Chemical Physics Letters 465 (2008) 238–240

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Reduction of Eu^{3+} to Eu^{2+} by an intense femtosecond laser pulse in solution

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ARTICLE INFO

Article history:
Received 6 August 2008
In final form 3 October 2008
Available online 8 October 2008

ABSTRACT

Europium 3+ ions in methanol were found to be reduced to the corresponding 2+ ions upon irradiation with intense femtosecond laser pulses. The excitation wavelength of 800 nm was nonresonant with their electronic transitions of Eu^{3+}. It is notable that femtosecond white-light laser was generated when the reactions occurred. The mechanisms can be explained in terms of solvated electron formation followed by the reduction. The electron ejection in a focused beam in solution has been known to be accompanied by white-light laser.

1. Introduction

Lanthanide and actinide ions show re-dox reactions in solution upon irradiation with UV light, γ-ray, and, recently, ultrashort laser pulses as reviewed in photochemistry of f-element ions [1]. One of photo-active f-element ions is europium. Eu^{3+} can be reduced to Eu^{2+} by excitation of the charge-transfer band in the UV region with reasonably high quantum yields [2,3]. Multiphoton reductions to Eu^{2+} in solution have been found by the present authors using nano- and picosecond laser pulses [4,5]. The f–f transitions are photochemically inactive by one photon excitation; however, focused laser pulses, multiphoton excitation, enable us to induce re-dox reactions.

Eu^{2+} in optical glasses can be created from Eu^{3+} by infrared femtosecond laser pulses. It has been suggested that an electron is ejected and that Eu^{3+} ions act as electron-trapping centers [6,7]. Reactions between electrons and Eu^{3+} ions have been found in radiation chemistry in solutions. Irradiation of γ-rays can produce an electron in solution and the electron reduces Eu^{3+} to Eu^{2+} [8,9].

The present paper reports on the formation of Eu^{2+} by irradiating solution with infrared femtosecond pulses, where the laser wavelength of 800 nm corresponds to an isolated resonance of the system. The product Eu^{2+} was detected by its fluorescence after laser irradiation. An interesting observation is that the solution emitted white-light laser whenever the Eu^{2+} fluorescence was observed. Based on this observation, the reduction mechanism can be explained in terms of reactions between electrons and Eu^{3+} ions, because femtosecond white-light laser is generated by a time-dependent nonlinear index in optical filaments in a medium. The filaments are created by balancing between the nonlinear index and the negative index by electrons, which are injected from a medium by focused, high-intensity femtosecond laser irradiation [10–12].

2. Experimental

A linearly polarized femtosecond laser pulse with a central wavelength of 800 nm was delivered from a 0.5 TW all-diode-laser pumped Ti:sapphire laser system Alpha 100/XS, Thales Laser, at a repetition rate of 100 Hz. The energy was reduced to less than 1 mJ/pulse. The transform-limited pulse had a duration of 45 fs. The pulse width was measured with a single-shot autocorrelator (Thales, TAIGA), and the total pulse energy was measured by a power meter (Gentec·eo, PS-310B). A 800-nm laser pulse was focused with a plano-convex lens with a focal length of 200 mm, and a sample cell was located 20 mm before the focal point. The cell contained 0.16 cm^3 Eu^{3+}solution in a quartz cell with a size of 2 (width) × 4 (depth) × 20 (height) mm^3. The Eu^{2+} product was detected by its fluorescence in the perpendicular direction of the incident laser after femtosecond laser irradiation, using an exciting light source of a 380-nm LED (LS-380, Ocean Optics). A spectrophotometer (USB2000, Ocean Optics) was used to measure the fluorescence with a typical spectral resolution of 10 nm. The Eu^{2+} concentrations after laser irradiation were determined by the fluorescence intensity. A calibration curve between its fluorescence intensity and the concentration was made, taking into account of the Eu^{2+} fluorescence quenched by Eu^{3+}, which has been discussed elsewhere [5].

$EuCl_3·6H_2O$ (Aldrich, 99.99%), methanol (Nacalai, fluorescent grade), and 15-crown-5-ether (Tokyo Kasei, >97%) were used without further purification. The solution was degassed to avoid oxidizing Eu^{2+} with dissolved oxygen. 15-Crown-5-ether can enhance the fluorescence yield of Eu^{2+} 690 times compared with that in the absence of the ether in methanol solution [16].

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doi:10.1016/j.cplett.2008.10.005

3. Results

Methanol solution of 0.1 M $EuCl_3 \cdot 6H_2O$ with 0.3 M 15-crown-5-ether was irradiated by Ti:sapphire laser pulses with a duration of 45 fs for 10 min at 100 Hz. After the irradiation, the photoproduct, Eu^{2+}, was detected by its fluorescence. The excitation wavelength of 800 nm corresponds to an isolated resonance of the electronic transitions of the system.

As shown in Fig. 1, the Eu^{2+} fluorescence intensity from a sample irradiated by 800-nm laser pulses was increased with increases in the irradiation laser energy of up to 307 μJ/pulse. The broad emission peaked at 428 nm is assignable to Eu^{2+} fluorescence, and a few peaks around 600 nm are due to Eu^{3+} luminescence. The Eu^{2+} fluorescence peak is affected in the presence of 15-crown-5-ether and shows a blue shift from 490 nm in the absence of the ether. Increases in the Eu^{2+} fluorescence intensity were accompanied by slight decreases in the Eu^{3+} luminescence intensity.

The Eu^{2+} fluorescence intensity increased nonlinearly with increases in the irradiation energy, as shown in Fig. 2. The log–log plots between the Eu^{2+} fluorescence intensity and irradiation laser energy have a slope of 2.9. One of the interesting observations is generation of white-light laser. Whenever the femtosecond white-light laser was generated during the irradiation, the Eu^{2+} fluorescence was observed after laser irradiation. The inserted pictures of the white-light laser in Fig. 2 are shown, which were taken on a paper 20 cm after the sample cell. The size of the central white portion is approximately 40 mm in diameter.

Other observations were bubble formation and a pink luminescence along with laser beam propagation, as shown in a side view of the sample during irradiation in Fig. 2. The pink color can be ascribed to the mixture of the blue luminescence of Eu^{2+} and the red one of Eu^{3+}. Bubble formation was also observed in the case of resonance excitation at 394 nm, which corresponds to the f–f transition of $^5L_6 \leftarrow {}^7F_0$, where the reduction of Eu^{3+} to Eu^{2+} occurred via three-photon excitation [5]. The bubbles can be assumed to be due to H_2 formation, because photo-excited Eu^{2+} is very active and efficiently converted to Eu^{3+}, accompanied by reductions of solvents and evolution of H_2. In the present experiments it is supposed that Eu^{2+} is excited by two-photon absorption by the 800-nm pulse and the excited Eu^{2+} reacts with the solvents. In fact, Eu^{2+} fluorescence and bubbles were observed from a sample containing Eu^{2+} without Eu^{3+} in response to 800-nm pulse excitation. The concentration of the Eu^{2+} product after 6×10^4 shots of a laser energy of 192 μJ/pulse was 1.4×10^{-3} M, which corresponded to an order of 2% of the irradiated photon numbers.

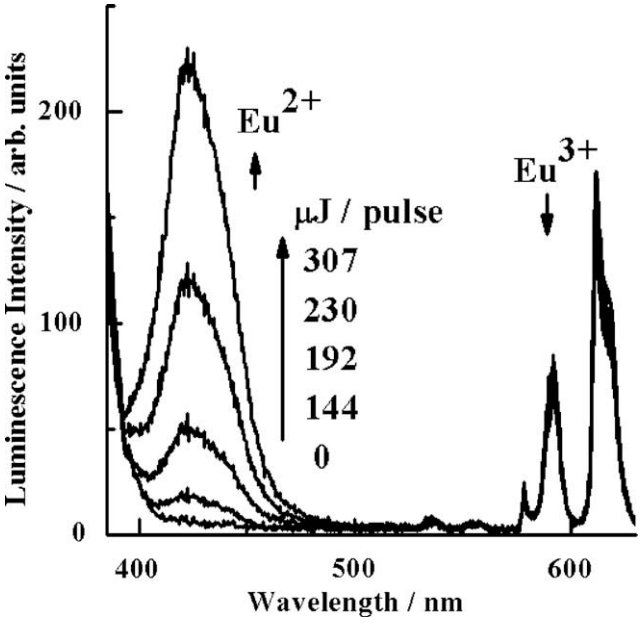

Fig. 1. Luminescence spectra by excitation with a LD 380 after irradiating methanol solution of 0.1 M $EuCl_3 \cdot 6H_2O$ with 0.3 M 15-crown-5-ether. Samples were irradiated by a Ti:sapphire laser pulse at 100 Hz for 10 min with laser energy from 0 to 307 μJ/pulse. The broad emission peaked at 428 nm is assignable to Eu^{2+} fluorescence and a few peaks around 600 nm are due to Eu^{3+} luminescence. The Eu^{2+} fluorescence intensities increase with an increase in irradiating laser energy and are accompanied by a slight decrease in the Eu^{3+} luminescence intensity.

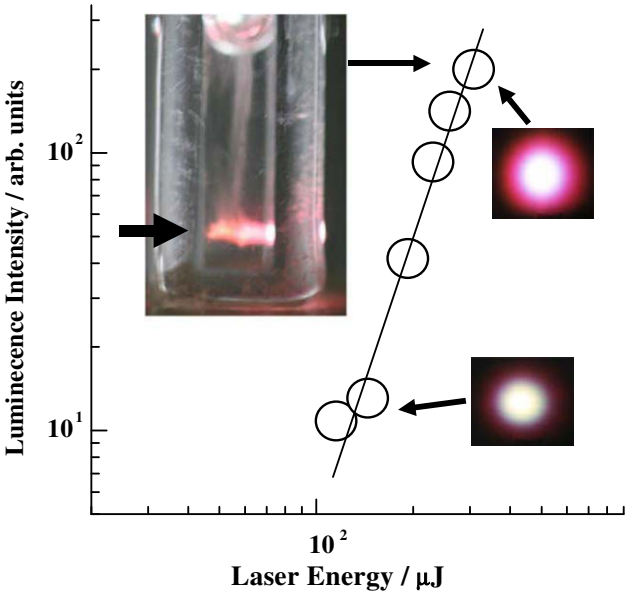

Fig. 2. The Eu^{2+} fluorescence intensity increases nonlinearly with increases in the irradiation energy. The solid line of the log–log plots has a slope of 2.9. The two right inserted figures are pictures of white-light laser on a paper 20 cm after laser passing through the sample cell for the cases of the highest and lowest irradiation energies. The size of the central white portion is approximately 40 mm in diameter. When the Eu^{2+} fluorescence was observed, the femtosecond white-light laser was emitted. The top picture is a side view of the cell, showing luminescence and bubbles during irradiation. The black arrow on the picture indicates the incident laser direction.

4. Discussion

4.1. Reaction mechanisms

The Eu^{2+} formation mechanisms are estimated as below

$$CH_3OH \overset{\text{fs laser}}{\rightarrow} CH_3OH^+ + e^- \quad (1)$$

$$Eu^{3+} + e^- \rightarrow Eu^{2+} \quad (2)$$

An electron is generated from solvent upon irradiation with high-intensity femtoseond pulses, as indicated Scheme (1). Once an electron is generated, Eu^{3+} captures the electron by Scheme (2). Details of the two reactions are explained below.

4.2. Electron formation by propagation of femtosecond pulse in sample solution

Self-focusing and filament formation in condensed matter accompanied by white-light laser have been well-studied [10–12]. The free-electron generation process in condensed matter occurs through the excitation of electrons from the valence to the conduction bands, followed by partial cascade ionization. The elec-

tron density is estimated to be as high as 10^{18} cm^{-3}, which is equivalent to 1.7×10^{-3} M, and far below the plasma critical electronic density of 10^{21} cm^{-3}. The pulse duration is too short to allow for a full breakdown unless there are tight focusing conditions. In the case of water, the break down was observed when a short focal length lens of $f < 43.1$ mm was used [13], while a much longer focal length of 200 mm was used in this Letter.

An input laser beam is converged by a focusing lens and nonlinear index n_2 of the medium. An electron is injected under a high intensity laser field and the electrons play a role of defocusing by the negative index. A balance between the positive and negative indexes maintains a small size of high intensity region, which is called a filament. The peak intensity in the filament is clamped and kept approximately 10^{13} W cm^{-2} [10–12], which is high enough to generate electrons. The order of the multiphoton transition to the conduction band of methanol is suggested to be 5 based on the band gap in methanol of 6.2 eV [14]. Once electron is ejected, the surrounding methanol molecules relax it to the solvated electron and is captured by Eu^{3+}. The laser pulse becomes steep in the filament, resulting in self-phase modulation, i.e., white-light laser. It is quite natural that the solution would emit white-light laser whenever the reduction was observed. White-light emission has been observed from femtosecond laser-induced plasma in a water droplet [15]. Such emission is not the white-light laser observed in a cell. The microdroplet acts as a lens and the tight focusing conditions are held. The electron density can be reach 10^{21} cm^{-3} at an irradiation intensity of 10^{13} W cm^{-2}. The size of the filament so-called near axis region in methanol is typically 10 μ φ in diameter, and the length is a few mm [14]. Many filaments would be produced, because the irradiation energy was approximately 100 times the critical power (P_{cr}) of filament formation using a focused beam. When the input power (P_{in}) is far above P_{cr}, the instability breaks up the beam into a large number of filaments [10–12]. Number of filaments (N) has been simply estimated by the equation, $N = P_{in}/P_{cr}$, when P_{cr} is an order of micro Joule with 100-fs pulse. Number of filaments could be an order of 100 in the present experiments. The capture efficiency of the electrons by Eu^{3+} based on the above parameters gave less than 1, but these parameters have to be directly measured and/or accurately clarified to finalize the efficiency.

4.3. Bubble formation

Bubbles were visually observed as shown by a picture at the highest laser intensity (307 μJ/pulse) in Fig. 2. The bubble formation can be attributed to H_2 production, as follows. Eu^{2+} has absorption below 400 nm and can be excited by the fundamental laser wavelength via two-photon absorption. The photoexcited Eu^{2+} is active, and hydrogen production in methanol has been reported [17,18]. Although Eu^{2+} was partially protected by crown ether in the present experiments, water molecule would be reduced by the excited Eu^{2+} and be finally converted to hydrogen molecule, as in Scheme (3)

$$Eu^{2+}H_2O \xrightarrow{h\nu} Eu^{3+} + OH^- + 1/2H_2 \quad (3)$$

The slope of 2.9 on a log-log scale between Eu^{2+} emission and laser intensities may indicate that Eu^{2+} forms by 5-photon ionization of methanol and that the Eu^{2+} returns to Eu^{3+} by two-photon excitation with hydrogen formation.

4.4. Multiphoton excitation of Eu^{3+} ions

Eu^{3+} ions can be excited by two-photon absorption upon irradiation with 800-nm fundamental pulses, which is followed by Eu^{3+} luminescence, as have been observed in Eu^{3+} ions and some other lanthanide ions [19]. Reactions of Eu^{3+} with solvent to Eu^{2+} could be expected via the multiphoton absorption processes. In the case of resonant excitation of the $^5L_6 \leftarrow {}^7F_0$ transition at 394 nm [5], three photon processes of 394-nm photons are assumed to induce the reactions of Eu^{3+} to Eu^{2+}; therefore, five or six photons at 800 nm could reach the active states of the reduction. The fundamental pulse at 800 nm has a broad spectrum approximately 30 nm; therefore, the $^5L_6 \leftarrow {}^7F_0$ transition at 394 nm would be excited via a two-photon process, but no Eu^{2+} signal was observed under the laser-intensity conditions where Eu^{3+} two-photon luminescence was seen but white-light laser was not emitted, indicating a low conversion efficiency from Eu^{3+} to Eu^{2+} by this mechanism.

4.5. On the same line with those in glass and radiation chemistry in solution

Eu^{3+} in glass can be reduced to Eu^{2+} by focused 800-nm femtosecond pulses [6,7]. They have suggested that glass bulk is ionized by multiphoton absorption and the electron is trapped by the Eu^{3+} ions. They also discussed that a short-wavelength part of white-light laser could induce a hole-trapped defect, in other words, ionize the glass. The white-light laser could have been observed from the glass samples, though no clear description.

A solvated electron can be created by radiation chemistry. γ-Ray of ^{60}Co efficiently induces Eu^{2+} formation from ethanol solution of $EuCl_3{\cdot}6H_2O$ at 77 K [7]. Eu^{2+} was identified by its fluorescence spectra, which peaked at 465 nm, and its lifetime of 780 ns at 77 K. An electron is produced by γ-ray irradiation in a low temperature matrix and Eu^{3+} captures the electron and forms Eu^{2+}. Another γ-ray experiment was carried out at room temperature in water, and Eu^{2+} ion was trapped by SO_4^{2-} as precipitation of $EuSO_4$ [9]. In the present Letter we are observing similar chemistry to those observed in the radiation chemistry.

Acknowledgement

This work was financially supported in part by a Grant-in-Aid (No 19350016) from the Ministry of Education, Culture, Sports, Science and Technology Japan to N.N.

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