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Modulation of photon-echo intensities by electric fields: Pseudo-Stark splittings in alexandrite and $YAlO_3:Er^{3+}$

Y. P. Wang* and R. S. Meltzer
Department of Physics and Astronomy, University of Georgia, Athens, Georgia 30602
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We describe and demonstrate a method for performing ultrahigh-resolution optical spectroscopy in the time domain which utilizes modulations in the intensity of the two-pulse photon echo in the presence of a perturbation that splits the optical transition frequencies of two or more subgroups of ions. The method is applied to a measurement of the pseudo-Stark effect in alexandrite and $YAlO_3:Er^{3+}$. Stark shifts of $\simeq 100$ kHz are observed but the technique is capable of resolutions < 10 kHz in some systems.

An optical time-domain experiment is described which uses modulations in the intensity of the two-pulse photon echo to measure the pseudo-Stark effect in optical transitions. The Stark effect has been an important technique for studying the electronic states and site symmetries of ions and molecules in solids. The electric field can either remove the electronic degeneracy in a single ion (Stark effect) or it can remove the equivalence of two ions (pseudo-Stark effect). Early studies required very high electric fields and only in materials with very sharp spectral features could splittings be directly resolved.[1] Laser spectroscopy techniques such as hole burning allowed measurements of Stark effects with much more modest fields[2] but these studies required long-lived holes. Nonetheless, the resolution was quite impressive.

However, much higher resolution can be obtained with time-domain spectroscopy which has the additional advantage that it does not require long-lived spectral holes. Echo modulations were first demonstrated by Mims[3] who measured the pseudo-Stark effect in the ground state of $CaWO_4:Ce^{3+}$ using electron spin (Hahn) echos. Much more recently van Oort and Glasbeek[4] optically detected the modulated Hahn echo in the ground state of the N-V center of diamond using a three-pulse spin-echo sequence to determine the pseudo-Stark splitting.

Here we demonstrate the extension of this concept to the pseudo-Stark effect in the optical domain. The electric field distinguishes the echo-producing ions in our samples into two subgroups, whose transition frequencies shift oppositely in the electric field. At the time 2τ after the first laser pulse, each subgroup of ions rephases and the macroscopic polarization is determined by the vector sum of the polarizations of the two rephased subgroups of ions. In the present examples we measure splittings of $\simeq 100$ kHz with fields as low as ≈ 10 V/cm but shifts < 10 kHz should be measurable in some systems. The use of electric-field-induced photon-echo modulations avoids the limitations imposed by laser frequency jitter encountered using Stark-shifted optical free-induction decay measurements.[5]

We first study the two-pulse photon-echo (TPPE) intensity modulation in alexandrite, $BeAl_2O_4:Cr^{3+}$ (0.05 at.%), with a pulsed uniform electric field and compare the time-domain results with those of hole burning psuedo-Stark measurements. Then, this modulation technique is applied to the $YAlO_3:Er^{3+}$ (0.1 at.%) system whose Stark shift is measured for two orientations of the electric field.

The experiment can be easily understood by examining the Bloch vectors in the rotating frame as shown in Fig. 1. The Bloch vectors associated with each site can be treated independently of those associated with the other site as they dephase and rephase. Consider first an electric-field pulse, of duration Δt, applied between the two excitation pulses. After the $\pi/2$ (first) excitation pulse, the high-frequency group of dipoles rotate in the 1-2 plane with an extra angular velocity given by

$$\Delta\omega = 2\pi\Delta\nu = 2\pi E_{\rm dc}(d\nu/dE)\,, \tag{1}$$

where $d\nu/dE$ is the Stark shift of the echo-producing ions. Similarly, for the low-frequency site dipoles, every pseudospin vector rotates with a reduction of their individual angular velocities by $\Delta\omega$. Therefore, when each group of pseudospin vectors rephase after the π pulse, they rephase at angles $\pm\alpha$ from the 2-axis (where the echoes would rephase without the electric-field pulse) given by $\alpha = -\Delta\omega\Delta t$. Therefore α is proportional to the electric pulse area $E_{\rm dc}\Delta t$.

From the macroscopic polarization density, which is the vector sum of the polarizations of the two groups of dipoles, one finds that the echo intensity I changes with the Stark pulse area as

$$I = I_0\cos^2\alpha \equiv I_0\cos^2[2\pi(d\nu/dE)(E_{\rm dc}\Delta t)]\,. \tag{2}$$

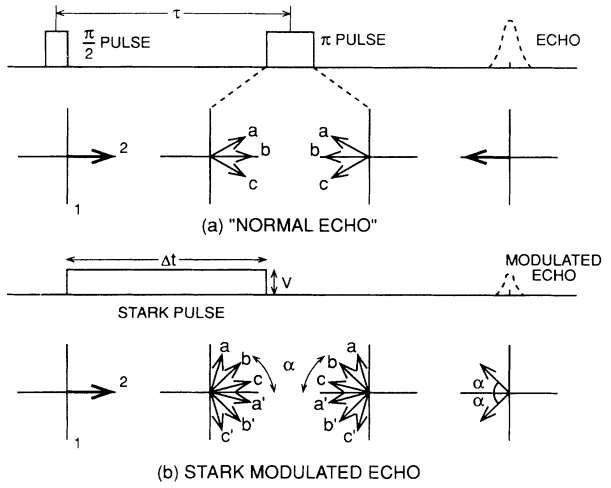

FIG. 1. Photon-echo time sequence (a) for the normal echo in the absence of the Stark pulse, the pseudospin vectors spread out in the 1-2 plane of the rotating frame after the $\pi/2$ pulse and converged after the π pulse is applied, and (b) for the Stark modulated echo, the fast (slow) group ions, represented by vectors **a**,**b**,**c** (a',b',c'), dephase in the 1-2 plane with an increase (reduction) of angular velocity $\Delta\omega$ due to the pseudo-Stark splittings. If the Stark pulse is applied between the two laser pulses as shown, these dipoles do not converge in the -2 direction; instead, they rephase at an angle $\pm\alpha$ from the -2 direction where $\alpha=\Delta\omega\tau$.

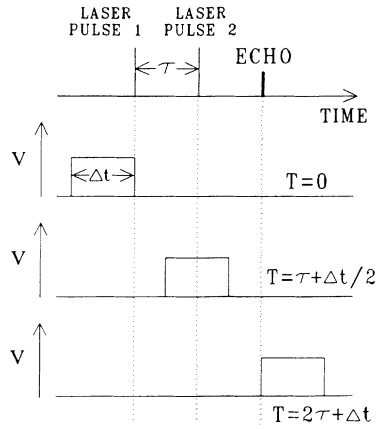

FIG. 2. Timing sequence of the experiment for alexandrite. The pulsed electric field is scanned in time relative to the echo pulse sequence. Three specific timing sequences are indicated. In the experiment, the echo intensity is measured as a function of T. Here, $\Delta t=\tau$.

I_0 is the echo intensity with the Stark pulse off. Therefore, by measuring the Stark-modulated echo intensity, we can obtain dv/dE. This technique turns out to be a very sensitive way to study the Stark effects. The ultimate resolution is limited by T_2, the transverse relaxation time of the system.

We first examine the pseudo-Stark effect for Cr^{3+} ions located on the mirror (C_s) Al^{3+} sites in alexandrite. This crystal has an orthorhombic structure with four molecules per unit cell.[6] An electric field in the ac plane introduces a pseudosplitting between the two subgroups of ions.[7,8]

The laser pulses used to prepare the coherence ($\pi/2$ and π pulses) are obtained from two independent Nd:YAG-pumped tunable dye lasers, adjusted for a time separation of $\tau=200$ ns and tuned to the R_1 transition of the mirror site ions. The timing of the experiment is shown in Fig. 2. The echo intensity is recorded as the electric-field pulse, of width $\Delta t=200$ ns ($\Delta t=\tau$) is scanned in time from before the first preparation pulse to beyond the time of the echo occurrence, using a programmable delay. Each data point is averaged over 100 shots for a particular timing of the pulse sequence characterized by the time delay T shown in Fig. 2. The whole modulation pattern was averaged over 2–4 scans of T so that the long-term fluctuation due to the lasers and other instruments is minimized.

The electric field is obtained by applying a voltage to a pair of electrodes painted on opposite faces of the crystal with the resulting electric field perpendicular to the laser beam. The experiments are carried out at 2 K in a large dc magnetic field along the electric-field direction which serves to increase the value of T_2, greatly enhancing the sensitivity of the pseudo-Stark measurement. The TPPE is generated on the ${}^4A_2(-\frac{1}{2})\rightarrow{}^2E(-\frac{1}{2})$ Zeeman transition,[9] selected in order to prevent overabsorption since this first excited spin component of the ground state is partially depopulated at 2 K.

Figure 3 shows the modulation of the intensity of the TPPE in alexandrite when voltage pulses of 3, 5, and 10

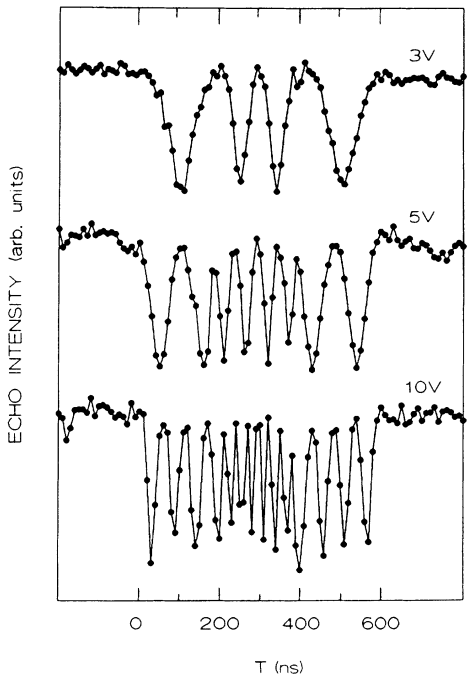

FIG. 3. Stark modulated photon-echo intensity in alexandrite as a function of time T (timing sequence is shown in Fig. 2) at three different Stark pulse voltages applied across a 1.6-mm sample. The three scans are displaced vertically for ease of viewing. Notice the modulation frequency increases with voltage and the pattern is symmetric around $T=300$ ns when the Stark pulse sits evenly on both side of the π pulse.

V, are applied across the a axis of a sample whose thickness is 1.6 mm. To analyze these modulations one must determine $\alpha_T(2\tau)$, the total field-induced phase accumulation at the time of echo formation. For a particular temporal pulse history, described by T,

$$\alpha_T(2\tau) = 2\pi(dv/dE) \times \left[\int_\tau^{2\tau} E_{dc}(T,t)dt - \int_0^\tau E_{dc}(T,t)dt\right]. \quad (3)$$

The dependence of $\alpha_T(2\tau)$ on T is shown at the top of Fig. 4. A theoretical best fit to the data using Eqs. (2) and (3) is obtained with $dv/dE = 141 \pm 5$ kHz/V cm^{-1}. This value is in excellent agreement with the hole burning result of Carter, Horne, and Moerner[10] who obtained, for E$\|a$, a value of 141 kHz/V cm^{-1}. This best fit is compared in Fig. 4 with the 5-V data of Fig. 3. Whereas the hole burning experiments required fields of 800 V/cm, the Stark modulated TPPE techniques utilize fields of < 60 V/cm.

The technique of Stark modulation of the photon-echo intensity is now used to study the pseudo-Stark effect in $YAlO_3:Er^{3+}$ for the transition between the lowest-crystal field components of the $^4I_{15/2}$ and $^4F_{9/2}$ states. The trivalent erbium ions enter the $YAlO_3$ lattice at the Y^{3+} sites. Based on the $YAlO_3$ crystal structure,[11] we find that the Y^{3+} ions have four energetically inequivalent sites for a general direction of the electric field. However, when the external electric field is applied along the crystal a or b axis, the transition frequencies of the four sites collapse into two pairs of inequivalent sites. If the electric field is applied along the c axis, all sites become equivalent.

In this experiment, a single-frequency gated-cw dye laser is used to produce the echo. A 30-kG magnetic field is applied along the c axis to increase T_2. Instead of scanning the timing of the Stark pulse relative to the laser pulses, we kept the Stark pulse fixed in time and on only during the time interval between the $\pi/2$ and π pulses. Since the echo intensity modulation is governed only by the Stark pulse area [Eq. (2)], we can achieve modulations by either changing the width Δt ($\Delta t < \tau$) or the voltage height V of the Stark pulse. Figure 5(a), obtained

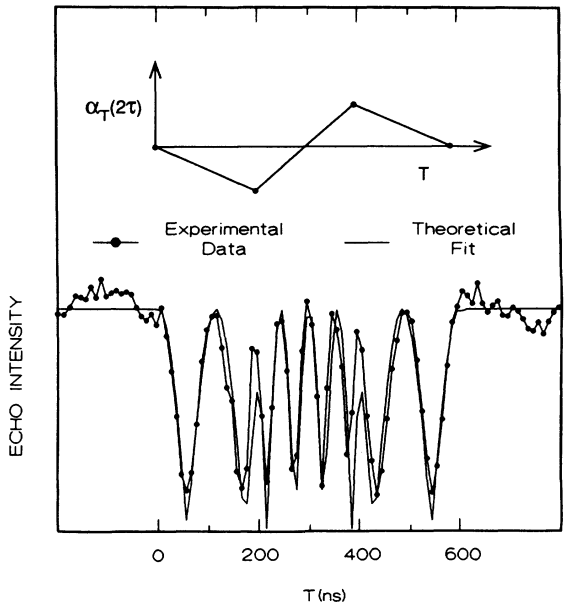

FIG. 4. Top: $\alpha_T(2\tau)$ as a function of T. Bottom: A theoretical best fit compared to the 5-V scan in Fig. 3. The excellent fit gives $dv/dE = 141$ kHz/V cm^{-1}. Notice that the modulations do not always go to zero [as should be expected from Eq. (2)] because of the 10-ns steps used for both the scanning and calculations.

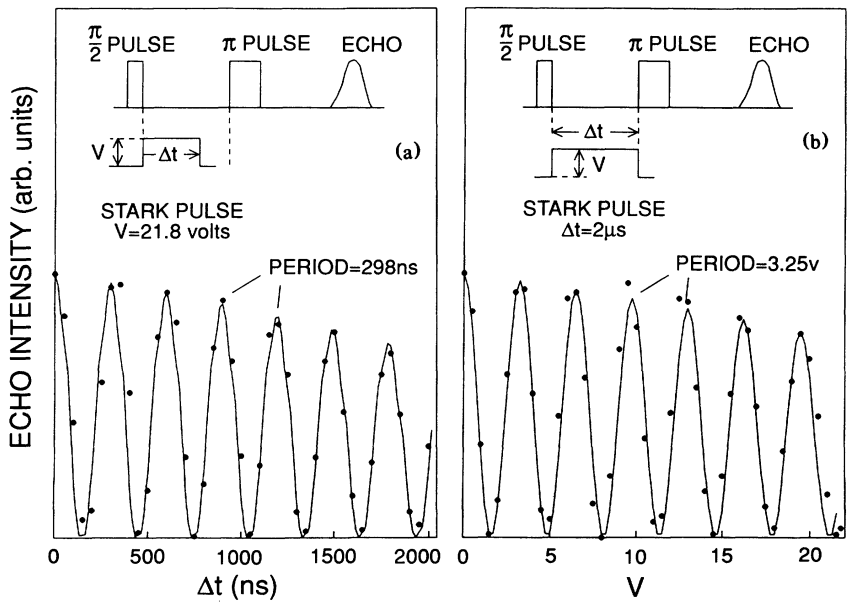

FIG. 5. (a) Periodic modulation of photon-echo intensity as a function of the Stark pulse width. The Stark pulse, set in time between the $\pi/2$ and π laser pulses, has a fixed amplitude of 21.8 V while its width increases from zero to τ ($=2$ μs). (b) Same as in (a) but the Stark pulse width is fixed at 2 μs while its amplitude increases from zero to 21.8 V.

with a 21.8-V pulse across the 2.3-mm crystal b axis, shows that the echo intensity varies periodically as the pulsewidth Δt is increased from zero to 2.1 μs. Based on Eq. (2) and the period of the modulations, we deduced the Stark shift to be

$$\frac{d\nu}{dE} = 17.7 \pm 0.3 \text{ kHz/V cm}^{-1},$$

$$\mathbf{E}_{dc}(\| b) = 21.8 \text{ V}/2.3 \text{ mm}, \ \Delta t \text{ variable}.$$

For $\mathbf{E}_{dc} \| a$, we found $d\nu/dE \simeq 14.8 \pm 1.0$ kHz/V cm^{-1}.

Alternatively, we varied V and kept Δt fixed at 2 μs. The resulting modulation, with period 3.25 V, is shown in Fig. 5(b), yielding for $\mathbf{E}_{dc} \| b$ a nearly identical result of $d\nu/dE = 17.7 \pm 0.3$ kHz/V cm^{-1}. These pseudo-Stark splittings are about an order of magnitude smaller than those for Cr^{3+}-doped alexandrite or ruby and would require large electric-field strengths ($\sim 10^4$ V/cm) to accurately measure if hole burning techniques were employed.

The slow overall decay of the echo intensity as the Stark pulse area gets larger (corresponding to $\alpha \geq 4\pi$) may be caused by the inhomogeneity of the Stark field across the echo-producing region, especially near the edges of the sample. This creates a distribution of Stark shifts, $\Delta\omega$, leading to incomplete phase coherence at the time of the echo formation.

By using this Stark modulation technique, we have measured pseudo-Stark splittings $\simeq 100$ kHz. In general, phase accumulations of $\alpha \simeq \pi/2$ (first minimum) are required for a reasonable ($\pm 10\%$) measurement of the Stark splitting. For the case of $YAlO_3:Er^{3+}$, this required fields as small as 1.6 V/cm. However, the frequency resolution can be improved by stretching out the Stark pulse width Δt. This requires increasing the separation between the echo preparation pulses which is ultimately limited by T_2 for the system. For example, for a system in which $T_2 \approx 100$ μs, splittings below 10 kHz can be detected. This has recently been demonstrated by Meixner, Jefferson, and Macfarlane[12] who have measured pseudo-Stark splittings of only 2 kHz in $YAlO_3:Eu^{3+}$, a system with $T_2 = 58$ μs. We note finally that gated cw echoes, as used in the $YAlO_3$ experiments, are preferable to echoes produced by short intense optical pulses, as used by us in the case of alexandrite, since these short pulses seem to limit T_2 due to effects of instantaneous diffusion.[13]

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*Present address: Physics Department, Oklahoma State University, Stillwater, OK 74078-0444.

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