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Laser Photochemistry of Lanthanide Ions

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Photochemical reactions of lanthanide ions in solution have been studied. One-photon and tow-photon reductions have been demonstrated.

Keywords: Lanthanide ions, Two-photon reduction

1. INTRODUCTION

The photoredox reactions of lanthanide and actinide ions are expected to be utilized for nuclear fuel reprocessing and partitioning of high level wastes. [1,2] Those ions have been widely used as laser active centers. Photochemical reactions in solution studied by this group are briefly reviewed in this paper.

Those ions in solution have broad charge transfer (CT) bands in the UV region and are photo-reactive by excitation the CT band. Several ions including Ce^{3+}, Sm^{3+}, and Eu^{3+} have been known to show photoredox reactions. For one photon reduction of Eu^{3+} to Eu^{2+}, the yields in alcoholic solution have been measured by the method of nanosecond laser photolysis. The highest yield was 0.97 ± 0.16 in methanol at 308 nm XeCl excimer laser excitation.

In the VIS and IR regions, sharp f'←f transitions can be seen, however, the f' excited states are not photo-reactive by one photon absorption. Two-

photon reduction of Eu^{3+} to Eu^{2+} has been found by excitation the f'←f transitions in the VIS wavelengths in solution. Laser fluence dependence, excitation spectra, and two photon and two color experiments suggested that the intermediates had a lifetime much shorter than the pulse width of the pumping laser (20ns). The threshold energy for the reduction has been found as 5.3 eV. Detailed investigation will open a method of high selective and efficient reduction.

The photochemistry of the lanthanide ion is hopefully applied for the actinide ion, because those atoms have f electrons. One of actinide elements, Am, is important in the nuclear waste. Eu and Am are in the same group with the electronic structure of f^7s^2 .

2. EXPERIMENTAL

For the two-photon chemistry, a dye laser (Lambda Physik FL 3002E) was used for excitation and for monitoring the concentration of Eu^{2+}. Eu^{2+} shows fluorescence peaked at 489 nm, therefore, the concentration was able to be determined by the fluorescence intensity. A conventional apparatus of the nanosecond laser flash photolysis was used for measuring absorbances of the product Eu^{2+}. The excitation source was an excimer laser (Lambda Physik EMG201MSC). The absorption spectrum of Eu^{2+} appears in the spectral region shorter than 400 nm and has a peak at 250 nm with the molar extinction coefficient of 1950 M^{-1} cm^{-1}. The yields were determined by comparing the concentration with the standard references.

3. RESULTS AND DISCUSSION

3.1 Reduction Quantum Yields of Eu^{3+} to Eu^{2+} by One-photon Absorption [3]

The CT spectra of Eu^{3+} in solution appear in the UV region. Four wavelengths of an excimer laser (193, 222, 248, and 308 nm) can be used to induce the following reactions.

$$Eu^{3+}(RHOH)_n + h\nu \rightarrow Eu^{2+}(RHOH)_{n-1} + RHOH^+ \quad (1)$$

The absorption spectrum of the photoproduct of Eu^{2+} was detected by the method of nanosecond laser photolysis. This method is suitable to determine the quantum yield, because secondary photoreactions and/or a dilution effect by the unirradiated volume can be avoided. Eu^{2+} formed immediately after laser irradiation. The reactions probably take places in a few picoseconds.

Interesting features have been observed in the quantum yields, although the detailed reasons are not very clear at the present stage. The first one is that the highest quantum was 0.97 ± 0.16 in methanol at 308 nm excitation, in other words, the charge separation yield is very high under some conditions. Secondary, wavelength effects were observed. Within a single CT band, shorter wavelength excitation showed higher yield. In H_2O it was 0.12 at 193 nm , and 0.06 at 222 nm. It was 0.23 at 248 nm, and 0.4 at 222 nm.

3.2 Reduction Induced by Two Photon Excitation to the Charge Transfer Band

Two-photon reactions via the f'←f transitions have been expected for lanthanide and actinide ions, because the reaction selectivity will be highly enhanced. [4,5] Photo-ejection of Sm^{2+} in BaClF crystal by two-photon absorption has been demonstrated and the intermediate is a f' excited state. [7] The similar two-photon reaction has been found to occur in solution as shown below. [6]

Dye laser lines were turned to the f'←f transitions, $^5L_6 \leftarrow {}^7F_0$ (394.2 nm), $^5D_2 \leftarrow {}^7F_0$ (464.7 nm), and $^5D_1 \leftarrow {}^7F_0$ (526.0 nm). The reaction (1) occurred except for 526.0 nm excitation. The concentration of Eu^{2+} was measured by the fluorescence intensity. The concentration quadratically increased as increasing in the laser intensity. The concentrations of Eu^{2+} were measured at several excitation wavelengths, which consist of excitation spectra. These spectra

reproduced the absorption spectra of the f'←f transitions. These results (shown in Figs.1 and 2) well indicate the intermediates are the the f'←f excited states and that the second photon pumps the CT levels and induces the reduction.

The reaction efficiency was unexpectedly low. The absorbed photon for evaluating the efficiency was calculated using the molar extinction coefficients of the f'←f transitions. Non-linear absorption under a high laser fluence was neglected under the first approximation. The concentration of Eu^{2+} was measured, then, the efficiency was evaluated to be 3×10^{-5} at 464.7 nm and 460 mJ/cm^2.

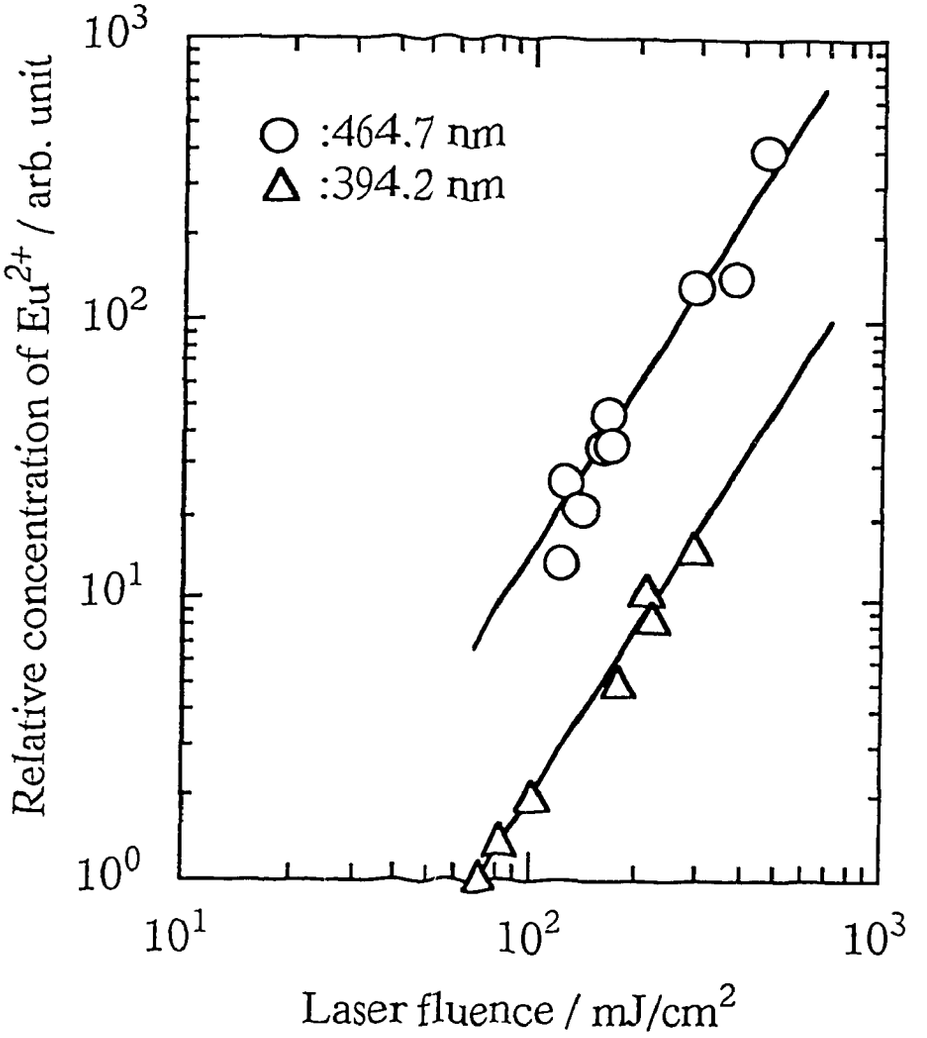

Figure 1. The laser power dependence of the concentration of Eu^{2+} vs. the irradiating laser fluence. The slope of the solid lines was 2.0.

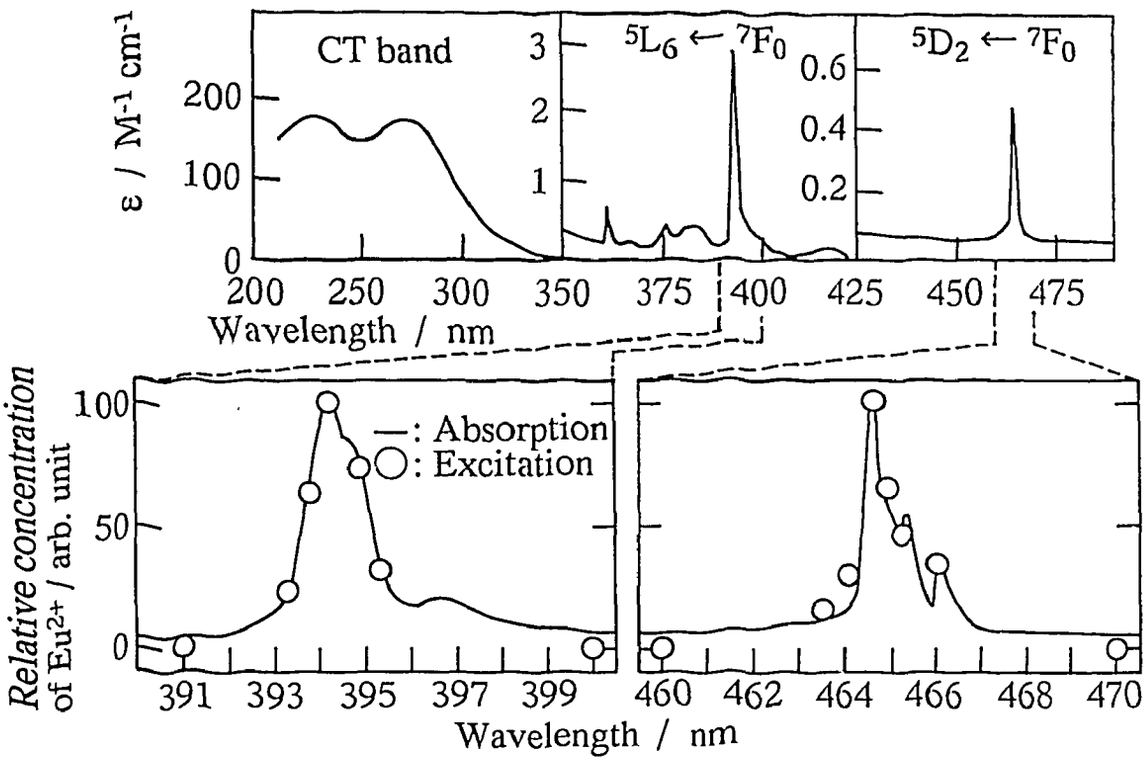

Figure 2. The concentration of Eu^{2+} formed by several wavelengths at the irradiating laser fluence of 290 mJ/cm^2. The symbols (O) are the normalized concentration of Eu^{2+} and the solid lines are the absorption spectra.

The two color and two photon excitation can induce the photo-reduction. The first photon was fixed at the transitions $^5L_6 \leftarrow {}^7F_0$ (394.2 nm) or $^5D_2 \leftarrow {}^7F_0$ (464.7 nm). Some of results are shown in Fig.3.

It is indicated that the reduction efficiency is enhanced when the wavelength of the second photon is shorter than 560 nm. The corresponding threshold energy for the reduction is 5.3 eV (233 nm) from the ground state. The same threshold energy has been observed for the case of 464.7 nm excitation. The photoreactive CT level by one photon absorption appears 3.5 eV (350 nm). There is a large difference in the CT levels.

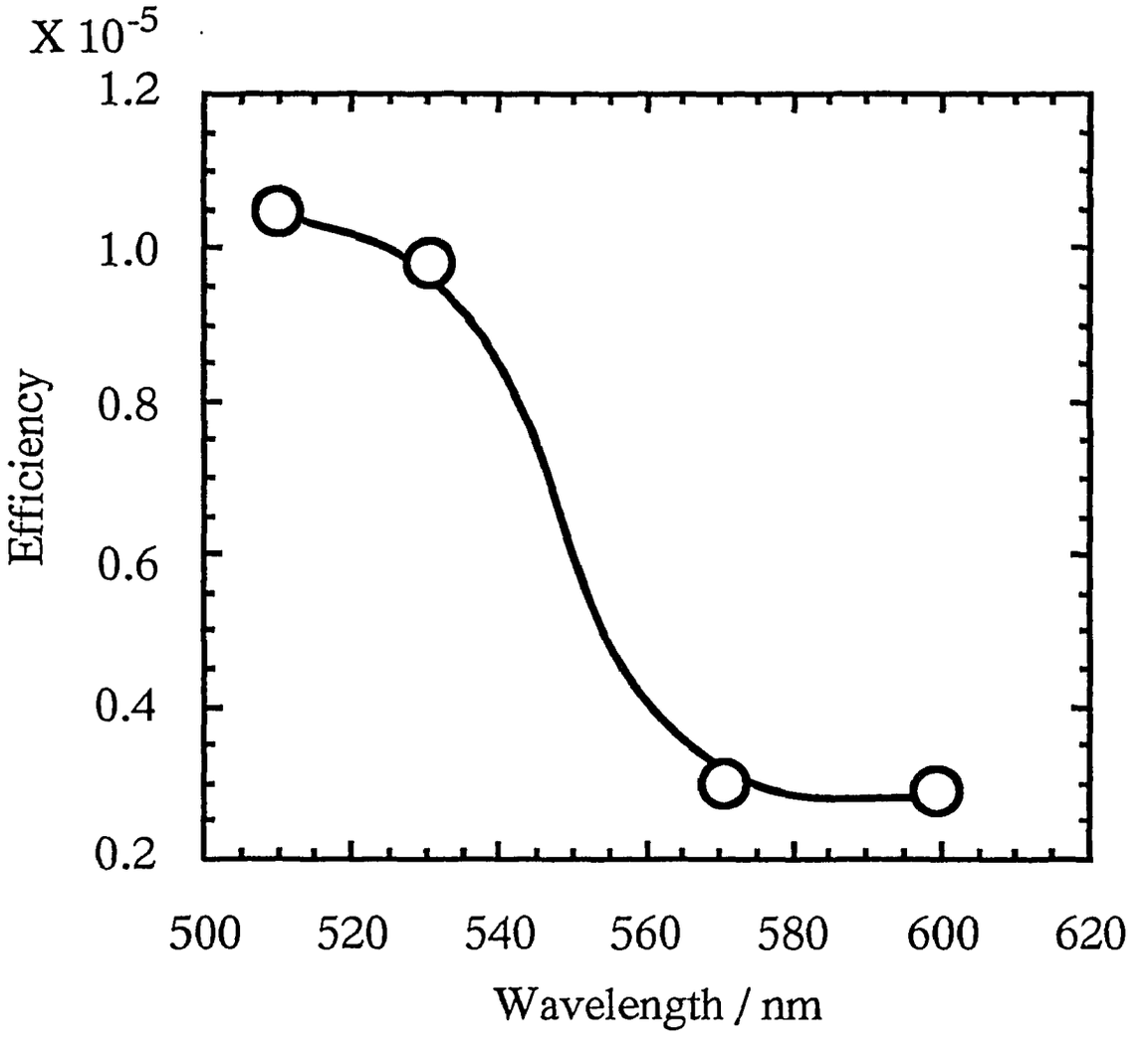

Figure 3 Photoreduction efficiency by the two color and two photon excitation at the same time. The first photon was fixed at the transitions $^5L_6 \leftarrow ^7F_0$ (394.2 nm) with the fluence of 440 mJ/cm^2. The efficiency was measured for the second photon at four wavelengths. The photon number second photon was 9.8×10^{17} photon/cm^2 (corresponding to 494 mJ/cm^2 at 394.2nm)

The efficiency of the two-photon reduction can be calculated assuming probable values for the second photon : the absorption coefficient to the CT band (ε = 100 $M^{-1}cm^{-1}$) and the reduction efficiency of the CT band (ϕ = 0.1). The theoretical analysis suggests that the lifetime of the intermediate is in a picosecond range. Therefore, the intermediate may not be the $^5D_0$ level, which has a lifetime of 230 μs. Detailed experiments are now in progress.

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