Anomalous photoacoustic effect from pulsed excitation of Eu^{3+} ions

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Abstract

When Eu^{3+} ions in aqueous solution are excited from ${}^7\text{F}_1$ state to ${}^5\text{D}_0$ state with a pulsed dye laser, the population of Eu^{3+} ions in the ${}^7\text{F}_1$ state decreases temporarily due to the slow decay of the ${}^5\text{D}_0$ state. The magnitude of transient photoacoustic signal from absorption of light by water and Eu^{3+} ions was found to decrease when the dye laser wavelength was tuned to the transition. This anomalous photoacoustic effect is attributed to the fast thermal equilibrium between "cold" Eu^{3+} ions and ambient water molecules.

1. INTRODUCTION

The sensitivity of photoacoustic detection is known to be 100 to 1000 times higher than that of absorption method (1,2). This is true, however, only when the absorbed photon energy is efficiently converted to thermal energy accompanying maximum pressure rise. When the excited state species relax down to the ground state mostly via radiative process or nonradiative relaxation is slow, the sensitivity of photoacoustic detection may be even lower than that of absorption method. The sensitivity of pulsed photoacoustic detection becomes quite low especially for a system with slow nonradiative decay. Even a cooling effect may be expected by pulsed photoexcitation for a system when an optical pumping effect is accompanied. Here, we present a direct evidence of anomalous temporal cooling effect of aqueous Eu^{3+} solution by pulsed photoexcitation, which is thought to originate from the slow nonradiative decay of the excited Eu^{3+} . This effect was not observed when cw photoacoustic method was employed(3). We found that the magnitude of the photoacoustic signal from the aqueous Eu^{3+} solution became smaller than that of neat water in case the dye laser wavelength was tuned to the transition from the ${}^7\text{F}_1$ state to the ${}^5\text{D}_0$ state of Eu^{3+} ion.

2. EXPERIMENTAL

Eu^{3+} solution was made from Eu_2O_3 (99.9%, Aldrich) by dissolving it in perchloric acid solution with pH of 0.5. The concentration of Eu^{3+} solution was in the range of 0.14 M through 0.57 M. The experimental setup is shown in Fig. 1. An excimer laser(Lambda-Physik LPX 305icc)-pumped dye laser(Lambda-Physik LPD3002) was employed to excite Eu^{3+} ions in aqueous solution. A quartz spectrophotometer cell with path length of 1 cm was used as the photoacoustic cell. PZT was purchased from Industrial Electronics (PZT-5A). The PZT is of 25 mm dia. and 6 mm thickness. The PZT photoacoustic detector designed after Tam et al (4) was mounted under the quartz photoacoustic cell.

Acoustic coupling between the quartz cell and a stainless steel PZT housing was greatly enhanced by dropping glycerin between them. Dye laser beam passed reference cell first and then sample cell. Photoacoustic signals from both sample and reference cell were amplified by a charge-sensitive preamplifier (EG&G Model 142B), filtered by a high pass filter. After filtering, both signals were properly attenuated to compensate the differences in incident laser power in front of both cells, the acoustic sensitivity of PZT, and the alignment of cells against laser beam and photoacoustic detector. The height of the cell was carefully adjusted in order to match the arrival time of the photoacoustic signal after the trigger from the firing of laser. Typical height of the laser beam was 1.4 cm above the detector surface. The photoacoustic signal after attenuation was sent to a boxcar integrator (SR250). The duration of the gate for the sample and reference cell was 0.8 μs . The repetition rate of dye laser was 10 Hz and the dye laser power at 580 nm was 13 mJ/pulse with duration of 25 nsec. After averaging by boxcar integrator, the photoacoustic signals and analog power meter signal were fed to a multichannel A/D converter (SR245) and then transferred to a laboratory computer (IBM PS/2), where both photoacoustic signals were normalized against dye laser power. At a wavelength where no absorption from Eu^{3+} is expected, the magnitudes of the two photoacoustic signals from sample and reference cells were made identical through the adjustment of attenuators. The dye laser wavelength was scanned 10 times to improve signal-to-noise ratio.

3. RESULTS AND DISCUSSION

The lines associated with the transitions between configurations of the electrons within the inner 4f shell of the rare earth ions are forbidden to the first approximation. With the perturbing field, the transition becomes allowed although these transitions are of intensities of magnetic dipole transition(3). Among $^5\text{D}_0 \rightarrow ^7\text{F}_j$ transitions of Eu^{3+} ions, $^5\text{D}_0 \rightarrow ^7\text{F}_1$ emission is the strongest, $^5\text{D}_0 \rightarrow ^7\text{F}_4$ is moderately strong, and other $^5\text{D}_0 \rightarrow ^7\text{F}_j$ emission intensities are extremely weak. The relevant energy levels of Eu^{3+} ion(5) are shown in Fig. 2. The quenching of the $^5\text{D}_0$ state of Eu^{3+} ion in aqueous solution is quite inefficient compared with $^7\text{F}_j$ states since high energy OH vibration is required for $^5\text{D}_0$ state(6,7). Therefore, Eu^{3+} ions in aqueous solution has been studied mostly by fluorescence technique instead of photoacoustic spectroscopy.

Figure 1. Schematic diagram of the experimental setup.

Figure 2. Energy level diagram of Eu^{3+} ion.

Photoacoustic spectrum of Eu^{3+} ion in aqueous solution was first obtained by Sawada et al (3) in 1979. They used Ar^+ ion laser-pumped dye laser for the generation of photoacoustic signal from aqueous solution of Eu^{3+} ion with concentration of 0.2 M. According to Sawada et al (3), the photoacoustic

spectrum of Eu^{3+} ions of the transition from ${}^7\text{F}_1$ state to ${}^5\text{D}_0$ state could not be observed for concentrations under 0.1 M in aqueous solution. This is quite abnormal considering the high sensitivity of photoacoustic detection although the absorption intensity of lines of the Eu^{3+} ion in the yellow region is known to be very weak.

In cw laser excitation, the mechanism of the generation of the photoacoustic signal is rather different from pulsed excitation in that the nonradiative decay of the excited ${}^5\text{D}_0$ state would be picked up as an acoustic signal as long as the inverse of the laser chopping frequency is longer than the nonradiative decay time. In this regard, cw excitation could be more sensitive than pulsed excitation in photoacoustic detection of ${}^7\text{F}_1 \rightarrow {}^5\text{D}_0$ transition of Eu^{3+} ion in aqueous solution.

In pulsed laser excitation, however, nonradiative decay longer than few μsec is hardly detectable as a positive photoacoustic signal. Instead, a cooling effect will show up when Eu^{3+} ions in a thermally excited state as ${}^7\text{F}_1$ state are optically pumped to a long-lived state as ${}^5\text{D}_0$ state. The aqueous solution then becomes instantaneously cold via energy exchange between water molecules and the Eu^{3+} ions in the ground ${}^7\text{F}_0$ state. Photoacoustic signal in aqueous Eu^{3+} solution is produced following the absorption processes (a) and (b) below. The quenching process (c) is a slow process, while the energy exchange between water molecules and ${}^7\text{F}$ electronic states of Eu^{3+} is fast (d). Similar cooling mechanism has been reported by Flynn and coworkers in gas phase(8).

Fig. 3 shows that the photoacoustic signal magnitude is reduced by about 25% at the peak of the absorption. In Fig. 4, the fine structure of ${}^7\text{F}_1 \rightarrow {}^5\text{D}_0$ transition is clearly visible.

Figure 3. Photoacoustic signal magnitudes from reference water cell (line) and sample Eu^{3+} solution cell (dots). The concentration of Eu^{3+} is 0.57 M.

Figure 4. Photoacoustic signal magnitude of sample cell after subtraction of photoacoustic signal from reference cell.

The molar absorptivity of $7F_1 \rightarrow 5D_0$ transition of Eu^{3+} ion in aqueous solution is known to be 0.014 and that of water at the same wavelength is 0.0008. The heat generated by absorption of light by water molecule seems to be partially lost due to the depletion of the population of Eu^{3+} ion in the $7F_1$ state. Concentration dependence is shown in Fig.5. Due to low signal-to-noise ratio, the linearity is not excellent for lower concentrations.

Recently, Terazima performed a similar experiment employing thermal lens method and observed the cooling effect in Eu^{3+} solution in real time: the thermal lens signal becomes negative (cooling) and then inverts sign, giving the normal positive (heating) thermal lens signal(9).

In conclusion, absorption of pulsed laser beam by Eu^{3+} ions makes themselves "cold" in msec time scale and "cold" Eu^{3+} ions exchange heat with ambient water molecules, thereby resulting negative photoacoustic signal. The mechanism of this anomalous photoacoustic effect and the details will be obtained with further experiments in D_2O solution.

Figure 5. Concentration dependence of the photoacoustic signal magnitude (sample signal minus reference signal).

Acknowledgements

One of the authors, S. M. P. is grateful to Kyung Hee University for supporting this work (University Research Fund 1993). We wish to thank Profs. G. J. Diebold and M. Terazima for fruitful discussions.

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