optically thin samples and resolution of satellite structure which was not previously resolved in straight absorption measurements of thicker samples. The agreement with the theoretical prediction is marginal and more measurements need to be taken with other dephasing atoms in order to make more stringent test of the calculations. The absolute absorption cross section on the wing due to dephasing and inelastic collisions was measured.

The present method yields photoionization cross sections of short-lived excited states. The saturated ionization is necessary in measurements of the photoionization cross sections of short-lived excited states, because, in the linear regime, big errors can be introduced due to the radiative decay to the lower excited states.

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Observation and Relaxation of the Two-Photon Echo in Na Vapor

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We have used a pair of simultaneously pumped dye lasers to produce in Na vapor the sum-frequency two-photon analog of the photon echo. Quantum-beat effects were observed. Relaxation of the $3^2S_{1/2}$-$4^2D_{3/2}$ superposition was measured.

We report the first observation of an optical two-photon echo and its application to the study of relaxation of the $3^2S_{1/2}$-$4^2D_{3/2}$ superposition state in atomic Na vapor. Although optical echo effects in two-photon transitions were discussed as early as 1968[1] and have been described by many authors,[2-5] it was only recently that echo experiments with two-photon character were reported. The first, a nuclear-spin-resonance experiment, was performed by Hatanaka and Hashi,[6] who, working on the ~10-MHz split ground-state levels of ^{27}Al in Al_2O_3, demonstrated the local rephasing character of the two-photon echo. Shortly thereafter Hu, Geschwind, and Jedju[7] used optical-frequency laser fields to create and probe via the two-photon "Raman" echo the coherence of the ~30-GHz magnetic-field-split donor-electron spin levels in a crystal of n-type CdS. In the present work, *all* transitions are in the optical regime. Utilizing the effective elimination of Doppler broadening, which is inherent in echo phenomena,[8,9] we have examined the foreign-gas-induced relaxation behavior of the Na $3^2S_{1/2}$-$4^2D_{3/2}$ superposition state.

The two-photon echo dynamics can most easily be visualized by approximating each atom by a three-level system with energy levels $\hbar\Omega_a < \hbar\Omega_b < \hbar\Omega_c$, such that the $|a\rangle$-$|b\rangle$ and $|b\rangle$-$|c\rangle$ transitions are electric-dipole allowed, while the $|a\rangle$=$|c\rangle$ transition is not. We restrict our discussion to a dilute gas. The atoms are excited by a sequence of two "pulses," each of length τ_p and each containing two optical fields (denoted by ′ and ″). Let $t_1 = 0$ ($t_2 = \tau$) be the time at which the first (second) pulse is centered, and let t_3 be the two-photon echo time. The traveling-wave fields are given by $E_i' \exp[i(\vec{k}_i' \cdot \vec{x} - \omega_i' t)] + \text{c.c.}$ and $E_i'' \times \exp[i(\vec{k}_i'' \cdot \vec{x} - \omega_i'' t)] + \text{c.c.}$, where the subscript i refers to the fields present at $t = t_i$. We require that $\omega_i' + \omega_i'' = \Omega_{ca} \equiv \Omega_c - \Omega_a$, assume that $|\omega_i' - \Omega_{ba}| \ll |\omega_i'' - \Omega_{ba}|$, and define $\Delta\omega = \omega_i' - \Omega_{ba}$, $\vec{K}_i = \vec{k}_i' + \vec{k}_i''$. Let $\vec{x}_i$ denote the position of a particular atom of velocity $\vec{v}$ at the time t_i. The $|a\rangle$-$|c\rangle$ superpositions dephase between the two pulses, but rephase at a later time t_3 to the extent to which the relative phase Φ of the atoms at each point $\vec{x}_3$, given by

$$\Phi = 2\vec{K}_2 \cdot (\vec{x}_3 - \vec{x}_2) - \vec{K}_1 \cdot (\vec{x}_3 - \vec{x}_1), \tag{1}$$

is independent of $\vec{v}$; this is a simple generalization of the condition for photon-echo rephasing in a gas.[9] Complete rephasing, i.e., Φ being independent of $\vec{v}$ at some time $t_3 > t_2$, only requires that $\vec{K}_1 \parallel \vec{K}_2$; t_3 is then given by $t_3 = 2\tau K_2/(2K_2 - K_1)$. The rephasing (i.e., two-photon echo) is observed by probing the medium at t_3 with a probe pulse of the form $E_3'' \exp[i(\vec{k}_3'' \cdot \vec{x} - \omega_3'' t)] + \text{c.c.}$ The medium responds instantaneously by emitting the two-photon echo "signal," a coherent pulse of frequency $\omega_3' = \Omega_{ca} - \omega_3''$ and wave vector $\vec{k}_3' = 2\vec{K}_2 - \vec{K}_1 - \vec{k}_3''$. The echo signal is phase matched if $k_3' = \omega_3'/c$. Two differences from an ordinary photon echo are evident. First, complete rephasing only requires that $\vec{K}_1 \parallel \vec{K}_2$; the individual waves need not propagate collinearly. Second, the two-photon echo occurs at 2τ only if $K_1 = K_2$; in general, it may be made to occur at any time between τ and ∞ by suitable choice of K_1 and K_2.

We now specialize to the case $\omega_1' = \omega_2' = \omega_3'$, $\vec{K}_1 = \vec{K}_2$. We assume first that the spectral widths of the optical waves are so wide that the entire Doppler profile is equally excited by each pulse, and second, that these waves are Fourier-transform limited. (The second assumption will be dropped below.) We consider two cases: (a) If $\Delta\omega$ is so large that, for each atom, state $|b\rangle$ is excited nonresonantly during each excitation pulse, then the dipole moment of frequency ω' induced in any atom located at $\vec{x}$ at the echo time is given in the "small-angle" limit of weak excitation by

$$p(\omega' = \Omega_{ba} + \Delta\omega) = p_{cb}{}^4 p_{ba}{}^4 E_1' E_1'' E_3'' \times (E_2' E_2'')^2 \tau_p{}^3 \hbar^{-7} (\Delta\omega)^{-4} \times \exp[i(\vec{k}_3' \cdot \vec{x} - \omega' t)], \tag{2}$$

where $p_{\alpha\beta}$ is the dipole matrix element between states α and β.[1] The echo signal intensity is proportional to $|p(\omega')|^2$. (b) If $\Delta\alpha = 0$, then state $|b\rangle$ is excited resonantly. The same two-photon echo, whose signature is the signal direction of propagation $\vec{k}_3'$, still occurs.[10] From the work of Aihara and Inaba[3] it follows that in the limit of weak excitation the induced dipole moment $p(\omega' = \Omega_{ba})$ has the *same form* as Eq. (2), but is a factor of $(\tau_p \Delta\omega)^4$ *larger*. It may also be shown that the ratio $p(\omega' = \Omega_{ba})/p(\omega' = \Omega_{ba} + \Delta\omega)$ is not modified if the optical excitation waves are not Fourier-transform limited, provided that the spectral width of at least one of the waves making up a pulse is comparable to the corresponding single-photon inhomogeneous linewidth.

Because of losses in our steering optics, the excitation pulses have peak powers of only a few watts as they traverse the sample volume. Therefore we optimize the size of the $3^2S_{1/2}$-$4^2D_{3/2}$ ($|a\rangle$-$|c\rangle$) superposition by exciting resonantly via the $3^2P_{1/2}$ ($|b\rangle$) state. The excitation pulses, of length $\tau_p = 7$ nsec, are supplied by two dye lasers which are pumped simultaneously by a N_2 laser. Each oscillates at one of the frequencies ω' (wavelength $\lambda' = 589$ nm) and ω'' (wavelength $\lambda'' = 568$ nm), corresponding respectively to the S-P and P-D transitions. The spectral width (full width at half-maximum) of the pulse of frequency ω' (ω'') is 0.8 GHz (10 GHz). The dye-laser pulses are divided, steered to a White-cell delay line,[8,11] recombined, and recollimated to a 4-mm^2 area such that (1) at $t = 0$ the pulses at ω' and ω'' overlap in the interaction region with their wave vectors $\vec{k}_1'$ and $\vec{k}_1''$ making an angle φ with respect to each other; (2) at $t = \tau$ the pulse configuration in the sample volume is the same as it was at $t = 0$; (3) at $t = 2\tau$ the "probe" pulse at ω_1'' which has traversed the White cell twice, is directed into the sample cell along the direction $\hat{k}_3'' \cong \hat{k}'$ where $\vec{k}' \equiv \vec{k}_1' = \vec{k}_2'$. The angle φ can be adjusted from 0 to 20 mrad, while τ can be adjusted from 21 to 40 nsec. Since $\vec{K}_1 = \vec{K}_2$, the rephasing condition is satisfied at $t = 2\tau$. The phase-matching condition ($k_3' = 2\pi/\lambda'$) demands that $\vec{K}_1$ make the same angle with $\vec{k}_3''$ as it does with $\vec{k}''$ where $\vec{k}'' \equiv \vec{k}_1'' = \vec{k}_2''$. (See Fig. 1.) With $\vec{k}_3''$ coplanar with $\vec{k}'$ and $\vec{k}''$, $|\vec{k}' - \vec{k}''| \ll k'$, and $\varphi \ll 1$, it follows that $\vec{k}_3''$ should make an angle $\theta = 2\varphi|\vec{k}' - \vec{k}''|/k'$ with $\vec{k}'$. Since in our case θ is smaller than the laser divergence of 1 mrad, the two-photon echo signal should be phase-matched with $\hat{k}_3'' \cong \hat{k}'$. Since the two-photon echo at ω' propagates along $\hat{k}_3' \cong \hat{k}''$, for φ sufficiently large the echo is not masked by excitation pulses at ω'. Furthermore, no single-photon coherent emission at ω' propagates in the direction of the two-photon echo signal. To eliminate stray light, the photomultiplier set up to detect the echo signal along $\hat{k}''$ is protected by an interference filter and two Pockels-cell shutters which are electronically gated to transmit at $t = 2\tau$.

The sample volume is contained by a stainless-steel heat-pipe–type cell whose central heated region is about 20 cm long. The Na density is about 10^{10} atoms/cm^3 at the cell temperature of 400 K. Provision is made to add Ar gas whose pressure is measured on a capacitance manometer

The experiment is begun with $\vec{k}'$ and $\vec{k}''$ parallel so that the ordinary[8] and excited-state[12] photon echoes may be observed through the Pockels-cell shutters at $t = 2\tau$. The next step is to insert the interference filter before the photomultiplier, so that only light of frequency ω' is detected. Then as $\hat{k}'$ is tilted away from $\hat{k}''$, the signal intensity observed at ω' continually diminishes, becoming undetectable at $\varphi = 10$ mrad, for which the direction $\hat{k}'$ is outside the acceptance angle (centered at $\hat{k}''$) of the phototube. At this point the probe pulse at ω'' along $\hat{k}_3'' \cong \hat{k}'$ is unblocked, and the two-photon echo signal at ω' along $\hat{k}_3' \cong \hat{k}''$ is observed. The two-photon echo signal disappears if any of the excitation pulses is blocked or if the probe is delayed by an additional 7 nsec.

In the limit of weak excitation, the two-photon-echo signal intensity should decrease as $(\tau_p \Delta\omega)^{-8}$ with laser detuning by $\Delta\omega$ from the $3^2P_{1/2}$ state (beyond δ, the S-P transition Doppler width). At $\Delta\omega = 2\times 10^{10}$ sec$^{-1} \cong 2\delta$, we obtain $(\tau_p\Delta\omega)^{-8} = 10^{-17}$. Thus, although echo intensity measurements (Fig. 2) indicate that we are only partially in the weak-excitation limit, it is not surprising, given our signal-to-noise ratio of ~30 (for a signal of 2×10^5 photons), that we observe the two-photon echo only when $|\Delta\omega| \lesssim \delta$. This echo signal is 30 times smaller than the signal observed at $t = \tau$ when the probe pulse is also made to occur at $t = \tau$; the latter signal arises from ordinary four-wave mixing.

In a two-photon echo the rephasing occurs on the same forbidden transition on which the dephasing occurs; thus, the echo intensity is independent of the decay of the intermediate state. This distinguishes the two-photon echo from the tri-level echo,[13] whose decay is determined by the relaxation of each superposition state the atoms pass through. This distinction is especially important if the intermediate state is very short lived. Using the two-photon echo, we have made a *direct* measurement of the relaxation of the S-D superposition state as a function of Ar-gas pressure p at fixed delay time τ. We find that the echo signal intensity decreases as $e^{-4\eta p\tau}$, with $(4\eta)^{-1} = 1.4\pm 0.5$ nsec Torr. This compares well with $(4\eta)^{-1} = 1.3\pm 0.2$ nsec Torr obtained in-

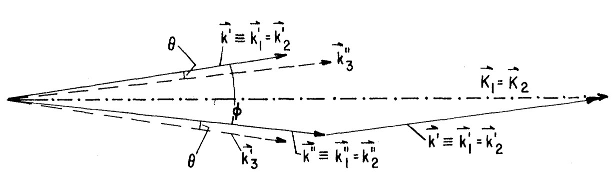

FIG. 1. The angular orientation of the pulses involved in the two-photon echo experiment as they emerge from the sample region is shown. The excitation pulses (solid arrows) at ω' (ω'') propagate along $\vec{k}'$ ($\vec{k}''$). The probe pulse and two-photon echo "signal" (dashed arrows) propagate along $\vec{k}_3''$ and $\vec{k}_3'$, respectively. $\vec{k}'$, $\vec{k}''$ and $\vec{k}_3'$, $\vec{k}_3''$ form the sides of a parallelogram with $\vec{K}_1 = \vec{K}_2$ as a diagonal. $\vec{k}'$ is drawn twice to illustrate this fact. Note that for $k' \cong k''$, $\theta \ll \varphi$.

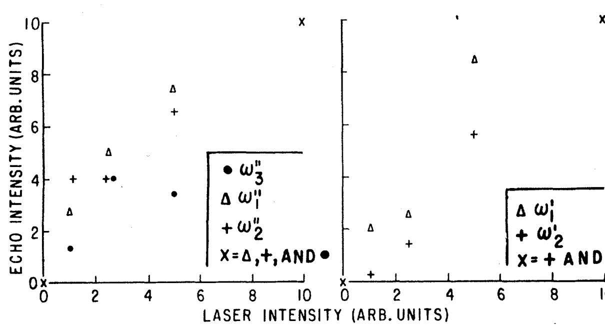

FIG. 2. Relative intensity of two-photon echo signal as a function of excitation-pulse intensities, attenuated one at a time. In the weak-excitation limit the signal intensity should vary linearly (quadratically) with the intensities at ω_1' ω_1'', and ω_3'' (ω_2' and ω_2''). The data reveal that several pulses are not entirely in the weak-excitation limit.

directly (i.e., by correcting for relaxation of the S-P state) for this S-D state from the tri-level measurements and agrees with the results of other Doppler-free two-photon techniques.[14,15]

To ensure that the intermediate P state, which was always resonantly excited in our experiment, indeed played no role in the decay of the two-photon echo, we measured the ratio $I_e(\tau)/I_e(\tau+13$ nsec) for $\tau=21$ and 27 nsec; here $I_e(\tau)$ represents the echo intensity at the pulse separation τ in the absence of foreign gas ($p_{\mathrm{Ar}}<5$ mTorr). In both cases the ratio was found to be 3. This is significantly smaller than the factor of 5 expected on the basis of the relaxation of the 16-nsec–lifetime[16] $3^2P_{1/2}$ state alone if its relaxation contributed to the decay of our signal. We believe that the observed decrease in echo intensity is due instead to the decay of the ~50-nsec–lifetime[17] $4^2D_{3/2}$ state and the additional ~10% reflection loss in power of the delayed laser pulses.

The intensity of the two-photon echo has also been observed qualitatively in the presence of a dc magnetic field H of up to 80 G at a pulse delay time of $\tau=27$ nsec. With $\vec{H}$ applied perpendicular to the propagation direction of the echo, the echo intensity is modulated as a function of H in an oscillatory fashion, with the first null occurring in the region of 10–20 G. The modulation is a type of quantum-beat effect which occurs because each atom is driven into a linear superposition of several ground and excited states.

Like all echo phenomena, the two-photon echo is well suited to the measurement of foreigh-gas–induced relaxation: With all other parameters fixed, the pressure dependence of the echo intensity may be observed directly. From it, a collisional relaxation rate may immediately be determined. In contrast, foreign-gas–induced, Doppler-free linewidth measurements, which can in principle be made to yield the same information, are complicated by the necessity to deconvolute the various contributions to the linewidth. Furthermore, laser monochromaticity, which is critical in linewidth measurements, is only of secondary importance in echo measurements. The two-photon echo itself is particularly important because (a) unlike the tri-level echo, it allows a *direct* measurement to be made of the homogeneous relaxation of a superposition of two levels which are not connected by a single-photon transition; and (b) it is, to our knowledge, the only effect allowing two-photon, Doppler-free measurements to be made even when resonant excitation via an intermediate state of arbitrary energy is required to lower the necessary laser powers.

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