Excitation-Induced Frequency Shift Probed by Stimulated Photon Echoes

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A stimulated photon-echo study has verified the instantaneous shift (≤ 1 MHz) and subsequent restoration (~ 2 ms) of the transition frequency of an impurity ion in a solid when its neighboring ions are exposed to pulsed optical excitation. Experiments were conducted by monitoring the echo intensity for the $^7F_0$-$^5D_0$ transition of Eu ions in one site of Y_2SiO_5, while exciting the other site. A photon-echo theory taking account of the stochastic frequency recovery is developed to explain the observations.

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High-resolution nonlinear laser spectroscopy in solids has been a powerful tool for studying small magnetic or electric interactions between optical centers and their circumstances. In 1987 Liu *et al.* [1] and in 1989 Huang *et al.* [2,3] used photon-echo experiments to show the existence of a small shift (20 to 300 kHz depending on the excitation intensity) in the optical transition frequency of an impurity ion in a solid, induced by the optical excitation of nearby ions. This excitation-induced frequency shift (EFS), also known as instantaneous spectral diffusion, can only be unveiled by nonlinear spectroscopy because otherwise the EFS would be totally buried within the huge inhomogeneous absorption linewidth ($\sim$GHz). Many recent observations of excitation-intensity-dependent optical dephasing times [1-5] can be well interpreted in terms of the EFS. The physical origin of the EFS is very clear. By optically exciting the surrounding ions (B ions) by an intense pulse, which we now call the scrambler, the two-level system of interest (A ion) experiences a sudden change in the local field (electric or magnetic), and this perturbation shifts the energy levels of the A ion. Of course A ions and B ions can be the same species, as they are in all the previous cases. The magnitude of the EFS should be random, depending on each A ion, which has its own distribution of the excited B ions around it. It is also important to note that this environmental change is instantaneous but temporary. In fact, sooner or later the original environment is restored when the B ions decay back to the ground state, but experimental verification of this restoration process has not been reported.

Such time evolution of the EFS can be studied by the measurement of *stimulated photon echoes* of A ions under the influence of the scrambler. The principal requirement for echo formation is that dephasing and rephasing be conducted with the same transition frequencies. If dephasing takes place with an unshifted frequency and rephasing with a shifted frequency, or vice versa, it will give imperfect rephasing, resulting in reduction of the echo intensity. On the other hand, the stimulated photon echo can vary the dephasing-to-rephasing period separation, or storage time, T very widely, and T can reach even several hours for persistent-hole-burning materials [6]. Therefore *the stimulated photon echo can be a strong tool for finding small transition-frequency imbalance of an atom between two different periods that can be arbitrarily separated.*

The purpose of this Letter is to study the effect of the EFS on the stimulated photon echo by the onset of the scrambler. A stochastic theory is developed for this purpose, experiments are performed to examine whether the physical picture given here is indeed applicable to the real case of Eu^{3+}:Y_2SiO_5, and finally the effect of the EFS on time-domain data storage is discussed.

First of all we assume that the optical frequency $\omega_j(t)$ of the jth A ion will be given in a general form as

$$\omega_j(t) = \omega_{j0} + \sum_k \epsilon_{jk}\delta_k(t) , \qquad (1)$$

where $\delta_k(t)$ takes the value 0 or 1 depending upon if the kth B ion is in the ground state or in the excited state, and ϵ_{jk} denotes the magnitude of EFS due to interaction between the jth A ion and the kth B ion. For an impact excitation, the very case we from now on investigate, the scrambler is applied at $t = t_0$ and an instantaneous EFS and subsequent recovery to ω_{j0} should be expected. Thus the stochastic average over all $\delta_k(t)$ will give the exponential decay of the frequency with the lifetime T_1, or γ^{-1}, of the excited state of the B ions:

$$\langle \omega_j(t) \rangle_{\rm st} = \omega_{j0} + \sum_k \epsilon_{jk}\delta_k(t_0)\exp[-\gamma(t-t_0)] , \qquad (2)$$

when $t > t_0$. Here $\langle \cdots \rangle_{\rm st}$ indicates the stochastic average over all the excited-to-ground decay processes of the B ion.

Now we consider the effect of the EFS given by Eq. (1) on the stimulated photon echo. Suppose that the first, second, and third pulses are applied to the A ions at $t = 0$, τ, and $T + \tau$, respectively, and the echo is observed at $T + 2\tau$, independent of t_0. We eventually need to obtain the echo intensity as a function of t_0, since it should give detailed information on the magnitude and the time evolution of the EFS.

The phase shift in the coherence of the jth A ion at the echo time as a function of t_0 is given by [2,7]

$$\phi_j(t_0) = \int_0^\tau \omega_j(t)dt - \int_{T+\tau}^{T+2\tau} \omega_j(t)dt . \qquad (3)$$

The excitation pulse widths were assumed to be negligible. The echo intensity $I(t_0)$ normalized by the perfect rephasing case is given simply as [2]

$$I(t_0)=\left|\sum_j \langle \exp[i\phi_j(t_0)]\rangle_{\text{st}}\right|^2 . \tag{4}$$

By substituting Eqs. (3) and (1), the above equation is

$$I(t_0)=\left|\sum_j \prod_k \left\langle \exp\left\{ i\epsilon_{jk}\left[\int_0^{\tau}\delta_k(t)dt-\int_{T+\tau}^{T+2\tau}\delta_k(t)dt\right]\right\}\right\rangle_{\text{st}}\right|^2 , \tag{5}$$

where we assumed that each B ion obeys totally independent statistics. Now we need to obtain the stochastic average in the above equation. Rewriting the stochastic averaging part in a more general form,

$$S_\epsilon(t_0)\equiv\left\langle \exp\left\{ i\epsilon\left[\int_0^{\tau}\delta(t)dt-\int_{T+\tau}^{T+2\tau}\delta(t)dt\right]\right\}\right\rangle_{\text{st}} . \tag{6}$$

Here $\delta(t)$ is the function which is 1 if $t_0 \le t \le t_p$ and 0 otherwise, and t_p is the time when the B ion returns to the ground state and is only probabilistically determined in such a way that the probability is given as $\mathcal{P}(t_p)=\gamma \times \exp[-\gamma(t_p-t_0)]$. An elaborate calculation [8] shows that $S_\epsilon(t_0)$ can be expressed using the function $\xi(t_1,t_2,t_3,t_4)$ as

$$S_\epsilon(t_0)=\begin{cases}\xi(\tau,T,\tau,-t_0), \text{ if } t_0<0,\\ \xi(\tau,T,\tau-t_0,0), \quad 0\le t_0<\tau,\\ \xi(\tau,T+\tau-t_0,0,0), \quad \tau\le t_0<T+\tau,\\ \xi(T+2\tau-t_0,0,0,0), \quad T+\tau\le t_0<T+2\tau ,\\ \xi(0,0,0,0), \quad t_0\ge T+2\tau ,\end{cases} \tag{7}$$

where the function ξ is defined as

$$\xi(t_1,t_2,t_3,t_4)\equiv\langle f|\exp[(\Gamma-i\epsilon\Delta)t_1]\exp[\Gamma t_2] \times\exp[(\Gamma+i\epsilon\Delta)t_3]\exp[\Gamma t_4]|e\rangle , \tag{8}$$

with matrices

$$\Gamma=\begin{pmatrix}-\gamma & 0\\ \gamma & 0\end{pmatrix},\quad \Delta=\begin{pmatrix}1 & 0\\ 0 & 0\end{pmatrix},\quad |e\rangle=\begin{pmatrix}1\\ 0\end{pmatrix},\quad |f\rangle=\begin{pmatrix}1\\ 1\end{pmatrix}. \tag{9}$$

Using this expression, Eq. (5) can be evaluated. However, a rigorous treatment of Eq. (5) is unrealistic and instead we will replace the product over k by the Nth power of $S_\epsilon(t_0)$ and the sum over j by the integral over ϵ with a distribution function $\mathcal{G}$:

$$I(t_0)=\left|\int_{-\infty}^{\infty}d\epsilon\,\mathcal{G}(\epsilon)S_\epsilon^N(t_0)\right|^2 . \tag{10}$$

A Lorentzian distribution for ϵ, $\mathcal{G}(\epsilon)=(\epsilon_0/\pi)/(\epsilon^2+\epsilon_0^2)$, is assumed [2,7] in the following calculation. The validity of the above expression is now discussed. The free parameter N represents the number of the excited B ions. The average magnitude of the EFS induced by one B ion is ϵ_0. The total shift ϵ_T of a given A ion at $t=t_0$ is therefore $\epsilon_T=N\epsilon_0$. As can be seen later, ϵ_T is the most important quantity in fitting the experimental results. In fact, a small variation of N or ϵ_0 with a fixed ϵ_T gives roughly the same curves. However, it does not necessarily mean that N can be arbitrary. N is like a number of steps in a staircase with the fixed initial height ϵ_T and the final height 0. If N is infinity (continuum limit), the staircase becomes the smooth exponential curve. However, this limit gives a kink in the curve $I(t_0)$ when $0<t_0<\tau$. This is because there is always some value of t_0 that satisfies $\phi_j(t_0)=0$ when $0<t_0<\tau$. At this t_0, $I(t_0)$ has a sharp peak, which is quite unrealistic. On the other hand, if N is chosen to be 1, the staircase has only one step. However, as shown later, to explain the experiment for the strong-excitation case we need to have many excited B ions. In the following analysis, we choose $N=20$, i.e., we pick up only the nearest twenty excited B ions that can contribute EFS.

A model calculation is performed for $I(t_0)$ expressed in Eq. (10) and the result is illustrated in Fig. 1. The parameters employed here are $\epsilon_T=40$ kHz, $T_1=2$ ms, $\tau=20$ μs, and $T=$(a) 0, (b) 100 μs, (c) 1 ms, and (d) 5 ms. The behavior of $I(t_0)$ shows clear contrast between short storage ($T\ll T_1$) and long storage ($T>T_1$). For short storage [Figs. 1(a) and 1(b)] $I(t_0)$ at $t_0<0$ is almost as strong as $t_0>t_{\text{echo}}\equiv T+2\tau$. The reason is that in this case the environment can be regarded as static

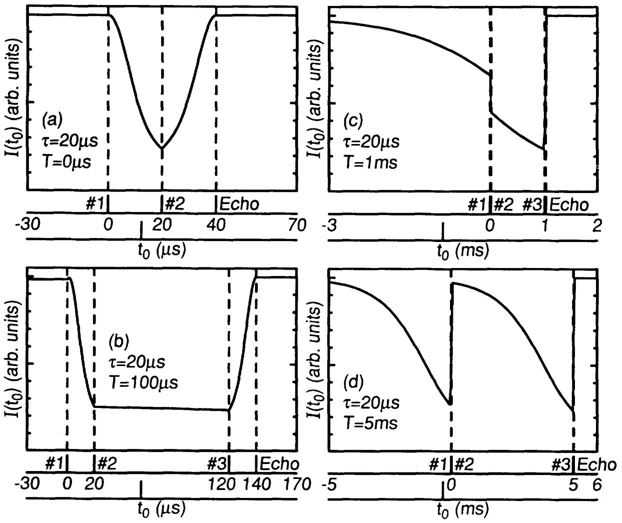

FIG. 1. Numerically calculated echo intensity I as a function of scrambler onset time t_0.

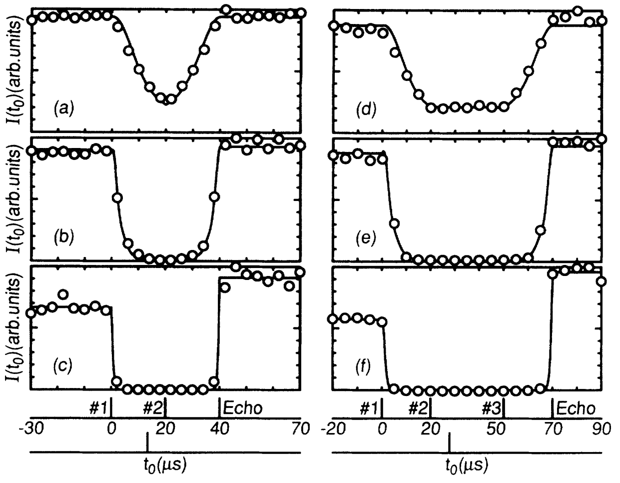

FIG. 2. Experimental plots of $I(t_0)$ (open circles) and least-squares-fit theoretical curves for (a)-(c) two-pulse photon echo and for (d)-(f) stimulated photon echo. Scrambler intensities are (a),(d) 14, (b),(e) 56, and (c),(f) 224 MW/cm^2.

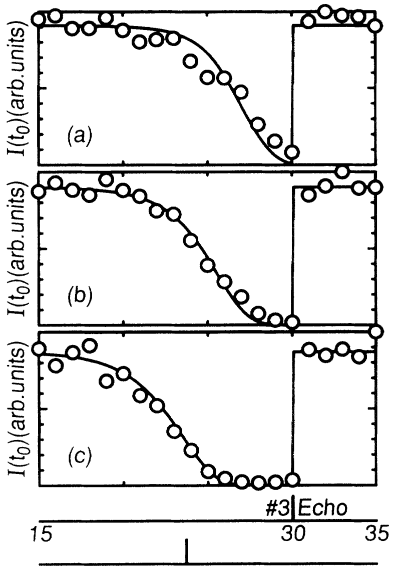

FIG. 3. Expermental plots of $I(t_0)$ (open circles) and least-squares-fit theoretical curves for long storage. First and second pulses are applied at $t=0$ and 20 μs. Scrambler intensities are (a) 11, (b) 45, and (c) 181 MW/cm^2.

during the echo formation. The echo intensity reaches a minimum as t_0 approaches the second pulse, where dephasing occurs with unshifted frequency while rephasing with shifted frequency. The echo stays almost constant during the storage period as long as $T \ll T_1$ and grows again to a maximum at $t_0 = t_{\text{echo}}$. When t_0 is later than the echo, $I(t_0)$ stays constant at this maximum, which is a trivial consequence of causality because a scrambler applied after the echo should not affect the echo intensity.

In the case of long storage [Fig. 1(d)] the behavior of $I(t_0)$ around $t_0=0$ is totally opposite to the previous case, i.e., $I(t_0)$ is at its minimum just before $t_0=0$ and has a maximum at $t_0=\tau$. This is because dephasing with unshifted frequency is required unlike the previous case. The scrambler becomes less and less effective as it moves away from the excitation pulses and finally has no effect when it is further away than T_1.

We now show experimental results. The sample was 0.1-at.% Eu^{3+}:Y$_2$SiO$_5$ (11.5 mm thick), an ideal crystal for the EFS study, because there are two inequivalent optical sites, sites 1 and 2, which give separated absorption spectra [9,10]. This enables independent excitation of the two sites which safely play the roles of A ions and B ions in the theoretical analysis.

A cw ring dye laser (RDL), tuned to the $^7F_0$-$^5D_0$ transition (580.049 nm) of site 2 of this crystal, was gated by a couple of acousto-optic modulators to obtain the stimulated-photon-echo pulse sequence. Typical widths of the three excitation pulses were 1 μs. The laser beam (power ~10 mW) impinged on the crystal sitting in a cryostat at 6 K, and the emitted photon-echo signal was monitored by a photomultiplier tube after a couple of acousto-optic shutters. At the same time a pulsed dye laser (PDL) with a 5-ns pulse width, tuned to the same transition of site 1 (579.879 nm), hit the same spot of the crystal in a noncollinear manner and played the role of the scrambler.

The experiment was performed for the two extreme cases of short-storage times and long-storage times. $I(t_0)$ for short storage is shown in Figs. 2(a) to 2(c) (two-pulse echo, $\tau=20$ μs) and 2(d) to 2(f) (stimulated echo, $\tau=20$ μs and $T=30$ μs) for three different excitation intensities along with least-squares-fit theoretical curves. For theoretical fitting, ϵ_T was 40, 200, 1280, 40, 158, and 800 kHz for 2(a) to 2(f). The agreement between the theory and the observations is quite good. For strong excitation (lower panels), the echo signal was totally unseen whenever t_0 is within the echo formation. Also, the echo intensities at $t_0<0$ are considerably lower than those at $t_0 > t_{\text{echo}}$. This is because, if many B ions are excited, some of them certainly decay back to the ground state even during the echo formation and the environment cannot be regarded as static anymore.

The long-storage case is shown in Fig. 3. The first and second pulses were applied at $t=0$ and 20 μs as before, but the third pulse was at $t=30$ ms with the echo signal 20 μs after that. Owing to the long hole lifetime (> 1 h) of this material [9], the echo signal is still observable even after 30 ms. The scrambler time t_0 was varied from 15 to 35 ms. As expected, the frequency recovery time is about $T_1=2$ ms for weak scrambler intensity and it becomes longer as the intensity increases. For theoretical fitting, ϵ_T was 122, 300, and 1120 kHz for 3(a) to 3(c).

It should be mentioned that the EFS has an important effect on time-domain data storage [10-12]. In this, a time-domain input datum is stored, by, for example, the

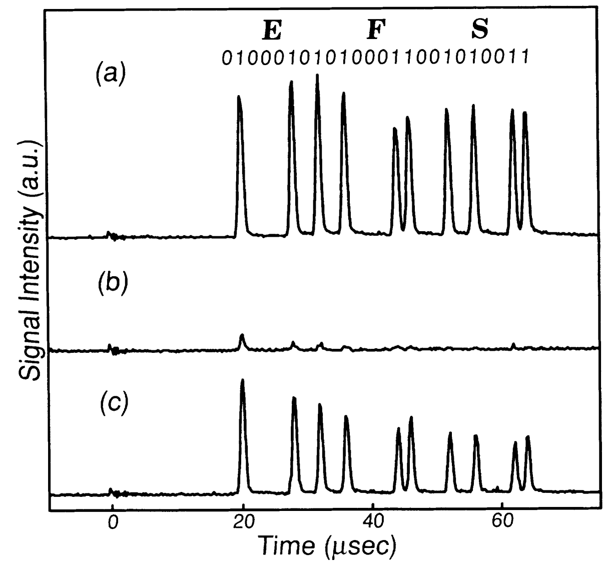

FIG. 4. (a) Accumulated photon-echo wave form after the read pulse (unseen) at $t=0$, representing 24-bit ASCII-coded data "EFS." (b) Scrambler is on just before the read pulse. Read pulse cannot read the stored datum due to shuffled inhomogeneous distribution. (c) Scrambler is again off and echo signal reappears, still keeping the input information.

bit-by-bit storage technique [12], into a medium as the modulated inhomogeneous absorption spectrum. The stored datum can be read out by applying a single read pulse as shown in Fig. 4(a). After this storage, if an environment is changed suddenly by the scrambler, the EFS causes a shuffled inhomogeneous distribution and the meaningful pattern representing the input datum virtually disappears temporarily [Fig. 4(b)]. This shuffled inhomogeneous distribution, though, will return to the original distribution after T_1 and the stored datum reappears [Fig. 4(c)] by another read pulse due to the reconstructed inhomogeneous distribution.

In summary, we have developed a stochastic theory which describes the dynamical properties of the EFS appearing in stimulated-photon-echo measurement. The experimental results undoubtedly indicated the existence of instantaneous EFS and its gradual recovery, consistent with the theoretical prediction. Further study should clarify quantitative aspects of dipole-dipole interaction between impurity ions.

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