Two-photon transition from $^3H_4$ to $^1S_0$ of Pr^{3+} in LaF_3

C. D. Cordero-Montalvo* and N. Bloembergen

Division of Applied Sciences, Harvard University, Cambridge, Massachusetts 02138

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A direct two-photon absorption between crystal-field components of the $^3H_4$ ground-state configuration to the highest excited state $^1S_0$ in the $4f^2$ manifold of Pr^{3+} in LaF_3 has been observed. The magnitude of the intensities and the polarization dependence require a third- and fourth-order theoretical analysis, similar to that developed for two-photon absorption of Gd^{3+} in LaF_3.

The importance of crystalline-field and spin-orbit perturbations of the virtual $4f^{n-1}5d$ intermediate states in the two-photon transitions between initial and final states belonging to the $4f^n$ configuration of Gd^{3+} in LaF_3 has been demonstrated by Downer and co-workers.[1-3] It is the purpose of this Rapid Communication to report a similar situation for the highly forbidden $^3H_4 \rightarrow {}^1S_0$ transition of Pr^{3+} in LaF_3, which involves $\Delta J = 4$, $\Delta L = 5$, and $\Delta S = 1$. A direct linkage between these two states can be mediated by the fourth-order matrix element

$$\sum_{l,m,n} \Delta_l^{-1}\Delta_m^{-1}\Delta_n^{-1} \langle g|\vec{E}\cdot\vec{D}|l\rangle \langle l|V_{cr}|m\rangle \langle m|V_{SO}|n\rangle \langle n|\vec{E}\cdot\vec{D}|f\rangle .$$

Here l, m, and n denote states in the $5d$ manifold, with respective energies Δ_l, Δ_m, and Δ_n above the ground state. $\vec{D} = \sum e_i \vec{r}_i$ is the electric dipole moment operator, V_{cr} is the crystalline-field potential which couples terms up to $\Delta L = 6$, and V_{SO} is the spin-orbit interaction.

The $^1S_0$ is the highest level of the $4f$ configuration, but for Pr^{3+} in LaF_3, it lies still about 3000 cm^{-1} below the $4f^{n-1}5d$ manifold. The energy level diagram[4,5] is presented in Fig. 1 in low resolution. Carnall, Fields, and Sarup[4] observed with one-photon uv spectroscopy that the $^1S_0$ lies at 46 985 cm^{-1} above the ground state. Yen, Levey, Huang, and Lai[6] reached this level by first populating the intermediate D levels with one-photon absorption, followed by a two-photon transition. They quote its position as 46 965 cm^{-1}.

We have observed the level in a direct two-photon transition from the ground state in a LaF_3 crystal, containing 0.5% Pr^{3+}, obtained from Optovac Inc. The experimental arrangement is the same as that described previously[2] for the study of Gd^{3+} two-photon absorption in LaF_3. In brief summary, a pulsed nitrogen laser pumped a dye laser of the Hänsch design at a repetition rate of 10 Hz. Tunable pulses of 0.5-ns duration and 0.15-mJ energy were focused with a 1-cm focal length lens into the crystal, which was kept in a Dewar at 77 K. The light propagation vector $\vec{k}$ was either parallel or perpendicular to the c axis. The following three polarization configurations which propagate in the birefringent crystal without change were used: $\vec{k}\|c, \vec{E}\perp c$ linearly polarized, $\vec{k}\|c, \vec{E}$ circularly polarized, and $\vec{k}\perp c, \vec{E}\|c$. The laser frequency was scanned over the range $2\nu = 46\,700-47\,100$ cm^{-1}. The ultraviolet fluorescence by one-photon transitions from the $^1S_0$ to the $^1G_4$ and $^3F_4$ multiplets was detected in the ranges 268–274 and 250.3–250.8 nm, respectively. This uv radiation was collected at right angles to the laser beam and detected by an EMI 9635 QB

photomultiplier with suitable bandpass filters. These fluorescent transitions from $^1S_0$ are strong and have been studied by Elias, Heaps, and Yen,[7] who pumped the $5d$ configuration with synchrotron radiation.

Figure 2 presents the experimental two-photon excitation recordings for three polarizations of the excitation beam.
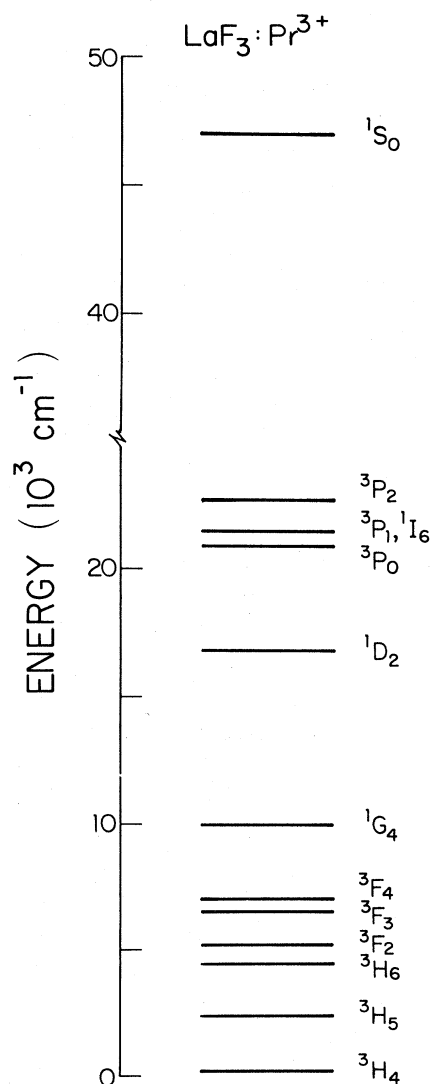
FIG. 1. Energy level diagram for Pr^{3+} in LaF_3. Only centers of gravity of each multiplet are shown.
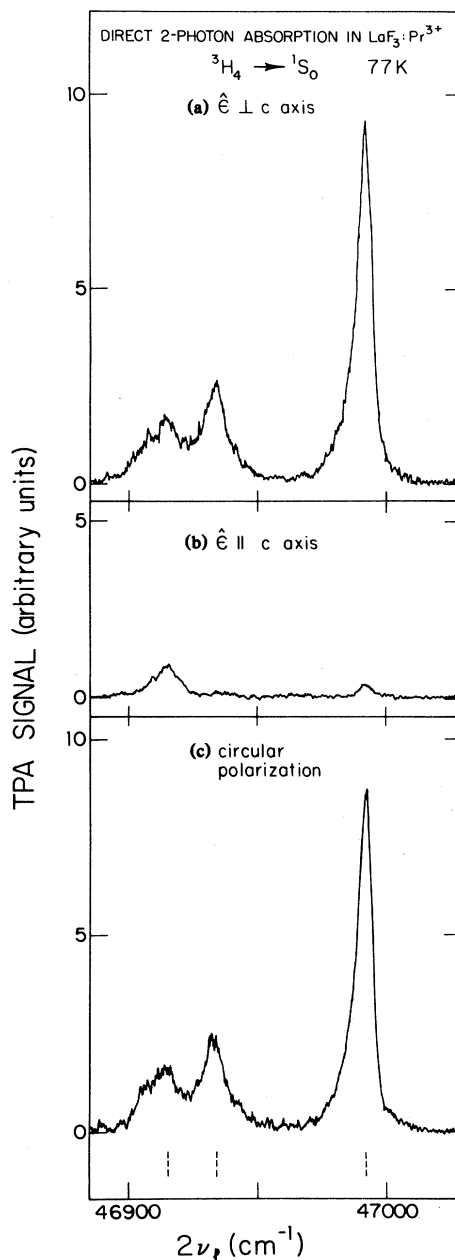
FIG. 2. Experimental two-photon excitation recordings of the $^1S_0$ level in Pr^{3+}:LaF$_3$ at 77 K for three polarizations of the excitation beam. Vertical marks on the horizontal axis show the experimental component positions as obtained by one-photon spectroscopy.

The vertical scale indicates the two-photon absorption (TPA) intensity in arbitrary units on an internally consistent scale. A determination of the variation of the fluorescence signal on incident intensity yielded a square law dependence. The position of the $^1S_0$ level was measured to be $46\,990 \pm 2$ cm^{-1}. This figure is in close agreement with the value re-

ported by Carnall et al.[4] The dye laser wavelength was determined with a one-meter Jarrell-Ash spectrometer calibrated against several lines from a Spectra Physics Model 171 argon laser.

In addition to the main line, there are two weaker lines displaced towards lower frequencies. These same lines have been observed in one-photon spectroscopy. Their intensity increases with temperature, and they arise from thermally populated components in the $^3H_4$ multiplet.

An additional line, of intensity smaller than that of the temperature-induced lines, was observed when filters were placed in front of the photomultiplier to allow fluorescence detection in the range 3400–4000 Å, found by Elias et al.[7] to be the strongest of those originating at $^1S_0$. The intensity of this additional line, which is located at $46\,965$ cm^{-1}, vanishes for $\vec{E} \perp c$. Its origin is unknown and it may be caused by an impurity.

The selection rule violation reported is analogous to those in several $^8S_{7/2} \rightarrow {}^6I$ transitions in Gd^{3+} observed by Downer. These and other transitions in this ion exhibit strong anisotropic features. He has given a detailed interpretation[2] based on crystal-field–induced admixtures among the multiplets of the $4f$ configuration. The admixed states may be connected by matrix elements of lower order, while the pure configurations are linked by the fourth-order element cited above. There is then an interference in the total matrix element responsible for the transition, which is constructive for $\vec{E} \perp c$ and destructive for $\vec{E} \parallel c$. For a transition to a final state with total angular momentum quantum number $J = 0$, it can be shown that, due to their azimuthal quantum number (M) dependence, the individual matrix elements vanish for $\vec{E} \parallel c$, unless the initial-state component has $M = 0$. For the latter case the total element must be evaluated, as is the case for the other polarizations. Reid and Richardson[8] have recently shown that ligand polarization effects lead to similar results.

Figure 2 shows that, in fact, a marked reduction in intensity, compared to the $\vec{E} \perp c$ or circular polarization measurements, is obtained when $\vec{E} \parallel c$. An analysis that takes into account the quantum number assignments of the $^3H_4$ Stark sublevels would be of assistance to elucidate the contribution made by the nonvanishing matrix elements to the observed intensity versus polarization dependence. In this regard, we point out that the contribution to the line strength due to the initial- to final-state direct linkage can be as large as that due to the linkage via admixed states, since the effective order of the corresponding terms may be comparable. Our observations thus suggest that terms arising from both third-order and fourth-order interactions will occur in a treatment that explains satisfactorily the behavior of the intensity of the $^3H_4$ to $^1S_0$ transition. Elaborate calculations beyond the scope of this note would be needed to verify this interpretation.

*On leave from Departamento de Matemática y Física, Colegio Universitario de Cayey, Cayey, Puerto Rico 00633.

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