Effects of Nearly Degenerate States on Photon-Echo Behavior*

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A density-matrix analysis is given of some properties of photon echoes arising from nearly degenerate ground and/or excited states. Modulations of the echo intensity as a function of pulse separation time are predicted as well as more complicated effects near level crossings. In particular, the analysis is applied to the 2.06-kG level crossing in the ground state of ruby.

Photon echoes have been interpreted in terms of simple two-level optical systems[1] and this approach is valid for the circularly polarized R_1 transitions in ruby under most experimental conditions. The observation of photon echoes arising from degenerate vibrational transitions of SF_6 has stimulated discussion of the characteristics of photon echoes which arise from completely degenerate states.[2,3] We wish to analyze some possible effects which may occur when photon echoes arise from *nearly* degenerate states such as occur near level crossings. The analysis which follows predicts effects resulting from the interference of these nearly degenerate states which in some circumstances produce a modulation of the echo intensity as the pulse separation time is varied, and which in other circumstances cause a decrease in echo signal at the level-crossing field. We shall apply the results of our analysis to the 2.06-kG ground-state level crossing in ruby, recently studied with photon-echo techniques.[4,5] Modulation of photon-echo intensity vs pulse separation recently has been suggested but without detailed theoretical development.[6] Modulation within the echo pulse has also been discussed,[6,7] but for experimental conditions quite different from those assumed in this paper.

The radiation from an optical system excited by short intense pulses of coherent radiation can readily be described by calculating semiclassically the expectation value of the electric dipole moment using a density-matrix formulism.[1] The electric dipole moment of a single atom, evaluated in a reference frame "rotating" at the frequency ω of the incident radiation field, is given simply as

$$\langle\vec{P}\rangle = \mathrm{Tr}[\vec{P}\rho(t)] = \mathrm{Tr}[\vec{P}e^{-i\mathcal{H}t/\hbar}\, e^{+i\vec{F}\cdot\vec{P}}\,\rho(0)\, e^{-i\vec{F}\cdot\vec{P}}\, e^{+i\mathcal{H}t/\hbar}], \quad (1)$$

where $\mathcal{H}$ is the effective Hamiltonian in the "rotating frame" and $\vec{F} = \int_0^{\Delta\tau} dt\, \vec{\mathscr{E}}(t)/\hbar$, where $\Delta\tau$ is the pulse width and the incident electric field of the pulse is given by $\vec{E}(t) = \vec{\mathscr{E}}(t)\cos(\omega t)$. The initial density matrix $\rho(0)$ characterizes a quasi-two-level system having sets of ground states $\{|a\rangle\}$ and excited states $\{|b\rangle\}$ which consist of two (or more) nondegenerate levels with splittings $\omega_a - \omega_{a'}$ and $\omega_b - \omega_{b'}$. In Eq. (1) we have made the usual resonance assumption that $\vec{\mathscr{E}}\cdot\vec{P} \gg \hbar|(\omega_b - \omega_a) - \omega|$ for all choices of $|a\rangle$ and $|b\rangle$. In addition, we shall assume that both $(\omega_a - \omega_{a'})$, $(\omega_b - \omega_{b'}) \ll 1/\Delta\tau$, so that all allowed transitions from states $|a\rangle$ to states $|b\rangle$ are simultaneously resonant. We note that these assumptions are not completely independent. If the system is initially in the ground state with all the $|a\rangle$ levels equally populated, then $\rho(0) = \sum_a |a\rangle\langle a|$. Furthermore, following the analysis of Gordon *et al.*,[2] when the pulse operator is written as $e^{-i\vec{F}\cdot\vec{P}} = \cos(\vec{F}\cdot\vec{P}) - i\sin(\vec{F}\cdot\vec{P})$ one may observe that the $\sin(\vec{F}\cdot\vec{P})$ operator is nonzero only for matrix elements between $|a\rangle$ and $|b\rangle$, while the $\cos(\vec{F}\cdot\vec{P})$ leaves the system in the ground or excited state. Thus one may easily identify the nonzero terms of the trace and obtain

$$\langle\vec{P}\rangle = \tfrac{1}{2}\sum_{ab} e^{-i\Delta\omega_{ba}t}\langle a|\vec{P}|b\rangle\langle b|\sin(2\vec{F}\cdot\vec{P})|a\rangle + \text{c.c.}\ , \quad (2)$$

where $\Delta\omega_{ba} = \omega_b - \omega_a - \omega$ and we have made use of the identity

$$\sum_{a'}\langle b|\sin(\vec{F}\cdot\vec{P})|a'\rangle\langle a'|\cos(\vec{F}\cdot\vec{P})|a\rangle = \tfrac{1}{2}\langle b|\sin(2\vec{F}\cdot\vec{P})|a\rangle\ . \quad (3)$$

The complex conjugate terms (c.c.) arise from the parts of the trace evaluated over the excited states $|b\rangle$.

For an assembly of N atoms, the intensity of the fluorescence, after the superradiant Bloch decay, is proportional to the sum of the squares of the electric dipole moments and is given by

$$I \sim \tfrac{1}{4}N\sum_{aa'bb'}\exp\{i[(\omega_b - \omega_{b'}) - (\omega_a - \omega_{a'})]t\} \times\langle a|\vec{P}|b\rangle\langle b|\sin(2\vec{F}\cdot\vec{P})|a\rangle\cdot\langle b'|\vec{P}|a'\rangle \times\langle a'|\sin(2\vec{F}\cdot\vec{P})|b'\rangle + \text{c.c.} \quad (4)$$

The result is obtained by first transforming the dipole moments of Eq. (2) back into the laboratory frame,[2] then squaring. Also we have assumed that the detector averages the intensity over times long compared to the optical frequency but short compared to the splitting frequencies, thus exponentials with a time dependence of approximately

$2\omega t$ are neglected. The terms we have included in Eq. (4) remain even in the presence of optical inhomogeneous broadening and give rise to oscillations of the fluorescent intensity at the ground- and/ or excited-state splitting frequencies. Such modulated fluorescence has been discussed in the literature[8] for weak excitation pulses and has been observed in experiments using beam-foil excitation,[9] pulsed electron-beam excitation,[10] and weak pulsed optical excitation.[11]

The analysis for two incident pulses is quite similar, but in this case we shall be interested in only those terms which contribute to the photon echo at $t=2\tau$, where τ is the pulse separation. Assuming the system has a large inhomogeneous linewidth, we retain terms with the time dependence of approximately $e^{-i\Delta\omega_{ba}(t-2\tau)}$, for only these terms contribute to the creation of the coherent superradiant echo state. With this restriction in mind we obtain for the relevant dipole moments in the "rotating frame"

$$\langle\vec{P}\rangle = \tfrac{1}{2}\sum_{aa'bb'} \exp\{-i[\Delta\omega_{ba}(t-\tau)-\Delta\omega_{b'a'}\tau]\}\langle a|\vec{P}|b\rangle \times\langle b|\sin(\vec{F}_2\cdot\vec{P})|a'\rangle\langle a'|\sin(2\vec{F}_1\cdot\vec{P})|b'\rangle \times\langle b'|\sin(\vec{F}_2\cdot\vec{P})|a\rangle + \text{c.c.} \tag{5}$$

The echo intensity, which is proportional to the square of this expression evaluated at $t\cong 2\tau$, again exhibits oscillatory terms at the splitting frequencies of the nearly degenerate states, since at $t=2\tau$ the above exponential reduces to $\exp\{-i[(\omega_{a'}-\omega_a)-(\omega_{b'}-\omega_b)]\tau\}$. The oscillatory terms can produce modulations of the echo intensity as a function of pulse separation time. For the completely degenerate case, $\omega_a=\omega_{a'}$ and $\omega_b=\omega_{b'}$, the oscillations vanish and the result is identical to that derived in Ref. 2.

The oscillatory terms appear whenever more than one of the nondegenerate ground (excited) states are coupled to the same excited (ground) state by the incident pulse. This is assured in the case of level "anticrossings"[12] where the states are mixed. If the splitting frequencies are the same for all atoms, the photon-echo intensity will exhibit well-defined modulations as a function of pulse separation; but if there is a large variation of splittings from atom to atom, then one might observe only a decrease of the echo signal resulting from interference of the different frequencies. The latter result will be obtained explicitly in the case of ruby, as one sweeps through the 2.06-kG level crossing.

In discussing Eq. (5) we have made the usual assumption that the echo system has a large inhomogeneous linewidth, i.e., $1/T_2^* > 1/\Delta\tau$, which implies that the echo-pulse duration is about the same as the duration of the incident pulses. If, on the other hand, the reciprocal pulse width and the splitting frequencies are greater than the inhomogeneous linewidth $1/T_2^*$, then the duration of the echo is determined by T_2^* and the modulations would occur during the echo pulse. In this case the modulations may appear even without the coupling referred to in the previous paragraph, since two independent photon-echo systems, radiating at slightly different frequencies, may interfere to produce beats in the total detected intensity. Modulation within the echo pulse is discussed in Refs. 6 and 7; however, our analysis applies to the regime $\omega_a-\omega_{a'} \ll 1/\Delta\tau$ and thus assures coherent excitation of both levels, a condition which is not clearly established by the authors of Refs. 6 and 7 in their assumption that $\omega_a-\omega_{a'} \gg 1/\Delta\tau$. For modulations to be observed, the incident pulses must have a frequency spectrum broad enough to simultaneously excite both levels in a single atom, and if $\omega_a-\omega_{a'} \gg 1/\Delta\tau$ the details of the frequency spectrum of the incident pulses must be included in the analysis.

To illustrate some of the effects embedded in these general expressions, we specialize to the 2.06-kG ground-state level crossing, ${}^4A_2(+\frac{3}{2}, -\frac{1}{2})$, in ruby. Photon echoes originating from each of these ground states have been observed with circular polarization.[4,5] In off-axis magnetic fields ($\vec{H}\nparallel c$ axis) the $M_s=+\frac{3}{2}$ and $M_s=-\frac{1}{2}$ states are strongly mixed and an "anticrossing" occurs. In this region the upper- and lower-energy states, respectively, may be written to a good approximation as

$$|a_1\rangle = \alpha|\tfrac{3}{2}\rangle + \beta|-\tfrac{1}{2}\rangle \quad\text{and}\quad |a_2\rangle = \beta|\tfrac{3}{2}\rangle - \alpha|-\tfrac{1}{2}\rangle\,, \tag{6}$$

where α and β are real numbers less than 1 and vary rapidly with $\vec{H}$ near the crossing as can be determined by diagonalizing the spin Hamiltonian.[13] If we consider the ${}^4A_2(\frac{3}{2})\to\bar{E}({}^2E)(+\frac{1}{2})$ transition which arises only from the $|\frac{3}{2}\rangle$ component of each of the above "anticrossing" states (by thermally tuning the laser[5] we can assure that only the $\frac{3}{2}\to\frac{1}{2}$ transition is on resonance), then

$$\begin{aligned}\langle a_1|\vec{P}|b\rangle &= \alpha\langle\tfrac{3}{2}|\vec{P}|\tfrac{1}{2}\rangle\,,\\ \langle a_2|\vec{P}|b\rangle &= \beta\langle\tfrac{3}{2}|\vec{P}|\tfrac{1}{2}\rangle\,,\end{aligned} \tag{7}$$

and, for example, the second pulse matrix elements are

$$\begin{aligned}\langle a_1|\sin(\vec{F}_2\cdot\vec{P})|b\rangle &= \alpha\langle\tfrac{3}{2}|\sin(\vec{F}_2\cdot\vec{P})|\tfrac{1}{2}\rangle\,,\\ \langle a_2|\sin(\vec{F}_2\cdot\vec{P})|b\rangle &= \beta\langle\tfrac{3}{2}|\sin(\vec{F}_2\cdot\vec{P})|\tfrac{1}{2}\rangle\,.\end{aligned} \tag{8}$$

The echo intensity is obtained by substituting Eqs. (7) and (8), and similar expressions for the first pulse, into Eq. (5), summing the polarization vectors of all N atoms and squaring. The resultant intensity is

$$I = I_0\{[\alpha^4+\beta^4+2\alpha^2\beta^2\cos(\delta\omega\tau)]_{\text{av}}\}^2\,, \tag{9}$$

where $\delta\omega=\omega_{a_1}-\omega_{a_2}$ and

$$I_0 \sim N^2 |\langle \tfrac{3}{2}|\vec{P}|\tfrac{1}{2}\rangle|^2 \times |\langle \tfrac{3}{2}|\sin(2\vec{F}_1\cdot\vec{P})|\tfrac{1}{2}\rangle|^2 \times |\langle \tfrac{3}{2}|\sin(\vec{F}_2\cdot\vec{P})|\tfrac{1}{2}\rangle|^4 . \quad (10)$$

Here α, β, and $\delta\omega$ are sensitive functions of the local magnetic field, thus the average should be taken over the magnetic field inhomogeneities in the sample. Asymptotically for magnetic fields considerably less than 2.06 kG, $\beta \rightarrow 1$ and $\alpha \rightarrow 0$, while above the crossing field $\beta \rightarrow 0$ and $\alpha \rightarrow 1$ so that in each $I \rightarrow I_0$. In ruby the spread of ~ 10 G in local magnetic fields due to neighboring nuclear moments produces a range of $\delta\omega$ sufficiently broad that the $\cos(\delta\omega\tau)$ term averages to zero for $\tau \gtrsim 20$ nsec. In this case one expects to observe in the region of the anticrossing a decrease in the echo intensity with a minimum of $\frac{1}{4}I_0$ where the states are equally mixed ($\alpha = \beta = \frac{1}{2}\sqrt{2}$). Analysis of the $^4A_2(-\frac{1}{2}) \rightarrow \bar{E}(^2E)(-\frac{1}{2})$ transition at the anticrossing leads to the same bracketed expression [Eq. (9)]; however, I_0 is reduced due to the slightly smaller value of the dipole matrix element for this transition.

Observations with pulse separations $\tau \gtrsim 70$ nsec have shown that this effect is obscured by a spin-dependent decay mechanism which results from the magnetic interaction of neighboring Al nuclei with the mixed Cr spin states at the crossing[4,5] and produces a decay which is greatly modified near the level crossing. However, the analysis predicts that at short pulse separation times ($\tau \sim 30$ nsec) where these decay mechanisms are relatively unimportant, there should be a dip with a minimum of about $\frac{1}{4}I_0$ for both the $(-\frac{1}{2} \rightarrow -\frac{1}{2})$ and $(\frac{3}{2} \rightarrow +\frac{1}{2})$ transitions.

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Surface-State Lifetimes and Current Flow in Liquid Helium

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The lifetime of electrons trapped at the free surface of liquid ^{4}He has been determined from the temperature dependence of the current flow in the liquid. These lifetimes are in substantial agreement with the values determined directly for the liquid-gas interface in ^{4}He. New results are presented for the ^{4}He-^{3}He interface which give lifetimes as long as 10^5 sec.

Several experiments have shown that a potential barrier exists for the passage of electrons from ^{4}He into gas[1-3] or liquid ^{3}He.[4] This surface barrier is believed to be caused by the repulsive image potential seen by the electron approaching the interface from the side having higher dielectric constant. These experiments were designed to measure current flow from an electron source in liquid ^{4}He to a collector located in the gas or ^{3}He region. The experimental evidence for the barrier is that the current decreases exponentially with decreasing temperature. The first direct evidence that electrons are trapped by this barrier was presented by Williams, Crandall, and Willis,[5] who measured