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Double-quantum photon echo in an adiabatic-vector-model approximation*

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The possible generation of photon echoes is discussed for a system where the incident radiation resonantly drives two-photon transitions. Use of the adiabatic-vector-model approximation of Grischkowsky, Loy, and Liao allows echo behavior to be calculated in a multilevel system by methods similar to those previously employed for two-level atoms. We find that observation of the double-quantum photon echo requires the presence of a nonresonant probe field at the time of formation of the echo pulse. The echo then radiates at the sum and difference of the probe and two-photon frequencies. As an example, we consider a possible experimental arrangement for the detection of double-quantum photon echoes in Rb vapor.

I. INTRODUCTION

In a recent paper, Grischkowsky, Loy, and Liao[1] introduce a useful adiabatic vector model to describe resonant optical two-photon parametric mixing and pulse propagation. This model, originally developed by Takatsuji,[2] extends the Feynman-Vernon-Hellwarth[3] treatment of resonance in a two-level atom to more general multilevel systems. In this paper we apply it explicitly to a new problem: the possible generation of double-quantum photon echoes.

A double-quantum photon echo is that process, in a system where the incident radiation excites two-photon transitions, which corresponds to the well-known photon echo[4] in the simple two-level system. To form a double-quantum echo, a coherent superposition of atomic ground and excited states is prepared by a sequence of intense light pulses. The frequency components of the preparation pulses are chosen so as to drive a two-photon resonance. After completion of the preparation-pulse sequence, the system can be made to emit an echo pulse whose characteristics are determined by the time evolution of the atomic density matrix, averaged over the many atoms of a macroscopic sample. In the double-quantum echo, unlike the usual photon echo, the ground and excited states are, in general, not connected by a dipole matrix element. Observation of the echo therefore requires the simultaneous presence of a probe light beam. The probe field mixes the superposition state with a set of intermediate states, allowing dipole transitions to occur. Its frequency may be different from that of any of the preparation pulses, and need not be in resonance with any atomic transition.

The echo appears at the sum and difference of the probe and two-photon resonance frequencies. In the case discussed here, the difference-frequency term is resonantly enhanced, and therefore dominates the observed emission. Zernik has studied a similar process: the incoherent quenching of excited hydrogen $2s$ metastables due to the mixing of states by nonresonant optical-frequency fields.[5]

The vector-model approximation we use in this calculation has previously been applied to studies of two-photon parametric frequency mixing,[1] self-induced transparency,[2] and adiabatic rapid passage.[6] Brewer and Hahn[7] have applied a somewhat different vector model, which yields exact solutions for the development of the density matrix of a three-level atom in the presence of resonant optical fields, to the calculation of transient emission following intense two-photon pulsed excitation. Hartmann[8] has analyzed the behavior of Raman echoes in a three-level system, a problem closely related to the one we discuss here. A "doubly-resonant" echo, in which an intermediate state is populated by the exciting field, has been described by Aihara and Inaba,[9] while Makhviladze and Shelepin[10] treat a three-level echo by means of a general group-theoretical formalism.

II. DOUBLE-QUANTUM ECHO CALCULATION

We begin our calculation of a double-quantum photon echo by considering an atom illuminated by two linearly polarized beams of light at frequencies ω_1 and ω_2. (The notation used here will closely follow that of Grischkowsky, Loy, and Liao.) The sum frequency $\omega = \omega_1 + \omega_2$ is assumed to be nearly equal to the energy separation $\Omega_{12} = \Omega_1 - \Omega_2$ of a pair of nondegenerate atomic states $|1\rangle$ and $|2\rangle$. Neither ω_1 nor ω_2 is resonant with any other atomic transition frequency. We also assume that the two beams propagate in the same direction, which we take to be the z axis. A schematic energy-level diagram appears in Fig. 1.

In the presence of the light beams, the Hamiltonian becomes

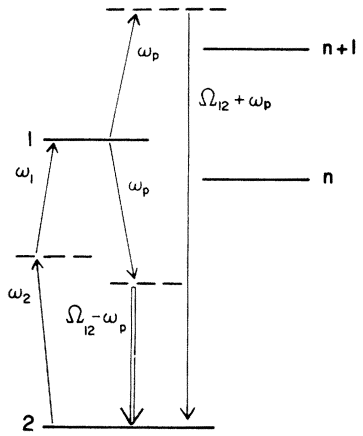

FIG. 1. Schematic energy-level diagram. Preparation pulses are applied simultaneously at ω_1 and ω_2, driving two-photon transitions between levels $|1\rangle$ and $|2\rangle$. To observe the double-quantum photon echo, a probe beam is applied at ω_p. The echo radiates at $\Omega_{12}-\omega_p$ and $\Omega_{12}+\omega_p$.

$$\mathcal{H}=\mathcal{H}_0-\vec{p}\cdot\vec{E}\,. \tag{1}$$

$\mathcal{H}_0$ is the unperturbed atomic Hamiltonian, $\vec{p}$ is the electric dipole moment operator, and $\vec{E}$ is the electric field, given by

$$\vec{E}=\hat{x}[\mathcal{E}_1(t)\cos(\omega_1 t-k_1 z)+\mathcal{E}_2(t)\cos(\omega_2 t-k_2 z)]\,. \tag{2}$$

We assume that the matrix elements $p_{1n}=\langle 1|\vec{p}|n\rangle$ and $p_{2n}=\langle 2|\vec{p}|n\rangle$ are nonzero for some intermediate state $|n\rangle$, but that $\langle 1|\vec{p}|2\rangle=0$. (For example, $|1\rangle$ and $|2\rangle$ could correspond to the ground and a higher-lying s state in an alkali metal; the states $|n\rangle$ would then correspond to the p states.)

The absence of a dipole matrix element between ground and excited states invalidates the two-level assumption commonly made in optical resonance problems; therefore, the simple Feynman-Vernon-Hellwarth vector model is no longer a correct representation of the problem. Takatsuji[2] shows, however, that the Bloch equation, and thus a vector model description, may be obtained as an approximation to the exact equation of motion for a many-level system by making an appropriate canonical transformation of the atomic basis states. Thus a new set of mixed states will replace the actual atomic levels. Use of this vector model approximation assumes that any optical pulses applied to the system are turned on and off adiabatically, i.e., for a given risetime, the detuning from resonance with any *intermediate state* must be sufficiently large. This adiabatic condition takes the form

$$\left|\frac{d\mathcal{E}}{dt}\right|\ll|\Delta\omega\mathcal{E}|\,, \tag{3}$$

where

$$\frac{1}{\Delta\omega}=\frac{1}{2}\left(\frac{1}{\omega_2-\Omega_{n2}}+\frac{1}{\Omega_{1n}-\omega_1}\right).$$

The adiabatic requirement can readily be satisfied experimentally by use of tunable dye laser excitation.

To make the adiabatic-vector-model approximation, we change coordinates to a "doubly-rotating" frame, using transformations developed by Grischkowsky, Loy, and Liao. For clarity and continuity in presentation of the echo calculations, we briefly restate some of their results as Eqs. (4)–(11). The density matrix $\rho''(t)$ and Hamiltonian $\mathcal{H}''$ in the new coordinate system are given by

$$\rho''(t)=R(t)e^{-iS(t)}\rho(t)e^{iS(t)}R^{-1}(t)\,, \tag{4}$$

$$\mathcal{H}''=R(t)\mathcal{H}'R^{-1}(t)+i\hbar\frac{\partial R}{\partial t}R^{-1}(t)\,,$$

where (5)

$$\mathcal{H}'=e^{-iS(t)}\mathcal{H}e^{iS(t)}+\hbar\frac{\partial S}{\partial t}+\frac{i\hbar}{2}\left[\frac{\partial S}{\partial t},S\right]$$

and $\rho(t)$ and $\mathcal{H}$ are the density matrix and Hamiltonian in the laboratory frame. $R(t)$ is the rotating-frame operator

$$R(t)=\begin{bmatrix} e^{+i(\omega t-kz)/2} & 0 & 0 & \cdots & 0\\ 0 & e^{-i(\omega t-kz)/2} & 0 & \cdots & 0\\ 0 & 0 & 1 & \cdots & 0\\ \cdots & \cdots & \cdots & & \\ 0 & 0 & 0 & & 1 \end{bmatrix}, \tag{6}$$

where

$$\omega=\omega_1+\omega_2 \quad\text{and}\quad k=k_1+k_2\,,$$

while $S(t)$ is an operator which represents the mixing of the ground and excited states $|1\rangle$ and $|2\rangle$ with the intermediate states $|n\rangle$ caused by the presence of the field $\vec{E}$. The new mixed states, designated by $|1'\rangle$ and $|2'\rangle$, are shifted in energy from $|1\rangle$ and $|2\rangle$ by the optical Stark shifts $\Delta\Omega_1$ and $\Delta\Omega_2$, where

$$\Delta\Omega_i=-\frac{1}{2\hbar^2}\sum_n p_{in}p_{ni}\Omega_{ni}\left(\frac{\mathcal{E}_1^2}{\Omega_{ni}^2-\omega_1^2}+\frac{\mathcal{E}_2^2}{\Omega_{ni}^2-\omega_2^2}\right). \tag{7}$$

Our coordinate transformation corresponds to taking $|1'\rangle$ and $|2'\rangle$ as a basis set for the density matrix and for representation of the Hamiltonian

in place of $|1\rangle$ and $|2\rangle$.

Unlike the unperturbed atomic states, the mixed states are connected by a dipole matrix element, allowing the density matrix equation of motion in the doubly-rotating frame to be written in the Bloch equation form

$$\frac{\partial \vec{r}}{\partial t} = \vec{\gamma} \times \vec{r}, \tag{8}$$

where

$$\begin{aligned} r_1 &= \rho''_{12} + \rho''_{21}, \\ r_2 &= i(\rho''_{12} - \rho''_{21}), \\ r_3 &= \rho''_{11} - \rho''_{22} \end{aligned} \tag{9}$$

and

$$\begin{aligned} \gamma_1 &= \kappa \mathcal{E}_1 \mathcal{E}_2, \\ \gamma_2 &= 0, \\ \gamma_3 &= \Omega_{12} - (\omega_1 + \omega_2) + \Delta\Omega_1 - \Delta\Omega_2. \end{aligned} \tag{10}$$

The two-photon gyroelectric ratio κ is given by

$$\kappa = \frac{1}{2\hbar^2} \left| \sum_n p_{1n} p_{n2} \left(\frac{1}{\Omega_{n2} - \omega_1} + \frac{1}{\Omega_{n2} - \omega_2} \right) \right|. \tag{11}$$

The operator $S(t)$ is proportional to the field amplitudes $\mathcal{E}_1$ and $\mathcal{E}_2$. The doubly-rotating density matrix $\rho''(t)$ therefore transforms smoothly into the conventional rotating frame density matrix $\rho'(t)$

$$\rho'(t) = R\rho(t)R^{-1} \tag{12}$$

as the fields are turned off adiabatically.

Explicit expressions for the matrix elements of $S(t)$ and a more detailed discussion of the properties of the adiabatic vector model approximation appear in the Grischkowsky-Loy-Liao paper.[1] The canonical transformation procedure employed is derived by Takatsuji.[2]

In the doubly-rotating frame, the effect of applying a pulse of duration Δt at frequencies ω_1 and ω_2 is to rotate the r vector around the γ vector through an angle θ equal to the two-photon pulse area

$$\theta = \kappa \int_0^{\Delta t} \mathcal{E}_1(t') \mathcal{E}_2(t')\, dt'. \tag{13}$$

If the pulse is nearly square (but still adiabatic with respect to the intermediate states) so that $\mathcal{E}_1$ and $\mathcal{E}_2$ quickly reach the constant values $\mathcal{E}_1^0$ and $\mathcal{E}_2^0$, we can approximate θ by

$$\theta \simeq \kappa \mathcal{E}_1^0 \mathcal{E}_2^0 \Delta t. \tag{14}$$

This approximation will be valid so long as the pulse risetime is small compared to the reciprocal of the two-photon Rabi flopping frequency

$$\Omega_R = (1/2\pi)\kappa \mathcal{E}_1^0 \mathcal{E}_2^0. \tag{15}$$

The risetime, however, cannot be too short, as the adiabatic condition of Eq. (3) must still be satisfied independently. A suitable choice for the pulse risetime exists only if the following inequality holds:

$$(\hbar\, \Delta\omega)^2 \gg \left| \sum_n p_{1n} p_{2n} \mathcal{E}_1^0 \mathcal{E}_2^0 \right|, \tag{16}$$

where $\Delta\omega$ is the detuning from the intermediate states as defined in Eq. (3).

To generate a double-quantum photon echo, we illuminate the atomic system with two pulses of areas θ_1 and θ_2, separated in time by an interval of length τ. The evolution of the doubly-rotating density matrix $\rho''(t)$ as the pulses are applied can be calculated by the same methods used for the single-quantum echo.[4,11] At time $t = t_0$, immediately following termination of the second pulse, the Bloch vector has components:

$$\begin{aligned} r_1 &= \sin\theta_1 \sin\gamma_3\tau + \zeta[(1 - \cos\theta_1 + \sin\theta_2 \sin\theta_1) \\ &\qquad \times \cos\gamma_3\tau + \cos\theta_1(1 - \cos\theta_2)], \\ r_2 &= -\cos\theta_2 \sin\theta_1 \cos\gamma_3\tau - \sin\theta_2 \cos\theta_1 \\ &\quad + \zeta[\sin\theta_2 \sin\theta_1 + \cos\theta_2(1 - \cos\theta_1)] \cos\gamma_3\tau, \\ r_3 &= \sin\theta_2 \sin\theta_1 \cos\gamma_3\tau - \cos\theta_2 \cos\theta_1 \\ &\quad - \zeta[(1 - \cos\theta_1)(\sin\theta_1 + \sin\theta_2)] \sin\gamma_3\tau, \end{aligned} \tag{17}$$

where $\zeta = \gamma_3 / \kappa \mathcal{E}_1^0 \mathcal{E}_2^0$. We can greatly simplify these expressions, while retaining the essential features of the echo, by assuming that we have applied the Carr-Purcell preparation pulse sequence, for which $\theta_1 = \frac{1}{2}\pi$ and $\theta_2 = \pi$.

The laboratory frame density matrix at $t = t_0$ can easily be found, since $S(t_0) = 0$ and the doubly-rotating frame has transformed smoothly into the conventional singly-rotating frame. Inverting the rotating-frame transformation, we obtain the following nonzero elements of $\rho(t_0)$:

$$\begin{aligned} \rho_{11}(t_0) &= \tfrac{1}{2} - (\gamma_3 / \kappa \mathcal{E}_1^0 \mathcal{E}_2^0) \sin\gamma_3\tau, \\ \rho_{22}(t_0) &= \tfrac{1}{2} + (\gamma_3 / \kappa \mathcal{E}_1^0 \mathcal{E}_2^0) \sin\gamma_3\tau, \\ \rho_{12}(t_0) &= -\tfrac{1}{2} i e^{+i\gamma_3 \xi} e^{-i(\omega t_0 - kz)}, \\ \rho_{21}(t_0) &= \tfrac{1}{2} i e^{-i\gamma_3 \xi} e^{+i(\omega t_0 - kz)}, \end{aligned} \tag{18}$$

where $\xi = \tau + 1/\kappa \mathcal{E}_1^0 \mathcal{E}_2^0$.

The intensity of radiation subsequently emitted by the system will be proportional to the square of the expectation value of the electric dipole moment $\langle p(t) \rangle$. For a single atom,

$$\langle p(t) \rangle = \mathrm{Tr} p\rho(t) = \sum_n [p_{1n} \mathrm{Re}\rho_{1n}(t) + p_{2n} \mathrm{Re}\rho_{2n}(t)]. \tag{19}$$

In the absence of any further perturbation, the evolution of the density matrix for $t > t_0$ will be

governed by the unperturbed Hamiltonian $\mathcal{H}_0$. As $\mathcal{H}_0$ is diagonal in the laboratory-frame energy representation, $\rho_{1n}(t)$ and $\rho_{2n}(t)$ will remain zero, implying $\langle p(t)\rangle = 0$. Since none of the intermediate states $|n\rangle$ have been populated, the atom has no dipole moment; except for spontaneous emission processes, it emits no radiation. Nonetheless, the states $|1\rangle$ and $|2\rangle$ retain a well-defined phase relationship, as evidenced by the nonzero off-diagonal density matrix elements $\rho_{12}(t)$ and $\rho_{21}(t)$. This phase coherence can be exhibited by probing the system with nonresonant beam of light.

We use time-dependent perturbation theory to evaluate $\rho(t)$ in the presence of the probe field

$$\vec{E}_p = \hat{x}\mathcal{E}_p \cos(\omega_p t - k_p z)\,. \tag{20}$$

The probe-field frequency ω_p is assumed to be far from resonance with any atomic transition frequency, but is otherwise arbitrary. Transforming to an interaction picture, the density matrix equation of motion becomes

$$\frac{d\rho_F}{dt} = \frac{i}{\hbar}[\rho_F, V_F]\,, \tag{21}$$

where

$$\begin{aligned} \rho_F &= e^{i\mathcal{H}_0 t/\hbar}\rho(t)e^{-i\mathcal{H}_0 t/\hbar}\,, \\ V_F &= e^{i\mathcal{H}_0 t/\hbar}Ve^{-i\mathcal{H}_0 t/\hbar}\,. \end{aligned} \tag{22}$$

To first order in V_F, this equation has the solution

$$\rho_F(t) \simeq \rho_F(t_0) + \frac{i}{\hbar}\int_{t_0}^{t}[\rho_F(t_0), V_F(t')]\,dt'\,. \tag{23}$$

Evaluating the commutator, returning to the Schrödinger picture, and calculating $\mathrm{Tr}[p\rho(t)]$, we obtain for the polarization the result:

$$\begin{aligned} \langle p(t)\rangle = -\sum \frac{p_{1n}p_{n2}\mathcal{E}_p}{4\hbar}\Bigg[&\left(\frac{1}{\Omega_{1n}-\omega_p}+\frac{1}{\Omega_{n2}-\omega_p}\right)\cos[(\Omega_{12}-\omega_p)t - k_a z - \gamma_3\xi] \\ &+\left(\frac{1}{\Omega_{1n}+\omega_p}+\frac{1}{\Omega_{n2}+\omega_p}\right)\cos[(\Omega_{12}+\omega_p)t - k_b z - \gamma_3\xi]\Bigg]\,, \end{aligned} \tag{24}$$

where $k_a = k - k_p$, $k_b = k + k_p$. Terms oscillating at frequency ω_p have been neglected. The probe field thus induces a dipole moment, allowing the system to radiate. Since the induced moment oscillates at ω_p while the probability amplitudes oscillate at Ω_{12}, sum and difference beat terms appear in the polarization. The polarization is proportional to $\mathcal{E}_p$, and exhibits resonant behavior as ω_p approaches Ω_{1n} or Ω_{n2}. The difference-frequency term will therefore be resonantly enhanced, and thus will dominate the observed emission, when the probe frequency lies in the optical region. Because we have explicitly treated the Carr-Purcell preparation pulse sequence, Eq. (24) shows no dependence of the polarization on the amplitudes of the exciting fields $\mathcal{E}_1^0$ and $\mathcal{E}_2^0$. For a more general choice of preparation pulse areas, the expression obtained above would have a factor $\sin\theta_1 \sin^2\frac{1}{2}\theta_2$ as has been found for photon echoes in a two-level system.[4]

An alternative method for producing an observable echo would be to apply a dc electric field in place of the ac probe field of Eq. (20). This procedure has been discussed by Zernik[5] as a means of quenching an incoherently populated hydrogen $2s$ state, which otherwise can decay only through spontaneous two-photon emission. Application of a dc perturbation corresponds to taking the limit of $\langle p(t)\rangle$ as $\omega_p \to 0$, with a probe field amplitude $\mathcal{E}_p$ replaced by the dc field strength $\mathcal{E}_0$. In this case, the two terms in Eq. (24) are equal, and the echo appears at the two-photon resonance frequency Ω_{12}. Use of a dc field, however, yields no resonant enhancement of the polarization; the emitted radiation may therefore be dominated by single-photon allowed transitions from the excited state $|1\rangle$ to a lower-lying intermediate level.

To evaluate the polarization for a macroscopic sample, we must average the single-atom polarization given by Eq. (24) over the inhomogeneous distribution of two-photon resonance frequencies $g(\Omega_{12})$:

$$\langle p(t)\rangle_M = N\int_{-\infty}^{\infty}\langle p(t)\rangle g(\Omega_{12})\,d\Omega_{12}\,, \tag{25}$$

where N is the number density of atoms in the sample. We assume that $g(\Omega_{12})$ has the Gaussian form:

$$g(\Omega_{12}) = (T_2^*/\pi)\exp[-(\Omega_{12}-\Omega_0)^2(T_2^*)^2/\pi]\,. \tag{26}$$

This averaging yields the result

$$\langle p(t)\rangle_M = \frac{N\mathcal{E}_p}{4\hbar^2}\exp\left[-\frac{\pi}{4(T_2^*)^2}\left(t-\tau-\frac{1}{\kappa\mathcal{E}_1^0\mathcal{E}_2^0}\right)^2\right]$$
$$\times\sum_n p_{1n}p_{n2}\left[\left(\frac{1}{\Omega_{1n}-\omega_p}+\frac{1}{\Omega_{n2}-\omega_p}\right)\cos[(\Omega_0-\omega_p)t-k_a z+\delta]\right.$$
$$\left.+\left(\frac{1}{\Omega_{1n}+\omega_p}+\frac{1}{\Omega_{n2}+\omega_p}\right)\cos[(\Omega_0+\omega_p)t-k_b z+\delta]\right], \quad (27)$$

where

$$\delta=(\omega_1+\omega_2-\Omega_0-\Delta\Omega_1+\Delta\Omega_2)(\tau+1/\kappa\mathcal{E}_1^0\mathcal{E}_2^0).$$

The exponential factor has a maximum at $t\simeq\tau$. Since we measure t from the end of the second pulse, this maximum corresponds to a sharp echo pulse at about 2τ following the start of the preparation pulse sequence.

III. NUMERICAL EXAMPLE: Rb 5S-7S

The expression for the polarization [Eq. (27)] suggests as a possible experimental arrangement the apparatus sketched in Fig. 2. We consider as an example the 5S-7S two-photon resonance in rubidium. A pulsed dye laser, transversely pumped by a Q-switched ruby laser, is tuned to 7601 Å, halfway between the Rb $5s$ and $7s$ levels, exciting two-photon transitions in the sample. Optical Stark shifts may displace the resonance from that predicted by the zero-field levels. Nevertheless, the resonance can be located experimentally by tuning the dye laser. Beamsplitter BS-2 divides the dye laser beam, sending about 50% of the intensity to an optical delay line, which introduces a delay τ. The delayed pulse is recombined collinearly with the undelayed dye laser beam by beamsplitter BS-3, forming the preparation pulse train. Beamsplitter BS-1 picks off a small fraction of the 6943 Å ruby laser pulse for later use as a probe. The probe pulse is delayed by 2τ in a second delay line, then fed into the sample along the original excitation direction, stimulating the echo at 8397 Å. This wavelength can be monitored by a photomultiplier with S-1 response. Since the double-quantum echo appears at a different wavelength than either the preparation pulse train or the ruby laser probe, a narrow-bandpass filter may be used to discriminate between the echo and probe pulses, as well as to prevent detector saturation. Although for clarity our figure shows two separate delay lines, both excitation and probe pulses may be delayed in the same set of mirrors through an appropriate choice of beam-steering optics.

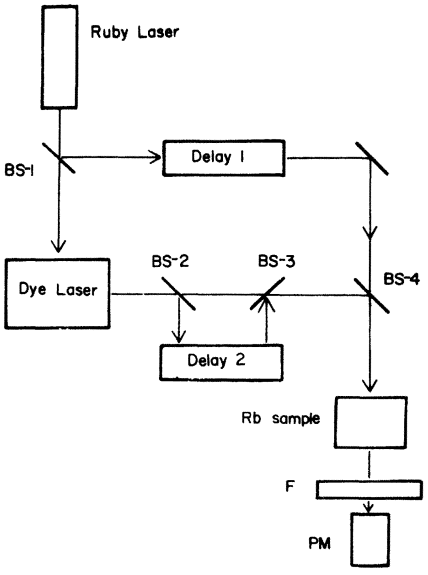

FIG. 2. Schematic experimental arrangement for observation of double-quantum photon echoes in rubidium. BS 1–4 are beamsplitters, F is a narrow-bandpass filter, and PM is an S-1 response photomultiplier.

For the energy levels and excitation wavelengths just discussed, the laser power required to generate a double-quantum photon echo can easily be estimated. Evaluating Eqs. (11) and (14) for the 5S-7S two-photon transition in rubidium, we find that a π pulse at 7601 Å corresponds to an intensity of 7 MW/cm^2 in a 10-nsec pulse. As the detuning from the nearest p state is 339 cm^{-1}, the adiabatic condition of Eq. (3) is clearly satisfied. Our calculation employs the published matrix elements of Heavens,[12] and assumes that only the $5p$, $6p$, and $7p$ intermediate states contribute significantly to κ.

The high-power levels necessary for the double-quantum echo effect imply substantial optical Stark shifts during the pulses. At 7601 Å the *net* shift calculated from Eq. (7) is found to be 750 MHz, largely in the ground state. If we assume transform-limited pulses, this shift exceeds the pulse linewidth. While the resonance can still be found experimentally, the magnitude of the Stark shift may impose a restriction on the relative amplitudes of the initial and delayed preparation pulses: if both pulses are to be in resonance, they must have comparable intensities. Such a

restriction is in practice readily satisfied.

Although the calculated power density for a double-quantum π pulse is much greater than that required to invert a typical single-photon transition in an alkali, it is still well within the range of output power available from a ruby-pumped dye laser. A substantial reduction in the power needed can readily be obtained by tuning one of the exciting frequencies close to resonance with an intermediate state, enhancing the transition probability. With this procedure, however, two-photon resonance can be attained only through the use of two separate dye lasers.

In view of the results obtained above, experimental observation of a double-quantum photon echo appears feasible. As in other resonant optical processes, generation of a double-quantum echo entails the creation of a coherently-oscillating superposition of a pair of atomic states in the many atoms of a macroscopic sample. In the double-quantum case, however, this coherent superposition no longer corresponds to a macroscopic dipole moment, thus requiring the use of a probe beam to produce an observable echo pulse. As the probe frequency is arbitrary, the echo can be obtained at a wavelength different from that of the exciting radiation, facilitating detection.

Use of this new technique can extend photon echo relaxation-time studies to atomic states previously inaccessible to single-photon excitation due to the operation of dipole selection rules. Although single-photon forbidden transitions can be driven by stepwise or doubly-resonant excitation, direct two-photon pumping eliminates many complications which arise when intermediate levels are populated. The greater energy available using double-quantum excitation would allow photon echo investigation of phase-changing collisions in high-lying Rydberg states.

Although we have restricted our attention to the simple example of collinear pulse preparation and detection, a more elaborate calculation, explicitly analyzing echo directionality and propagation effects, would be straightforward. In particular, the work of Brewer and Hahn[7] suggests the possibility of echo generation with counter-propagating beams, allowing the selective excitation of particular fine and hyperfine components under the Doppler-broadened atomic linewidth. Even though the two-photon resonance would then be "Doppler free," the motion of individual atoms following the preparation pulses would dephase the excited state in the usual manner, and an echo would subsequently form. Our calculations could also be extended to include interference effects arising from level degeneracy, as has previously been done for the photon echo[13] and for other two-photon processes.[7,14]

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[1]D. Grischkowsky, M. M. T. Loy, and P. F. Liao, Phys. Rev. A 12, 2514 (1975).

[2]M. Takatsuji, Phys. Rev. A 11, 619 (1975).

[3]R. P. Feynman, F. L. Vernon, and R. W. Hellwarth, J. Appl. Phys. 28, 49 (1957).

[4]I. D. Abella, N. A. Kurnit, and S. R. Hartmann, Phys. Rev. 141, 391 (1966).

[5]W. Zernik, Phys. Rev. 132, 320 (1963).

[6]D. Grischkowsky and M. M. T. Loy, Phys. Rev. A 12, 1117 (1975).

[7]R. G. Brewer and E. L. Hahn, Phys. Rev. A 11, 1641 (1975).

[8]S. R. Hartmann, IEEE J. Quantum Elec. QE-4, 802 (1968).

[9]M. Aihara and H. Inaba, J. Phys. A 6, 1709 (1973).

[10]T. M. Makhviladze and L. A. Shelepin, Zh. Eksp. Teor. Fiz. 62, 2066 (1972) [Sov. Phys.-JETP 35, 1080 (1972)].

[11]L. Allen and J. H. Eberly, *Optical Resonance and Two-Level Atoms* (Wiley, New York, 1975), pp. 195–209.

[12]O. S. Heavens, J. Opt. Soc. Am. 51, 1058 (1961).

[13]L. Q. Lambert, A. Compaan, and I. D. Abella, Phys. Rev. A 4, 2022 (1971); I. D. Abella, A. Compaan, and L. Q. Lambert, in *Laser Spectroscopy*, edited by R. G. Brewer and A. Mooradian (Plenum, N. Y., 1975), p. 457.

[14]R. G. Brewer and E. L. Hahn, Phys. Rev. A 8, 464 (1973); A 9, 1479(E) (1974).