Distinction between resonance Raman scattering and hot luminescence

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(Received 3 August 1973)

Using density-matrix formalism which takes into account relaxation more correctly, we show that resonance Raman scattering and hot luminescence are two distinct physical processes, although they are always simultaneously present and can interfere with each other. The transient response of the two processes are, however, different.

With the advance of tunable lasers, resonance Raman scattering has become a subject of much investigation.[1-5] There is, however, apparent confusion in the literature on the difference between resonance Raman scattering (RRS) and hot luminescence (HL). Recently, Klein[6] showed that in some cases the RRS efficiency could be written as the product of the absorption coefficient and the quantum yield for hot luminescence. He then concluded that RRS was often equivalent to HL. In the literature, usually either one or the other was used to interpret the observed resonant-Raman data.[1-5] We want to present in this paper expressions for the cross sections of RRS and HL derived from the density-matrix formalism which takes into account relaxation due to random processes more properly than the golden-rule approach.[7] We show that RRS and HL are, in fact, two distinct physical processes although they are simultaneously present in ordinary RRS experiments.

The physical differences between the two processes are perhaps quite obvious intuitively. RRS is a two-photon direct process, while HL is a two-step process. HL arises from radiative decay of the excess population pumped into the intermediate state by the exciting field, but RRS does not. The two processes have in general different line shapes. If the exciting field is abruptly shut off, HL should have an exponential decay corresponding to the decay of the excess population in the intermediate state, aside from the usual induction decay. These differences can be seen more clearly in the following derivation.

Since we are dealing with a resonance phenomenon, relaxation for transitions must be taken into account properly. For this reason, we use the density-matrix formalism. The equation of motion for the density-matrix operator ρ is[8,9]

$$i\hbar\frac{\partial\rho}{\partial t}=[\mathcal{H}_0+\mathcal{H}',\rho]+i\hbar\left(\frac{\partial\rho}{\partial t}\right)_{\text{damping}}, \tag{1}$$

where $\mathcal{H}_0$ is the Hamiltonian of the unperturbed system, $\mathcal{H}'$ is the interaction Hamiltonian between light and matter, and $(\partial\rho/\partial t)_{\text{damping}}$, responsible for relaxation, comes from interaction of the system with random fields. We can use the semiclassical approach to find the transition probability for the system to change from the ground state to an excited state by absorbing a photon at ω_l and emitting a photon at ω_s. We first solve $\rho(t)$ from Eq. (1) using the iterative-perturbation procedure, and obtain the third-order polarization at ω_s from $\langle\vec{p}^{(3)}(\omega_s,t)\rangle=\mathrm{Tr}[\rho^{(3)}(\omega_s,t)\vec{p}_s]$. Then, the differential probability for spontaneously emitting a photon at ω_s per unit volume per unit time is given by[9]

$$\frac{d^2W}{d\omega_s d\Omega}=-\frac{\omega_s^3}{2\pi^2C^3}\frac{\mathrm{Im}\langle\vec{p}^{(3)}(\omega_s)\cdot\vec{E}(\omega_s)\rangle}{|E(\omega_s)|^2}. \tag{2}$$

In the steady state, the corresponding differential scattering cross section is

$$\frac{d^2\sigma}{d\omega_s d\Omega}=-\frac{\hbar\omega_l\omega_s^3}{\pi C^4}\frac{\mathrm{Im}\langle\vec{p}^{(3)}(\omega_s)\cdot\vec{E}(\omega_s)\rangle}{|E(\omega_l)|^2|E(\omega_s)|^2}. \tag{3}$$

Consider first a three-level system with a ground state $\langle g|$, an intermediate state $\langle n|$, and a final state $\langle f|$, as shown in Fig. 1. The frequency ω_l of the exciting light is close to the transition frequency ω_{ng} between $|n\rangle$ and $|g\rangle$, and the frequency ω_s of the scattered radiation is close to ω_{nf}. We can

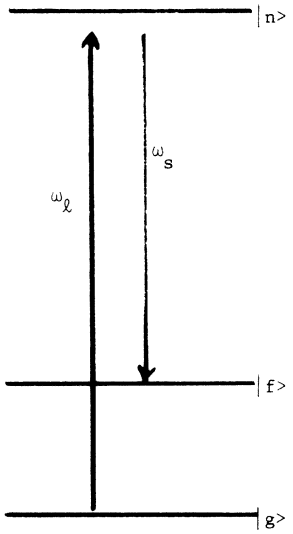

FIG. 1. A three-level system interacting with an exciting field at frequency $\omega_l\sim\omega_{ng}$ and a Stokes field at $\omega_s\sim\omega_{nf}$.

write

$$\mathcal{H}' = \mathcal{H}'(\omega_l) + \mathcal{H}'(\omega_s) + \mathcal{H}'(-\omega_l) + \mathcal{H}'(-\omega_s) \ , \qquad (4)$$

where

$$\mathcal{H}'(\omega_{l,s}) = [\mathcal{H}'(-\omega_{l,s})]^\dagger = -\vec{p}^\dagger_{l,s} \cdot \vec{E}(\omega_{l,s}) \ ,$$

$$\vec{E}(\omega_{l,s}) = \vec{\mathcal{E}}_{l,s}\, e^{-\omega_{l,s} t} \ .$$

We expand ρ into a series of ascending orders, $\rho = \rho^{(0)} + \rho^{(1)} + \rho^{(2)} + \rho^{(3)} + \ldots$, and find each term successively through the iterative solution of Eq. (1).[8,9] In each iterative process, we need to keep only those density matrix elements which are near resonance. We assume, for simplicity, $\langle i|\rho^{(0)}|j\rangle \equiv \rho^{(0)}_{ij} = 0$ except that $\rho^{(0)}_{gg} = 1$. As a result, we obtain from the various orders of interaction the following set of equations:

$$\langle \vec{p}^{(3)}(\omega_s)\rangle \cong (\vec{p}_s)_{fn}\, \rho^{(3)}_{nf}(\omega_s) \ ,$$

$$\frac{\partial \rho^{(3)}_{nf}(\omega_s)}{\partial t} + (i\omega_{nf} + \Gamma_{nf})\rho^{(3)}_{nf}(\omega_s) = \frac{1}{i\hbar}[-\rho^{(2)}_{nn}(0)\mathcal{H}'_{nf}(\omega_s) + \mathcal{H}'_{ng}(\omega_l)\rho^{(2)}_{gf}(\omega_s - \omega_l)] \ ,$$

$$\frac{\partial \rho^{(2)}_{nn}(0)}{\partial t} + \Gamma_{nn}\rho^{(2)}_{nn}(0) = \frac{1}{i\hbar}[\mathcal{H}'_{ng}(\omega_l)\rho^{(1)}_{gn}(-\omega_l) - \rho^{(1)}_{ng}(\omega_l)\mathcal{H}'_{gn}(-\omega_l)] \ ,$$

$$\frac{\partial \rho^{(2)}_{gf}(\omega_s - \omega_l)}{\partial t} + (i\omega_{gf} + \Gamma_{gf})\rho^{(2)}_{gf}(\omega_s - \omega_l) = \frac{1}{i\hbar}\rho^{(1)}_{gn}(-\omega_l)\mathcal{H}'_{nf}(\omega_s) \ ,$$

$$\frac{\partial \rho^{(1)}_{ng}(\omega_l)}{\partial t} + (i\omega_{ng} + \Gamma_{ng})\rho^{(1)}_{ng}(\omega_l) = \frac{1}{i\hbar}\mathcal{H}'_{ng}(\omega_l) \ ,$$

$$\rho^{(1)}_{ng}(\omega_l) = [\rho^{(1)}_{ng}(-\omega_l)]^* \ . \qquad (5)$$

In the above equations, the damping constants Γ's come from the $(\partial\rho/\partial t)_{\text{damping}}$ term in Eq. (1). How Γ's result from interaction of the system with random fields has been a subject of extensive studies in magnetic resonance,[10] but is not well understood in optical cases. It is usually believed that the lifetime broadening often dominates the linewidth of an optical transition.[8,9] Then, we can write $\Gamma_{ij}(i \neq j) = \frac{1}{2}(1/T_i + 1/T_j)$, where T_i and T_j are the lifetimes of $\langle i|$ and $\langle j|$. Since $\langle n|$ is far above $\langle g|$, we also have $\Gamma_{nn} = 1/T_n$. Normally, we also expect $T_g \gg T_n$, T_f. We must, however, emphasize that in general Γ_{ij} does not necessarily have any simple relation with T_i and T_j or Γ_{ii} and Γ_{jj}.

The solution of the set of equations in (5) is straightforward. Assume the exciting radiation is switched on at $t = -\infty$ and then suddenly shut off at $t = t_0$, as described by $\mathcal{E}(t) = A[1 - u(t - t_0)]$ in Eq. (4), where $u(t)$ is a unit step function. We then find from Eqs. (5)

$$\langle \vec{P}^{(3)}(\omega_s)\rangle = \langle \vec{P}^{(3)}(\omega_s)\rangle_{\text{RRS}} + \langle \vec{P}^{(3)}(\omega_s)\rangle_{\text{HL}} \ ,$$

$$\langle \vec{P}^{(3)}(\omega_s)\rangle_{\text{RRS}} = \frac{(\vec{P}_s)_{fn}|(\vec{P}^\dagger_l \cdot \vec{\mathcal{E}}_l)_{ng}|^2 (\vec{P}^\dagger_s \cdot \vec{\mathcal{E}}_s)_{nf}}{\hbar^3(\omega_l - \omega_s - \omega_{fg} - i\Gamma_{fg})(\omega_l - \omega_{ng} - i\Gamma_{ng})(\omega_s - \omega_{nf} + i\Gamma_{nf})} \times\{[1 - u(t - t_0)]e^{-i\omega_s t} + e^{[-i\omega_{nf} - \Gamma_{nf}](t - t_0)}u(t - t_0)\}$$

$$\langle \vec{P}^{(3)}(\omega_s)\rangle_{\text{HL}} = \frac{-2\Gamma_{ng}T_n}{\hbar^3[(\omega_l - \omega_{ng})^2 + \Gamma^2_{ng}]}(\vec{P}_s)_{fn}(\vec{P}^\dagger_s \cdot \vec{\mathcal{E}}_s)_{nf}|(\vec{P}^\dagger_l \cdot \vec{\mathcal{E}}_l)_{ng}|^2 \times\left[\frac{1 - u(t - t_0)}{\omega_s - \omega_{nf} + i\Gamma_{nf}} e^{-i\omega_s t} + \frac{u(t - t_0)}{\omega_s - \omega_{nf} + i(\Gamma_{nf} - 1/T_n)} e^{(-i\omega_s - 1/T_n)(t - t_0)} + \left(\frac{1}{\omega_s - \omega_{nf} + i\Gamma_{nf}} - \frac{1}{\omega_s - \omega_{nf} + i(\Gamma_{nf} - 1/T_n)}\right) u(t - t_0)e^{(-i\omega_{nf} - \Gamma_{nf})(t - t_0)}\right] . \qquad (6)$$

We note that $\langle \vec{P}^{(3)}(\omega_s)\rangle$ consists of two terms. The term $\langle \vec{P}^{(3)}(\omega_s)\rangle_{\text{RRS}}$ comes from the $\rho^{(2)}_{gf}(\omega_s - \omega_l)$ contribution to $\rho^{(3)}_{nf}(\omega_s)$ in Eq. (5) and the term $\langle P^{(3)}(\omega_s)\rangle_{\text{HL}}$ comes from the $\rho^{(2)}_{nn}(0)$ contribution to $\rho^{(3)}_{nf}(\omega_s)$ in Eq. (5). They can be identified as the Raman scattering part and the luminescence part, respectively, for the following obvious reasons. $\langle \vec{P}^{(3)}(\omega_s)\rangle_{\text{RRS}}$ does not depend on the excess population $\rho^{(2)}_{nn}(0)$ pumped into the immediate state $\langle n|$ by the exciting field, while $\langle \vec{P}^{(3)}(\omega_s)\rangle_{\text{HL}}$ is directly connected with $\rho^{(2)}_{nn}(0)$. In the steady state (corresponding to $t < t_0$), if ω_l is sufficiently far away from resonance such that

$$|\omega_l - \omega_{ng}| \cong |\omega_s - \omega_{nf}| \gg \Gamma_{ng}, \Gamma_{nf} \ ,$$

then $\text{Im}\langle \vec{E}^*(\omega_s) \cdot \vec{P}^{(3)}_{\text{HL}}(\omega_s)\rangle$ is negligible compared with $\text{Im}\langle \vec{E}^*)\omega_s) \cdot \vec{P}^{(3)}_{\text{RRS}}(\omega_s)\rangle$, and the substitution of $\langle \vec{P}^{(3)}(\omega_s)\rangle_{\text{RRS}}$ in Eq. (3) leads to the well-known expression for the differential Raman scattering cross section. Near resonance ($\omega_l \simeq \omega_{ng}$), the term $\text{Im}\langle \vec{E}^*(\omega_s) \cdot \vec{P}^{(3)}_{\text{HL}}(\omega_s)\rangle$ becomes important. If, however, the linewidths are dominated by lifetime

broadening with $2\Gamma_{ng}T_n = 1$ and $T_g \gg T_n, T_f$, then by substitution of $\langle \vec{P}^{(3)}(\omega_s)\rangle_{RRS} + \langle \vec{P}^{(3)}(\omega_s)\rangle_{HL}$ into Eq. (3), we find[11]

$$\frac{d^2\sigma}{d\omega_s d\Omega} = \frac{\omega_l \omega_s^3}{\pi C^4} \frac{\Gamma_{fg}}{(\omega_l - \omega_s - \omega_{fg})^2 + \Gamma_{fg}^2} \times \left| \frac{(P_s)_{fn}(P_l^\dagger)_{ng}}{\hbar(\omega_l - \omega_{ng} + i\Gamma_{ng})} \right|^2 . \quad (7)$$

This is the usual expression one normally uses for the differential cross section of RRS when there is only one intermediate state effective in the resonance scattering process. Note that Eq. (7) is usually derived from the golden-rule approach which implicitly assumes lifetime broadening for the states $2\Gamma_{ng}T_n = 1$, and $T_g \gg T_n, T_f$.[7] As shown in Eq. (6), Raman scattering and hot luminescence have, in general, different line shapes, as one would expect. In the transient state ($t > t_0$), both $\mathrm{Im}\langle \vec{E}^*(\omega_s) \cdot \vec{P}^{(3)}_{RRS}(\omega_s)\rangle$ and $\mathrm{Im}\langle \vec{E}^*(\omega_s) \cdot \vec{P}^{(3)}_{HL}(\omega_s)\rangle$ have a term which decays in the form of a damped oscillation with an oscillating frequency of $(\omega_s - \omega_{nf})$ and a decay rate of Γ_{nf}. This is due to luminescence from $|n\rangle$ to $|f\rangle$ induced by the abrupt change of the exciting field, and is the source of coherent Raman beat recently observed by Shoemaker and Brewer.[12] However, the HL term has an additional pure expotential decay term which reflects the decay of the excess population pumped into the intermediate state $|n\rangle$ by the exciting field.

One limiting case in the steady state is of interest. As seen from Eq. (6), if $\Gamma_{ng} \approx \Gamma_{nf} \gg \Gamma_{fg}$, then $(d^2\sigma/d\omega_s d\Omega)_{RRS}$ obtained from $\mathrm{Im}\langle \vec{E}^*(\omega_s) \cdot \vec{P}^{(3)}_{RRS}(\omega_s)\rangle$ reduces to the usual expression for resonance Raman scattering as given in Eq. (7), while $(d^2\sigma/d\omega_s d\Omega)_{HL}$ would appear as a broad background (with a half-width Γ_{nf}).

The total scattering efficiency is given by

$$\sigma = \int \frac{d^2\sigma}{d\omega_s d\Omega}\, d\omega_s d\Omega . \quad (8)$$

Assuming Eq. (7) with $2\Gamma_{ng}T_n = 1$ is valid, we then recognize that

$$2|(P_l^\dagger)_{ng}|^2 \Gamma_{ng}/[(\omega_l - \omega_{ng})^2 + \Gamma_{ng}^2]$$

is proportional to the absorption coefficient $\alpha(\omega_l)$, and $|(P_s)_{fn}|^2$ proportional to the inverse radiative lifetime T_R for radiative transition from $|n\rangle$ to $|f\rangle$. It is then easy to show that[6]

$$\sigma = \alpha(\omega_l) T_n / T_R , \quad (9)$$

i.e., the total scattering efficiency is equal to the absorption coefficient multiplied by the quantum yield for radiative transition from $|n\rangle$ to $|f\rangle$. This equality has led Klein to believe that RRS and HL are equivalent.[6] However, we should again emphasize that there are assumptions involved in deriving Eq. (7). On the other hand, we can easily show from the steady-state expression of $\langle \vec{P}^{(3)}(\omega_s)\rangle_{HL}$ in Eq. (6) that the total HL efficiency σ_{HL} is given rigorously by

$$\sigma_{HL} = \alpha(\omega_l) T_n / T_R \quad (10)$$

as one would expect. We should of course consult Eq. (6) for the more subtle differences between RRS and HL.

The case with several intermediate states which are close to resonance with the exciting field is more complicated. The first few equations in (5) must be modified as follows[8,9]:

$$\begin{aligned}
&\langle \vec{P}^{(3)}(\omega_s)\rangle = \sum_n (\vec{P}_s)_{fn} \rho^{(3)}_{nf}(\omega_s) ,\\
&\left(\frac{\partial}{\partial t} + i\omega_{nf} + \Gamma_{nf}\right) \rho^{(3)}_{nf}(\omega_s) \\
&\quad = \frac{1}{i\hbar}\left(- \sum_{n'} \rho^{(2)}_{nn'}(0) \mathcal{H}'_{n'f}(\omega_s) + \mathcal{H}'_{ng}(\omega_l) \rho^{(2)}_{gf}(\omega_s - \omega_l) \right) ,\\
&\left(\frac{\partial}{\partial t} + i\omega_{gf} + \Gamma_{gf}\right) \rho^{(2)}_{gf}(\omega_s - \omega_l) = \frac{-1}{i\hbar} \sum_n \rho^{(1)}_{gn}(-\omega_l) \mathcal{H}'_{nf}(\omega_s) \\
&\left(\frac{\partial}{\partial t} + \Gamma_{nn}\right) \rho^{(2)}_{nn}(0) - \sum_{n' \neq n} W_{nn'} \rho^{(2)}_{n'n'}(0) \\
&\quad = \frac{1}{i\hbar}\left[\mathcal{H}'_{ng}(\omega_l) \rho^{(1)}_{gn}(-\omega_l) - \rho^{(1)}_{ng}(\omega_l) \mathcal{H}'_{gn}(-\omega_l) \right] ,\\
&\left(\frac{\partial}{\partial t} + i\omega_{nn'} + \Gamma_{nn'}\right)_{n \neq n'} \rho^{(2)}_{nn'}(0) = \frac{1}{i\hbar} \mathcal{H}'_{ng}(\omega_l) \rho^{(1)}_{gn'}(-\omega_l) \\
&\qquad\qquad - \rho^{(1)}_{ng}(\omega_l) \mathcal{H}'_{gn'}(-\omega_l).
\end{aligned} \quad (11)$$

The major difference between this case and the previous case is in the last two equations of (11). Through interaction with random fields, the intermediate states can be strongly coupled with one another. Here, $W_{nn'}$ represents the transition rate from $|n'\rangle$ to $|n\rangle$ induced by the random fields. We have actually[8,9]

$$\Gamma_{nn} = W_{gn} + W_{fn} + \sum_{n'} W_{n'n}$$

and

$$W_{n'n}/W_{nn'} = e^{\hbar\omega_{nn'}/kT} .$$

In the equation of $\rho^{(2)}_{nn}(0)$, we have neglected the term $W_{ng}\rho^{(2)}_{gg}(0)$ which is usually small. The resulting polarization $\langle \vec{P}^{(3)}(\omega_s)\rangle$ again consists of an RRS part and an HL part, coming, respectively, from the $\rho^{(2)}_{gf}(\omega_s - \omega_l)$ and $\sum_{n'} \rho_{nn'}(0)$ contributions to $\rho^{(3)}_{nf}(\omega_s)$.

The RRS part of $\langle \vec{P}^{(3)}(\omega_s)\rangle$ leads to a differential scattering cross section

$$\left(\frac{d^2\sigma}{d\omega_s d\Omega}\right)_{RRS} = \frac{\omega_l \omega_s^3}{\pi C^4} \mathrm{Im}\left(\frac{1}{(\omega_l - \omega_s - \omega_{fg}) - i\Gamma_{fg}} \times \sum_{n,n'} \frac{(P_l)_{gn}(P_s^\dagger)_{nf}(P_s)_{fn'}(P_l^\dagger)_{n'g}}{(\omega_l - \omega_{ng} - i\Gamma_{ng})(\omega_s - \omega_{n'f} + i\Gamma_{n'f})} \right) \quad (12)$$

If $|\omega_l - \omega_{ng}| \simeq |\omega_s - \omega_{nf}| \gg \Gamma_{ng}, \Gamma_{nf}$, then the above equation reduces to the usual expression for differential Raman scattering cross section (near resonance) as it should be. The HL part is nonnegligible only when ω_l is close to resonance. Because of coupling between intermediate states through relaxation, it is difficult to derive a general expression for the differential cross section of HL. We shall therefore discuss only a few limiting steady-state cases in the following. We shall present only the results, the derivation of which is straightforward and will not be reproduced here.

Consider first the ideal case where the intermediate states are not coupled, i.e., $W_{nn'} = 0$. If we assume lifetime broadening of the states with $2\Gamma_{ng}T_n = 1$ and $T_g \gg T_n$, T_f, we have

$$\left(\frac{d^2\sigma}{d\omega_s d\Omega}\right)_{\mathrm{HL}} = \frac{\omega_l \omega_s^3}{\pi C^4} \operatorname{Im}\left(\sum_{n,n'} \frac{-(P_s)_{fn}(P_s^\dagger)_{n'g}(P_l^\dagger)_{ng}(P_l)_{gn'}}{(\omega_l - \omega_{ng} + i\Gamma_{ng})(\omega_s - \omega_{nf} + i\Gamma_{nf})(\omega_l - \omega_{n'g} - i\Gamma_{n'g})}\right) . \tag{13}$$

Then, the total differential scattering cross section becomes

$$\begin{aligned}\frac{d^2\sigma}{d\omega_s d\Omega} &= \left(\frac{d^2\sigma}{d\omega_s d\Omega}\right)_{\mathrm{RRS}} + \left(\frac{d^2\sigma}{d\omega_s d\Omega}\right)_{\mathrm{HL}} \\ &= \frac{\omega_l \omega_s^3}{\pi C^4} \frac{\Gamma_{fg}}{(\omega_l - \omega_s - \omega_{fg})^2 + \Gamma_{fg}^2} \\ &\quad \times \left|\sum_n \frac{(P_s)_{fn}(P_l^\dagger)_{ng}}{\omega_l - \omega_{ng} + i\Gamma_{ng}}\right|^2 \equiv \left(\frac{d^2\sigma}{d\omega_s d\Omega}\right)_S \end{aligned} \tag{14}$$

which is the expression one often uses for RRS.

Consider next the case where only one intermediate state $|n_0\rangle$ is being effectively pumped. The other intermediate states are populated only through relaxation from the excess population in $|n_0\rangle$. With the assumption of lifetime broadening, we find

$$\frac{d^2\sigma}{d\omega_s d\Omega} = (d^2\sigma d\omega_s d\Omega)_S + \text{luminescence}, \tag{15}$$

where the luminescence part[13] comes from $(\rho_{nn}^{(2)})_{n \neq n_0} \neq 0$. In the limit when $|\omega_{nn_0}| \gg \Gamma_{n_0 g}$, we have $(d^2\sigma/d\omega_s d\Omega)_S$ reduce to Eq. (7); in other words, so far as scattering is concerned, the system becomes effectively a three-level system. This is the approximation often used, for example, in the work of Yu *et al.*[5]

Consider finally the case where the relaxation rates between the intermediate states are so large that the excess populations in $|n\rangle$ are always close to thermal equilibrium. We then find

$$\begin{aligned}\rho_{nn}^{(2)}(0) &= A_n \sum_{n'} \frac{2\Gamma_{n'g}/\Gamma}{\hbar^2[(\omega_l - \omega_{n'g})^2 + \Gamma_{n'g}^2]} \\ &\quad \times \left|(\vec{\mathbf{P}}_l^\dagger \cdot \vec{\mathcal{E}}_l)_{n'g}\right|^2 , \end{aligned} \tag{16}$$

where the constant coefficients A_n describe the thermal distribution among $|n\rangle$ and Γ is the average relaxation rate from the set of intermediate states $|n\rangle$ to other states. The differential cross section for hot luminescence (or luminescence in general) is given by

$$\begin{aligned}\left(\frac{d^2\sigma}{d\omega_s d\Omega}\right)_{\mathrm{HL}} &= \frac{\omega_l \omega_s^3}{\pi C^4} \operatorname{Im}\Bigg[\Bigg(\sum_n \frac{-|(P_s)_{fn}|^2}{\omega_s - \omega_{nf} + i\Gamma_{nf}} \\ &\quad \times \sum_{n'} \frac{2A_n(\Gamma_{n'g}/\Gamma)|(P_l^\dagger)_{n'g}|^2}{\hbar^2[(\omega_l - \omega_{n'g})^2 + \Gamma_{n'g}^2]} \\ &\quad + \sum_{n' \neq n} \frac{(P_l^\dagger)_{ng}(P_l)_{gn'}}{(\omega_l - \omega_{ng} + i\Gamma_{ng})(\omega_l - \omega_{n'g} - i\Gamma_{n'g})}\Bigg)\Bigg] . \end{aligned} \tag{17}$$

As seen from Eqs. (12) and (17), both RRS and HL are simultaneously present in this case, but they would have different spectral distribution.

We have seen in the above discussion that RRS and HL are in fact two different physical processes, but they are always simultaneously present and can interfere with each other. In experiments measuring only steady-state response, they are not clearly distinguishable except that HL usually has a broader emission spectrum. Both RRS and HL have been observed, for example, by Gross *et al.*[2] In some cases, the two processes can probably be distinguished in the transient time-resolving experiments, since RRS is essentially an instantaneous two-photon direct process and HL is a two-step process which depends on the relaxation of the excess population in the intermediate states. Our discussion here will of course apply to other two-photon processes as well, such as two-photon absorption. Using picosecond pulses, Reintjes and McGroddy[14] have recently demonstrated the importance of the indirect two-step process in the two-photon absorption in Si at 1.06 μm.

The author acknowledges useful discussions with Dr. C. Flytzanis, Professor G. Mayer, and Professor M. L. Cohen.

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