COMMENTS

Time-Resolved Resonance Fluorescence and Resonance Raman Scattering

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Light emission under near-resonant excitation by a pulsed optical field is described using a semiclassical (Bloch) model for the near-resonant transition. Adiabatic excitation of this transition leads to Raman emission, whereas nonadiabaticity gives fluorescence. The model describes quantitatively observed relaxation effects. It further predicts that such experiments can determine the power spectrum of the correlation function characterizing collisions, offering an alternative to off-resonance spectroscopy.

The availability of tunable pulsed lasers has made possible the investigation of time-resolved resonant scattering. For example, Williams, Rousseau, and Dworetsky have recently reported measurements on molecular iodine.[1] In their experiment a nondissociative transition is excited by a quasirectangular argon-laser pulse and the emission to a third level is time resolved, showing both a fast component (Raman) and a slow tail (fluorescence). The ratio of the strength of these components was found to depend both on pressure and on the tuning of the laser, at least for small detunings, beyond which the ratio became constant. Such behavior can be explained using second-order perturbation and scattering theories.[2,3] The purpose of the present comment is to develop a simple model able to describe such experiments quantitatively while clarifying several concepts involved. In particular, it will be shown that relaxation can be taken into account in a simple way and that time-resolved scattering is related to the study of line shapes far from resonance (off-resonance spectroscopy). Furthermore, the analysis suggests some new experiments.

Consider the nondegenerate three-level system of Fig. 1(a). Transitions 1-2 and 2-3 are dipole allowed, and the system is excited by an optical pulse of frequency ω close to ω_{21}. One is interested in the time dependence and in the frequency of the spontaneous emission to 3. In the model, the pair 1-2, described by a density matrix ρ whose elements obey a Bloch equation,[4] evolves under the influence of a classical field. Appropriate elements of ρ contribute to the emission to 3, which is a well-known result that can be derived from perturbation theory.[5] Let $\vec{S}$ be the normalized pseudospin ($S_x + iS_y = 2\rho_{12}$; $S_z = \rho_{22} - \rho_{11}$) in a frame rotating at the field frequency ω. It obeys the equation

$$d\vec{S}/dt = \vec{S} \times \vec{E}_{\text{eff}} - \vec{\Gamma} \cdot (\vec{S} - \vec{S}_0), \tag{1}$$

where $\vec{E}_{\text{eff}}$ is an effective field whose x component is the Rabi precession frequency $2\mu\mathcal{E}/\hbar$ ($\mathcal{E}$ is the field amplitude), and whose z component equals $-\Delta = \omega_{21} - \omega$, the frequency offset; $\vec{\Gamma}$ accounts for relaxation. The effective field makes

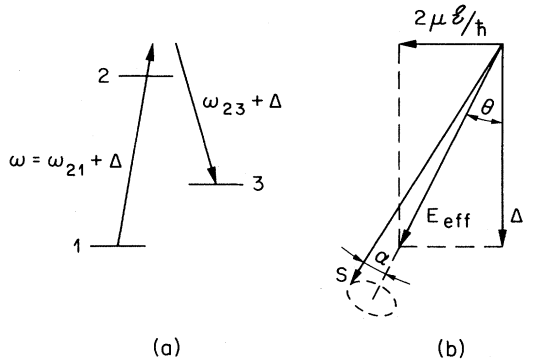

FIG. 1. (a) The three-level scheme of the simplest scattering model; (b) the geometry of adiabatic following in the frame rotating at the field frequency ω.

an angle θ with the $-z$ axis, $\tan\theta = 2\mu\mathcal{E}/\hbar\Delta$. Off resonance, the polarization in the system 1-2 is proportional to ρ_{12} and precesses at the field frequency ω. The emission from 2 to 3, whose *amplitude* is proportional to ρ_{12}, occurs therefore at frequency $\omega_{23}+\Delta$; its intensity is proportional to $|\rho_{12}|^2$. On the other hand, in the absence of coherence ($\rho_{12}=0$), but with upper-state excitation ($\rho_{22}\neq 0$), the emission intensity is proportional to $\rho_{22}=(1+S_z)/2$ and takes place at frequency ω_{23}. In the case of inhomogeneous broadening, these conclusions remain valid for each independent isochromat, as the Raman emission is incoherent. These considerations can also be extended to degenerate systems and more complicated level schemes.

Consider now the evolution of the system of Fig. 1(a) during and after the application of the pulse, first neglecting relaxation. If Δ is sufficiently large, the effective field varies slowly, and $\vec{S}$ follows $\vec{E}_{\rm eff}$ adiabatically.[6] This will turn out to be a very useful concept. For the angle α between $\vec{S}$ and $\vec{E}_{\rm eff}$ to remain smaller than θ [Fig. 1(b)], the condition $|d\theta/dt| \approx \alpha E_{\rm eff} \ll E_{\rm eff}$ has to be satisfied. For Δ constant this leads to $|\mathcal{E}^{-1}d\mathcal{E}/dt| \ll |\Delta|$, which is just the condition that the pulse be off resonance, i.e., its Fourier components on resonance are relatively small. The same criterion is derived from perturbation theory.[7] This being satisfied, $|\vec{S}| = S = 1$ and $S_x = 2\rho_{12} = 2\mu\mathcal{E}/\hbar\Delta$. A pulse whose intensity is proportional to $S_x^2/4 = \mu^2\mathcal{E}^2/\hbar^2\Delta^2$ is radiated at frequency $\omega_{23}+\Delta$. At the end of the pulse, no coherent dipole remains and the emission terminates. This process can properly be called Raman scattering. On the other hand, if the pulse is turned on nonadiabatically, the pseudospin does not follow $\vec{E}_{\rm eff}$. Radiation is then emitted both around the shifted frequency $\omega_{23}+\Delta$ and around the resonant frequency ω_{23}. This follows immediately when one considers the precession of $\vec{S}$ in the rotating frame. For an arbitrary pulse shape the result is complicated, especially in the presence of inhomogeneous broadening. When the pulse subsides, ρ_{12} components will in general remain. They emit resonance fluorescence at ω_{23}, a phenomenon known in NMR by the name of ringing.[6] For inhomogeneous lines and intermediate detunings, it is clear that part of the line can produce Raman scattering while another part produces fluorescence. In this regime the ratio of these components will be a strong function of detuning, as observed by Williams, Rousseau, and Dworetsky.[1]

One may now allow for collisional relaxation, still assuming a pulse length much shorter than radiative lifetimes. With Δ sufficiently large, $\vec{S}$ follows $\vec{E}_{\rm eff}$, but S is not conserved. From the Bloch equation and the adiabatic-following approximation, one obtains

$$\frac{dS}{dt} \cong -\left(\frac{\sin^2\theta}{T_2}+\frac{\cos^2\theta}{T_1}\right)S+\frac{\cos\theta}{T_1} \equiv -a(t)S+b(t). \tag{2}$$

In the optical region collisions contribute to transverse relaxation only and $T_1=\tau_R$, the radiative lifetime. In this model collisional relaxation to close-lying levels is included in T_2 and the overall population of the pair 1-2 is accounted for by rate equations. It will also be assumed that the driving field is weak in the sense that $(2\mu\mathcal{E}/\hbar\Delta)^2 \ll T_2/T_1$, and we will also specialize to the case $T_2 \ll T_1$; i.e., the line is strongly pressure broadened. Then, for a quasirectangular pulse, with a and b in (2) constant, one finds that

$$1-S \cong \left(1-\frac{b}{a}\right)[1-\exp(-at)] \cong \left(\frac{2\mu\mathcal{E}}{\hbar\Delta}\right)^2\frac{T_1}{T_2}\left[1-\exp\left(-\frac{t}{T_1}\right)\right] \qquad (0<t<\tau_p). \tag{3}$$

During the pulse, radiation near $\omega_{23}+\Delta$ with intensity proportional to $|\rho_{12}|^2 = (S^2\sin^2\theta)/4$ is emitted. It decays slightly, while radiation near ω_{23} grows; its intensity is proportional to $(1-S)/2$ for small θ. After the pulse $\theta\approx 0$, and only the latter remains, decaying with the relaxation of level 2. If τ_p is sufficiently short ($\tau_p \ll T_2$), expansion of (3) shows that the ratio of resonance fluorescence to resonance Raman scattering equals $2\tau_p/T_2$. This is independent of Δ for constant T_2 and is proportional to the relaxation rate.[8] It should be noted that emission at ω_{23} again corresponds to nonadiabatic excitation of the pair 1-2, the nonadiabaticity being caused here by collisions. The adiabatic-following property of Raman emission has the further consequence that the linewidth of the intermediate level 2 does not appear in the spectral width of the scattered light.

Collisional relaxation in a dilute gas is treated adequately by a binary collision approximation. If $\hbar\Delta \ll \tau_c^{-1}$, the reciprocal of the mean collision time, the line is a Lorentzian characterized by a single relaxation time T_2.[9] If Δ is further increased, collisions become less effective in sup-

plying or absorbing the energy $\approx\hbar\Delta$ required to produce the nonadiabatic excitation of level 2. Indeed it is well known that no resonance fluorescence is seen in a Raman experiment far from resonance. The frequency dependence of T_2 has been treated adequately by Redfield and Bloch.[10] From the latter's treatment [Eqs. (4.58) to (4.60) and (4.72)], using the adiabatic-following approximation, one obtains

$$T_2^{-1}=2T_1^{-1}+\phi_0[(\Delta^2+4\mu^2\mathcal{E}^2/\hbar^2)^{1/2}], \quad (4)$$

where $\phi_0(\omega')$ is the power spectrum of the quantum-mechanical correlation function of the collision operator. For collisions characterized by a single relaxation time τ_c, the power spectrum is

$$\phi_0(\omega')=\varphi(1+\omega'^2\tau_c^2)^{-1}, \quad (5)$$

where φ is proportional to the collision frequency. Therefore, the ratio of strengths $2\tau_p/T_2$ should decrease as the excitation frequency is tuned further away from resonance.[11] This provides an attractive alternative to "off-resonance" spectroscopy for the determination of τ_c.[12]

Our treatment also describes resonance scattering and fluorescence from level 2 to level 1. In this case, there is an important coherent contribution that enhances the emission. For samples smaller than a wavelength, with inhomogeneous broadening and nonadiabatic excitation, the enhanced emission at the resonant frequency stops after a time comparable to the inverse of the excited part of the inhomogeneous width, and can be restored only in an echo experiment. In a sample much larger than a wavelength, the coherent dipole S_x is phased so that it describes radiation in the forward direction only. It properly describes the index of refraction and superradiance effects. The Rayleigh-scattered radiation is proportional to density fluctuations whereas the nonadiabatic part can be called fluorescence proper.

Further effects can be predicted in the case where the direct 2-3 transition is forbidden, with level 2 being able to relax to a nearby level 4 from which transition to 3 is allowed. This would, for instance, be the case when one excites near resonantly the singlet manifold of an organic crystal while observing the triplet emission. In this case, there will be no appreciable adiabatic component whereas the delayed fluorescence will exhibit the strong temperature dependence of the 2-4 relaxation, as well as its frequency dependence.

In conclusion, the semiclassical model is extremely helpful for describing resonance scattering. With careful handling, it provides quantitative predictions which agree with elaborate quantum electrodynamical treatments.[13] The association of Raman scattering with adiabatic excitation and that of fluorescence with nonadiabaticity is a new clarifying concept.

Thanks are due to the authors of Ref. 13 for a preprint of their paper and for stimulating discussions.

[1]P. F. Williams, D. L. Rousseau, and S. H. Dworetsky, Phys. Rev. Lett. 32, 196 (1974).

[2]N. M. Kroll, in *Quantum Optics and Electronics, Les Houches Lectures, 1964,* edited by C. De Witt, A. Blandin, and C. Cohen-Tannoudji (Gordon and Breach, New York, 1965).

[3]P. P. Shorygin, Usp. Fiz. Nauk 109, 293 (1973) [Sov. Phys. Usp. 16, 99 (1973)].

[4]R. P. Feynman, F. L. Vernon, Jr., and R. W. Hellwarth, J. Appl. Phys. 28, 49 (1957). The notation will be similar to that used by E. Courtens, in *Laser Handbook*, edited by F. T. Arecchi and E. O. Schulz-DuBois (North-Holland, Amsterdam, 1972), Chap. E5.

[5]G. E. Notkin, S. G. Rautian, and A. A. Feoktistov, Zh. Eksp. Teor. Fiz. 52, 1673 (1967) [Sov. Phys. JETP 25, 1112 (1967)].

[6]A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, England, 1961); D. Grischkowsky and J. Armstrong, Phys. Rev. A 6, 1566 (1972).

[7]Take a wave function $\psi=\sum_i a_i(t)\psi_i$, with initial conditions $a_1(0)=1$, $a_2(0)=a_3(0)=0$. The field pulse is

$$E(t)=\mathcal{E}(t)\cos\omega t=(2\pi)^{-1}\int\mathcal{E}(\omega')e^{i\omega' t}\,d\omega'.$$

First-order perturbation theory gives $a_1=1$, $a_3=0$, and $a_2=\mu\mathcal{E}(\omega')/\hbar(\omega'-\omega_{21}+i\Gamma)$. Hence

$$a_2(t)=\frac{1}{2\pi}\int a_2(\omega')e^{i\omega' t}\,d\omega'$$

$$=\frac{1}{2\pi}\int\frac{\mu\mathcal{E}(\omega')}{\hbar(\omega'-\omega_{21}+i\Gamma)}e^{i\omega' t}\,d\omega'.$$

If the range of Fourier components of $\mathcal{E}(\omega')$ is smaller than Δ, the denominator can be taken out of the integral sign and $a_2(t)\approx\mu\mathcal{E}(t)/\hbar\Delta$, which is just the adiabatic-following result $S_x=2\rho_{12}=2\mu\mathcal{E}/\hbar\Delta$.

[8]This was also found by Williams, Rousseau, and Dworetsky, Ref. 1. The details of their experiment can be described by a refined version of these simple ideas including radiative lifetimes.

[9]M. Baranger, Phys. Rev. 111, 481, 494 (1958), and 112, 855 (1958).

[10]A. G. Redfield, IBM J. Res. Develop. 1, 19 (1957); F. Bloch, Phys. Rev. 105, 1206 (1957).

[11]An experiment is being carried out by J. Liran,

G. Erex, and L. Levine (to be published).
[12]Near resonance the linewidth is determined by pressure broadening, while far from resonance only the radiative width counts.
[13]S. Mukamel, A. Ben Reuven, and J. Jortner, to be published.

Singularities in the Critical Surface and Universality for Ising-Like Spin Systems

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It is shown that singularities appear in the shape of the critical surface of Ising-like spin systems for special interactions such as occur in the symmetric eight-vertex model. The nature of the singularity and the connection with breakdown of universality are given.

Universality of critical behavior appears quite naturally in the renormalization theory.[1] However, the exactly solvable symmetric eight-vertex model yields critical exponents which vary continuously with the interaction parameters.[2] Recently Nauenberg and Nienhuis[3] determined, by a renormalization calculation, the *location* of the critical surface for a quadratic lattice in surprisingly good agreement with the known critical lines of the eight-vertex model. Their critical *exponents*, however, are universally equal to the Ising exponents, also along the eight-vertex critical lines, where the exact solution yields interaction-dependent exponents. In this note it is shown that this discrepancy is due to the fact that usual renormalization procedures[3,4] fail to ensure the invariance of the antiferromagnetic ground state. An improved renormalization scheme yields new fixed points and eigenvalues, implying a cusp in the critical surface at the intersection of the ferromagnetic and antiferromagnetic surfaces (in which the eight-vertex critical lines are located). Also a marginal eigenvalue appears, indicating the existence of a line of fixed points, along which the exponents may depend on the interaction. The set of critical points with non-universal exponents remains of lower dimensionality than the class of Ising-like critical points.

Consider a quadratic lattice with sites i and spins $s_i = \pm 1$. The general spin Hamiltonian $\mathcal{H}(s)$ is written as

$$\mathcal{H}(s) = \sum_\alpha K_\alpha \sum_i s_{\alpha,i}, \tag{1}$$

where α stands for the type of the interaction and $s_{\alpha,i}$ for the product of spins of the sites involved in the interaction; e.g.,

$$\mathcal{H}_1 = K_1 \sum_i \sum_{\text{nn}} s_i s_{i+\delta_{\text{nn}}},$$
$$\mathcal{H}_2 = K_2 \sum_i \sum_{\text{nnn}} s_i s_{i+\delta_{\text{nnn}}}, \tag{2}$$
$$\mathcal{H}_3 = K_3 \sum_i s_i s_{i+\delta_1} s_{i+\delta_2} s_{i+\delta_3}$$

(the factor $-1/k_B T$ is included in the interaction constants K_α). $\mathcal{H}_1$ is the (nearest neighbor) Ising Hamiltonian, $\mathcal{H}_2$ (involving only next-nearest neighbor interactions) is also an Ising Hamiltonian for the uncoupled (black and white) sublattices (Fig. 1) and $\mathcal{H}_2 + \mathcal{H}_3$ is the symmetric eight-vertex model Hamiltonian. In Fig. 1 the interaction types are shown. By flipping all the spins of a sublattice one derives the following symmetry

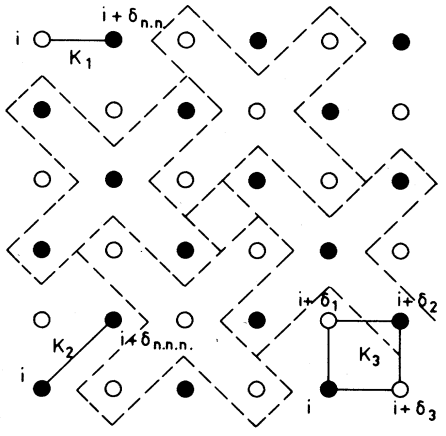

FIG. 1. Quadratic lattice with black and white sublattices. K_1 nearest nieghbor, K_2 next-nearest neighbor, and K_3 a four-spin coupling. Cells involve either black or white sites.