scattering method may make a significant contribution to analyzing the relaxation mechanism from the view point of the band structure mentioned above.

In this paper we present an applicability of the time-resolved Raman spectroscopy to analyzing the relaxation mechanism of the canonically hot molecules and show how the collisional vibrational relaxation reflects the time-resolved Raman spectra. For this purpose we derive an expression for the cross section of the time-resolved resonance Raman scattering. To our knowledge, there are few theoretical papers on the time-resolved Raman spectroscopy applied to highly non-equilibrium system so far. Luzzi and Vasconcellos,[6] and Vasconcellos and Luzzi[7] have developed a theoretical study of the time-resolved Raman scattering from a highly photoexcited semiconductor plasma by using the Zubarev non-equilibrium ensemble method. In the next section we use the generating function method to derive the time-resolved resonance Raman scattering cross section. This method has been proved to be a powerful method for deriving the Raman scattering cross section of molecules.[8,9]

Theory

We consider a resonance Raman scattering (RRS) from initial state $a\{v\}$ to final state $a\{v'\}$ *via* resonant state $b\{m\}$ where a and b denote the initial (final) and resonant electronic states, respectively, and { } denote the relevant vibrational states. The time-resolved RRS differential cross section in a solid angle $d\Omega$ per unit scattered photon frequency ω_2, $d^2\sigma(\omega_1,\omega_2,t)/d\Omega d\omega_2$ is defined as

$$\frac{d^2\sigma(\omega_1,\omega_2,t)}{d\Omega d\omega_2} = \sum_v \rho_v(t)\,\frac{d^2\sigma_v(\omega_1,\omega_2)}{d\Omega d\omega_2}, \tag{3}$$

where ω_1 is the incident photon frequency, $d^2\sigma_v(\omega_1,\omega_2)/d\Omega d\omega_2$ is the RRS differential cross section from single vibronic level (SVL) v, and $\rho_v(t)$ is the population of the initial vibrational state v at time t. In this treatment, it is assumed that the time-dependence of the population can be observed after transient effects have terminated. The single vibronic level RRS cross section is expressed as

$$\frac{\mathrm{d}^2\sigma_v(\omega_1,\omega_2)}{\mathrm{d}\Omega \mathrm{d}\omega_2} = C\omega_1\omega_2^3\sum_{v'}\frac{\Gamma_{av',av}}{(\omega_{v',v}-\omega_1+\omega_2)^2+\Gamma^2_{av',av}} \times \left|\sum_m \frac{M_{av',bm}(2)M_{bm,av}(1)}{i(\omega_{bm,av}-\omega_1)+\Gamma_{bm,av}}\right|^2, \tag{4}$$

where $C=(2\pi\hbar^2\varepsilon_0 c^4)^{-1}$, and $M_{bm,av}$ (1)represents the component of the transition moment along the polarization direction $\hat{e}_1$ between two vibronic states bm and av. $\Gamma_{av',av}$ and $\Gamma_{bm,av}$ are the dephasing constant associated with the initial and final states, and that with the resonant and initial states, respectively.

In order to derive an expression for the time-resolved RRS differential cross section, it is convenient to express Eq. 4 in terms of the generating function,

$$\frac{\mathrm{d}^2\sigma_v(\omega_1,\omega_2)}{\mathrm{d}\Omega \mathrm{d}\omega_2} = \frac{1}{2}C\omega_1\omega_2^3|M^0_{ab}(2)M^0_{ba}(1)|^2\int_0^\infty \mathrm{d}\tau\int_0^\infty \mathrm{d}\tau'\int_{-\infty}^\infty \mathrm{d}\xi \times \exp[\mathrm{i}\xi(\omega_1-\omega_2)+\mathrm{i}\omega_1(\tau'-\tau) - \Gamma_{\mathrm{ba}}(\tau+\tau')-\Gamma_{v'v}|\xi|]G_v(\tau,\tau',\xi), \tag{5}$$

where the generating function for the single vibronic level RRS, $G_v(\tau,\tau',\xi)$ takes the form,

$$G_v(\tau,\tau',\xi) = \langle v|\exp[\mathrm{i}\hat{H}_{\mathrm{b}}\tau/\hbar]\exp[-\mathrm{i}\hat{H}_{\mathrm{a}}\xi/\hbar]\exp[-\mathrm{i}\hat{H}_{\mathrm{b}}\tau'/\hbar] \times \exp[\mathrm{i}\hat{H}_{\mathrm{a}}(\xi-\tau+\tau')/\hbar]|v\rangle. \tag{6}$$

In deriving Eq. 5, the vibrational quantum number dependence of the dephasing constants has been omitted, that is, Γ_{ba} and $\Gamma_{v'v}$ should be interpreted as the average electronic and vibrational dephasing constants, respectively, and the Condon approximation has been used, that is, electronic transition moments $M^0_{ab}(2),M^0_{ba}(1)$ are independent of the nuclear coordinates.

In the displaced harmonic oscillator model, in which the Hamiltonians of the initial (final) electronic and the resonant electronic states are given by

$$\hat{H}_a = \frac{\hbar\omega}{2}(\hat{p}^2+q^2) = \hbar\omega(\hat{b}^\dagger\hat{b}+\frac{1}{2}), \tag{7a}$$

and

$$\hat{H}_b = \frac{\hbar\omega}{2}[\hat{p}^2+(q-\Delta)^2]+\varepsilon^0 = \hat{H}_a-\frac{\hbar\omega\Delta}{\sqrt{2}}(\hat{b}+\hat{b}^\dagger)+\frac{\hbar\omega\Delta^2}{2}+\varepsilon^0, \tag{7b}$$

we can derive the generating function, Eq. 6 as

$$G_v(\tau,\tau',\xi) = \exp\left[\frac{\mathrm{i}\varepsilon^0(\tau-\tau')}{\hbar}+\frac{\Delta^2}{2}\{\exp(\mathrm{i}\omega\tau)-1\}\right.$$

$$\left. +\frac{\Delta^2}{2}\{\exp(-\mathrm{i}\omega\tau')-1\} + \lambda^*(\tau)\lambda(\tau')\exp(-\mathrm{i}\omega\xi)\right]L_v(|\alpha(\tau,\tau',\xi)|^2), \tag{8}$$

where ω is the frequency of the harmonic oscillator, Δ is the dimensionless displacement between the equilibrium positions in the initial and resonant states and ε^0 represents the electronic energy gap between the bottoms of the two electronic states. A detailed derivation is given in Appendix A. In Eq. 8, L_v, the Laguerre polynomials, is defined as

$$L_v(|\alpha(\tau,\tau',\xi)|^2) = \sum_{k=0}^{v}\frac{v!(-|\alpha(\tau,\tau',\xi)|^2)^k}{(k!)^2(v-k)!}, \tag{9}$$

with

$$\alpha(\tau,\tau',\xi) = \lambda(\tau)-\lambda(\tau')\exp(-\mathrm{i}\omega\xi), \tag{10}$$

and

$$\lambda(\tau) = \frac{\Delta}{\sqrt{2}}\{1-\exp(-\mathrm{i}\omega\tau)\}.$$

Substituting Eqs. 1 and 5 with Eq. 8 into Eq. 3, and carrying out summation over v, we obtain

$$\frac{\mathrm{d}^2\sigma(\omega_1,\omega_2,t)}{\mathrm{d}\Omega \mathrm{d}\omega_2} = \frac{1}{2}C\omega_1\omega_2^3|M^0_{ab}(2)M^0_{ba}(1)|^2\int_0^\infty \mathrm{d}\tau\int_0^\infty \mathrm{d}\tau'\int_{-\infty}^\infty \mathrm{d}\xi \times \exp[\mathrm{i}\xi(\omega_1-\omega_2)+\mathrm{i}\omega_1(\tau'-\tau) - \Gamma_{ba}(\tau+\tau')-\Gamma_{v'v}|\xi|]G(\tau,\tau',\xi), \tag{11}$$

where

$$G(\tau,\tau',\xi) = \exp\left[\mathrm{i}\varepsilon^0(\tau-\tau')/\hbar-\{v(t)+1\}\left\{\frac{\Delta}{\sqrt{2}}\lambda^*(\tau) + \frac{\Delta}{\sqrt{2}}\lambda(\tau')-\lambda^*(\tau)\lambda(\tau')\exp(-\mathrm{i}\omega\xi)\right\} - v(t)\left\{\frac{\Delta}{\sqrt{2}}\lambda(\tau)+\frac{\Delta}{\sqrt{2}}\lambda^*(\tau') - \lambda(\tau)\lambda^*(\tau')\exp(\mathrm{i}\omega\xi)\right\}\right], \tag{12}$$

and $v(t)=\{\exp[u(t)]-1\}^{-1}$, which is the average vibrational occupation number at time t. In deriving Eq. 11 the following formula has been used,

$$\sum_{v=0}^{\infty}\exp[-vu(t)]L_v(|\alpha(\tau,\tau',\xi)|^2) = \frac{\exp[-|\alpha(\tau,\tau',\xi)|^2 v(t)]}{1-\exp[-u(t)]}. \tag{13}$$

Equation 12 has the same structure as that of the generating function for the RRS cross section of molecules in the thermal equilibrium.[8)] An analytical expression for the time-resolved RRS cross section can easily be derived from Eq. 11 with Eq. 12:

$$\frac{\mathrm{d}^2\sigma(\omega_1,\omega_2,t)}{\mathrm{d}\Omega \mathrm{d}\omega_2} = C\omega_1\omega_2^3|M^0_{ab}(2)M^0_{ba}(1)|^2\exp[-\{2v(t)+1\}\Delta^2] \times\left(\sum_{k=0}^{8}\sum_{l=0}^{\infty}\frac{\left[\{v(t)+1\}\frac{\Delta^2}{2}\right]^k\left\{v(t)\frac{\Delta^2}{2}\right\}^l}{k!l!}\right.$$

$$\times \frac{\Gamma_{v'v}}{[\{\omega_1-\omega_2-(k-l)\omega\}^2+\Gamma_{v'v}^2]}\Bigg)$$

$$\times \left|\sum_{p=0}^{k}\sum_{q=0}^{l}\sum_{r=0}^{\infty}\sum_{u=0}^{\infty}\binom{k}{p}\binom{l}{q}(-1)^{r+u}\frac{\left[\{v(t)+1\}\dfrac{\Delta^2}{2}\right]^r}{r!}\frac{\left\{v(t)\dfrac{\Delta^2}{2}\right\}^u}{u!}\right.$$

$$\left.\times \frac{1}{[\mathrm{i}\{\omega_1-\varepsilon^0/\hbar-(p-q+r-u)\omega\}+\Gamma_{ba}]}\right|^2. \tag{14}$$

In the case in which the molecular system is characterized by a high temperature, that is, $\{2v(t)+1\}\Delta^2/2 \gg 1$ is satisfied, an approximate expression for the time-resolved RRS can be used. In this case expanding $\exp(\pm \mathrm{i}\omega\tau)$ and $\exp(\pm \mathrm{i}\omega\tau')$ in Eq. 12 to the second order,[10] substituting the resulting expression into Eq. 11 and carrying out the integration over ξ, we obtain

$$\frac{\mathrm{d}^2\sigma(\omega_1,\omega_2,t)}{\mathrm{d}\Omega\mathrm{d}\omega_2} \simeq C\omega_1\omega_2^3|M_{ab}^0(2)M_{ba}^0(1)|^2$$

$$\times\sum_{k=0}^{\infty}\sum_{l=0}^{\infty}\frac{\{S_{v1}(t)\}^k\{S_v(t)\}^l}{k!\,l!}\frac{\Gamma_{v'v}|F^{(k+l)}(\omega_1)|^2}{[\{\omega_1-\omega_2-(k-l)\omega\}^2+\Gamma_{v'v}^2]}, \tag{15}$$

where

$$F^{(k+l)}(\omega_1) = \int_0^\infty \mathrm{d}\tau(\omega\tau)^{k+l}$$

$$\times \exp\left[\mathrm{i}\left(\frac{\varepsilon^0}{\hbar}+\frac{\Delta^2\omega}{2}-\omega_1\right)\tau-\Gamma_{\mathrm{ba}}\tau-\frac{S(t)\omega^2\tau^2}{2}\right], \tag{16}$$

$S_{v1}(t)=\{v(t)+1\}\Delta^2/2$, $S_v(t)=v(t)\Delta^2/2$, and $S(t)=S_{v1}(t)+S_v(t)$. Equation 16 can be expressed in terms of the repeated integrals of the error function defined by[11]

$$\mathrm{i}^{(n)}\mathrm{erfc}(z) = \frac{2}{\sqrt{\pi}}\int_z^\infty \frac{(x-z)^n}{n!}\exp(-x^2)\mathrm{d}x, \tag{17}$$

as

$$F^{(k+l)}(\omega_1) =$$

$$\frac{\sqrt{\pi}}{2}\frac{(k+l)!}{\omega}\left\{\frac{2}{S(t)}\right\}^{(k+l+1)/2}\exp(z^2)\mathrm{i}^{(k+l)}\mathrm{erfc}(z), \tag{18}$$

with

$$z = \left\{\Gamma_{ba}-\mathrm{i}(\varepsilon^0/\hbar+\frac{\Delta^2}{2}\omega-\omega_1)\right\}^2/[\{2S(t)\}^{1/2}\omega]. \tag{19}$$

In the high temperature case, anti-Stokes bands as well as Stokes bands make a significant contribution to the Raman spectra. Expressions for the time-resolved RRS, Eqs. 14 and 15 consist of the Rayleigh, Stokes, and anti-Stokes components:

$$\frac{\mathrm{d}^2\sigma(\omega_1,\omega_2,t)}{\mathrm{d}\Omega\mathrm{d}\omega_2} = \frac{\mathrm{d}^2\sigma^{(R)}(\omega_1,\omega_2,t)}{\mathrm{d}\Omega\mathrm{d}\omega_2}$$

$$+\sum_{n=1}^{\infty}\left\{\frac{\mathrm{d}^2\sigma^{(ST-n)}(\omega_1,\omega_2,t)}{\mathrm{d}\Omega\mathrm{d}\omega_2}+\frac{\mathrm{d}^2\sigma^{(AST-n)}(\omega_1,\omega_2,t)}{\mathrm{d}\Omega\mathrm{d}\omega_2}\right\}, \tag{20}$$

where the first, second and the last terms represent the Rayleigh scattering, n-th order Stokes and n-th order anti-Stokes cross sections, respectively. For example, the cross sections for the n-th order Stokes and anti-Stokes bands in Eq. 15 can be expressed by putting $n=k-l$ and $n=l-k$ as

$$\frac{\mathrm{d}^2\sigma^{(ST-n)}(\omega_1,\omega_2,t)}{\mathrm{d}\Omega\mathrm{d}\omega}$$

$$=\sum_{l=0}^{\infty}\frac{S_{v1}^{n+l}S_v^l}{(n+l)!\,l!}|F^{(n+2l)}(\omega_1)|^2\frac{\Gamma_{v'v}}{\{(\omega_1-\omega_2-n\omega)^2+\Gamma_{v'v}^2\}}, \tag{21}$$

and

$$\frac{\mathrm{d}^2\sigma^{(AST-n)}(\omega_1,\omega_2,t)}{\mathrm{d}\Omega\mathrm{d}\omega_2} = \sum_{l=0}^{\infty}\frac{S_{v1}^{l}S_v^{n+l}}{l!\,(n+l)!}|F^{(n+2l)}(\omega_1)|^2$$

$$\times\frac{\Gamma_{v'v}}{\{(\omega_1-\omega_2+n\omega)^2+\Gamma_{v'v}^2\}}, \tag{22}$$

respectively where $S_{v1}=S_{v1}(t)$, $S_v=S_v(t)$ and the expression for the Rayleigh scattering band is equivalent to Eqs. 21 or 22 with $n=0$. The cross sections for the n-th order Stokes and anti-Stokes bands in Eq. 14 can be evaluated in the similar way.

Discussion

In the previous section we have derived an expression for the time-resolved RRS from molecules in which the initial distribution is characterized by a canonical distribution with higher temperature than that of the heat bath. One of the merits of carrying out the summation over v in Eq. 3 to derive the expression for the time-resolved RRS differential cross section is spontaneously to bring about concept of time-dependent average occupation numbers $v(t)$. The average occupation number decreases as the molecular system becomes cool because of the collisional vibrational relaxation. Intensities of anti-Stokes bands originate from the nonzero average occupation numbers. In order to demonstrate the time-dependence of the RRS spectra we perform a model calculation of the Raman band intensity. Figure 1 shows the time-resolved RRS spectra of molecules whose initial distribution is characterized by a canonical distribution with temperature T^0=800 K at the initial time and relaxes to the equilibrium one with 300 K after collisional vibrational relaxations. The broken and solid lines represent the RRS spectra at κt=0 and 2 in a unit of κ, respectively. These Raman bands are calculated by using Eq. 14 under the rigorous resonance condition $\omega_1=\varepsilon^0/\hbar$. The average vibrational occupation numbers $v(t)$ at κt=0, and 2 are 3.52 and 1.99, respectively. The parameters used in the calculation are vibrational frequency ω=200 cm^{-1}, dimensionless displacement Δ=0.5, the damping constants Γ_{ba}=100 cm^{-1}, and $\Gamma_{v'v}$=20 cm^{-1}. We can see the increase in the intensities of the Rayleigh and first-order Stokes Raman bands with the development of time. Higher order Stokes and anti-Stokes Raman bands, on the other hand, decrease in their intensities.

Figure 2 shows time-resolved RRS spectra in the

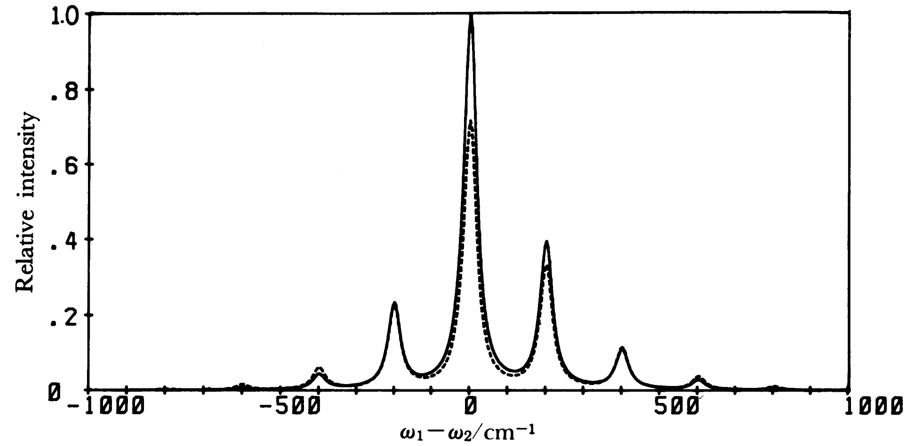

Fig. 1. The calculated time-resolved resonance Raman spectra. The broken and solid lines represent the Raman spectra for $\kappa t=0$ and 1.0 in a unit of κ, respectively. The resonant condition $\omega_1=\varepsilon^0/\hbar$ is assumed. The constants used are $T^0=800\,\mathrm{K}$ and $T=300\,\mathrm{K}$ for the initial and thermal equilibrium temperatures, $\omega=200\,\mathrm{cm}^{-1}$ for the frequency of the displaced harmonic oscillator with dimensionless displacement $\Delta=0.5$, and $\Gamma_{ba}=100\,\mathrm{cm}^{-1}$, and $\Gamma_{v'v}=20\,\mathrm{cm}^{-1}$ for the dephasing constants. The calculation is carried out by using Eq. 14.

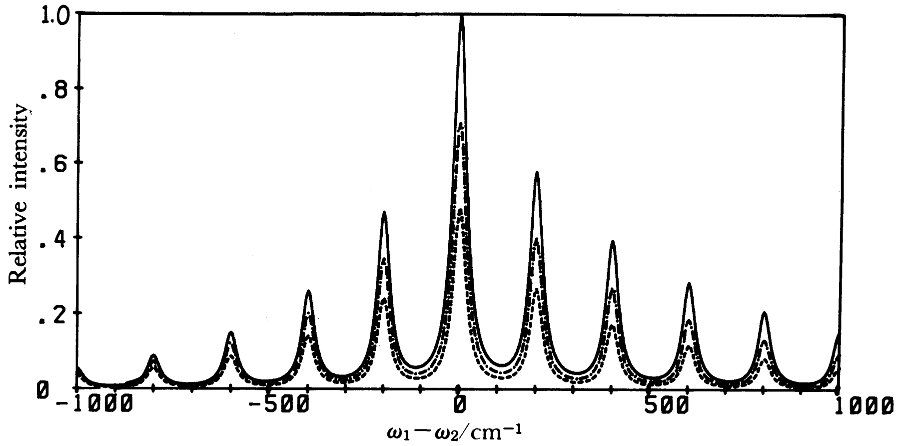

Fig. 2. The calculated time-resolved resonance Raman spectra in a strong coupling case. The broken, dotted broken, and solid lines represent the Raman spectra at $\kappa t=0$, 1.0 and 2.0, respectively. The constants used are $T^0=2000\,\mathrm{K}$ and $T=300\,\mathrm{K}$, $\Delta=2.0$ and the other constants are the same as those in Fig. 1. The resonant condition $\omega_1=\varepsilon^0/\hbar+\Delta^2\omega/2$ is assumed. The calculation is carried out by using Eq. 15. The average occupation numbers $v(t)$ at $\kappa t=0$, 1.0 and 2.0 are 9.51, 6.25 and 4.25, respectively.

strong coupling case. Here $\Delta=2.0$ and $T^0=2000\,\mathrm{K}$ are taken, and the other parameters are the same as those in Fig. 1. The calculation has been carried out by using Eq. 15. It was assumed that $\omega_1=\varepsilon^0/\hbar+\omega\Delta^2/2$ which corresponds to the classical resonance condition. From Fig. 2, we can see that in the strong coupling case n-th order anti-Stokes bands as well as the Stokes bands increase in their intensities with the time development. The average occupation numbers at $\kappa t=0$, 1, and 2 are $v(t)=9.51$, 6.25, and 4.25, respectively. In order to understand this time-dependent behavior we derive an analytical expression for the time-dependent Raman scattering cross section, Eq. 16 in the resonance condition. In the strong coupling case and further in the case in which $\{v(t)+1/2\}^{1/2}\Delta\omega>\Gamma_{ba}$ is satisfied and the damping effects (Γ_{ba}) can be neglected, noting that

$$F^{(p)}(\omega_1=\varepsilon^0/\hbar+\omega\Delta^2/2)$$
$$=\frac{1}{\omega}\left(\frac{\pi}{2}\right)^{1/2}S^{-1/2}(p-1)!!S^{-p/2}, \tag{23a}$$

for even p, and

$$F^{(p)}(\omega^1=\varepsilon^0/\hbar+\omega\Delta^2/2)=\frac{1}{\omega}S^{-1/2}(p-1)!S^{-p/2}, \tag{23b}$$

for odd p, we can obtain an analytical expression for Stokes band intensity, Eq. 21 as

$$\frac{\mathrm{d}^2\sigma^{(ST-n)}(\omega_1,\omega_2,t)}{\mathrm{d}\Omega\mathrm{d}\omega_2}=S^{-1}\Xi^{(ST-n)}, \tag{24}$$

with

$$\Xi^{(ST-n)} = \frac{1}{\omega^2}\sum_{l=0}^{\infty}\left(\frac{S_{v1}}{S}\right)^{n+l}\left(\frac{S_v}{S}\right)^{l} \times \frac{\{(n+2l-1)!\}^2}{(n+l)!\,l!}\,\frac{\Gamma_{v'v}}{\{(\omega_1-\omega_2-n\omega)^2+\Gamma^2_{v'v}\}}, \tag{25a}$$

for odd n, and with

$$\Xi^{(ST-n)} = \frac{\pi}{2\omega^2}\left[\sum_{l=0}^{\infty}\left(\frac{S_{v1}}{S}\right)^{n+l}\left(\frac{S_v}{S}\right)^{l} \times \frac{\{(n/2+l-1)!!\}^2}{(n+l)!\,l!}\,\frac{\Gamma_{v'v}}{\{(\omega_1-\omega_2-n\omega)^2+\Gamma^2_{v'v}\}}\right], \tag{25b}$$

for even n, where $S=S(t)$. Equation 24 indicates that the time-dependence of the Stokes band intensities originates mainly from S^{-1} for high temperatures because $S_{v1}/S_v\sim 1$ and therefore $\Xi^{(ST-n)}$ is independent of time. Similarly, the time-dependence of the anti-Stokes bands originates from S^{-1}:

$$\frac{d^2\sigma^{(ST-n)}(\omega_1,\omega_2,t)}{d\Omega d\omega_2} \propto S^{-1}(t) \propto v(t), \tag{26a}$$

and

$$\frac{d^2\sigma^{(AST-n)}(\omega_1,\omega_2,t)}{d\Omega d\omega_2} \propto S^{-1}(t) \propto v(t). \tag{26b}$$

These expressions explain why the Raman bands in the strong coupling case increase in their intensities with the time development as shown in Fig. 2. It should be noted that Eqs. 26 are valid for the short time domain in which the strong coupling can be defined.

In summary in this paper we have developed a theory of the time-resolved RRS from molecules. The time-resolved RRS cross section is defined as a product of the SVL RRS cross section and its time-dependent population which is derived from the master equation. As an example we have applied the theory to the RRS from molecules whose population distribution is given by a canonical distribution characterized by temperature T^0 higher than that of the heat bath. It is shown that the time-resolved resonance Raman scattering method can be used to clarify the relaxation mechanism of canonically hot molecules. In a subsequent paper other types of the populations relaxation will be taken into account.

Appendix A

Derivation of the generating function for the SVL resonance Raman scattering cross section. In this Appendix we derive the generating function of the cross section for the resonance Raman scattering from single vibronic level v in the displaced harmonic oscillator model. In theory section it is shown that the generating function $G_v(\tau,\tau',\xi)$ takes the form,

$$G_v(\tau,\tau',\xi) = \langle v|\exp[i\hat{H}_b\tau/\hbar]\exp[-i\hat{H}_a\xi/\hbar]\exp[-i\hat{H}_b\tau'/\hbar] \times \exp[i\hat{H}_a(\xi-\tau+\tau')/\hbar]|v\rangle \tag{A.1}$$

Substituting the following expression into Eq. (A. 1)

$$\exp[i\hat{H}_b\tau/\hbar] = \exp[i\varepsilon_a^0\tau/\hbar$$

$$+ \frac{\Delta^2}{2}\{\exp(i\omega\tau)-1\}]\exp[i\hat{H}_a\tau/\hbar] \times \exp[-\lambda(\tau)\hat{b}^\dagger]\exp[\lambda^*(\tau)\hat{b}], \tag{A.2}$$

we obtain

$$G_v(\tau,\tau',\xi) = \exp[i\varepsilon_a^0(\tau-\tau')/\hbar + \frac{\Delta^2}{2}\{\exp(i\omega\tau)-1\} + \frac{\Delta^2}{2}\{\exp(-i\omega\tau')-1\}]\,\Lambda_v(\tau,\tau',\xi), \tag{A.3}$$

where

$$\begin{aligned}\Lambda_v(\tau,\tau',\xi) = {} & \langle v|\exp[i\hat{H}_a\tau/\hbar]\exp[-\lambda(\tau)\hat{b}^\dagger]\exp[\lambda^*(\tau)\hat{b}] \\ & \times \exp[-i\hat{H}_a\xi/\hbar]\exp[-i\hat{H}_a\tau'/\hbar] \\ & \times \exp[-\lambda(-\tau')\hat{b}^\dagger]\exp[\lambda^*(-\tau')\hat{b}] \\ & \times \exp[i\hat{H}_a(\xi-\tau+\tau')/\hbar]|v\rangle,\end{aligned} \tag{A.4}$$

with $\lambda(\tau)=\Delta/\sqrt{2}\{1\text{-}\exp(\text{-}i\varepsilon\tau)\}$. Equation A. 2 has been derived by using the Feynman disentangle technique.[9] Applying the Boson operator technique[9] to Eq. A. 4, we can obtain

$$\begin{aligned}\Lambda_v(\tau,\tau',\xi) = {} & \exp[\lambda^*(\tau)\lambda(\tau')\exp(-i\omega\xi)]\langle v| \\ & \times \exp[-\alpha(\tau,\tau',\xi)\exp(i\omega\tau)\hat{b}^\dagger] \\ & \times \exp[\alpha^*(\tau,\tau',\xi)\exp(-i\omega\tau)\hat{b}]|v\rangle,\end{aligned} \tag{A.5}$$

where

$$\alpha(\tau,\tau',\xi) = \lambda(\tau)-\lambda(\tau')\exp(-i\omega\xi). \tag{A·6}$$

Noting that

$$|v\rangle = \frac{1}{\sqrt{v!}}(\hat{b}^\dagger)^v|0\rangle, \tag{A.7}$$

we can rewrite Eq. A. 5 as

$$\begin{aligned}\Lambda_v(\tau,\tau',\xi) = {} & \exp[\lambda^*(\tau)\lambda(\tau')\exp(i\omega\xi)]\frac{1}{v!} \\ & \times \langle 0|\hat{b}^v\exp[-\alpha(\tau,\tau',\xi)\exp(-i\omega\tau)\hat{b}^\dagger] \\ & \times \exp[\alpha^*(\tau,\tau',\xi)\exp(i\omega\tau)\hat{b}](\hat{b}^\dagger)^v|0\rangle,\end{aligned} \tag{A.8}$$

which is expressed as

$$\begin{aligned}\Lambda_v(\tau,\tau',\xi) = {} & \exp[\lambda^*(\tau)\lambda(\tau')\exp(i\omega\xi)]\frac{1}{v!} \\ & \times \langle 0|\{b-\alpha(\tau,\tau',\xi)\exp(-i\omega\tau)\}^v \\ & \times \{\hat{b}^\dagger+\alpha(\tau,\tau^\dagger,\xi)\exp(i\omega\tau)\}^v|0\rangle \\ = {} & \exp[\lambda^*(\tau)\lambda(\tau')\exp(i\omega\xi)]\frac{1}{v!} \\ & \times\sum_{k=0}^{\infty}\frac{(v!)^2\{-|\alpha(\tau,\tau',\xi)|^2\}^{(v-k)}}{(k!)^2(v-k)!},\end{aligned} \tag{A.9}$$

where we have used the relation

$$(\hat{b}^\dagger+\alpha^*)^v|0\rangle=\sum_{k=0}^{v}\frac{v!(\alpha^*)^{v-k}}{(v-k)!\sqrt{k!}}|k\rangle. \tag{A.10}$$

Equation A. 9 can be expressed in terms of the Laguerre polynomials which is defined by

$$L_v(|\alpha|^2) = \sum_{k=0}^{v}\frac{v!(-|\alpha|^2)^k}{(k!)^2(v-k)!}, \tag{A.11}$$

as

$$\Lambda_v(\tau,\tau',\xi) = \exp[\lambda^*(\tau')\lambda(\tau)\exp(i\omega\xi)]L_v(|\alpha(\tau,\tau',\xi)|^2). \tag{A.12}$$

Substituting Eq. A. 12 into Eq. A. 3 we obtain the expression for the generating function:

$$\begin{aligned} G_v(\tau,\tau',\xi) = \exp[&i\varepsilon^0(\tau-\tau')/\hbar \\ &+\frac{\Delta^2}{2}\{\exp(i\omega\tau)-1\}+\frac{\Delta^2}{2}\{\exp(-i\omega\tau')-1\} \\ &+\lambda^*(\tau)\lambda(\tau')\exp(-i\omega\xi)]L_v(|\alpha(\tau,\tau',\xi)|^2). \end{aligned} \tag{A.13}$$

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