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Cooperative energy transfer among Pr^{3+} ions in LaF_3

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We report the discovery of population in the $^1S_0$ state (46 986 cm^{-1}) of Pr^{3+} following the excitation of the $^3P_0$ state (20 925 cm^{-1}) by a 477.8-nm pulse laser. The energy upconversion is attributed to a cooperative energy transfer from a pair of Pr^{3+} ions in the $^3P_0$ state to a nearby ion in the same state. A PrF_3 crystal and three LaF_3:Pr^{3+} crystals doped with 10, 20, and 60 at. % Pr^{3+} are tested in our experiment. The lifetime of the $^1S_0$ state and the decay of the $^3P_0$ state of each of the crystals are investigated. The results are used to solve the rate equations for calculating the temporal variations of the populations in the $^1S_0$ state in different crystals. The calculated result agrees with the measured variation of the uv emission ($^1S_0 \rightarrow {}^3P_1 + {}^1I_6$, 393 nm).

I. INTRODUCTION

We have found that ultraviolet lines from the $^1S_0$ state of Pr^{3+} (see Fig. 1) can be generated through the excitation of the $^3P_0$ state by a 477.8-nm pulsed laser, even though the energy needed to excite the $^1S_0$ state is more than can be supplied by two of the visible photons. The energy upconversion is attributed to a three-ion interaction, termed cooperative energy transfer, in which the two donor ions and the acceptor ion participating are all Pr^{3+} in the same excited state ($^3P_0$). Through this interaction process the two donor ions can de-excite to $^1G_4$ (9716–10 499 cm^{-1}) and $^3F_2$ (5136–5280 cm^{-1}) states while releasing enough energy to upconvert the acceptor ion to the $^1S_0$ state with an excess of 10–1000 cm^{-1} (see Fig. 2). This process can be expressed by the equation

$$D(^3P_0)+D(^3P_0)+A(^3P_0) \rightarrow D(^1G_4)+D(^3F_2)+A(^1S_0)\ , \quad (1)$$

in which D denotes donor ion and A denotes acceptor ion.

Cooperative energy transfer among rare-earth ions has been studied since the 1960s.[1] However, three-body cooperative effects have been reported in only one system which contained a pair of Yb^{3+} ions in the excited state ($^2F_{5/2}$) as the donors and a Tb^{3+} ion in the ground state as the acceptor. Livanova, Saitkulov, and Stolov[2] observed luminescence due to transitions from $^5D_4$ (20 400 cm^{-1}) level of Tb^{3+} ions when exciting the $^2F_{5/2}$ (10 200 cm^{-1}) level of Yb^{3+} in single crystals of CaF_2 and SrF_2 activated with Tb^{3+} and Yb^{3+}. The decay of the luminescence was in agreement with their calculated time dependence based on the energy-transfer theory. Ostermayer, Jr. and VanUitert[3] investigated the correlation between the Tb $^5D_4$ intensity and the Yb $^2F_{5/2}$ and Tb $^5D_4$

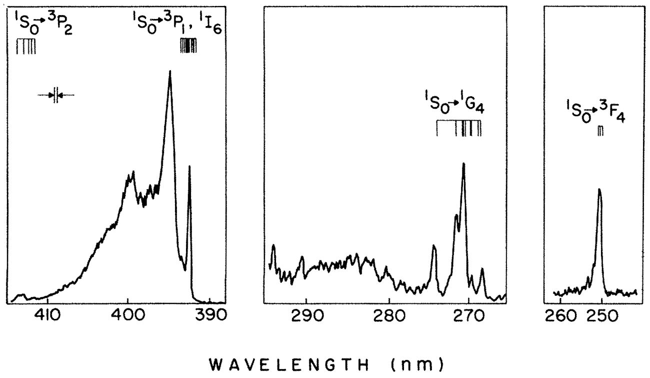

FIG. 1. Ultraviolet spectra due to transitions from $^1S_0 \rightarrow {}^3P_1$, $^1I_6$, $^1G_4$, and $^3F_4$, following the excitation of the $^3P_0$ state of Pr^{3+}.

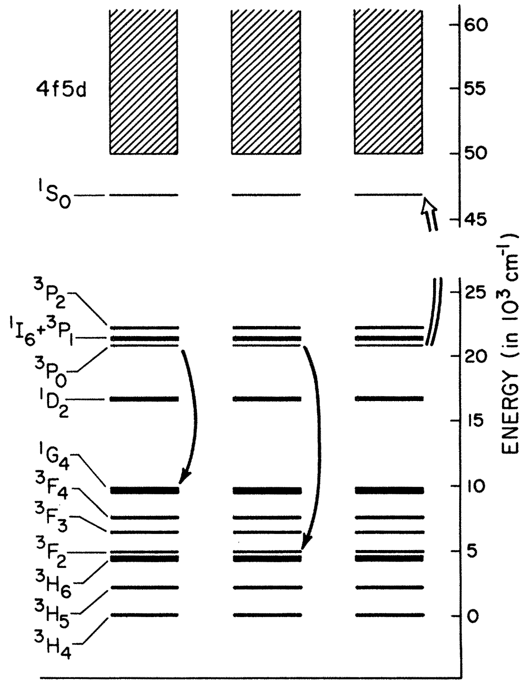

FIG. 2. Schematic representation of cooperative energy transfer. The two donor ions (left and middle) de-excite from $^3P_0$ to lower levels ($^1G_4$ and $^3F_2$, for example) and transfer the released energy to upconvert the acceptor ion (right) to its $^1S_0$ state.

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lifetimes as a function of Tb concentration to verify the cooperative transfer in the YF_3 crystals doped with Tb^{3+} and Yb^{3+}. Miyakawa and Dexter[4] first estimated the probability of the energy transfer by considering multipolar interaction for the ion coupling. Kushida[5] later extended the consideration to the individual character of different energy levels in the three-ion interaction and calculated the transfer rate to get $\sim 2.4\ s^{-1}$, a number less than Miyakawa's by 8 orders of magnitude.

Carnall, Fields, and Sarup[6] determined the position of the ${}^1S_0$ state of Pr^{3+} in LaF_3 and placed it at 46 986 cm^{-1} above the ground state. Elias, Heaps, and Yen[7] investigated uv emissions originating from the ${}^1S_0$ state by illuminating LaF_3:Pr^{3+} crystals with uv synchrotron radiation from a 240-MeV electron storage ring.

II. THEORY

The rate equations for the cooperative energy transfer among Pr^{3+} ions are

$$\frac{dN_p(t)}{dt} = -N_p(t)/\tau_p - \chi 3 N_p^3(t)\ , \tag{2}$$

and

$$\frac{dN_s(t)}{dt} = -N_s(t)/\tau_s + \chi N_p^3(t)\ , \tag{3}$$

where N_p and N_s denote the number densities of the Pr^{3+} ions in the ${}^3P_0$ and ${}^1S_0$ states, respectively, τ_p and τ_s denote the lifetimes of the ${}^3P_0$ and ${}^1S_0$ states, respectively, and χ denotes the probability for cooperative energy transfer. Self-quenching is implicitly included since τ_p and τ_s in this work are determined as a function of Pr^{3+} concentration and are accurate exponents of the decays for the initial 10 μs. Because three ${}^3P_0$ ions are required for one interaction event to occur, there is a factor of 3 in the last term of Eq. (2).

The analytical solution to Eq. (2) takes the following form:

$$N_p(t) = N_0[(1+\alpha)\exp(2t/\tau_p) - \alpha]^{-1/2}\ ,$$

where $\alpha = 3\tau_p \chi N_0^2$ and $N_0 = N_p(t=0)$, the initial condition. When $\alpha \to 0$, we obtain $N_p(t) \to N_0 \exp(-t/\tau_p)$.

The relative variation of $N_s(t)$ can be calculated by numerical methods if both τ_s and relative $N_p(t)$ are known. In our experiment, relative $N_p(t)$ is monitored by observing the decay of a visible emission (${}^3P_0 \to {}^3H_5$ or ${}^3P_0 \to {}^3H_6$). The details of measuring τ_s by a two-photon (266 nm plus 477.8 or 592.5 nm) excitation method will be described in Sec. III. We will then compare the relative $N_s(t)$ obtained through calculation and the measured variation of the uv fluorescence (${}^1S_0 \to {}^1I_6$, 393 nm).

We have noticed that the decay of $N_p(t)$ is nonexponential because of quenching effects by cross-relaxation transfer, donor-donor transfer,[8,9] three-ion interaction, and other nonlinear processes. It is conceivable that the lifetime τ_p might depend in some way on the concentration of ions excited to the ${}^3P_0$ state, as it does on the concentration of Pr ions. However, the exponential and cubic terms in Eq. (2) fit the observed decay quite well. Since some of the uv fluorescence is emitted within 1.6 μs after the pulsed excitation from the PrF_3 crystals, only $N_p(t)$ in this short duration is of interest when solving $N_s(t)$ in Eq. (3) numerically. Similarily, the visible emission [$\alpha\ N_p(t)$] from $La_{0.9}Pr_{0.1}F_3$, $La_{0.8}Pr_{0.2}F_3$, and $La_{0.4}Pr_{0.6}F_3$ during 4, 5, and 10 μs, respectively, after the pulse will be measured for solving $N_s(t)$. It will be shown by our experimental results that the visible fluorescent decay can be approximated by the function

$$[(1+\alpha)\exp(2t/\tau_p) - \alpha]^{-1/2}$$

with proper choice of τ_p and α values. In a dilute crystal (10 at. % Pr^{3+}, for example), α could be very small such that the visible fluorescent decay looks exponential in a short duration (10 μs).

III. EXPERIMENT

Crystals of $La_{1-x}Pr_xF_3$ with $x = 0.1$, 0.2, and 0.6 were obtained from Optovac, Inc. A laser using Coumarin 480 dye was pumped by the third harmonic of an Nd:YAG (yttrium aluminum garnet) laser to give the pulse of ~ 8 ns width, $\sim 0.3\ cm^{-1}$ bandwidth, and ~ 0.6 mJ energy. The laser was focused along the optical axis of each of the crystals and tuned to 477.8 nm to excite the Pr ions in the crystals. A PrF_3 crystal with impurity less than 0.01% was obtained from Ames Laboratory, Iowa. With an intracavity etalon installed in the resonator, the laser was tuned to 477.7882 nm with 0.01-cm^{-1} bandwidth and ~ 0.25 mJ pulse energy to irradiate the PrF_3 crystal. The wavelength was measured by a multiple-wedge wavemeter.[10] All the samples were cooled to below 10 K in a liquid-helium cryostat. Care was taken to avoid dielectric breakdown, with consequent intense uv emissions by defocusing the laser such that the spot size on the front surface of each crystal was 0.24 nm in diameter. Visible (${}^3P_0 \to {}^3H_6$ or ${}^3P_0 \to {}^3H_5$) and uv (${}^1S_0 \to {}^1I_6$) fluorescence from the first 20—40 μm of the excitation volume and propagating perpendicularly to the input beam was focused into a 1.4-m Czerny-Turner spectrometer fitted with a S-13 photomultiplier tube. A Princeton Applied Research model 162/164 boxcar integrator triggered by the pulsed signals from the Q-switch board of the Nd:YAG laser was used to measure the photomultiplier tube output. Time-resolved fluorescent variations with a resolution of ~ 30 ns were obtained by narrowing the gatewidth and scanning the gate of the boxcar integrator.

A two-photon excitation method was used to determine τ_s in different samples. The transition from the ground to the ${}^1S_0$ state by the excitation of two photons with combined energy of 46 986 cm^{-1} is forbidden because of the $J \le 2$ selection rule.[1] Therefore we irradiated the crystal with the fourth harmonic from the Nd:YAG laser (266 nm) and the dye laser output (477.8 or 592.5 nm) to pump the Pr^{3+} ion to the $4f5d$ band. After a quick and nonradiative decay to ${}^1S_0$, uv fluorescence due to the transition from ${}^1S_0$ to ${}^1I_6$ state was observed and the decay-time constant was measured to determine the τ_s in each of the samples.

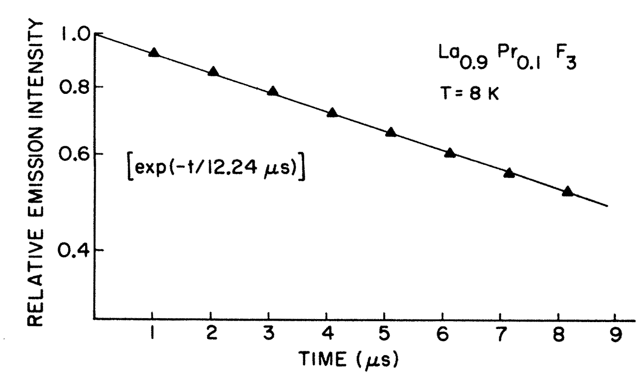

FIG. 3. The measured decay of a visible emission ($^3P_0 \rightarrow {}^3H_6$) from the first ~40 μm of the excitation volume is shown by the solid triangles. The solid line is the asymptote, $\exp(-t/12.24\ \mu\mathrm{s})$.

IV. RESULTS

A. $\mathrm{La}_{0.9}\mathrm{Pr}_{0.1}\mathrm{F}_3$

Figure 3 shows the decay of the $^3P_0$ state within 10 μs after the pulsed excitation. Although long-term decay may look different (i.e., nonexponential) as explained earlier, only fluorescence in this duration is important for analysis because little uv fluorescence is observed 10 μs after the excitation or later. τ_s, the measured lifetime of the $^1S_0$ state, is 760±40 ns. By taking $\tau_s = 760$ ns and $N_p = N_o \exp(-t/12.24\ \mu\mathrm{s})$ as an asymptote of the decay of the $^3P_0$ population, we can solve Eq. (3) analytically and obtain

$$N_s(t) \propto [\exp(-3t/12.24\ \mu\mathrm{s}) - \exp(-t/0.76\ \mu\mathrm{s})] \ .$$

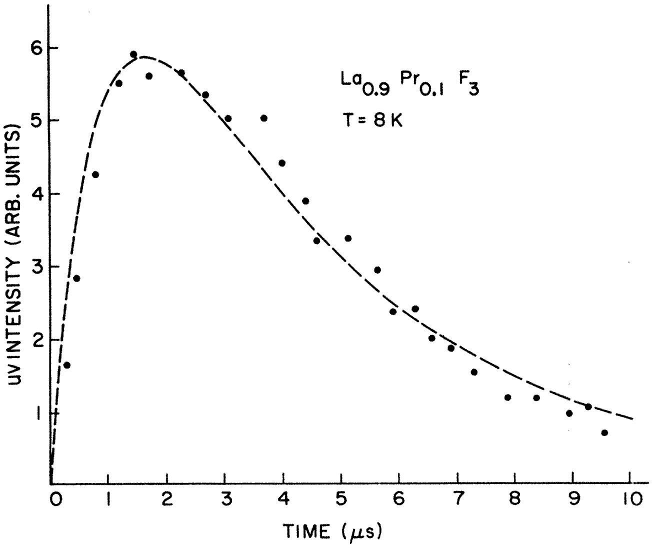

FIG. 4. The calculated $N_s(t)$, which is proportional to $[\exp(-3t/12.24\ \mu\mathrm{s}) - \exp(-t/0.76\ \mu\mathrm{s})]$, is shown by the dashed curve. The measured variation of the uv emission ($^1S_0 \rightarrow {}^1I_6$) from the same excitation volume as that in Fig. 3 is shown by the dots.

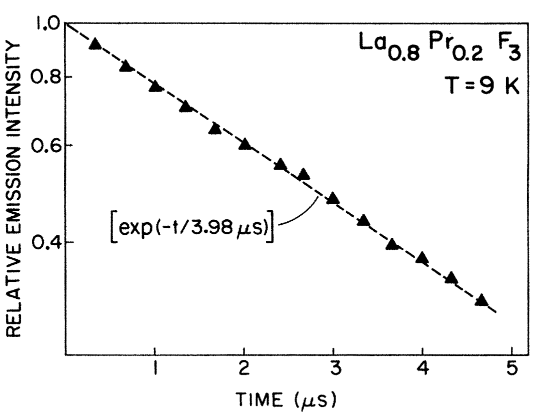

FIG. 5. Measured decay of a visible emission ($^3P_0 \rightarrow {}^3H_6$) from the first ~40 μm of the excitation volume.

Figure 4 shows good agreement between this calculated result and the relative variation of the uv fluorescence observed in the experiment.

B. $\mathrm{La}_{0.8}\mathrm{Pr}_{0.2}\mathrm{F}_3$

Figure 5 shows that the decay of the $^3P_0$ population can be approximated by $N_p = N_0 \exp(-t/3.98\ \mu\mathrm{s})$. This result, along with 750±30 ns, the measured lifetime of the $^1S_0$ state, could be used to solve $N_s(t)$ analytically and yield

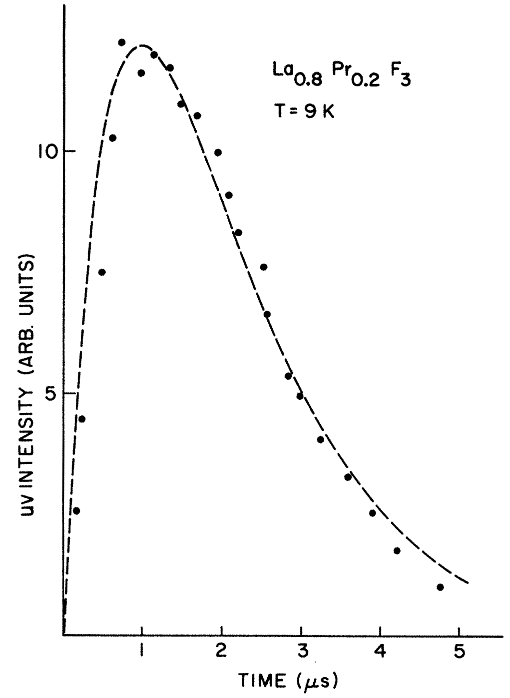

FIG. 6. The calculated $N_s(t)$, which is proportional to $[\exp(-3t/3.98\ \mu\mathrm{s}) - \exp(-t/0.75\ \mu\mathrm{s})]$, is shown by the dashed curve. The measured variation of the uv emission ($^1S_0 \rightarrow {}^1I_6$) from the same excitation volume as that in Fig. 5 is shown by the dots.

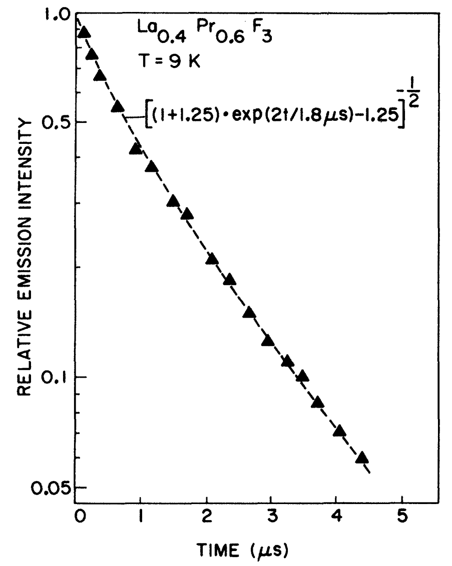

FIG. 7. Measured decay of a visible emission ($^3P_0 \rightarrow {}^3H_6$) from the first ~25 μm of the excitation volume. By choosing $\alpha = 1.25$ and $\tau p = 1.8$ μs the function $[(1+\alpha)\exp(2t/\tau p) - \alpha]^{-1/2}$, shown by the dashed curve, is a good asymptote of the decay.

$$N_s(t) \propto [\exp(-3t/3.98\ \mu s) - \exp(-t/0.75\ \mu s)] \ .$$

Figure 6 shows the agreement between this function and the experimental result.

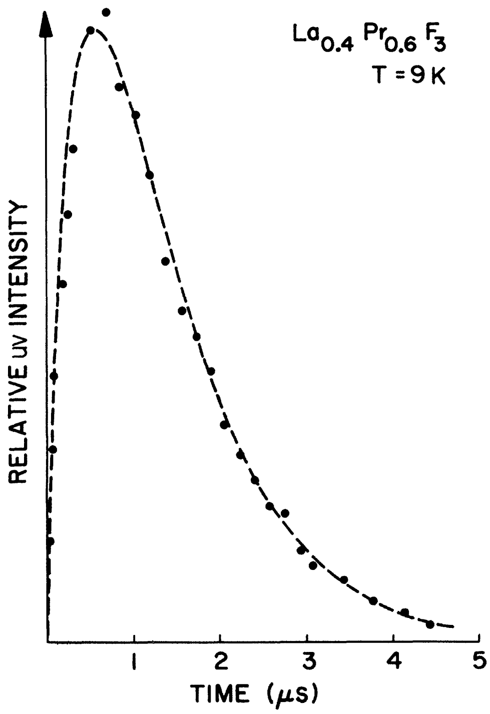

FIG. 8. $N_s(t)$, which has been calculated by numerical methods, is shown by the dashed curve. The measured variation of the uv emission from the same excitation volume as that in Fig. 7 is shown by the dots.

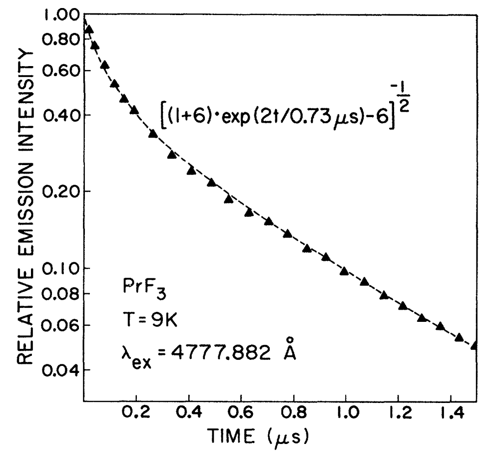

FIG. 9. Measured decay of a visible emission [$^3P_0 \rightarrow {}^3H_5(4)$] from the first ~20 μm of the excitation volume.

C. $La_{0.4}Pr_{0.6}F_3$

Figure 7 shows the decay of the $^3P_0$ state. We have chosen $\alpha = 1.25$ and $\tau_p = 1.8$ μs in order to make the function

$$N_p(t) = [(1+\alpha)\exp(2t/\tau_p) - \alpha]^{-1/2}$$

fit the observed fluorescent decay well. The lifetime of the $^1S_0$ state in this crystal is ~730 ns by measurement. Utilizing this τ_s value and $N_p(t)$, we could solve Eq. (3) numerically and obtain relative $N_s(t)$, which is shown in Fig. 8 along with the observed temporal variation of the uv emission.

D. PrF_3

Figure 9 shows the decay of the $^3P_0$ state and its asymptote,

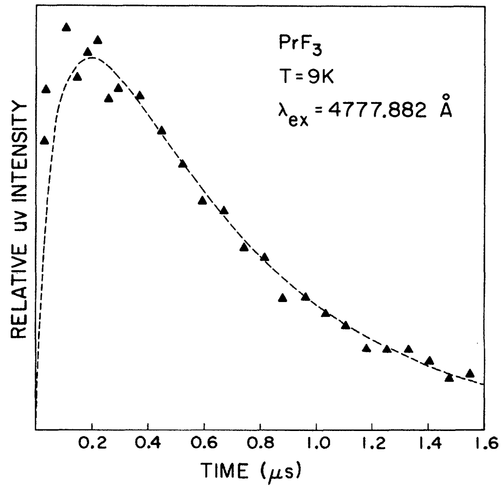

FIG. 10. $N_s(t)$, which has been calculated by numerical methods, is shown by the dashed curve. The measured variation of a uv emission from the same volume as that in Fig. 9 is shown by the solid triangles.

$$N_p(t)=N_0[(1+6)\exp(2t/0.73\ \mu s)-6]^{-1/2} .$$

This result and the fact that $\tau_s \simeq 590$ ns enable us to calculate relative $N_s(t)$ numerically. Figure 10 shows the calculated result and the observed uv radiation. The uv fluorescent intensity was roughly 50 times weaker than the visible emission.

V. DISCUSSION

We have seen disagreement between the calculated $N_s(t)$ and relative uv variation in PrF_3 by fixing the laser at 477.782 nm, the center of the absorption line. Because N_p represents the number density of the ions in the $^3P_0$ state, in order to obtain a reliable $N_s(t)$ by solving the rate equations, the decay behavior should be roughly the same throughout the volume under investigation. When the laser was at the center of the absorption line, the absorption length was only 9 μm (Ref. 12) and the concentration of the $^3P_0$ ions varied significantly throughout the first ~20 μm of the excitation volume. Under this condition the observed visible fluorescence was not a good approximation of $N_p(t)$ for solving Eq. (3). When the laser was tuned off-center by 0.27 cm^{-1} to deepen the penetration, a good agreement was obtained as shown in the preceding section.

Unless there is a sideband above the $^1S_0$ state, the energy transfer shown by Eq. (1) is not quite resonant. A release of phonon with (10—1000)-cm^{-1} energy is expected.

It is also possible that the two donor ions could deexcite to levels lower than the $^1G_4$ and $^3F_2$ combination while the acceptor ion is resonantly upconverted to the $4f5d$ band, followed by a decay to the $^1S_0$ state. The resultant $N_s(t)$ should be similar to that of direct upconversion to the $^1S_0$ state, provided the transition from the $4f5d$ states takes a very short time ($\ll \tau_s, \tau_p$). Elias, Heaps, and Yen[7] have observed the absorption and located three Stark components of the $5d$ bands in LaF_3:Pr^{3+} near 53 200, 56 000, 59 000 cm^{-1}. The change of the uv emission intensity is insignificant ($\leq 15\%$) when raising the temperature from 5 to 30 K, which suggests that the ions could be resonantly upconverted to real levels. Thus it appears that lattice phonons are not involved in the upconversion process.

We have observed in addition a broadband uv emission between 280—320 nm in every crystal obtained from OptoVac. It is believed to be from impurities (Ce^{3+}, Nd^{3+}, etc.) since it does not occur in the highly purified PrF_3 crystal grown by Dr. B. J. Braudry at Ames Laboratory. We have seen sideband absorption near the $^3P_1$, $^1I_6$, and $^3P_2$ levels (21 600—23 000 cm^{-1}). The emission between 394 and 410 nm, which was seen in every crystal, could be attributed to the transitions from the $^1S_0$ state to the $^3P_1$ and $^1I_6$ sideband. The same emission was also observed by Elias, Heaps, and Yen.[7] Near 335 nm, we have seen uv emission due to transitions from $^1S_0$ to $^1D_2$ and the accompanying sideband.

The absorption coefficient of PrF_3 at 477.7882 nm was measured by the transmission through thin slices of crystal, and found to be 435 cm^{-1}. This value, along with the roughly known laser power density, allows us to estimate N_0 and obtain $\sim 3.8\times10^{20}$ cm^{-3} near the surface. Furthermore, by using the known τ_p, α, and N_0 values we can calculate χ and obtain 1.87×10^{-35} cm^6/s. If every ion in the system is excited to the $^3P_0$ state ($N_0=1.9\times10^{22}$ cm^{-3}), the interaction rate will be $\chi N_0^3=1.28\times10^{32}$ events/cm^3 s. The transfer rate for an individual ion under this condition will be 6.7×10^9 s^{-1}, which greatly exceeds the spontaneous single-ion decay rate. However, this estimate is rough because it is difficult to determine the exact laser power density and N_0 is not a constant in the first 20 μm of the excitation volume.

Since

$$\int_0^\infty [(1+\alpha)\exp(2t/\tau_p)-\alpha]^{-1/2}dt=(\tan^{-1}\sqrt{\alpha})/\sqrt{\alpha} ,$$

the integrated visible and uv fluorescent intensities should be proportional to N_0 $(\tan^{-1}\sqrt{\alpha})/\sqrt{\alpha}$ and $[1-(\tan^{-1}\sqrt{\alpha})/\sqrt{\alpha}]N_0/3$, respectively. When α is very small the integrated uv fluorescent intensity could be proportional to αN_0, as well as the cube of the integrated visible fluorescent intensity. By using a neutral density filter to lessen the laser excitation on the $La_{0.9}P_{0.1}F_3$ crystal, we have seen decreases of the integrated uv and visible fluorescent intensities by factors of 950 and 9.5, respectively, which has suggested a cubic dependence. The integrated uv fluorescent intensity does not have to be proportional to the cube of the input laser power[13] if α is not small (PrF_3 in the experiment, for example) or the absorption reaches saturation under intense excitation.

VI. CONCLUSION

We have found a new system in which cooperative energy transfer can take place. Unlike the old one in which the acceptor (Yb^{3+}) is in the ground state before the transfer, in this system the acceptor (Pr^{3+}) is in an excited state and therefore can be upconverted to a state ($^1S_0$ or $4f5d$) with energy more than twice the input photon energy. We have also introduced a new method to verify the three-ion interaction by comparing the solution of the rate equations with the temporal variation of the uv fluorescence. The nonexponential decay of the visible emission from PrF_3 is an indication of strong competition between the decay and upconversion processes. The investigation of the decay and the measurement of the absorption coefficient have led to a rough estimate of the transfer rate.

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