Excess Dephasing in Photon-Echo Experiments Arising from Excitation-Induced Electronic Level Shifts

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(Received 3 January 1989)

Working on the $^7F_0$-$^5D_0$ transition of Eu^{3+} in Y_2O_3, we provide the first detailed characterization of excitation-induced shifts in optical transition frequencies and demonstrate their exaggeration of nominally homogeneous dephasing rates. The shifts (found to vary in rough proportion to the number of Eu^{3+} ions excited and to be as small as one part in 10^{12}) were identified through their unique signature in specially designed photon-echo experiments. The effects reported may constitute a rather general complication in optical measurements of homogeneous relaxation rates in solids.

PACS numbers: 78.50.Ec, 42.50.Md

Coherent transient optical techniques have been employed with great advantage over the last ten years or so to study the slow optical dephasing of rare-earth and transition-metal impurities in insulators.[1-9] Kilohertz-scale homogeneous linewidths have been observed,[5] and interesting effects such as the variation of homogeneous linewidths across inhomogeneous absorption profiles have been observed[5] and analyzed.[10] In this Letter, we provide the first unambiguous demonstration of a novel new type of optical dephasing that occurs as a result of excitation-induced optical frequency shifts. The shifts have intrinsic interest insofar as studies of their properties may provide useful information about the materials in which they occur. Importantly, however, they also exaggerate the homogeneous linewidths deduced from experiments employing coherent transient techniques and may provide a heretofore unappreciated explanation for frequency-dependent relaxation rates.

The existence of excitation-mediated optical frequency shifts was proposed some time ago by Taylor and Hessler[11] who suggested that such shifts may be responsible for the concentration-dependent photon-echo relaxation rates observed in ruby by Liao and Hartmann.[12] It was suggested, based on analogy with the well known and closely related nuclear magnetic resonance (NMR) effect of instantaneous diffusion,[13,14] that excitation-mediated frequency shifts arise because of a change in the static electric-dipole moment of Cr sites accompanying state changes of the resident Cr ion. Dipole-moment changes of this type are possible in any noncentrosymmetric site. In this model, electric-dipole changes at one site modify the electric field at surrounding sites and thereby shift the transition frequencies of the neighboring ions. In the earlier NMR work, instantaneous diffusion was presumed to arise similarly, but from magnetic interactions. It was shown that the precise type of magnetic interaction responsible for the excitation-induced frequency shifts could be identified through studies of shift-induced spin-echo relaxation. Similar results are expected in the optical case. Interestingly, an experimental follow up[15] of Taylor and Hessler's suggestion[11] revealed no clear evidence for excitation-induced frequency shifts in the ruby system. In subsequent work, excitation-induced frequency shifts have been invoked to explain intensity-dependent dephasing rates seen in other photon-echo experiments,[6] but the results reported do not actually allow for an unambiguous determination of the relaxation mechanism involved.

Coherent transient techniques are particularly sensitive to small random shifts in the transition frequencies of echo-producing (or active) ions. This has been demonstrated both in spin[14,16] and in optical[17] systems. However, in ordinary coherent-transient-type experiments, relaxation due to excitation-induced frequency shifts tends to be difficult to distinguish from other relaxation mechanisms. We have therefore designed novel photon-echo excitation schemes involving pulses of widely different bandwidths that enable us to control the relative contribution of excitation-induced frequency shifts to the overall relaxation rate, and thereby enable us to unambiguously identify and characterize frequency-shift–mediated relaxation.

The experiments were conducted on the $^7F_0$-$^5D_0$ transition of Eu^{3+} in 2 at.% Eu^{3+}:Y_2O_3 at $\simeq$4.5 K. The excitation pulses employed were acousto-optically gated from the output of a single-mode cw dye laser. Temporally long (0.1–6 μsec) pulses (gated-cw pulses) were obtained by direct coupling of the cw dye-laser beam into the sample. Temporally short (6 nsec) pulses (amplified pulses) were obtained by excimer-pumped-dye amplification of gated-cw pulses. In both cases, pulse bandwidths were given roughly by the Fourier-transform limit. For equal pulse areas, the amplified pulse excites 1 to 2 orders of magnitude more ions than the gated-cw pulse.

Our apparatus provides excitation sequences at 7 Hz containing a variable number of gated-cw pulses together with one amplified pulse. The time ordering of the pulses is varied to highlight different aspects of the relaxation. All pulses were spatially coincident and collinear

(with a beam waist of 70 μm) as they passed through the 4-mm-long $Eu^{3+}:Y_2O_3$ crystal. The "standard" intensity (maximum intensity) of the gated-cw (amplified) pulse was $\simeq$400 W/cm^2 ($I_0 \simeq 30$ MW/cm^2). The area of the gated-cw pulse varies linearly with duration and at standard intensity is roughly π for a pulse duration of 2 μsec. The area of the amplified pulse varies linearly with the square root of its intensity and is roughly π at intensity I_0. To avoid complications from spectral hole burning,[5,8,18] the cw dye-laser frequency was swept over a range of 0.5–1.0 GHz every 2.5 sec. Periodically, the sample temperature was raised to $\simeq$20 K for $\simeq$1 min to thermalize the ground-state sublevel populations. Except as noted, the laser frequency was tuned to the approximate center of the inhomogeneous absorption line.

First, we measured the decay of two-excitation-pulse photon echoes generated with one gated-cw pulse and one amplified pulse as a function of the temporal separation $t_{21} \equiv t_2 - t_1$ between the excitation pulses. Here t_i ($i=1,2$) is the time of the ith echo excitation pulse. In Fig. 1(a) [Fig. 1(b)], we present measurements of echo intensity versus t_{21} with the amplified pulse temporally second (first) for three different amplified-pulse intensities. With the amplified pulse second [Fig. 1(a)], the echo decays exponentially with a rate 2 *orders of magnitude* larger than expected on the basis of the hundreds-of-microseconds-scale T_2 measured previously.[7] With the amplified pulse first [Fig. 1(b)], the echo decays at a substantially smaller rate (still larger than derived from the earlier T_2 measurement), and the decay takes on a nonexponential character. For both time orderings, the decay rate increases with the amplified-pulse intensity.

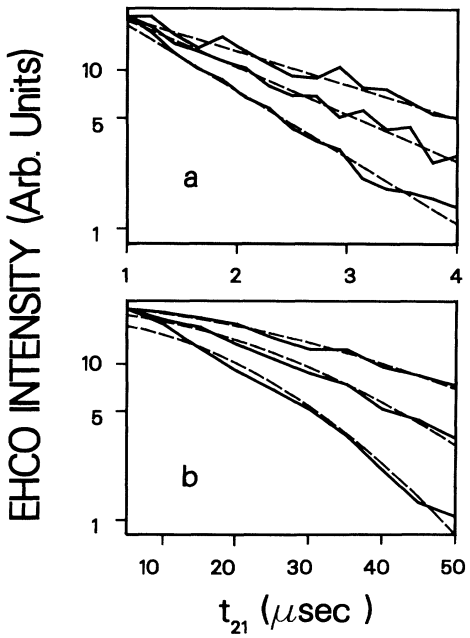

FIG. 1. Two-excitation-pulse photon-echo intensity vs excitation pulse separation t_{21}. (a) The gated-cw excitation pulse precedes the amplified pulse. (b) The amplified excitation pulse precedes the gated-cw pulse. From bottom to top, the traces in each figure correspond to amplified-pulse intensities of $I_0 \simeq 30$ MW/cm^2, $I_0/2$, and $I_0/4$, respectively. Dashed lines are calculated, as described in the text, assuming that the observed relaxation is caused by frequency shifts induced by the amplified excitation pulse. The gated-cw pulses had the standard intensity, and in (a) [(b)] a duration of $\simeq$100 nsec [$\simeq$2 μsec].

Next, two gated-cw pulses were employed to generate a photon-echo signal whose intensity was monitored as a relatively weak, small-area, amplified pulse was applied at various times $t_s > t_1$. In these experiments, the separation between the two gated-cw pulses, t_{21}, was held fixed, and the detector was gated to ignore three-pulse (stimulated) echo signals created by application of the amplified pulse. Figures 2(a)–2(c) display the echo intensity as a function of $t_s - t_1$ for several different amplified-pulse intensities. For this figure, $t_s - t_1 = 0$ ($t_s - t_1 = t_{21}$) when the amplified pulse is simultaneous with the first (second) gated-cw pulse.

For analysis of the above results, we note that the intensity I_e of a two-excitation-pulse echo obeys the proportionality[17,19]

$$I_e \propto \left| \sum_j \exp[i\phi_j(t_e)] \right|^2 , \tag{1}$$

where t_e denotes the time of the echo, and ϕ_j is the relative phase of the jth active ion. We also have

$$\phi_j(t_e) = \int_{t_1}^{t_2} \omega_j(t)dt - \int_{t_2}^{t_e} \omega_j(t)dt , \tag{2}$$

where $\omega_j(t)$ is the instantaneous transition frequency of the jth active ion. Clearly, for ω_j constant throughout the interval t_1 to t_e, $\phi_j = 0$, and I_e is maximized.

We now consider the echo decay properties expected in an environment of excitation-induced frequency shifts and compare them with our experimental observations.

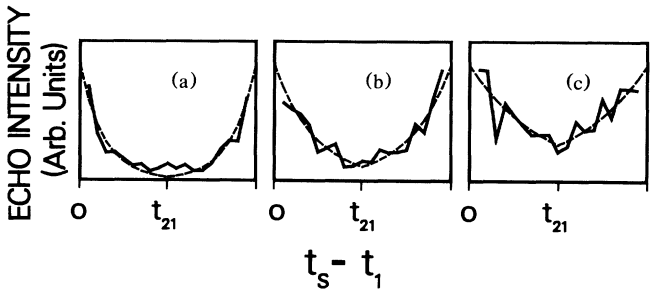

FIG. 2. Intensity of two-excitation-pulse photon echoes ($t_{21} = 80$ μsec) generated by two gated-cw pulses and perturbed by an amplified pulse applied at the time t_s as a function of $t_s - t_1$. For (a), (b), and (c), respectively, the intensity of the amplified pulse is $I_0/8$, $I_0/16$, and $I_0/32$. Dashed lines are simulations based on Lorentzian frequency-shift distributions. The first and second gated-cw pulses had the standard intensity and durations of $\simeq$1 and $\simeq$2 μsec, respectively.

We first note, in light of the mechanism assumed responsible for excitation-induced frequency shifts, that the magnitude of the shifts will depend on the number of ions excited and hence on the ion concentration, the excitation-pulse intensity, and the excitation-pulse bandwidth. Thus, as a first approximation, made reasonable by the relatively small number of ions excited, we ignore frequency shifts introduced by the gated-cw pulses. We assume that the amplified pulse introduces shifts ϵ_j in the transition frequency of each active ion, and that the shifts are described by a distribution function $\rho(\epsilon_j)$. From NMR work,[14,16] one expects ρ to have a Lorenztian form if the interaction responsible for the shifts is dipolar. We assume that conventional homogeneous dephasing mechanisms perturb the various ω_j in a manner independent of the excitation conditions and that their effect can be accounted for through a simple exponential decay factor.

In the case of Fig. 1(a) (amplified pulse second), frequency shifts ϵ_j are introduced at time t_2, and because of the long $^5D_0$-state lifetime they remain approximately constant thereafter. Frequency shifts will thus degrade the echo intensity by a factor

$$I_e \propto \left| \int_{-\infty}^{\infty} \rho(\epsilon) \exp[-i\epsilon t_{21}] d\epsilon \right|^2 . \quad (3)$$

The dashed lines in Fig. 1(a) are calculated using Eq. (3) assuming a Lorentzian $\rho(\epsilon)$ with a half width at half maximum (HWHM) Δ_0 of, from top to bottom, 40, 57, and 83 kHz, respectively. The growth of Δ_0 with amplified-pulse intensity (which in this case provides for a relatively large pulse area) roughly mirrors the growth in excited Eu^{3+}-ion population.

In the case of Fig. 1(b) (amplified pulse first), the situation is quite different. If the ϵ_j induced at t_1 are assumed time independent as in the previous paragraph, frequency-shift–mediated decay should vanish. If, however, the 860-μsec excited-state lifetime[7] is taken into account, the excited-state population and hence the ϵ_j (being dependent on the excited-state population) relax partially toward their initial (in this case zero) values before the echo is emitted. The dashed lines of Fig. 1(b) were calculated assuming that the initial frequency-shift distribution $\rho(\epsilon)$ is a Lorentzian whose width decays exponentially on a time scale equal to the excited-state lifetime. Best fit values of Δ_0, the HWHM of the initial $\rho(\epsilon)$, were found to be, from top to bottom, $\Delta_0 = 24$, 45, and 80 kHz, respectively, in excellent agreement with the values of Δ_0 deduced from Eq. (3) and Fig. 1(a).

In the three-pulse experiments of Fig. 2, the frequency shifts are introduced by the amplified pulse at some time t_s between t_1 and t_e. In this case (assuming as a first approximation that the frequency shifts ϵ_j are time independent), I_e should obey a relation identical to Eq. (3) except that t_{21} is replaced by the term $\delta = \min[|t_1 - t_s|, |t_e - t_s|]$. For reasonable $\rho(\epsilon)$ and fixed t_{21}, I_e is then minimized when it coincides with the second excitation pulse. This is just the behavior seen in Fig. 2. We have fitted Eq. (3), modified as described, to the data of Fig. 2 assuming a Lorentzian $\rho(\epsilon)$. The Δ_0 values obtained from the fits to the observed data exhibit an approximately linear dependence on the intensity of the amplified pulse and hence (because of the small area of the amplified pulse in this set of experiments) on the number of Eu^{3+} ions excited. For the weakest intensities used [see Fig. 2(c)], the frequency-shift distribution has a width on the order of 1 kHz.

It is clear that the excitation-induced–frequency-shift relaxation mechanism assumed provides an excellent description of our observations. Traditional optical relaxation mechanisms, on the other hand, cannot account for the very different relaxation behavior observed when the order of the excitation pulses is reversed (see Fig. 1), nor can they account for the behavior of Fig. 2. The fact that a Lorentzian distribution function provides a reasonable quantitative description of our results supports[14] Taylor and Hessler's contention[11] that the excitation-induced frequency shifts are mediated by a dipolar field. The magnitude of the shifts depends upon the amount by which the site electric dipoles are modified on excitation. The frequency shifts observed in our experiments indicate[11] an electric dipole change of $\simeq 10^{-32}$ C m.

In our analysis above, we assumed for simplicity that frequency shifts introduced by the gated-cw pulses were unimportant. Although this approximation is reasonable in the context of the previous discussion, it is not correct in general. In Fig. 3, we show the decay of photon echoes generated with two gated-cw pulses as a function of t_{21}. In the top trace, the intensity (duration) of each excitation pulse is reduced (increased) by a factor of 10

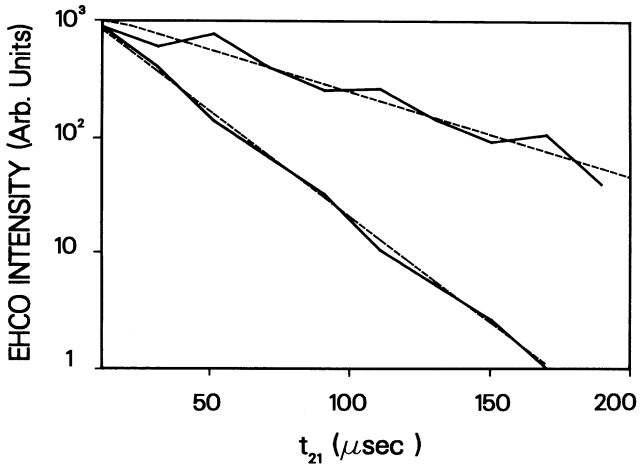

FIG. 3. Intensity of photon echoes generated with two gated-cw pulses vs t_{21} for different excitation pulse intensities but equal pulse areas. The pulse area was roughly $\pi/2$ (π) for the first (second) pulse.

(3) compared to the situation of the bottom trace. (For the bottom trace, the gated-cw pulses had standard intensity.) These intensity-time ratios provide for nominally constant pulse areas. If excitation-induced frequency shifts contribute to the observed decay, the lower-intensity pulses (which because of their smaller bandwidth excite roughly one-third as many Eu^{3+} ions) should produce photon echoes displaying a smaller decay rate. This is observed. A factor of 3 change is not expected because on the relevant time scale normal homogeneous broadening is also important. In the limit of weak excitation, photon echoes generated near line center with gated-cw pulses were observed to exhibit a decay rate several times smaller than the line-center decay rate observed in Ref. 7. In fact, as will be discussed elsewhere, the variation in the homogeneous decay rate across the inhomogeneous absorption profile that was reported in Ref. 7 appears to arise primarily because of the variation in the number of ions excited and the concomitant variation in frequency-shift–mediated decay.

In summary, we have observed and characterized excitation-induced optical frequency shifts. The properties of the frequency shifts appear to be consistent with the electric-dipole frequency-shift mechanism proposed by Taylor and Hessler.[11] The excitation-induced frequency shifts were shown to result in the spurious enhancement of relaxation rates ordinarily understood to represent homogeneous rates, and to provide a means of studying ion-ion interactions. In line-shape measurements, excitation-induced frequency shifts may lead to a spurious broadening of lines.

We would like to thank R. M. Shelby and R. S. Meltzer for interesting conversations and R. M. MacFarlane for the extended loan of the $Eu^{3+}:Y_2O_3$ crystal. We gratefully acknowledge financial support from the Army Research Office under Contract No. DAAL03-89-K-0004. One of us (A.L.) acknowledges support from Conselho Nacional de Desenvolvimento Científico e Tecnológico (Brazil).

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