PHYSICAL REVIEW B VOLUME 14, NUMBER 4 15 AUGUST 1976

Comment on "Resonant scattering or absorption followed by emission"

Y. R. Shen
Department of Physics, University of California, Berkeley, California 94720
and Inorganic Materials Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

(Received 14 August 1975)

The resonant scattering which is governed by transverse relaxation is physically different from absorption followed by emission which is affected by longitudinal relaxation. A number of physical examples are given.

Solin and Merkelo in a recent article[1] claimed that there is no difference between resonant Raman scattering (RRS) and hot luminescence (HL) (or emission after absorption). They extended Klein's intuitive theoretical derivation[2] to support their argument. Their conclusion is in contradiction with that derived from the density-matrix formalism.[3] The density-matrix approach shows that RRS is connected only with the off-diagonal density matrix elements and is governed by transverse relaxation, while HL is connected with real population change in the excited state and is affected by longitudinal relaxation. Here we want to reassert that RRS and HL are different physical processes and to point out that the apparent contradiction arises because Solin and Merkelo have ignored the difference between transverse and longitudinal relaxation.

Solin and Merkelo[1] considered only the collisionless case where the linewidths of all states are naturally broadened. Their conclusion was then based solely on the result that in the steady state, the resonant emission cross section derived from an intuitive argument agrees with the Raman scattering cross section from the *usual* scattering formula. In fact, for this special case, the same mathematical result was obtained in Ref. 3 with the density-matrix formalism but the physical interpretation is different. As shown there [Eqs. (7)-(10) of Ref. 3 with $u(t-t_0)=1$], in the limiting case of lifetime broadening with $2T_n\Gamma_{ng}=1$ and $T_g \gg T_n, T_f$ (we use the same notations here as in Ref. 3), it is the *overall* differential cross section for Stokes emission (HL+RRS) which reduces to the *usual* expression for resonant Raman scattering.[2] The integrated HL cross section is equal to the integrated (HL+RRS) Stokes emission cross section. This happens because of interference between HL and RRS in some frequency regions. In the more general cases, however, these results are not valid but the overall Stokes emission cross section still consists of two parts, HL and RRS, as pointed out in Ref. 3. We emphasize here that even in the limiting case of lifetime broadening, the *usual* expression for resonant Raman scattering has actually had contributions from both HL and RRS. Therefore, the conclusion of Solin and Merkelo[1] is not correct.

For the matter of clarification, we should point out that the definitions of HL and RRS existing in the literature are not unique. Here, we follow the definition in Ref. 2. We start from a rather general definition of differential scattering cross-section

$$\frac{d^2\sigma}{d\omega_s\, d\Omega} \propto \operatorname{Im}\langle \vec{\mathrm{p}}^{(3)}(\omega_s)\cdot\vec{\mathrm{E}}(\omega_s)\rangle .$$

We can write

$$\langle \vec{\mathrm{p}}^{(3)}(\omega_s)\rangle = \langle \vec{\mathrm{p}}^{(3)}_{\mathrm{HL}}(\omega_s)\rangle + \langle \vec{\mathrm{p}}^{(3)}_{\mathrm{RRS}}(\omega_s)\rangle ,$$

and hence

$$\frac{d^2\sigma}{d\omega_s\, d\Omega} = \left(\frac{d^2\sigma}{d\omega_s\, d\Omega}\right)_{\mathrm{HL}} + \left(\frac{d^2\sigma}{d\omega_s\, d\Omega}\right)_{\mathrm{RRS}} .$$

The HL part (or absorption followed by emission) arises from the excess population $\rho^{(2)}_{nn}(0)$ (longitudinal excitation) pumped into the intermediate state $\langle n|$ by the exciting field. The RRS part is connected only with the off-diagonal density-matrix elements (transverse excitation). Clearly from our definition HL and RRS can interfere,[4] and therefore cannot really be separated from each other, at least in steady-state measurements.

However, the relaxations of longitudinal and transverse excitations (and hence the relaxations of HL and RRS) are in general very different and are most appropriately taken care of by the density-matrix formalism. We have, for the density matrix operator ρ, the equation of motion[5-8]

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

We normally assume for optical transitions,[8,9]

$$\left(\frac{\partial\rho_{ij}}{\partial t}\right)_{\mathrm{damping}} = \begin{cases} \sum_{n\neq i}(W_{in}\rho_{nn}-W_{ni}\rho_{ii}) & \text{for } i=j ,\\ -\Gamma_{ij}\rho_{ij} & \text{for } i\neq j , \end{cases} \qquad (2)$$

where W_{in} is the transition probability from $\langle n|$ to $\langle i|$. The same equations have been used in many magnetic resonance problems.[5-7] It is seen clearly from Eq. (2) that the relaxations for longitudinal excitations ($\Delta\rho_{ii}$) and for transverse excitations ($\Delta\rho_{ij}$ with $i \neq j$) are different. Only in special cases, the two are connected. For a two-level system, Eq. (2) leads to the well-known longitudinal and transverse relaxations times, T_1 and T_2, respectively. Recently, Rousseau *et al.*[10] have indeed observed these two relaxation processes in their work on resonant Raman scattering and fluorescence in I_2 vapor.

In response to the suggestion of Ref. 1 that the results of Ref. 3 [Eqs. (6) and (7)] may not be correct, we now feel obliged to give a brief discussion on the derivation in Ref. 3 to confirm those results.[11] We consider only the steady-state case [$u(t-t_0)=1$ with $t_0 \rightarrow \infty$ in Eqs. (6) and (7) of Ref. 3]. The transient case follows essentially the same derivation. The detailed procedure of deriving Eq. (6) of Ref. 3 has been spelled out clearly by Bloembergen.[12] In fact, the expression of $\langle P^{(3)}(\omega_s)\rangle_{\mathrm{RRS}}$ follows directly from his derivation, taking into account only the resonant term with the damping constants incorporated. A similar derivation leads to $\langle P^{(3)}(\omega_s)\rangle_{\mathrm{HL}}$. That the steady-state expression of $\langle P^{(3)}(\omega_s)\rangle_{\mathrm{HL}}$ in Eq. (6) of Ref. 3 is correct can be seen as follows. For hot luminescence from $\langle n|$ to $\langle f|$, the system is equivalent to a two-level system with the populations $\rho_{nn} = \rho_{nn}^{(2)}(0)$ and $\rho_{ff}=0$. It is well known that for such a system, we have[8,12]

$$\langle \vec{\mathrm{P}}(\omega_s)\rangle = \frac{(\vec{\mathrm{P}}_s)_{fn}(\vec{\mathrm{P}}_s^{\dagger}\cdot\vec{\mathscr{E}}_s)_{nf}}{\hbar(\omega_s-\omega_{nf}+i\Gamma_{nf})}(\rho_{ff}-\rho_{nn})e^{-i\omega_s t}\,. \tag{3}$$

We also know from the well-known formula for resonance saturation that the second-order population change $\rho_{nn}^{(2)}$ induced by the exciting field is[7,8,13]

$$\rho_{nn}^{(2)} = \frac{2\Gamma_{ng}T_n|(\vec{\mathrm{P}}_l^{\dagger}\cdot\vec{\mathscr{E}}_l)_{ng}|^2}{\hbar^2[(\omega_l-\omega_{ng})^2+\Gamma_{ng}^2]}\,. \tag{4}$$

Substitution of Eq. (4) into Eq. (3) leads immediately to the steady-state expression of $\langle P^{(3)}(\omega_s)\rangle_{\mathrm{HL}}$ in Eq. (6) of Ref. 3. We should also comment in passing that the damping term which appears in the equation for $\rho_{nn}^{(2)}$ in Eq. (5) of Ref. 3 is an approximation. According to Eq. (2), it should be

$$\left(\frac{\partial\rho_{nn}^{(2)}}{\partial t}\right)_{\mathrm{damping}} = -(W_{gn}+W_{fn})\rho_{nn}^{(2)} + (W_{nf}\rho_{ff}^{(2)}+W_{ng}\rho_{gg}^{(2)})\,, \tag{5}$$

but since $\rho_{ff}^{(2)}=0$, $\rho_{gg}^{(2)}=-\rho_{nn}^{(2)}$, and $W_{ng}/W_{gn} \ll 1$ from thermal statistical consideration, we have, as a good approximation,

$$\left(\frac{\partial\rho_{nn}^{(2)}}{\partial t}\right)_{\mathrm{damping}} = -\Gamma_{nn}\rho_{nn}^{(2)}\,, \tag{6}$$

where $\Gamma_{nn}=W_{gn}+W_{fn}$. This approximation is not generally true for ρ_{nn}, especially when $\rho_{nn}^{(0)}$ is nonnegligible.

In Sec. III A of Ref. 1, Solin and Merkelo tried to elucidate the "damping approximation," but they used a rather specific model which led to some incorrect statements. In their model, the system is initially ($t=t_0$) in an excited state $|i\rangle$. Using the lifetime-broadening approximation, they calculated the total time-integrated (from $t=t_0$ to $t=\infty$) transition probability for the system making transition from $|i\rangle$ to another excited state $|l\rangle$ while scattering a photon at ω_l into a photon at ω_s. They then defined a scattering cross section as proportional to this time-integrated transition probability. There is no steady-state population in any state involved in the transition as seen, for example, from Eq. (13a) of Ref. 1. This is clearly a light scattering problem different from the one we normally deal with. The scattering cross section we are usually interested in is proportional to the steady-state transition rate from an initial state with finite equilibrium population. The results expressed in Eq. (14) of Ref. 1 are not valid when the equilibrium populations of either $|i\rangle$ or $|l\rangle$ or both are non-negligible. Thus, the claim by Solin and Merkelo that they had essentially the same expression for transition probability as in Ref. 3 was wrong. The first and second terms of Eq. (14) of Ref. 1 do not correspond to the HL and RRS terms in Eq. (6) of Ref. 3. Specifically, we note that in the expression for the steady-state scattering cross section, the $\frac{1}{2}(\Gamma_a-\Gamma_b)$ factor, which is in Eq. (14) of Ref. 1, could never appear as a damping coefficient in a denominator. Since the scattering cross sections obtained from Eqs. (4) and (14) of Ref. 1 do not follow the same definition, it is not clear how they can be equivalent as claimed in Ref. 1.

According to the definitions of HL and RRS in Ref. 3, the distinction between the two processes comes mainly from the difference between longitudinal and transverse relaxations of the intermediate state $\langle n|$. While it may be difficult to distinguish unambiguously HL and RRS without transient time-resolving measurements,[10,14] there are innumerable physical cases[15] which are based on the difference between longitudinal and transverse relaxations, some of them being similar to the case of HL and RRS. A few examples have already been given in Ref. 3. Here, we consider a few more. One well-known example is anti-Stokes scattering[16,17] in a medium in the presence of strong laser and Stokes fields. It can be generated by both direct and indirect (two-step) processes. In the direct process, the laser and the Stokes fields excite the vibrational wave (proportional to the off-diagonal density matrix element between the ground state and the excited vibrational state), and the vibrational wave in turn couples with the laser field to create the anti-Stokes field. The response is governed by the transverse relaxation time T_2 of the vibrational state. In the indirect process, the laser and the Stokes fields actually pump a non-negligible excess population into the vibrational excited state via the Raman process. This excess population can then yield an anti-Stokes scattering which decays with the longitudinal relaxation time T_1 of the vibrational state. Kaiser and his co-workers[18] have used these direct and indirect processes in their time-resolving experiments to measure, respectively, T_1 and T_2 of vibrational or phonon relaxation in liquids and solids. They are also contemplating the method of exciting the vibrational excitation directly by a coherent infrared source.[19] The same situation should appear if a laser beam at ω_1 is used to excite an optically excited state, and another laser beam at ω_2 is used to induce emission at $\omega_1 - \omega_2$. This latter case is equivalent to the case of HL and RRS, except that induced two-photon emission to the ground state occurs instead of one-photon emission to a lower-excited state. In the discussion of Solin and Merkelo,[1] they have ignored the question of longitudinal and transverse relaxations.

ACKNOWLEDGMENT

This work was supported by the U. S. Energy Research and Development Administration.

---

[1] J. R. Solin and H. Merkelo, Phys. Rev. B 12, 624 (1975).

[2] M. V. Klein, Phys. Rev. B 8, 919 (1973).

[3] Y. R. Shen, Phys. Rev. B 9, 622 (1974).

[4] While $d^2\sigma/d\omega_s d\Omega$ is always positive for $\rho_{gg}^{(0)} = 1$, its RRS component can be negative at certain ω_l and ω_s.

[5] R. K. Wangsness and F. Bloch, Phys. Rev. 89, 728 (1953).

[6] A. G. Redfield, IBM J. Res. Dev. 1, 19 (1957).

[7] See, for example, A. Abragam, *Principles of Nuclear Magnetism* (Oxford U. P., Oxford, 1961), p. 276; C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row, New York, 1963), p. 127.

[8] N. Bloembergen and Y. R. Shen, Phys. Rev. 133, A37 (1964).

[9] See, for example, L. R. Wilcox and W. E. Lamb, Phys. Rev. 119, 1915 (1960); W. E. Lamb and T. M. Sanders, *ibid.* 119, 1901 (1960); W. E. Lamb, Phys. Rev. A 134, 1429 (1964); M. O. Scully and W. E. Lamb, *ibid.* A 159, 208 (1967).

[10] D. L. Rousseau, G. D. Patterson, and P. F. Williams, Phys. Rev. Lett. 34, 1306 (1975).

[11] In Eq. (6) of Ref. 2, there should be a factor $\exp(-i\omega_s t_0)$ attached to $u(t-t_0)$ in each term, except those terms proportional to $[1-u(t-t_0)]$.

[12] N. Bloembergen, *Nonlinear Optics* (Benjamin, New York, 1965), Chap. II.

[13] F. Bloch, Phys. Rev. 102, 104 (1956).

[14] P. F. Williams, D. L. Rousseau, and S. H. Swortesky, Phys. Rev. Lett. 32, 196 (1974). In this case, the transverse relaxation is too short to be seen. The results have been averaged over Doppler broadening and hyperfine splittings.

[15] Many examples are associated with magnetic resonance phenomena. See, for example, Ref. 7.

[16] Y. R. Shen and N. Bloembergen, Phys. Rev. 137, A1786 (1965).

[17] J. A. Giordmaine and W. Kaiser, Phys. Rev. 144, 676 (1966).

[18] D. von der Linde, A. Lauberearu, and W. Kaiser, Phys. Rev. Lett. 26, 954 (1971); A. Laubereau, D. von der Linde, and W. Kaiser, *ibid.* 27, 802 (1971); 28, 1162 (1972); Opt. Commun. 7, 173 (1973).

[19] A. Laubereau, A. Grieter, and W. Kaiser, Appl. Phys. Lett. 25, 87 (1974).