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Brief Reports

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Photon-echo nuclear double resonance in $LaF_3:Pr^{3+}$

K. Chiang,* E. A. Whittaker, and S. R. Hartmann
Columbia Radiation Laboratory, Department of Physics, Columbia University, New York, New York 10027
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Using the photon-echo-nuclear-double-resonance technique, we have measured the nuclear hyperfine splittings in the excited $^1D_2$ state of $LaF_3:Pr^{3+}$. Our measurements are in agreement with the results obtained by Erickson from his saturated-and-enhanced-absorption study of the $^3H_4$-$^1D_2$ transition in $LaF_3:Pr^{3+}$.

Photon-echo modulation in $LaF_3:Pr^{3+}$ has been a valuable source for obtaining the various spectroscopic and relaxation parameters associated with the $^3H_4$-$^3P_0$ transition.[1] This technique when applied to the $^3H_4$-$^1D_2$ transition, however, has only had modest success.[2] In particular, echo modulation data taken in the standard manner are not altogether consistent[3] with the measured excited-state splittings as obtained by Erickson.[4,5] It was therefore felt that an independent measurement of the $^1D_2$ excited-state splittings was necessary to build confidence in their accuracy. To this end we have performed a photon-echo-nuclear-double-resonance (PENDOR) experiment[6] on the $^3H_4$-$^1D_2$ transition of this system.

The PENDOR technique was first applied to the measurement of energy splittings of ^{13}Al nuclei in a single crystal of ruby, and was used to obtain the interaction parameters of the Cr^{3+} ion with its surrounding nuclear neighbors in both the ground $^2A_4$ and excited $^2E(\bar{E})$ states of ruby.[7] Until our use of this technique to measure nuclear hyperfine splittings in $LaF_3:Pr^{3+}$, PENDOR had not been applied to the study of any material other than ruby.

A PENDOR experiment may be summarized as follows: Three laser pulses of resonant radiation are made incident on a sample to produce a stimulated photon echo, with a pulsed rf field applied to the sample during the interval between the second and third pulses. When the rf field is resonant with a nuclear transition in either of the two terminal levels of the echo transition, there will be a degradation of the echo intensity. This decrease in echo size is the double resonance signal. As is generally true in optical-rf double-resonance experiments, one obtains a sensitivity greatly increased over purely NMR or optical methods for several reasons. With PENDOR, the resolution is limited not by the linewidth of the laser used, as was the case in Erickson's enhanced-and-saturated-absorption method,[4] but only by the length of time over which the rf field is applied to the sample. Secondly, there are no ambiguities in the interpretation of the observed line shape. For example, in order to obtain the true inhomogeneous line shape of the nuclear transitions in the $^1D_2$ state in $LaF_3:Pr^{3+}$, Erickson had to deconvolve the measured line shape from the linewidth of the laser that he used. The inferred linewidths are quite sensitive to whether the measured line shape is assumed to be Gaussian or Lorentzian. A third and important advantage of PENDOR is that it can be used to study nuclear hyperfine structure in excited states of ions in solids that are not accessible to cw dye lasers because of power or spectral range considerations.

Stimulated photon echoes were produced on the transition (592.5 nm) connecting the lowest levels of the crystal-field-split components of the $^3H_4$ and $^1D_2$ states. These levels are electronic singlets that are further split into three doubly degenerate nuclear levels by the combined influence of the Pr^{3+} nuclear quadrupolar and second-order magnetic hyperfine dipolar interactions. The previously measured[1,4] nuclear splittings for both the $^3H_4$ and $^1D_2$ states are small compared to the 10-GHz bandwidth of the laser excitation pulses. The timing sequence for a PENDOR experiment is shown in Fig. 1.

Our experimental setup utilized two independently triggered nitrogen-laser-pumped dye lasers, which produce multiple-kW, 5-nsec-long pulses in a bandwidth of approximately 10 GHz. The output of one of the lasers was divided into two beams of roughly equal intensity by beam splitter BS (see Fig. 2). One beam was steered into an optical delay line (consisting of a White cell with spherical mirrors having radius of curvature equal to 2.9 m), while the

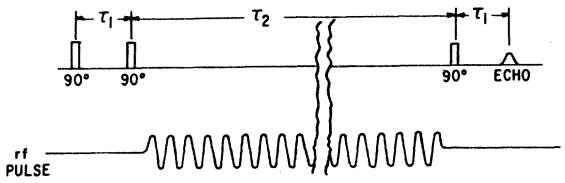

FIG. 1. Laser and radio-frequency excitation pulses for PENDOR experiment.

other was combined and made collinear with the output of the second laser by beam combiner BC1. The delayed beam from the White cell was then combined with the other two beams at BC2. The temporal separation between laser pulses 1 and 2 was adjusted to be 130 nsec, and the separation between pulses 2 and 3 was adjusted to be either 20 or 40 μsec. The three collinear pulses were focused to a 100-μm-diameter spot in the sample by a 20-cm-focal-length lens. The sample, whose Pr^{3+} concentration was 1.0 at. wt.%, had a thickness of 2.5 mm, and was mounted in a cryostat that was maintained at a temperature of 2.5 K. The c axis of the crystal was perpendicular to its optically buffed surface, and parallel to the direction of propagation of the laser pulses. The rf pulse was applied to the sample by means of a 1-μH, 4-mm-diameter coil consisting of 10 turns of 30-gauge copper wire wound about the sample in such a way that the oscillating rf field was parallel to the crystal c axis. The coil was energized by a broadband 3-W amplifier (ENI model 300 L) driven by a Hewlett-Packard frequency synthesizer whose output

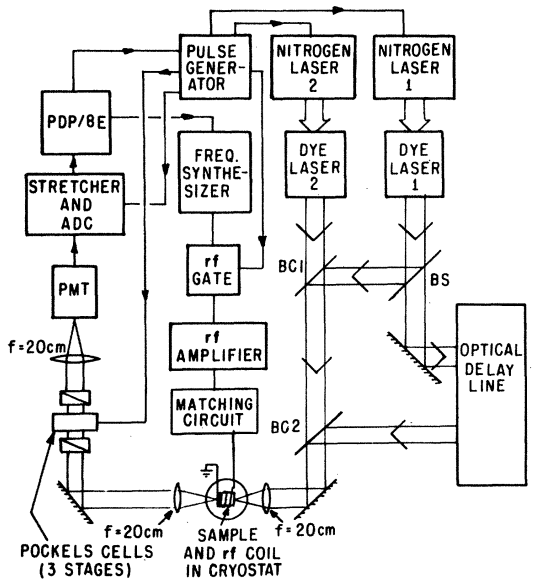

FIG. 2. Experimental arrangement for PENDOR measurements. See text for detailed explanation.

was gated on between the second and third laser pulses. The rf gating circuit was triggered by a multipulse-generator unit that was interfaced to a PDP 8/e minicomputer, making it possible to gate the rf field on and off under program control. The output of the frequency synthesizer was also controlled by the PDP 8/e. To enhance the rf field at the sample, an impedance matching circuit was inserted between the rf amplifier and the coil at the sample. After passing through the sample, the laser beams were recollimated by another 20-cm-focal-length lens and then directed into an RCA-C31034 photomultiplier tube (PMT). The three excitation pulses were prevented from saturating the PMT by three stages of crossed polarizers and Pockels cells that were pulsed open about 30 nsec before the arrival time of the stimulated echo. The output of the PMT was amplified and fed into a gated stretcher and then directed to an analog-to-digital converter. To eliminate the effects of long-term drift in the echo signal due to changes in laser intensity or optical alignment, the rf field was alternately gated on and off, with the computer separately averaging the stimulated photon echo intensity for the two cases. The average was taken over 200 shots. The value of $(I_{rf}-I_{nrf})/I_{nrf}$, where $I_{rf}(I_{nrf})$ stands for the echo intensity with (without) the rf field gated on, is then printed out by the computer as a function of rf frequency. The Q of our matching circuit was ~ 100 and we had to adjust the matching circuit capacitors whenever the frequency was changed.

Figure 3 shows the percentage decrease in the stimulated photon echo intensity as a function of the applied rf frequency. The dips at 3.7 and 4.65 MHz correspond to the energy splittings in the excited $^1D_2$ state, and agree well with Erickson's reported values of 3.7 and 4.7 MHz.[4] Our measured linewidths of 350 kHz [full width at half maximum (FWHM)] for the two resonances are, however, larger than the 200 $\pm$50-kHz linewidth that he reported.[8] This discrep-

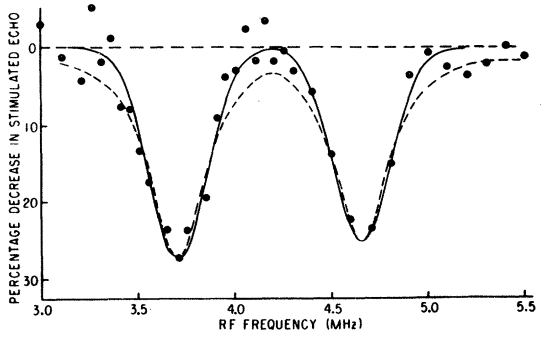

FIG. 3. PENDOR resonance curve, showing $^1D_2$ excited state splittings in $LaF_3:Pr^{3+}$.

ancy can perhaps be explained by the suppositon that the 200-kHz linewidth he inferred is a consequence of his assuming a Lorentzian line shape for deconvolving the observed line shape from the laser line shape. For a Gaussian line shape, the inferred linewidth can be a factor of 2 larger.[9] In Fig. 3 the solid and dotted lines are Gaussian and Lorentzian fits, respectively, to the data points with a (FWHM) linewidth of 350 kHz. The quality of our data prevents our preferring one over the other, but since a large part of the inhomogeneity of the nuclear hyperfine levels is due to the perturbing effects of eleven ^{19}F neighbors,[10] one would expect the linewidth to be Gaussian rather than Lorentzian.

Previous work which Fourier analyzed photon-echo-modulation data for the $^3H_4$-$^3P_0$ transition[1] has shown that the inhomogeneous linewidth of the nuclear transitions in the $^3P_0$ state is approximately 20 kHz, while the inhomogenous linewidth of the $^3H_4$ ground state is approximately 200 kHz. For the $^3P_0$ state, $J=0$, and the linewidth is due primarily to the static dipolar and quadrupolar interactions of the ^{141}Pr nucleus with the neighboring ^{19}F nuclei and the electric field gradient at the ^{141}Pr site, respectively. For the $^3H_4$ state, $J=4$ and the close spacing of the crystal-field-split levels of the $^3H_4$ multiplet gives rise to an enhanced nuclear moment that interacts strongly with the surrounding nuclear neighbors and leads to an increased linewidth. In like manner the $^1D_2$ multiplet levels are broadened beyond the 20-kHz width of the $^3P_0$ state. According to a second moment calculation, the contribution to the inhomogeneous linewidth from the unenhanced Pr-F nuclear dipolar interaction is 13 kHz.[11] When we take into account the experimentally determined enhanced nuclear gyromagnetic ratio of $\gamma/2\pi = 10$ kHz/G for the $^1D_2$ state[11,12] we obtain an inhomogeneous linewidth of approximately 120 kHz. The contribution from other sources such as lifetime broadening (~ 600 Hz) and phonon processes (~ 800 Hz) (Ref. 4) are negligible. Since we typically used rf pulses 20-μsec long, the contribution to the linewidth due to the finite duration of the rf field is 8 kHz. The remaining 220 kHz of the measured 350-kHz linewidth that must be accounted for is possibly due to rf power broadening.

In conclusion, using a photon-echo nuclear-double-resonance technique, we have shown that the nuclear splittings in the $^1D_2$ state, as inferred by Erickson from his saturated-and-enhanced-absorption study of the $^3H_4$-$^1D_2$ transition in LaF_3:Pr^{3+}, are correct.

ACKNOWLEDGMENTS

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*Present address: IBM Research Laboratory, San Jose, Calif. 95193.

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[5] It also seemed something of a coincidence that the excited-state splittings of 3.7 and 4.7 MHz should almost sum to the well-verified 8.47-MHz ground-state splitting. See Refs. 3, 4, and 9.

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