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Resonant Raman scattering versus luminescence

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Résumé. — Nous étudions l'importance relative, dans le spectre de diffusion de la lumière, de la diffusion Raman électronique résonnante et de la luminescence, sur un modèle simple à trois niveaux du à Takagahara et al., qui suppose les électrons couplés, dans l'état intermédiaire, à un champ de « phonons » localisés. Le modèle est exactement solvable. Nous montrons que le poids relatif des pics Raman et luminescents est contrôlé par un paramètre de mémoire unique \( \gamma_b/\Gamma \) où \( \gamma_b \) et \( \Gamma \) sont les largeurs de l'état électronique intermédiaire et du niveau de phonons. Si \( \gamma_b/\Gamma \gg 1 \), la mémoire est presque parfaite, et le spectre est de type Raman. Dans le cas contraire, la luminescence domine. Pour \( \gamma_b/\Gamma \sim 1 \), les deux types de structure coexistent, et il apparaît des satellites anormaux caractéristiques de la luminescence « chaude ».

Abstract. — We study the competition, in the light scattering spectrum, between electronic resonant Raman scattering and luminescence, on a simple three-level model due to Takagahara et al., where electrons are assumed to couple, in the intermediate state, with a field of localized « phonons ». The model can be solved exactly. We show that the relative weight of Raman versus luminescence peaks is controlled by a single memory parameter \( \gamma_b/\Gamma \) where \( \gamma_b \) and \( \Gamma \) are the damping rates of the intermediate electronic state and of the phonons. If \( \gamma_b/\Gamma \gg 1 \), memory is quasi-perfect, and the spectrum is purely Raman; in the opposite limit luminescence predominates. For \( \gamma_b/\Gamma \sim 1 \), both structures are present, as well as anomalous satellites characteristic of « hot » luminescence.

1. Introduction. — The relationship between resonant Raman scattering and hot luminescence (absorption-reemission of a photon) has been the subject of a controversy [1] which essentially revolves around the discussion of the effect of interactions in the intermediate state. In a series of recent articles [2, 3, 4], Takagahara et al. have clarified this problem with the help of a simple three-level model with a coupling to, e.g., a vibrational field in the intermediate state, the effect of which is treated with the help of a stochastic approach.

In this article, we present an exact calculation of the scattered light spectrum for this same model, in which the effect of the vibrational field is treated microscopically, with the help of techniques developed to deal with effects of incomplete relaxation in solid-state high-energy spectroscopies [5].

This provides a basis for discussing the influence of the various physical parameters of the model (vibrational frequency, coupling strength and damping rates) on the respective weights of the Raman and luminescence peaks (or, more generally, structures) in the spectrum, as well as the possibility itself of identifying separately the two types of structures.

2. Complete expression for the scattered light spectrum. — Let us first recall the details of the model. We consider a system with three narrow well separated electronic levels a, b, c (see Fig. 1). We study the second order optical process in which an incident photon of frequency \( \omega_1 \) excites an electron from the initially occupied state (a) up to the intermediate state (b). The system then decays into the final state (c) by emission of a photon of frequency \( \omega_2 \).

We assume, for simplicity, that (a) and (c) have infinite lifetimes, and that it is only in state (b) that the electrons are subject to interactions, which we divide into two parts:

1) Interactions with a non-dispersive boson (e.g. optical phonon or molecular vibration) field, characterized by a « phonon » frequency \( \omega_0 \) (much smaller
The energy levels of the system: $\omega_1$ is the photon energy, $\epsilon_a$, $\epsilon_b$, $\epsilon_c$ respectively the energies of the initial, intermediate and final electronic states.

than the electronic splittings $\epsilon_b - \epsilon_a$ and $\epsilon_b - \epsilon_c$ and a damping rate $\Gamma$. The coupling hamiltonian is taken to be:

$$H_C = gc_b^+ c_b (a^+ + a)$$

where $c_b^+$ (resp. $c_b$) creates (resp. destroys) an electron in state (b), and $a^+$ (resp. $a$) creates (resp. destroys) a phonon.

2) All the other interactions, which we take into account phenomenologically by means of an electronic linewidth $\gamma_b$. These describe, for example, the radiative and Auger decays. More generally, we include in this group all the interactions involving energy exchanges much larger than the scale, $\omega_b$, on which we want to study the photon spectrum. So, only virtual transitions due to these processes are important, and they can legitimately be taken into account by means of a constant linewidth.

Since we are interested in the resonant Raman scattering ($\omega_1 \approx \epsilon_b - \epsilon_a$), the scattering cross-section is essentially due to the dipolar electron-phonon coupling (acting to second order), and direct $a \rightarrow c$ transitions due to the diamagnetic coupling (acting to first order) are negligible [6].

So, when calculating the number of photons scattered at frequency $\omega_2$, we are looking for the quadratic response to the incident electromagnetic field. Applying the techniques which have been developed to calculate quadratic responses [7], we find that the rate of scattering $I(\omega_1, \omega_2)$ can be represented, in the absence of interactions with the vibrations in state (b), by one single Keldysh diagram, shown in figure 2.

The corresponding algebraic expression is, for a system at $T = 0$ K:

$$I_0(\omega_1, \omega_2) = - |M_{ab}|^2 |M_{bc}|^2 \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' \int_{-\infty}^{\infty} du' G_{b}^{+\dagger}(-t) \times$$

$$G_{a}^{\dagger}(-t') G_{b}^{\dagger}(t') G_{c}^{\dagger}(u') e^{-i\omega_1 t} e^{-i\omega_2 u'} (2)$$

where $M_{ab}$ and $M_{bc}$ are the dipolar matrix elements corresponding to the $a \rightarrow c$ and $b \rightarrow c$ transitions. The Keldysh electron propagators [8] in the absence of the electromagnetic field are:

$$G_{a}^{\dagger}(t) = - i e^{-i\epsilon_a t} \theta(t)$$

$$G_{b}^{\dagger}(t) = - i e^{-i\epsilon_b t} \theta(t)$$

$$G_{c}^{\dagger}(t) = i e^{-i\epsilon_c t}$$

$$G_{c}^{\dagger}(t) = - i e^{-i\epsilon_c t}$$

where we have taken into account the fact that states (b) and (c) are initially empty, and state (a) is initially occupied. Then:

$$I_0(\omega_1, \omega_2) = |M_{ab}|^2 |M_{bc}|^2 2 \pi \frac{\delta(\epsilon_a - \epsilon_c + \omega_1 - \omega_2)}{(\epsilon_b - \epsilon_a - \omega_1)^2 + \gamma_b^2}$$

i.e., of course, the value predicted by the Fermi golden rule for the resonant (electronic) Raman $a \rightarrow b \rightarrow c$ process.

Taking into account the coupling to phonons in state (b) simply amounts to renormalizing the diagram of figure 2 in all possible ways. That is, one must sum all the diagrams of the type shown in figure 3, containing an arbitrary number of phonon lines connected to either of the two (b) electron lines.
Fig. 3. — An example of renormalization of the diagram of figure 2 in the presence of electron-phonon interactions in the intermediate state. The internal wavy lines represent phonon propagators.

It is well known that, when the electron is non propagating, this sum can be performed exactly with the help of the linked cluster theorem [9], and one obtains:

\[
I(\omega_1, \omega_2) = - |M_{ab}|^2 |M_{bc}|^2 \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' \int_{-\infty}^{\infty} du \ e^{-i\omega s(t-t')} G_b^+(t) \times \\
G^-(t-t') G_b^-(t'-u) G^+(u) \exp \{ C^+(t) + C^-(t'-u) + C^+(-0, t, t', u) \}
\]

where the \( C^\alpha \)s are given by:

\[
C^+(t) = [C^-(t)]^* = - i g^2 \int_{t}^{t_2} dt_2 \int_{t_1}^{t_0} dt_1 D^+(t_1 - t_2)
\]

\[
C^+(0, t, t', u) = i g^2 \int_{t}^{t'} dt_2 \int_{t_1}^{t_0} dt_1 D^+(t_1 - t_2)
\]

and the phonon Keldysh propagators are:

\[
D^+(t) = - i e^{-i(\omega_0 - \Gamma t)}
\]

\[
D^-(t) = - i e^{i(\omega_0 - \Gamma t)}
\]

Using the same algebraic technique as Langreth [10], we find, after a tedious but straightforward calculation:

\[
I(\omega_1, \omega_2) = 2 \text{ Re } \{ A_1 + A_2 + A_3 \}
\]

\[
A_1(\omega_1, \omega_2) = \sum_{n,m,p,q,r,s=0}^\infty e^{-a(\omega_0 + 2\omega_1 + \omega_2)} \left( \frac{n! m! p! q! r! s!}{(r+s)!} \right) [x_s^+ + \Delta \varepsilon + (m + r + s) \omega_+ - (m + r + s) \omega_-]^{-1} \times \\
\left[ x_2 + \Delta \varepsilon + \omega_+ + (p + r) \omega_- \right]^{-1} [x_1 - x_2 - (p + q + r + s) \omega_- + i\eta]^{-1}
\]

\[
A_2(\omega_1, \omega_2) = \sum_{n,m,p,q,r,s=0}^\infty e^{-2a} \frac{a^{m+p+r+q+s}}{n! m! p! q! r! s!} [x_s^+ + \Delta \varepsilon + (m + r + s) \omega_+ - (m + r + s) \omega_-]^{-1} \times \\
\left[ x_2^+ + \Delta \varepsilon - n\omega_- + (p + r) \omega_+ \right]^{-1} [2 i \gamma_1 + (m + r) \omega_+ - (n + q) \omega_-]^{-1}
\]

\[
A_3(\omega_1, \omega_2) = \sum_{n,m,p,q,r,s=0}^\infty e^{-a(\omega_0 + 2\omega_1 + \omega_2)} \frac{a^{m+p+r+q+s}}{n! m! p! q! r! s!} [x_1 + \Delta \varepsilon + \omega_+ - (n + p + q) \omega_-]^{-1} \times \\
\left[ x_2 + \Delta \varepsilon - (n + p + q) \omega_+ \right]^{-1} [2 i \gamma_1 + (q + n) \omega_+ - (m + s) \omega_-]^{-1}
\]

with

\[
a = \frac{2}{(\omega_0 + i\Gamma)^2}, \quad \Delta \varepsilon = (\omega_0 + i\Gamma) a, \quad \omega_0 = \omega_0 \pm i\Gamma
\]

\[
x_1 = \omega_1 + \varepsilon_a - \varepsilon_b - i\gamma_1 \quad x_2 = \omega_2 + \varepsilon_c - \varepsilon_b - i\gamma_1.
\]

This exact expression of the spectrum calls for a few simple comments:

— it provides a complete, although very heavy, expression for the scattered intensity, and explicits the results which can be obtained from the method of reference [2] by numerical matrix inversion.
one immediately sees on equations (8-9) that two types of structures are to be expected:

1. Raman peaks at energies

\[ \omega_2 = \omega_1 - (\varepsilon_b - \varepsilon_a) - N \omega_0, \]

of widths \( N \gamma \), \( N = 0, 1, 2 \ldots \), i.e. the central \( N = 0 \) (electronic Raman) line retains a \( \delta \)-function shape. Only Stokes satellites of the main Raman peak are present, since we assume the system to be at zero temperature.

2. Luminescence structures, at frequencies

\[ \omega_2 \approx \varepsilon_b - \varepsilon_e - (P - M) \omega_0 - \text{Re} \Delta \epsilon \]

(11)
of widths \( \gamma_b + (P + M) \Gamma \), where \( P \) and \( M = 0, 1, 2 \ldots \).

So, besides the main luminescence peak, centred at \( \omega_2 = \varepsilon_b - \varepsilon_e - \text{Re} \Delta \epsilon \), one can distinguish between two types of luminescence satellites:

(i) "Normal" ones \( (P > M) \). These satellites are the only ones present if reemission takes place after complete relaxation in the intermediate state, i.e. after the excited electron has relaxed into the ground state \( \psi_0 \) (of energy \( \varepsilon_b - \text{Re} \Delta \epsilon \approx \varepsilon_b \) of the \((b) + \) phonon) coupled system. They then correspond to the decay from that part of \( \psi_0 \) in which the \((b) \) electron is dressed with \( P \) phonons \([10]\) (i.e., complete relaxation entails \( M = 0 \) in equation (11)).

(ii) Anomalous ones \( (P < M) \), the presence of which characterizes the phenomenon of incomplete relaxation in the intermediate state. The reemission process then occurs from an excited state \( \psi_{\text{exc}} \) (of energy \( \approx \varepsilon_b + M \omega_0, \ M > 0 \)) of the \((b) + \) phonon) coupled system, which has not had time enough to relax into \( \psi_0 \). The anomalous structures then come from that part of \( \psi_{\text{exc}} \) in which the \((b) \) electron is dressed with \( P < M \) phonons. Obviously, incomplete relaxation, when present, also contributes to the normal satellites (i.e. \( P > M \)).

— Absorption resonances are located at energies

\[ \omega_1 \approx \varepsilon_b - \varepsilon_e + Q \omega_0 \] 

\( Q = 0, 1, 2 \ldots \)

and have widths \( \gamma_b + Q \Gamma \).

Let us finally insist that, as already pointed out by Takagahara et al. [2], resonant Raman and hot luminescence structures all result from one single second-order optical process and, consequently, cannot be considered as independent phenomena.

In order to make the above remarks more concrete, we will now study in more detail the shape of the spectrum in the weak coupling limit \( \langle a \rangle \ll 1 \), which will enable us to discuss the influence of the various physical parameters.

3. Analysis of the low-order structures. — We now assume that:

— \( \gamma_b \) and \( \Gamma < \omega_0 \), so that the various structures in the spectrum can be separated and identified. (Note that, anyhow, the condition \( \Gamma < \omega_0 \) is necessary for phonons to be well-defined excitations.)

— \( a \) is very small (this condition will be made more precise below), so that we only retain in equations (8-9) terms up to order \( a^2 \).

At this stage, a problem arises, connected with the existence of the complex shift \( \Delta \epsilon = a \omega_0 = g^2/\omega_0 \) of the absorption and emission resonances which appears in equations (9). The corresponding terms can be developed, near the resonances, in powers of \( \Delta \epsilon \) (i.e. of \( a \)), if and only if \( \text{Im} \Delta \epsilon \ll \gamma_b \), i.e. if the phonon-induced broadening of level (b) is small compared with the width due to other processes. Since \( \Gamma < \omega_0 \), this means

\[ (g^2/\omega_0) \Gamma < \gamma_b. \]

(12)

If this condition is satisfied, the development of expressions (8-9) up to a given order \( l \) in powers of \( a \) is equivalent to a standard perturbation calculation, i.e. to summing all diagrams containing up to \( l \) phonon lines.

If, on the contrary, condition (12) is not fulfilled, a development in powers of \( a \) is no longer meaningful and one must perform, either a direct computation of expression (8-9), or a more elaborate perturbation calculation, where it is the self-energy itself, instead of the \((b) \) propagator, which is calculated to a given order in \( a \).

We will assume from now on that condition (12) holds. We then find, to second order in \( a \):

\[ I(\omega_1, \omega_2) = I^{(0)} + I^{(1)} + I^{(2)} \]

(13)

where \( I^{(0)} \) is the contribution to \( I \) corresponding to processes in which \( n \) real phonons have been emitted (i.e., \( I^{(0)} \) contains terms involving at most \( (2 - n) \) virtual phonons).

\[ I^{(0)}(\omega_1, \omega_2) = 2 \pi \delta(x_1 - x_2) \left\{ 1 + 2 \text{Re} \left[ \frac{g^2}{x_1(x_1 - \omega_+)} \right] + \left[ \frac{g^2}{x_1(x_1 - \omega_+)} \right]^2 + 2 \text{Re} \left[ \frac{g^4(3x_1 - 2\omega_+)}{x_1^2(x_1 - \omega_+)^2(x_1 - 2\omega_+)} \right] \right\} \]

(14)

\[ I^{(1)}(\omega_1, \omega_2) = \frac{2 \Gamma g^2}{|x_1x_2|^2|x_1 - x_2 - \omega_+|^2} \left\{ 1+2g^2 \text{Re} \left[ \frac{1}{x_2(x_2 - \omega_+)} + \frac{1}{x_1(x_1 - \omega_+)} + \frac{1}{(x_2 - \omega_+)(x_1 - \omega_+)} \right] \right\} \]

(15)
It is seen on the above expressions of the $I^{(n)}$ that our development is valid provided that the various terms of $I^{(0)}$ decrease with increasing powers of $g^2$. The condition for this is $g^2/\gamma_b \omega_0 \ll 1$, which also ensures that the $g^4$ correction to $I^{(1)}$ is everywhere small compared with its first term, of order $g^2$. (Of course, $I^{(1)} \gg I^{(0)}$ in the region of the first Raman satellite, and $I^{(2)} \gg I^{(1)}$ around the second one, since these structures only appear, respectively, to order $g^2$ and $g^4$.)

As expected, the $I^{(0)}$ term, corresponding to the central Raman peak at $\omega_2 = \omega_1 + \epsilon_a - \epsilon_c - \omega_0$, has the $\delta$-function shape which results from energy conservation. This remains true to all orders in $a$, as far as levels (a) and (c) are assumed to be infinitely narrow. Of course, the weight of this peak has a main resonance at $\omega_1 \approx \omega_0 - \epsilon_b$. It also exhibits secondary resonances at $\omega_1 = \epsilon_b - \epsilon_c + n\omega_0$ ($n = 1, 2, ...$), which correspond to excitation into the phonon satellites of the spectral density of level (b). We will not study these secondary resonances in detail since, for small $a$, they are only small corrections to the main resonance. It is more convenient in practice to study phonon effects on the rest of the spectrum, which exists only in the presence of interactions in state (b) i.e. has no contribution of zeroth order in $a$.

That is, we now study qualitatively the various structures on $I^{(1)} + I^{(2)}$.

a) **Raman satellites.** — The first one, at $\omega_2 = \omega_1 + \epsilon_a - \epsilon_c - \omega_0$, has a width $\Gamma$ and a maximum intensity

$$I_{\text{1st Raman}} \cong \frac{2g^2}{\Gamma_x |x_1|^2 |x_1 - \omega_0|^2}$$

while, for the second one, of width $2\Gamma$,

$$I_{\text{2nd Raman}} \cong \frac{g^2}{|x_1 - 2\omega_0|^2}$$

b) **Central luminescence peak** ($\omega_2 \approx \epsilon_b - \epsilon_c$). — Its intensity is

$$I_{\text{CL}} \cong \frac{2\Gamma g^2}{\gamma_b |x_1|^2 |\bar{x}_1 - \omega_0|^2}$$

where

$$\bar{x}_1 = \text{Re} x_2 = \omega_1 + \epsilon_a - \epsilon_b$$

and its width $\Delta_{\text{CL}} \cong \gamma_b$.

c) **First normal luminescence satellite** ($\omega_2 = \epsilon_b - \epsilon_a - \omega_0$). — It has a width $\gamma_b + \Gamma$ and a maximum intensity

$$I_{\text{NLS}} \cong \frac{2\Gamma g^4}{\gamma_b |x_1|^2 |\bar{x}_1 - \omega_0|^2}(\gamma_b + \Gamma).$$

Its weight is:

$$W_{\text{NLS}} \cong W_{\text{CL}} g^2/\omega_0^3$$

thus, $W_{\text{NLS}}/W_{\text{CL}}$ only depends on the coupling strength, and not on the memory parameter, which expresses the fact that it is a normal satellite. However, while, for increasing $\Gamma/\gamma_b$, the intensity of the central luminescence peak grows at constant width, $I_{\text{NLS}}$ remains almost constant, the increase in $W_{\text{NLS}}$ being due to that of the width ($\gamma_b + \Gamma$).

d) **First anomalous luminescence satellite** ($\omega_2 = \epsilon_b + \epsilon_c + \omega_0$). — It has a width $\gamma_b + \Gamma$, an antiresonant shape, and its maximum intensity is of order

$$I_{\text{ALS}} \cong \frac{\Gamma g^4}{|x_1|^2 |\omega_0^2| |\bar{x}_1 - 2\omega_0 - i\Gamma|^2(\gamma_b + \Gamma)} \text{Max}(|x_1 - \omega_0|, \gamma_b + \Gamma)$$
so that its half-weight

\[ W_{ALS} \approx W_{CL} \frac{g^2}{\omega_0^2} \frac{\gamma_b}{\max(0, \gamma_b + \Gamma)} < W_{CL} \frac{g^2}{\omega_0^2} \frac{\gamma_b}{\gamma_b + \Gamma}. \]  

(24)

As discussed above, the relative weight of the anomalous structure decreases when the loss of memory increases: the characteristic time for relaxation of the optically excited state into the ground state of the \((\text{b}) + \text{phonon}\) system is, at most, of order \((\gamma_b + \Gamma)^{-1}\). When \(x_1\) moves away from the resonant value \(\omega_0\), this time reduces to \(|x_1 - \omega_0|^{-1}\), the time for losing phase coherence between the wave packet \(\psi(t)\) (at energy \(\omega_1 + \varepsilon_a\)) and \(\psi_{\text{exc}}(t)\) (at energy \(\approx \varepsilon_a + \omega_0\)).

It is clear that the effects we have discussed will be most important when the memory parameter is of order 1. Indeed, if \(\gamma_b/\Gamma \gg 1\), only Raman peaks show up, while, if \(\gamma_b/\Gamma \ll 1\), anomalous luminescence effects become negligible.

Figure 4 illustrates our discussion for the case \(\gamma_b/\Gamma \sim 1\), by showing the spectrum as computed from the second order expression (15-16). Obviously, this is only valid for very small couplings

\[ \frac{g^2}{\omega_0^2} \ll \frac{\gamma_b}{\omega_0} \ll 1, \]

in which case second order effects are correspondingly small. For larger couplings, one should compute \(I(\omega_1, \omega_2)\) directly from equations (9). Such a calculation has been performed with a different technique by Takagahara et al. [3], whose numerical results show the same qualitative dependence on the memory parameter as that predicted from the perturbation calculation.

In conclusion, the crucial physical parameter which determines the relative importance of resonant Raman scattering and luminescence is the « memory parameter » \(\gamma_b/\Gamma\). It appears, from the physical interpretation we have given for the various contributions to the spectrum, that this qualitative result, deduced here from a very simplified model, is general. Of course, in a more realistic model, one should include, for example, into \(\Gamma\) the effect of phonon dispersion and, clearly, the existence of a continuous electron spectrum would complicate very much the shape of the emission spectrum.

Let us however mention that the present model can be used as a reasonable first approximation for a system of molecules — the « phonons » being in this case the vibrational and rotational molecular excitations.

Two particular aspects of the above qualitative discussion should be of physical interest:

(i) a study of the relative weights of the first Raman satellite (in a resonant Raman experiment) and of the central luminescence peak seems to be usable as a tool (e.g. in the case of molecular crystals) to estimate the ratio of the electronic (b) lifetime and of the phonon — or vibration — one;

(ii) the analysis of the anomalous luminescence satellites (in the very low temperature limit where phonon emission processes, which we have neglected here, become negligible) would provide a definite test of the fact that luminescence is effectively hot. Their existence, as well as that of the Raman peaks, corresponds to the memory, in the reemitted spectrum, of the excitation process.

These memory effects are analogous to incomplete relaxation effects in X-ray emission from solids, or interference effects and anomalous plasmon satellites in Auger emission.
References