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# Two-photon excitation of $Ho^{3+}$ in the $CaF_2$, $SrF_2$, and $CdF_2$ lattices

D. Narayana Rao, Jagdish Prasad, and Paras N. Prasad
*Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214*

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The observation of two-photon absorption by a very efficient up-converted emission is reported for $Ho^{3+}$ in $CaF_2$, $SrF_2$, and $CdF_2$ with both cw- and pulse-laser excitations. The two-photon excitation spectra are found to be highly structured and consist of two bands: The band $A$ is excited by the dye-laser photons of frequencies 15 400—15 700 $cm^{-1}$: The band $B$ is excited by the dye-laser photons of frequencies 15 800—16 400 $cm^{-1}$. No one-photon absorption is observed for $Ho^{3+}$ in the above lattices at twice these frequencies. Studies of concentration dependence, temperature dependence, and dependence on the pulse repetition rate are used for the assignment of the band. The investigation shows that the two bands $A$ and $B$ arise fom two different modes of two-photon excitation. The band $A$ is assigned to arise from a sequential (stepwise) two-photon excitation $^5I_8 \rightarrow {}^5F_5 \rightarrow {}^5D_2$. The band $B$ is assigned to arise from the direct two-photon absorption $^5I_8 \rightarrow {}^3L_8$. Our results are in agreement with the prediction of the Judd-Ofelt theory of lanthanide transition intensities.

## INTRODUCTION

The study of two-photon processes involving the $f \rightarrow f$ transitions in the rare-earth ions can provide valuable information. One can conveniently investigate high-energy excited states. The two-photon absorption processes can be used as a test for the Judd-Ofelt theory. The investigation of luminescence resulting from the two-photon excitation is also important in relation to the quantum up conversion and spectral diffusion. The two-photon processes for the rare-earth ions, however, have received limited attention.[1–6] Recently, the two-photon absorption[5] of the $Gd^{3+}$ ion in the $LaF_3$ host has been observed by using a cw dye-laser excitation. In the above-mentioned paper, the authors have discussed how the observed two-photon absorption could be used to test the method of Judd and Ofelt for calculating the oscillator strengths of $f \rightarrow f$ transitions in lanthanide ions. In a more recent paper[6] Downer *et al.* have shown that if the crystal-field interaction with $4f^{n-1}5d$ levels is strong, it can give rise to two-photon transitions with $\Delta J > 2$. This violates the selection rule $\Delta J \leq 2$ which the Judd-Ofelt theory requires for a direct two-photon absorption.

Some studies of the two-photon processes in $CaF_2$:$Ho^{3+}$ have been reported in the past.[2–4] For these studies, the high peak power Nd laser and Ruby laser were used. Furthermore, the past work focused on the low-lying ($< 30 000$ $cm^{-1}$) two-photon levels. Also, the thrust of these earlier studies on $Ho^{3+}$ has been the investigation of the step wise (sequential) two-photon resonance.

The objective of our study has been the investigation of the high-energy states ($> 30 000$ $cm^{-1}$) excited by the two-photon processes and the resulting up-converted emissions. The fluorite-type hosts ($CaF_2$, $SrF_2$, $CdF_2$) are highly suitable for this study because the host absorption bands lie above 40 000 $cm^{-1}$. Furthermore, some interesting crystal-field effects can be expected in these lattices because the substitution of trivalent rare-earth ions require charge compensation.[7,8] Consequently, the rare-earth ions can experience crystal fields of different strengths and symmetries.[9]

In the present paper we report the observation of two-photon excitations for $Ho^{3+}$ in $CaF_2$, $SrF_2$, and $CdF_2$ lattices in the spectral region 30 800—32 400 $cm^{-1}$ for which no one-photon absorption was found. A highly structured two-photon resonance spectrum was obtained as an excitation spectrum by monitoring the up-converted green emission. Also, the two-photon excitation was obtained with both the cw and the pulse dye lasers. In each case, a highly efficient up-converted emission was found. This, therefore, represents only the second report of the observation of two-photon resonance in rare-earth ions which uses a cw dye laser.[10] A detailed analysis of the two-photon excitation spectra reveals another unusual feature, i.e., it consists of two bands which are exicted by different two-photon processes. A comparison is made of the observed transition strength with that calculated by using the Judd-Ofelt theory.

## EXPERIMENTAL

The crystals of $CaF_2$:$Ho^{3+}$ grown from a vacuum furnace in fluorine atmosphere were obtained from Optovac, Inc. The five different concentrations of $Ho^{3+}$ used in this study were 5%, 0.65%, 0.3%, 0.09%, and 0.01%. The crystals of $CdF_2$ and $SrF_2$ with 1% $Ho^{3+}$ were also purchased from Optovac, Inc. Two types of excitation sources were used for the two-photon excitation. In the cw mode a dye laser, pumped by an 8-W argon-ion laser (both from coherent radiation), was used. A home-built grazing angle incidence dye laser (one oscillator and two amplifiers) was pumped by the second harmonic of the Nd-YAG (yttrium aluminum garnet) laser (Quantel, model 481). This dye laser was used as a pulse source with the maximum repetition rate of 10 Hz. The pulse width of the dye output was estimated to be several nanoseconds. Both in the cw and the pulse dye lasers, the dyes used were Rhodamine-6G and DCM, depending on the spectral region desired.

The spectra were recorded by using a Spex double

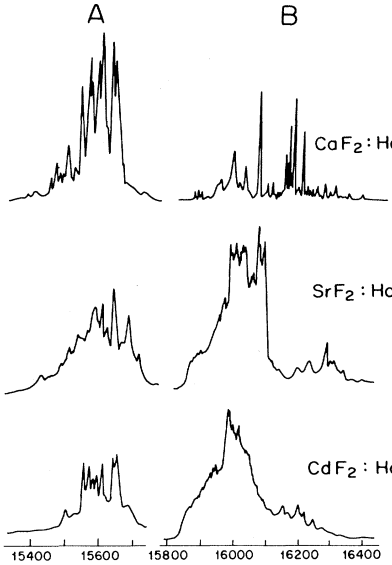

FIG. 1. Two-photon excitation spectra of $Ho^{3+}$ in $CaF_2$, $SrF_2$, and $CdF_2$ lattices at 77 K. The up-converted green emission at $\sim 18\,200$ cm$^{-1}$ ($^5S_2 + {}^5F_4 \rightarrow {}^5I_8$) was monitored in each case. The concentration of $Ho^{3+}$ used was 0.65% in $CaF_2$ and 1% in both $SrF_2$ and $CdF_2$. The excitation profile *A* is obtained with the dye DCM while *B* is obtained with Rhodhamine-6G.

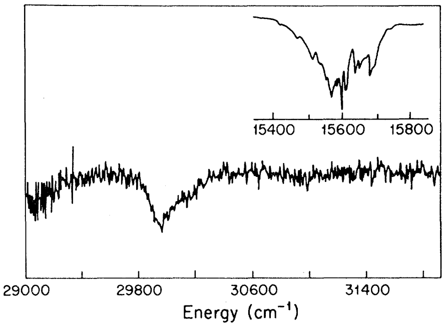

FIG. 2. One-photon absorption spectra of 0.65% $Ho^{3+}$ in the $CaF_2$ lattice at 77 K are displayed for the selected regions 15 400—15 800 cm$^{-1}$ and 29 000—31 800 cm$^{-1}$.

monochromator (model 14018). They were obtained at room temperature as well as at 77 and 6 K. For the latter two temperatures, the sample was cooled in a Janis Supervaritemp liquid-helium cryostat. The temperature was monitored by a copper-constantan thermocouple. For recording the spectra, a dc detection mode was used. To obtain the one-photon absorption spectra in the region (13 000—16 500 cm$^{-1}$) a 75-W halogen lamp was used. A 60-W deuterium lamp was used to obtain the one-photon absorption spectra in the region 29 000—33 000 cm$^{-1}$.

## RESULTS

The two-photon processes are observed as an up-converted emission when the laser excitation is tuned through the region 15 500—16 500 cm$^{-1}$. Figure 1 shows the two-photon excitation profile in this region obtained with the cw dye laser. To obtain the excitation spectra, the green emission, at 18 644 cm$^{-1}$, was monitored. For this purpose, two dyes were used: Rhodhamine-6G and DCM. These spectra were obtained at 77 K. The excitation spectra show two highly structured bands *A* and *B*, which were obtained with dyes DCM and Rhodhamine-6G, respectively. The spectra shown in Fig. 1, however, are not normalized with respect to the dye-emission profile. The room-temperature excitation profiles are similar, except that they are broad as compared to those presented in Fig. 1. In general, the excitation profiles observed in the $CaF_2$ lattice are sharper than those observed in $SrF_2$ and $CdF_2$ lattices. This difference may result due to the difference in concentrations used, i.e., 0.6% $Ho^{3+}$ in $CaF_2$ but 1% $Ho^{3+}$ in $SrF_2$ and $CdF_2$. Within the uncertainty of our measurements, the excitation-power dependence is found to be very close to quadratic, confirming the two-photon nature of these transitions.

The relevant one-photon absorption regions are 15 400—16 500 cm$^{-1}$ and 30 000—33 000 cm$^{-1}$. The one-photon absorption spectra of $Ho^{3+}$ in the $CaF_2$ lattice are shown, for these selected regions, in Fig. 2. In the region 29 000—33 000 cm$^{-1}$, we see only one broad-photon absorption which peaks at 29 000 cm$^{-1}$. The two bands, *A* and *B*, observed in the two-photon excitation spectra (Fig. 1), would correspond to the energy levels at $\sim 31\,200$ and $\sim 32\,000$ cm$^{-1}$. No absorption is observed at these energies in the one-photon absorption spectra. These levels of $Ho^{3+}$ in the fluorite-type lattice must, therefore, have considerably small oscillator strength for one-photon process. The emission spectra, obtained with the two-photon excitation profiles, as shown in Fig. 1, are displayed in Fig. 3. Figure 3 spectra were obtained with a cw dye laser. It shows that up-conversion is seen as emission from states as high in energy as 30 000 cm$^{-1}$. All the emissions observed are the same as seen by the direct one-photon absorption. There are some differences in the relative emission intensities of various bands when the host lattice is

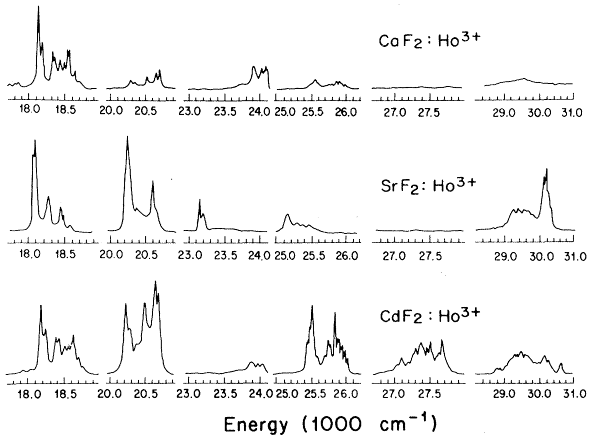

FIG. 3. Up-converted emission spectra observed by two-photon excitation profiles of Fig. 1 are displayed for $Ho^{3+}$ in the $CaF_2$, $SrF_2$, and $CdF_2$ lattices at 77 K. The concentrations of $Ho^{3+}$ in these lattices are the same as those for Fig. 1.

changed from $CaF_2$ to $CdF_2$ and $SrF_2$. This difference may be the result of nonradiative processes which are highly dependent on the host phonon density of states.[11] It is worth noting that the detailed high-resolution fluorescence spectra, shown in Fig. 3, were made possible because of a highly efficient up conversion which points to a relatively strong two-photon excitation with the cw dye laser. This observation is different from the recent and the only other report of the cw dye-laser excitation of two-photon absorption by $Gd^{3+}$ in $LaF_3$, where a relatively weak two-photon process was found.[5]

In order to investigate the dependence on the concentration, we studied $CaF_2$ crystals doped with various concentrations of $Ho^{3+}$. The crystals used had 5%, 0.65%, 0.3%, 0.09%, and 0.01% of $Ho^{3+}$ in the $CaF_2$ lattice. Even in the most dilute sample, the up conversion was observed. The concentration dependence was not strong enough to suggest any biexcitation annihilation mechanism (discussed below) for the up conversion.

The two-photon excitation profiles observed with the pulse dye laser (pumped by the Nd-YAG laser) are similar to that shown in Fig. 1. The up conversion does not depend on the pulse repetition rate which was varied from 2 to 10 Hz. The two-photon excited decay curves were obtained at several emission wavelengths and were found to be exponential.

## DISCUSSION

The up-conversion process in a solid may occur by one of the following mechanisms: (a) two-photon sequential absorptions, (b) biexcitation annihilation process analogous to triplet-triplet exciton annihilation observed in organic solids,[12] and (c) direct two-photon absorption. The biexcitation annihilation mechanism is not operative here, because no strong dependence of the up-conversion efficiency, with respect to the concentration of the $Ho^{3+}$ ion, is observed. A comparison of Figs. 1 and 2 reveals that the two-photon excitation profile of $Ho^{3+}$ in $CaF_2$ in the region 15 400—15 800 $cm^{-1}$ (band *A*) correlates with the observed one-photon absorption spectra (${}^5I_8 \rightarrow {}^5F_5$) of $Ho^{3+}$ in the same lattice. This points out that the up conversion starting with the laser excitation in this spectral region results from a sequential absorption, where the intermediate level is ${}^5F_5$. There is no one-photon absorption observed in the region 15 800—16 200 $cm^{-1}$ (corresponding to band *B*). Therefore, we conclude that the two-photon excitation in this region (band *B*) is the result of a direct two-photon absorption.

The band *A*, which involves the ${}^5F_5$ level, can be a result of either a direct sequential two-photon absorption or it may involve another intermediate level populated by a nonradiative relaxation from the ${}^5F_5$ level. The latter process would require a finite time lag between the sequential absorption. But we observe that, even with a single-pulse shot from the Nd-YAG pumped dye laser (Nd-YAG pulse is 13 nsec), up conversion is observed and no dependence of it on the repetition rate of the YAG dye pulse is observed. This observation is not consistent with the involvement of another intermediate state populated by relaxation from a state (${}^5F_5$) reached with the first photon. We therefore conclude that the band *A* corresponds to a two-photon sequential absorption without relaxation in the middle level. We have conducted the temperature dependence study of up conversion up to 4 K. The emission, resulting from the up conversion for both excitations *A* and *B* (Fig. 2), as a matter of fact, gets stronger as the temperature is lowered. From this we conclude that the up conversion does not involve any thermally activated process. In other words, the two-photon processes start from the ground level ${}^5I_8$. There have been theoretical and experimental investigations[13–16] of energy-level structures of $Ho^{3+}$ in several hosts. We first analyze the band *A* of the two-photon excitation profile as shown in Fig. 1. The final state reached in a two-photon sequential absorption for the band *A* would be in the region 30 800—31 400 $cm^{-1}$. The published[13,14] energy-level structure of $Ho^{3+}$ in $LaCl_3$ shows the level ${}^3D_2$ at 30 746 $cm^{-1}$ above ${}^5I_8$. This level is the closest to the two-photon excitation of band *A*. As discussed below, in Judd-Ofelt theory a direct two-photon absorption requires that $\Delta J \leq 2$. On this basis, the direct two-photon absorption ${}^5I_8 \rightarrow {}^3D_2$ is forbidden. However, the one-photon absorption ${}^5F_5 \rightarrow {}^3D_2$ is allowed by the *J* selection rule ($\Delta J \leq 6$). We therefore assign the observed two-photon excitation band *A* of Fig. 1 as the two-photon sequential absorption ${}^5I_8 \rightarrow {}^5F_5 \rightarrow {}^3D_2$.

The direct two-photon excitation, resulting from the laser photons of energy between 15 800 and 16 400 $cm^{-1}$, will lead to excited states in the region 31 400—32 800 $cm^{-1}$. About this energy, the published studies[13–16] show two levels: ${}^3L_8$ and ${}^3M_{10}$. The intensity *S* of a direct two-photon absorption, for both photons of the same frequency and polarization, has been shown to be (by Judd-Ofelt method)

$$S = C\Omega_2 \langle \gamma J \mid U^{(2)} \mid \gamma' J' \rangle^2 \cdots . \qquad (1)$$

In the above equation *C* is a polarization-dependent factor and $\Omega_2$ contains integrals over radial parts. The matrix element $U^{(2)}$ determines the *J* selection rule for the direct two-photon absorption, i.e., $\Delta J \leq 2$. Both the transitions ${}^5I_8 \rightarrow {}^3L_8$ and ${}^5I_8 \rightarrow {}^3M_{10}$ are allowed on the $\Delta J$ selection rule basis. We therefore assign the observed two-photon excitation in the region 31 400—32 800 $cm^{-1}$ to arise from the ${}^5I_8 \rightarrow {}^3L_8$ and/or ${}^5I_8 \rightarrow {}^3M_{10}$ transitions. For $Ho^{3+}$ in $LaCl_3$ the ${}^3L_8$ and ${}^3M_{10}$ levels have been listed at 33 999 and 34 101 $cm^{-1}$.

In order to compare the strengths of these two transitions, we use Eq. (1). As is customary, we assume that $\Omega_2$ has the same value for all excited states. Then the relative integrated intensities of the two-photon transition are determined by the square of the $U^{(2)}$ matrix element. This matrix element has been calculated[16] for various transitions of $Ho^{3+}$ in $LaF_3$. If we assume that the matrix element does not change significantly from host to host, as has been found to be the case, the strongest two-photon absorption in the region 32 000—34 000 $cm^{-1}$ would be ${}^5I_8 \rightarrow {}^3L_8$. We therefore assign the observed two-photon absorption around 32 000 $cm^{-1}$ to the ${}^5I_8 \rightarrow {}^3L_8$ transition. The level ${}^3L_8$ has been reported[16] for $Ho^{3+}$ in $LaF_3$ at 33 894 $cm^{-1}$ and carries a considerable one-photon absorption oscillator strength ($1.20 \times 10^6$). The same transition is reported[16] in the $YAlO_3$ host at 33 890 $cm^{-1}$ with a considerably reduced oscillator strength ($0.18 \times 10^6$). For $Ho^{3+}$ in $CaF_2$, our assignment would predict a considerable host-induced shift for the ${}^3L_8$ level ($\sim 32\,000$ $cm^{-1}$ in $CaF_2$). This host-induced shift may be a result of the requirement of charge-compensation when $Ho^{3+}$ is substituted in the $CaF_2$ lattice. Furthermore, the one-photon absorption spectra do not show any detectable one-photon transition to this level. As a matter of fact, we observed no one-photon absorption for $Ho^{3+}$ in $CaF_2$ in the spectral region 30 000–33 000 $cm^{-1}$. Our observation is consistent with a previous study which reveals that the oscillator strength of the one-photon absorption to the $^3L_8$ level is dependent on the host lattice.[16]

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