Capillary shear flow was also measured in an untreated viscometer of circular cross section (diam = 2 mm) in a vertical field; i.e., with the flow along the helix axis. In this geometry the fluid becomes nearly immobile at lower shear rates, yielding apparent viscosities several orders of magnitude higher than in the isotropic phase. In the absence of the field the flow is still non-Newtonian but the effective viscosity is smaller, indicating that the field helps produce substantially more orientation of the helix axis along the flow. This supports the Helfrich permeation model. Attempts to force flow with high pressure yield a significantly smaller effective viscosity, which we interpret to be a consequence of defect flow. The system does not easily recover from the defect structure; large hysteresis effects are present. The structure is found to cure only after heating to the isotropic phase.

In conclusion, we have observed, for what we believe is the first time, the following confirmations of theoretical predictions: (1) Newtonian capillary shear flow in a cholesteric for flow perpendicular to the helix axis; (2) Newtonian flow near the isotropic-cholesteric phase transition; (3) an oscillatory temperature dependence of the viscosity near T_N.

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Optically Detected Coherent Transients in Nuclear Hyperfine Levels

R. M. Shelby, C. S. Yannoni, and R. M. Macfarlane
IBM Research Laboratory, San Jose, California 95193
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Using optical detection, we have observed rf nutation, free-induction decay, and echoes, on the 16.70-MHz nuclear hyperfine transition of dilute Pr^{3+} in LaF_3 at 2 K. From a comparison of free-induction decay and echo decay we find that the previously observed linewidth of 200 kHz is inhomogeneous and that the homogeneous width is 19 kHz. On the basis of these measurements it is suggested that optical dephasing times for the $^1D_2 \leftrightarrow {}^3H_4$ and $^3P_0 \leftrightarrow {}^3H_4$ transitions are as long as $\sim 20\,\mu$sec.

Coherent-transient techniques in pulsed NMR have proven themselves in recent years to be a very effective means of studying magnetic interactions in solids.[1] In particular they have elucidated the way in which these interactions contribute to homogeneous and inhomogeneous broadening,[1,2] thus allowing high-resolution measurements to be made in inhomogeneous environments.

It is known that optical detection can substantially improve the sensitivity of magnetic-resonance experiments, providing a simple method of studying dilute-spin systems.[3] This idea has found widespread application in ESR[3] and electron-nuclear double resonance[4] and has recently been demonstrated in solid-state NMR.[5] In this paper we report the extension of optical-detection techniques to the study of rf coherent transients in nuclear hyperfine levels. Because of its greatly enhanced sensitivity, it should significantly expand the application of these techniques to dilute-spin systems where nuclear polarization can be induced by optical pumping.

We have chosen to illustrate these techniques with a system of great current interest, viz. LaF_3:Pr^{3+}. Optical-dephasing (i.e., T_2) measurements have been carried out on $^1D_2 \leftrightarrow {}^3H_4$ (Refs. 6–8) and $^3P_0 \leftrightarrow {}^3H_4$ (Refs. 8–10) transitions using a variety of laser techniques. Although laser

frequency instabilities often limit the resolution which can be achieved,[6,7] it seems clear that nuclear hyperfine interactions are prime candidates for the source of optical dephasing at very low temperatures. (Specifically, the nuclear dipolar interaction between the ^{141}Pr nucleus and the surrounding ^{19}F and ^{139}La nuclei.) As a necessary step in establishing this, it is important to characterize the static and dynamic hyperfine interactions independently. A specific example is the $^1D_2 \rightarrow {}^3H_4$ transition at 5925.2 Å, where Erickson[11] has proposed that the optical linewidth at 2 K is 200 kHz and corresponds to the difference in the width of the hyperfine levels in the ground and excited states. He has measured a width of 180 ±10 kHz in the ground state.[5] Using optically detected coherent transients [echo and free-induction decay (FID)] we show that this width is in fact inhomogeneous and that the homogeneous width is an order of magnitude smaller. This has the implication that the homogeneous width of the optical transition is much less than 200 kHz. Optical FID measurements have already suggested that this may be the case.[7]

The relevant energy-level diagram for the 5925.2-Å transition is shown in Fig. 1. The optical detection scheme is that used by Erickson[5] in his rf absorption measurements. In the case of the 16.7-MHz hyperfine splitting, a large nuclear polarization is produced by pumping, say, the $2 \rightarrow 2'$ transition and transferring population to 3, for example, by the relaxation $2' \rightarrow 3$. [The laser linewidth of ≤ 2 MHz is less than the hyperfine splittings in the ground (8.47 and 16.7 MHz)[5] or excited (3.7 and 4.7 MHz)[11] states so that a single transition is pumped for any given ion.] This burns a hole, and the absorption of light decreases. The application of rf pulses at 16.7 MHz transfers population between levels 2 and 3, and this can be detected by the change in optical absorption. However, since this detection scheme monitors the populations of the hyperfine levels, only the z component of the nuclear magnetization (or in this case the pseudomagnetization) can be optically detected. Transient effects such as free-induction decay or spin echo, which are associated with coherence of the precessing moments in the x-y plane cannot be observed directly. A similar situation exists in the case of optically detected magnetic resonance in excited triplet states of organic molecules. It was shown by Harris and co-workers[12] that the problem could be surmounted by the use of a $\pi/2$ probe pulse to rotate the coherent component of the magnetization to the z axis in order to observe its magnitude. The coherent transient can then be mapped out point by point in time.

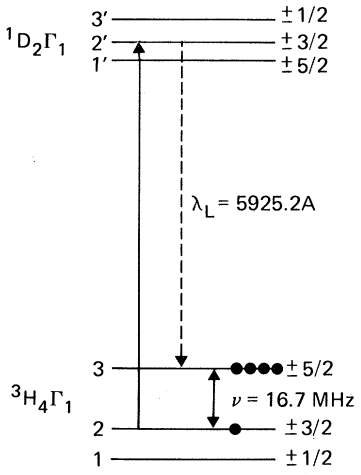

FIG. 1. Energy level diagram for the 5925.2-Å transition of LaF_3:Pr^{3+} showing one optical pumping pathway. The laser connects the levels $2 \rightarrow 2'$, and nuclear polarization is produced by the relaxation $2' \rightarrow 3$ (see Ref. 11). The rf coherent transients are detected by the change in optical absorption produced by the nuclear population changes.

A $2 \times 2 \times 3$-mm^3 sample of LaF_3:Pr^{3+} (0.05 at.%) was mounted with its c axis parallel to the rf magnetic field in a coil tuned for 16.7 MHz and immersed in a liquid helium cryostat. The absorption of the laser was monitored either directly with a photodiode or by the fluorescence detected at 90° by a photomultiplier. For some experiments the full power (50–100 mW) of the laser was used continuously, while for others it was attenuated by $\sim 10^4$ to minimize optical pumping during the period in which the rf pulse sequence was applied. A 50-W rf amplifier provided field strengths of up to 45 G.

A typical optically detected transient nutation signal is shown in Fig. 2(a). This signal was obtained by monitoring laser transmission while applying a 100-μsec rf pulse. The decay of the nutation is quite long (~ 40 μsec for an rf field of 39 G) and appears to be dominated by the rf-field inhomogeneity of about 2%. This result is to be expected[13] since the Pr-F and Pr-La interactions are averaged to zero by the rapidly nutating Pr leaving only the width due to homonuclear Pr-Pr interactions (estimated to be <100 Hz). Measurements of the nutation frequency as a function of rf field strength yields a value of 13.3 kHz/G for

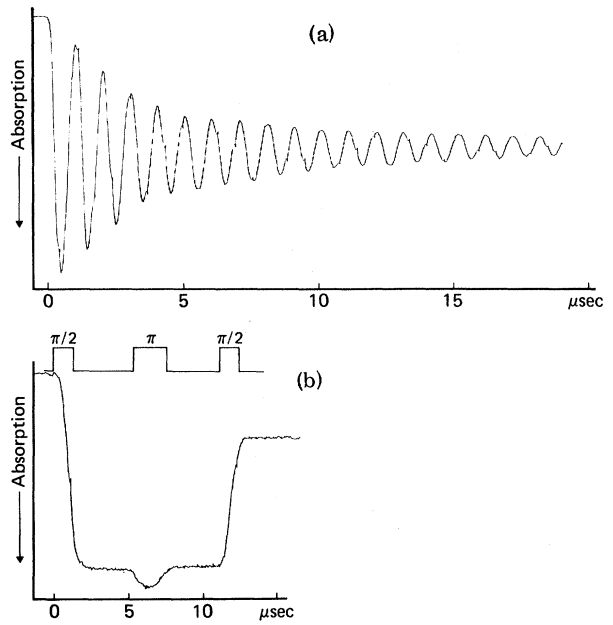

FIG. 2. (a) Optically detected transient nutation (ν = 200 kHz) for the 16.7-MHz hyperfine transition of $LaF_3:Pr^{3+}$ at 2 K. The rf field strength H_{rf} is 18 G. (b) The pulse sequence and observed signal is shown for the optically detected spin echo at 3 K. For this sequence $\tau = \tau' = 6$ μsec, and $H_{rf} = 18$ G. The "bump" in the signal during the π pulse is due to imcomplete "fanning out" of the magnetization and is equivalent to the FID signal at $t = \tau$.

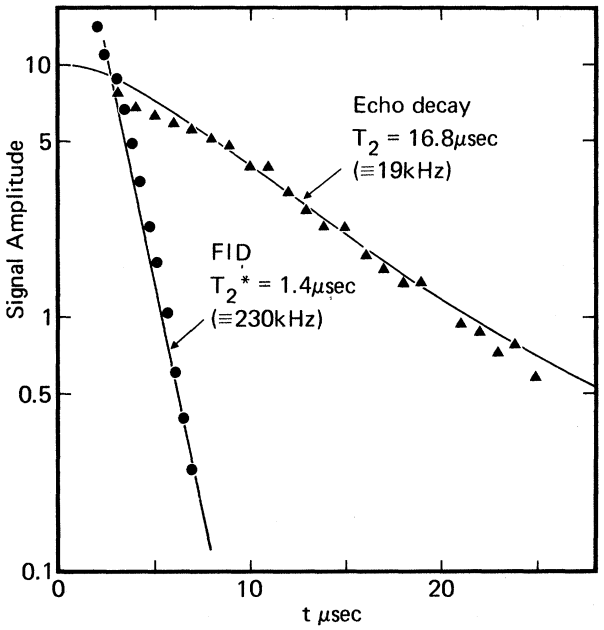

FIG. 3. FID and echo decay for the 16.7-MHz transition of $LaF_3:Pr^{3+}$ at 2.0 K. For the echo, the solid line is calculated using Eq. (5.7) of Ref. 15.

the 16.7-MHz transition. A similar measurement for the 8.47-MHz transition gives 10.8 kHz/G. This is almost as large as the enhanced nuclear moment of 23 kHz/G observed for static fields.[5]

The nutation frequency was used to determine the appropriate pulse widths for $\pi/2$ and π pulses used in the FID and spin-echo pulse sequences. The FID experiment consists of two $\pi/2$ pulses separated by a time interval t, the rf field being sufficiently strong to excite the entire line. The change in laser absorption induced by the second $\pi/2$ pulse represents the magnitude of the precessing magnetization (i.e., the FID signal) at time t. This signal decays as the magnetization "fans out" as a result of the inhomogeneous distribution of local fields. We find a decay time of $T_2^* = 1.4 \pm 0.15$ μsec (see Fig. 3), corresponding to a linewidth of 230 ± 25 kHz which is close to Erickson's measured spectral linewidth of 180 ± 10 kHz.[5]

The spin-echo pulse sequence consists of length $\pi/2$, π, and $\pi/2$ separated by intervals τ and τ'. This sequence together with the experimentally observed changes in laser absorption is shown in Fig. 2(b). This differs from the FID experiment in the presence of the π pulse which removes the effects of inhomogeneous dephasing by refocusing the magnetization at $t = 2\tau$. The change in laser absorption induced by the third pulse gives the amplitude of the echo signal at $t = \tau + \tau'$ and is maximum when $\tau = \tau'$. To trace out the echo shape, the signal is plotted as a function of τ' for a fixed value of τ. To obtain the echo decay, we set $\tau = \tau'$ and plot the signal as a function of τ. This procedure gives an approximately exponential decay over about $1\frac{1}{2}$ orders of magnitude with a decay time corresponding to $T_2 = 16.8$ μsec, i.e., to a linewidth of 19 kHz. This is an order of magnitude narrower than the inhomogeneous width and is independent of laser intensity.

The very good signal-to-noise ratios possible with this method are evident in the experimental data shown in Fig. 2. These data were obtained by monitoring the laser intensity transmitted by the sample with a photodiode. The peak of the inhomogeneous optical line corresponded to absorption of about 8% of the laser light. The hole burned by the laser reduced this value to about 2% and application of a π pulse to the 16.7-MHz transition "refilled the hole" more than half way. Thus, the nutation signal in Fig. 2(a) corresponds to several-percent modulation of the transmitted

laser intensity (or 300–400% modulation of the fluorescence). The transient nutation of the 8.47-MHz transition was observed, but the signal corresponded to at least a factor of 5 less modulation of the laser absorption, apparently because a smaller nuclear polarization is induced by the optical pumping for this transition.

A comparison of the FID and echo data (Fig. 3) clearly shows that the nuclear hyperfine transition is inhomogeneously broadened. The inhomogeneous linewidth of ~200 kHz corresponds to the distribution of local fields felt by the various Pr nuclei as a result of Pr-F dipolar interactions. On the other hand, the relatively long phase-memory time measured by the echo decay implies either that the major part of this interaction must be effectively static in nature, or that the rate of modulation of the local fields due to fluorine mutual spin flips must be very small. These spin flips occur at a rate given by the fluorine T_2 which has been measured in LaF_3 to be 17 μsec.[14] We calculated the spin-echo decay based on one[15] of several models[2,15-17] which incorporate the effects of spectral diffusion. Using the fluorine T_2 of 17 μsec and a fluctuating local field of magnitude $\delta = 50$ kHz we obtain good agreement with the echo decay curve (see Fig. 3). Note that δ is much less than the inhomogeneous linewidth. This is interpreted as evidence that the nearest-neighbor fluorines are unable to take part in resonant flip-flop processes because of detuning by their proximity to the Pr^{3+} ion. This effect is well documented in the case of electron-spin resonance[17] and might be expected to be important here due to the large enhanced nuclear moment of Pr.[5,18] Thus, the fluorine fields which account for the bulk (200 kHz) of the Pr-F interactions are effectively static, and the fluctuating part of the local field is much smaller (50 kHz).

With these experiments in mind, it would seem important to take the inhomogeneity of the Pr-F interaction into account when estimating the contribution of these interactions to optical dephasing times. It is reasonable to expect that the optical linewidth contribution due to Pr-F interactions is directly related to the difference between the ground- and excited-state broadening of the hyperfine levels.[5,11] The large inhomogeneity of the hyperfine transition indicated by the nuclear FID and echo data presented here implies a similar inhomogeneity for the nuclear contribution to the optical linewidth. The homogeneous part of this linewidth measured by third-order optical-FID or photon-echo experiments at ~2 K is expected to be on the order of 20 kHz, the width implied by the echo decay of the hyperfine transition. This is an order of magnitude narrower than any homogeneous optical width derived for this system so far, suggesting that instrumental contributions to the optical measurements are significant.[6,7]

In conclusion, we have demonstrated the optical detection of nuclear coherent transients. Further, we have shown their utility in understanding magnetic interactions in $LaF_3:Pr^{3+}$ and discussed implications of these results for optical dephasing experiments.

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