Quantum interference between resonant and nonresonant contributions in nearly resonant Raman scattering

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Time-resolved secondary-radiation spectra have been calculated for a three-level system coupled with a reservoir under pulsed-light excitation. It has been found that a dip is observed in the time profile of the secondary-radiation intensity near the resonance-excitation condition, when the spectral bandwidth of the detection system is increased. If the secondary radiation is divided into the Raman and luminescence components that are, respectively, due to the mean value and fluctuation of the photoinduced emission dipole, the dip is observed only in the former. A simple analysis reveals that this dip originates from the quantum interference between the resonant and nonresonant contributions to the Raman scattering.

INTRODUCTION

The time behavior of Raman scattering under pulsed-light excitation has been the subject of much controversy.[1-8] Namely, when the exciting pulse duration is shorter than the excited-state lifetime, the total secondary-radiation intensity exhibits an exponential decay with the excited-state lifetime under just-resonance excitation, while it shows the same time profile as the exciting light under far off-resonance excitation. Therefore, some people consider that the secondary radiation varies from luminescence to Raman scattering continuously when the excitation frequency is detuned from resonance. This is based on the interpretation that the time profile of the Raman intensity is always the same as that of the exciting pulse. However, this is not considered to be true near the resonance condition, because among various frequency components of the exciting light, those that are close to resonance should mainly contribute to Raman scattering on account of the resonance enhancement effect, so that the spectral width of the scattered light can be narrower than that of the exciting pulse.[8]

It is not possible directly to clarify the transient response of Raman scattering under just-resonance excitation by using a short exciting pulse and a fast-response detector, because the Raman scattering is discernible from luminescence neither spectrally nor temporally in this case. Namely, under just-resonance short-pulse excitation, the secondary-radiation spectrum shows only a broad component, whose width is almost determined by the width of the absorption spectrum, and the time behavior of the total secondary-radiation intensity shows only a single exponential decay with the lifetime of the intermediate state. However, this does not mean that Raman scattering is absent under just-resonance excitation. In fact, for the exciting light whose spectral width is narrower than the width of the absorption spectrum, the Raman scattering is clearly observable even under just-resonance excitation.[9]

In the present paper, we calculate the time-resolved secondary radiation spectrum using a simple model and show that a peculiar dip appears in the time profile of the secondary-radiation intensity under near-resonance excitation. This dip appears only when the spectral resolution of the detection system is broader than the detuning energy of the excitation and is interpretable in terms of a quantum interference effect between the resonant and nonresonant Raman processes. This fact indicates the existence of a coherent process in the secondary emission, even when the secondary-radiation spectrum is not separable into narrow Raman and broad luminescence components. Therefore, it supports the view of the present authors that the secondary radiation should be considered to consist of both scattering and luminescence components even under just-resonance short-pulse excitation.[8-10]

THEORY

Let us consider a three-level system (denoted as g, m, and f) coupled with a reservoir, in which the secondary radiation is emitted by the $g \rightarrow m \rightarrow f$ transition under a weak pulsed-light excitation. We designate the mean angular frequencies of the incident and the emitted light as ω_1 and ω_2, respectively. In addition to the spontaneous emission of photons, relaxations of the three-level system occur through the system-reservoir interaction. We assume, for simplicity, that only the intermediate state m suffers from relaxations. Further, we treat the adiabatic perturbation due to the system-reservoir interaction, which causes the dephasing relaxation, as a random modulation of the transition energy, and assume that this modulation is represented by a Gaussian process. On the other hand, the nonadiabatic perturbation is assumed to give population decay with a constant rate. Then, using the general formula derived by Aihara and Kotani,[5] the time-resolved secondary-radiation spectrum is given as[7]

$$I(\omega_1,\omega_2,t)=\pi^{-1/2}\delta_0\int_{-\infty}^{\infty}d\mu\int_{-x}^{x}d\sigma\int_{(1/2)|\mu-\sigma|}^{x}d\tau_0\exp[i(\omega_2-\omega_{mf})\mu-i(\omega_1-\omega_{mg})\sigma-2\gamma_m\tau_0-(\delta_m^2/4)\mu^2$$
$$-(\delta_p^2/4)\sigma^2-\delta_0^2(\tau_0-t)^2-S^*(\mu)-S(\sigma)$$
$$-S(\tau_0+\tfrac{1}{2}(\mu-\sigma))-S^*(\tau_0+\tfrac{1}{2}(\sigma-\mu))$$
$$+S^*(\tau_0+\tfrac{1}{2}(\mu+\sigma))+S(\tau_0-\tfrac{1}{2}(\mu+\sigma))]\ , \tag{1}$$

where ω_{ij} is the energy difference between the states i and j (we put $\hbar=1$), and $2\gamma_m$ is the population relaxation rate of the intermediate state. Here, we have assumed that both the time profile of the exciting light and the temporal response function of the detection system are Gaussians, expressed by

$$I_p(t)=(\delta_p/\sqrt{\pi})\exp(-\delta_p^2t^2)\ , \tag{2}$$

$$F_m(t)=(\delta_m/\sqrt{\pi})\exp(-\delta_m^2t^2)\ , \tag{3}$$

with $\delta_0^{-2}=\delta_p^{-2}+\delta_m^{-2}$. In Eq. (1), the minimum uncertainty has been assumed to be between energy and time, and, accordingly, δ_p and δ_m correspond to the spectral width of the incident light and the spectral resolution of the detection system, respectively. The second cumulant $S(t)$ is given by

$$S(t)=\int_0^t ds_1\int_0^{s_1}ds_2\langle\delta V(s_1)\delta V(s_2)\rangle\ , \tag{4}$$

where δV represents the energy modulation of the state m and $\langle\ \rangle$ denotes the ensemble average. If the energy modulation is represented by a Gaussian-Markovian process, we have

$$S(t)=D^2\tau_c^2(e^{-|t|/\tau_c}+|t|/\tau_c-1)\ , \tag{5}$$

where D and τ_c are the amplitude and the correlation time of the energy modulation, respectively. In the following we consider, for simplicity, the fast-modulation limit case of $D\tau_c\ll1$, in which $S(t)=\Gamma|t|$, where Γ ($\equiv D^2\tau_c$) is the pure dephasing rate of the intermediate state.

When the detector's spectral bandwidth δ_m is increased, Eq. (1) approaches the following expression asymptotically in the fast-modulation limit:

$$I(t)=2(\delta_p/\delta_m)\int_0^{\infty}dt_1\int_0^{\infty}dt_2\exp[-\tfrac{1}{2}\delta_p^2(t_1-t)^2-\tfrac{1}{2}\delta_p^2(t_2-t)^2+i\Delta\omega_1(t_2-t_1)-\gamma_m(t_1+t_2)-\Gamma|t_1-t_2|]\ , \tag{6}$$

where $\Delta\omega_1=\omega_1-\omega_{mg}$. The secondary-radiation intensity is proportional to $\langle|\ddot{P}(t)|^2\rangle$, where $\ddot{P}(t)$ is the second time derivative of the emission dipole moment induced by the exciting light, and $\langle|\ddot{P}(t)|^2\rangle$ can be generally divided into two parts as follows:[8] $\langle|\ddot{P}(t)|^2\rangle=|\langle\ddot{P}(t)\rangle|^2+\langle|\ddot{P}(t)-\langle\ddot{P}(t)\rangle|^2\rangle$. The first part originates from the mean value of the emission dipole, while the second from the fluctuation around the mean value. If we adopt the definition that Raman scattering is a single coherent quantum process, while luminescence is a two-step process consisting of independent light absorption and emission, the secondary radiations due to the first and second parts correspond to Raman scattering and luminescence, respectively.[8-10] The explicit expressions for the above two are

$$I_R(t)=2(\delta_p/\delta_m)\left|\int_0^{\infty}dt_1\exp[-\tfrac{1}{2}\delta_p^2(t_1-t)^2+i\Delta\omega_1t_1-(\gamma_m+\Gamma)t_1]\right|^2\ , \tag{7}$$

and

$$I_L(t)=I(t)-I_R(t)\ . \tag{8}$$

Numerical calculations of Eqs. (1) and (6)–(8) give the time-resolved spectrum and transient behavior of the secondary-radiation intensity under various excitation and detection conditions.

RESULTS AND DISCUSSION

First, we have calculated the time-resolved spectra for various detuning energies of the exciting light from resonance to off-resonance. The results are shown in Figs. 1–3. The temporal width of the detector's response function has been set to be the same as that of the exciting pulse, i.e., $\delta_m=\delta_p$. Under just-resonance excitation (Fig. 1), the secondary radiation appears around the energy of ω_{mf}, and its intensity shows a gradual rise and subsequent slow decay after pulsed excitation. This time behavior is insensitive to the emission energy. The rise time is determined by the temporal profiles of the exciting light and the detector's response function, while the decay time coincides with the lifetime of the intermediate state, $1/2\gamma_m$. Under off-resonance excitation (Fig. 2), a fast component appears around the energy of $\omega_1-\omega_{fg}$ in addition to a slow component around ω_{mf}. The temporal shape of the fast component is determined by the convolution of the exciting pulse and the detector's temporal

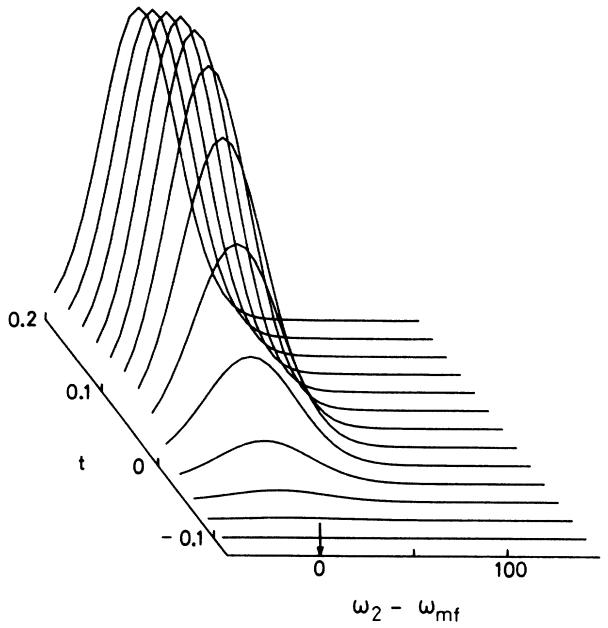

FIG. 1. Time-resolved secondary-radiation spectra calculated for a three-level system in the fast modulation limit under pulsed-light excitation at $\Delta\omega_1=0$. The time-resolved spectra are calculated between $t=-0.1$ and 0.2, with the interval of 0.025. Parameter values employed are $\delta_p=\delta_m=28.284$, $\gamma_m=1.0$, and $\Gamma=0.4$. The arrow indicates the energy position expected for the ordinary Raman scattering: $\omega_2=\omega_1-\omega_{fg}$.

response function, while that of the slow component is almost coincident with that under just-resonance excitation. For the near-resonance excitation (Fig. 3), on the other hand, the fast and the slow components are not discriminated spectrally. The secondary-radiation spectrum in the early stage changes with time, and the peak energy does not coincide with that expected for the ordinary Raman scattering, i.e., $\omega_1-\omega_{fg}$. At a sufficiently

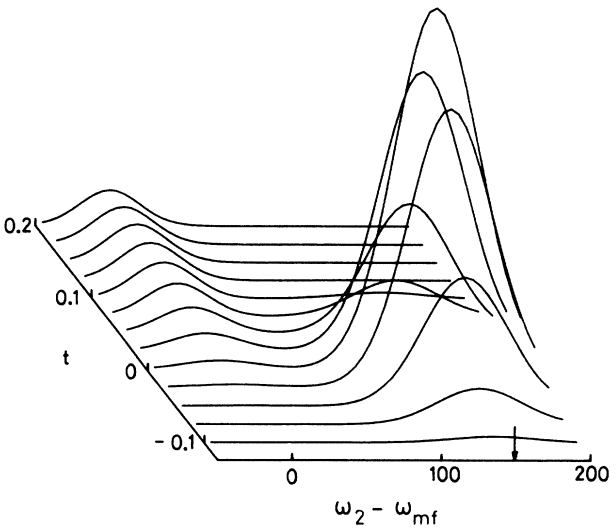

FIG. 2. Time-resolved secondary-radiation spectra calculated for the pulsed excitation at $\Delta\omega_1=150$. Parameter values are the same as those in Fig. 1.

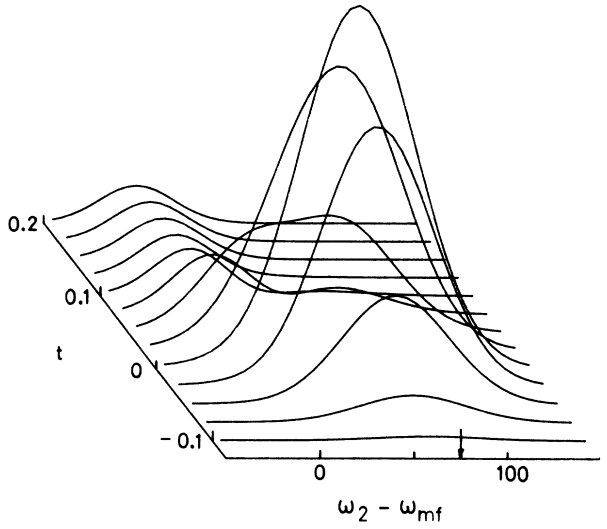

FIG. 3. Time-resolved secondary-radiation spectra calculated for the pulsed excitation at $\Delta\omega_1=75$. Parameter values are the same as those in Fig. 1.

late stage, the time behavior of the slowly decaying component coincides with that under just-resonance excitation.

To obtain more detailed information on the transient response under near-resonance excitation, we have further calculated the time profile of the secondary-radiation intensity by fixing the center of the energy spectrum of the detection system, while varying its energy width δ_m. The results are shown in Fig. 4. The right-hand side of

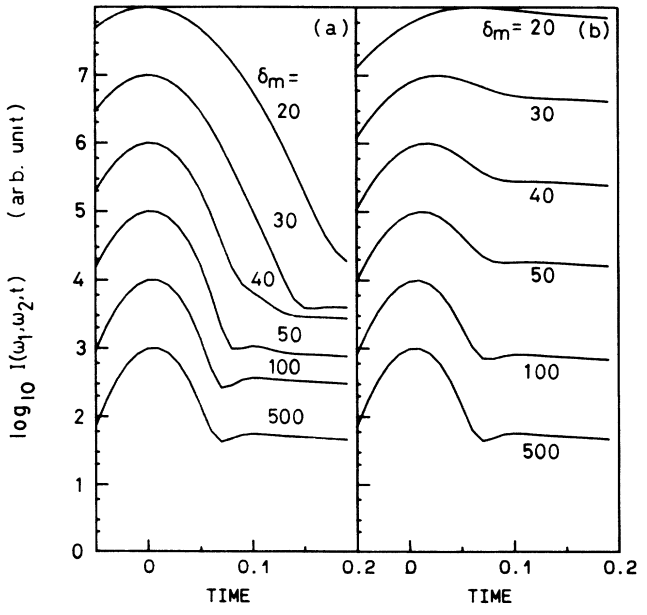

FIG. 4. Logarithmic plot of the time profile of the secondary-radiation intensity for various detector's energy widths: $\delta_m=20$, 30, 40, 50, 100, and 500. The center of the energy spectrum of the detection system is fixed at $\omega_2-\omega_{mf}=75$ and 0 for (a) and (b), respectively. The other parameters are the same as those in Fig. 1.

this figure shows the transient response observed at ω_{mf}, while the left-hand side shows that at $\omega_1-\omega_{fg}$. The time behavior of the former is similar to that under just-resonance excitation and shows an exponential decay with the rate $2\gamma_m$ when δ_m is small. With increasing δ_m, a fast component becomes observable, and finally a dip appears between the fast and the slow components. In the case of the emission around $\omega_1-\omega_{fg}$, on the other hand, only the fast component appears when δ_m is small. With increasing δ_m, a slow component becomes prominent, accompanied by the deformation of the transient response near the boundary of the fast and slow components, and finally the same response curve as observed at ω_{mf} is obtained. Since the dip appears only when the detector's spectral bandwidth is comparable to or broader than the detuning energy, both components around ω_{mf} and $\omega_1-\omega_{fg}$ are considered to contribute to the dip in the transient behavior.

To clarify the origin of the dip, we have investigated an extreme case where the detector's energy width is infinitely large. The transient response has been calculated using Eq. (6). As shown by a solid curve in Fig. 5, the result is essentially the same as that in Fig. 4 for the broad detector's energy width, e.g., $\delta_m=500$. We have further divided the transient emission intensity into the Raman scattering and luminescence components according to the method described in Sec. II, i.e., Eqs. (7) and (8). The results are plotted by dashed and dotted curves in Fig. 5. It is evident that the dip appears only in the Raman component. The luminescence component shows an ordinary slowly decaying response.

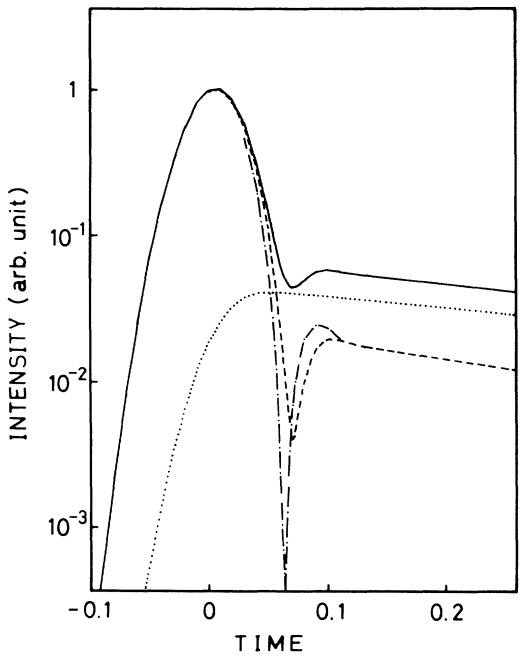

FIG. 5. Time profile of the secondary-radiation intensity for infinitely broad energy width of the detection system. The solid, dashed, and dotted curves indicate the intensities for the total, Raman, and luminescence components calculated using Eqs. (6), (7), and (8), respectively. The dot-dashed curve is the result of the calculation using Eq. (14). Parameter values are the same as those in Fig. 1.

The above result is interpreted in terms of the quantum interference effect between the resonant and nonresonant Raman processes, i.e., the Raman component which has a peak around ω_{mf} and that around $\omega_1-\omega_{fg}$. Let us express the temporal shape of the electric field of the exciting pulse as

$$E(t)=\tilde{E}(t)e^{-i\omega_1 t}+\tilde{E}^*(t)e^{i\omega_1 t} . \tag{9}$$

Then, Eq. (7) can be written in a more general form as

$$I_R(t)=\left|\int_0^\infty dt_1\tilde{E}(t-t_1)\exp[(i\Delta\omega_1-\gamma_m-\Gamma)t_1]\right|^2 , \tag{10}$$

where we have omitted unimportant factors. This equation becomes

$$I_R(t)=\left|\frac{\int_{-\infty}^{\infty}d\omega e^{-i\omega t}\tilde{E}(\omega)}{i(\omega+\Delta\omega_1)-(\gamma_m+\Gamma)}\right|^2 , \tag{11}$$

using the following Fourier transform:

$$\tilde{E}(t)=\int_{-\infty}^{\infty}d\omega\tilde{E}(\omega)e^{-i\omega t} . \tag{12}$$

Since $\tilde{E}(t)$ is a slowly varying function of t, $|\tilde{E}(\omega)|^2$ is peaked at $\omega=0$, and $|i(\omega+\Delta\omega_1)-(\gamma_m+\Gamma)|^{-2}$ has its peak at $\omega=-\Delta\omega_1$. Therefore we employ the following approximation:

$$\frac{\tilde{E}(\omega)}{i(\omega+\Delta\omega_1)-(\gamma_m+\Gamma)}\approx\frac{\tilde{E}(\omega)}{i\Delta\omega_1-(\gamma_m+\Gamma)}+\frac{\tilde{E}(-\Delta\omega_1)}{i(\omega+\Delta\omega_1)-(\gamma_m+\Gamma)} . \tag{13}$$

Then, denoting the temporal shape of the electric field of the emitted light due to the above two components as $C_{\rm nr}(t)$ and $C_{\rm r}(t)$, we can express the total Raman intensity as

$$\begin{aligned}I_R(t)&=|C_{\rm nr}(t)+C_{\rm r}(t)|^2\\&=I_{\rm nr}(t)+I_{\rm r}(t)+2{\rm Re}[C_{\rm nr}^*(t)C_{\rm r}(t)] ,\end{aligned} \tag{14}$$

where

$$\begin{aligned}I_{\rm nr}(t)&\equiv|C_{\rm nr}(t)|^2\\&=|\tilde{E}(t)|^2/[\Delta\omega_1^2+(\gamma_m+\Gamma)^2] ,\end{aligned} \tag{15}$$

and

$$\begin{aligned}I_r(t)&\equiv|C_{\rm r}(t)|^2\\&=4\pi^2|\tilde{E}(-\Delta\omega_1)|^2\exp[-2(\gamma_m+\Gamma)t] \quad \text{for } t>0 ,\\&=\pi^2|\tilde{E}(-\Delta\omega_1)|^2 \quad \text{for } t=0 ,\\&=0 \quad \text{for } t<0 ,\end{aligned} \tag{16}$$

correspond to the approximate expressions for the time profiles of the intensities of the Raman components centered at $\omega_1-\omega_{fg}$ and ω_{mf}, respectively. $I_{\rm nr}(t)$ is attribut-

able to the nonresonant Raman scattering, which shows the same time profile as the exciting light. On the other hand, $I_r(t)$ is ascribed to the Raman scattering which occurs through the resonant excitation by the spectral tail of the exciting pulse, and shows a slowly decaying transient response. This component is not ascribable to luminescence, because its decay time is not determined by the excited-state lifetime, but by the reciprocal of the homogeneous width of the $g \rightarrow m$ absorption band. Equation (14) coincides with the usual expression for an interference phenomenon, and the calculation of the interference term of Eq. (14) gives

$$\begin{aligned} I_{\rm int}(t) &= 4\pi[\Delta\omega_1^2+(\gamma_m+\Gamma)^2]^{-1/2}\tilde{E}(t)\tilde{E}(-\Delta\omega_1) \\ &\quad \times \exp[-(\gamma_m+\Gamma)t]\cos(\omega_1 t-\phi) \quad \text{for } t>0\ , \\ &= 2\pi[\Delta\omega_1^2+(\gamma_m+\Gamma)^2]^{-1/2} \\ &\quad \times \tilde{E}(0)\tilde{E}(-\Delta\omega_1)\cos\phi \quad \text{for } t=0\ , \\ &= 0 \quad \text{for } t<0\ , \end{aligned} \tag{17}$$

where $\tan\phi=\Delta\omega_1/(\gamma_m+\Gamma)$ and we have assumed that $\tilde{E}(t)$ and $\tilde{E}(\omega)$ are real. The dip appears as a result of the cosine term multiplied by $\tilde{E}(t)\exp[-(\gamma_m+\Gamma)t]$ and is prominent when the above two components are comparable in intensity, i.e., around the boundary of the fast and the slow components. As shown by a dot-dashed curve in Fig. 5, the transient behavior of the secondary radiation under nearly resonant excitation has been found to be reproduced fairly well by a calculation using Eq. (14). Discrepancies in the position and depth of the dip are ascribed to the crude approximation made in Eq. (13). Since the dip is explained by the interference effect, its appearance in the transient response clearly indicates the coherent nature of the secondary-emission process and gives evidence for the presence of coherent Raman scattering, even when the fast and the slow components are not separable spectrally. This supports our view that the secondary radiation should be interpreted in terms of the sum of the scattering and luminescence components, even near the resonance and under just-resonance short-pulse excitations. In the latter case, Raman component decays within the time roughly equal to the reciprocal of the homogeneous width of the absorption band, while the luminescence component decays exponentially with the lifetime of the excited state at sufficiently later time after the excitation.[8,9]

In actual systems, inhomogeneous broadening in the $g \rightarrow m$ transition obscures this interference because of the convolution of the cosine term over the inhomogeneous broadening. Therefore, to observe the above interference phenomenon, it is necessary that the following conditions are satisfied: (i) The spectral bandwidth of the detection system is comparable to or larger than the detuning energy of the exciting pulse, (ii) the detuning energy is so large that the contributions of the above two Raman-scattering processes to the total Raman intensity are comparable, (iii) the width of the inhomogeneous broadening is much smaller than the detuning energy.

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