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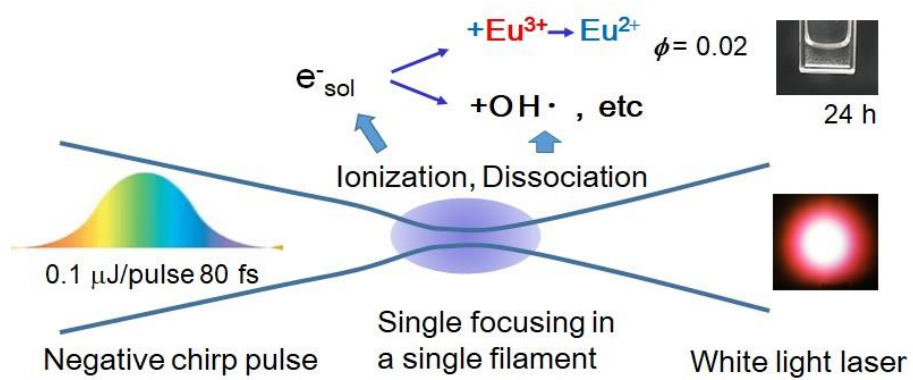
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HIGHLIGHTS

- Reduction efficiencies from Eu^{3+} to Eu^{2+} by femtosecond IR and one-photon UV pulses.
- An estimation of electron-capture efficiency in a femtosecond filament.
- Halogen ions enhance absorption of focused IR femtosecond pulses.

ABSTRACT

This paper reveals one of the primary chemical processes in femtosecond filaments. Reduction yields from Eu^{3+} to Eu^{2+} by focused femtosecond 800 nm pulses in ethanol solution were determined to be 0.021 (Eu^{2+} molecule/800 nm photon absorbed) or 0.14 (micro mol/ absorbed laser energy(J)) under single filament conditions. The Eu^{3+} captured an electron which was formed by filamentation, leading to Eu^{2+} . About half of the solvated electrons that initially survived were estimated to be captured by Eu^{2+} . Halogen ions are found to make a contribution to femtosecond pulse absorption with an increasing tendency with $\text{Cl} < \text{Br} < \text{I}$.

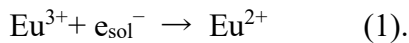


1. Introduction

Femtosecond filamentation produces weak plasma accompanied by white continuum generation which leads to the breakdown of water and/or solvents at a high laser intensity [1-7]. It results in violent conditions in regard to chemical reactions. Hence, chemical products starting from hydrogen, oxygen, and hydrogen peroxide [8, 9], as well as reduction of metal ion [10, 11] have been reported. This is also followed by the formation of nanoparticles (the most studied example): gold, Au_n [12-18]; carbon nanoparticles [19]; diamond formation [20]; and DNA base modification [21], and ultimately, cancer therapy [22]. Femtosecond filamentation is accompanied by white light laser. It should be noted that the white light laser and its spectra are directly related to the high electron density and electron capture reactions [23, 24].

Although Au_n formation mechanisms have been extensively studied in a filament, they involve multistep reactions. To reach the final products Au_n, the reactions involve at least three electron reduction steps followed by mediation with H₂O₂ [12-18]. On the other hand, carbon nanoparticle formation and application to biological systems are promising [18, 20-22], and would also be composed of multistep reactions. Therefore, it is desirable to consider the elementary reaction in the femtosecond filaments.

A simple reaction is suitable for this purpose. The Reaction (1) was reported by the present group and can be regarded as a one-step electron-capturing reaction in a filament [10].



Electrons denoted as e_{sol}⁻ in Reaction (1) are produced by ionization and followed by solvation in a filament. A single focusing in a single filament [4] is necessary to study the efficiency. This can be achieved by using a pulse with a low input energy. In this study, an order of 0.1 μJ /pulse femtosecond laser was used as the lowest energy/pulse for chemical reaction in the filaments known [4, 5, 8-22].

A high intensity of femtosecond pulse, typically, $1 \times 10^{13} \text{ Wcm}^{-2}$, would create a filament with an electron density of $3 \times 10^{18} \text{ cm}^{-3}$ [7]. The electron e_{sol}^- would react with a neighboring cation, radicals such as $\text{H}\bullet$, $\text{OH}\bullet$, and with e_{sol}^- itself in the small volume. When Eu^{3+} salt is added, Reaction (1) occurs and rigorously competes with the above electron-capturing reactions. In this study, we measured the overall yield and attempted to estimate the ratio of Reaction (1) and the e_{sol}^- quenching reactions.

The product Eu^{2+} concentrations were determined on the basis of the newly fixed absorption Eu^{2+} coefficients. Furthermore, we re-examined the ultraviolet (UV) one-photon reaction of Eu^{3+} to Eu^{2+} in relation to the significance of Reaction (1) and showed how to evaluate reaction yield. Next, we determined the yield and efficiency of the femtosecond filamentation reaction. During the course, we found that halogen ions can enhance absorption of focused femtosecond pulses to some extent.

2. Experimental

The femtosecond laser used was a Coherent Legend Elite (USP-HE 30 fs, 5 kHz, 0.8 mJ/pulse, $1/e^2$ width of 6.2 mm) [25, 26]. The output of the amplifier was reflected by wedged plates and thereby weakened 1.5×10^{-4} times down to a typical 0.1 μ J/pulse. The averaged power of the laser pulses was monitored using a Coherent PM10 power meter, and the pulse width was monitored using an equipped single-shot autocorrelator. Transmission through sample of femtosecond laser pulses was measured using the same optical arrangements and detectors [12]. The laser beam was focused into a cell located at the focal point through a plano-convex lens with a focal length of 12 or 15 cm. Furthermore, a negative chirp pulse was generated by adjusting the output grating of the laser to obtain the maximum absorption by water. A certain negative chirp pulse is known to be absorbed more effectively than the transformed limited pulse at a fixed laser energy [6]. The apparent pulse width with a negative chirp character was 80 fs elongated from the transformed limited pulse of 30 fs. A white light laser was accompanied at typical energy of 0.14 μ J/pulse on the cell surface with the 80 fs pulse. It is worthy of note that no absorption and white light laser was generated at the 30 fs pulse with the same pulse energy. The quartz cell with a bottom area of $0.5 \times 1 \text{ cm}^2$ contained a solution of 0.6 cm^3 . The absorption of the solution was measured after 1–24 h irradiation. The Eu^{3+} was almost transparent at 800 nm and visible wavelengths observed with a spectrometer.

The UV excitation source was an excimer laser (COHERENT Compex Pro 110) at 308 nm with a beam size of $2.5 \times 0.7 \text{ cm}^2$, and its parallel beam was introduced on the quartz cell with an internal area of $1 \times 1 \text{ cm}^2$ and energy of 63 mJ/pulse with a pulse width of 20 ns.

Absorption spectra were measured using a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer with a spectral resolution of 2 nm. Samples for laser reactions were degassed with freeze and thaw cycles under rotary pump vacuum conditions and fused off. Europium(III) chloride hexahydrate ($\text{Eu(III)Cl}_3 \cdot 6\text{H}_2\text{O}$) with a stated purity of 99.9%

(Aldrich), europium(II) chloride (Eu(II)Cl_2) with a stated purity of 99.99% (Aldrich), and ethanol (EtOH , 99.5%) and methanol (MeOH , 99.8%) specially prepared reagents (spectral grade; Nacalai Tesque) were used. EtOH containing 3–5% percent water was also used. Many of the halide metal salts, including calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) extra pure, were obtained from Nacalai Tesque.

3. Results

3.1 UV one-photon reaction and its quantum yield

The UV light ($h\nu$) Reaction (2) has been re-examined to determine the yield ϕ . The Reaction (2) was previously studied using UV nanosecond laser photolysis [27], where the products of Eu^{2+} were detected in a transient spectrum. A medium-pressure mercury lamp was irradiated and Eu^{2+} was recovered as the insoluble salt of EuCl_2 [28]. The UV pulse at 308 nm pumps the longer wavelength edge of the absorption peaked 275 nm, which has been assigned to the Eu-Cl 4f-5d charge transfer (CT) transition [29]. The formation of Eu^{2+} was observed in the absorption spectra as a stable product in this study, as shown in Fig. 1.

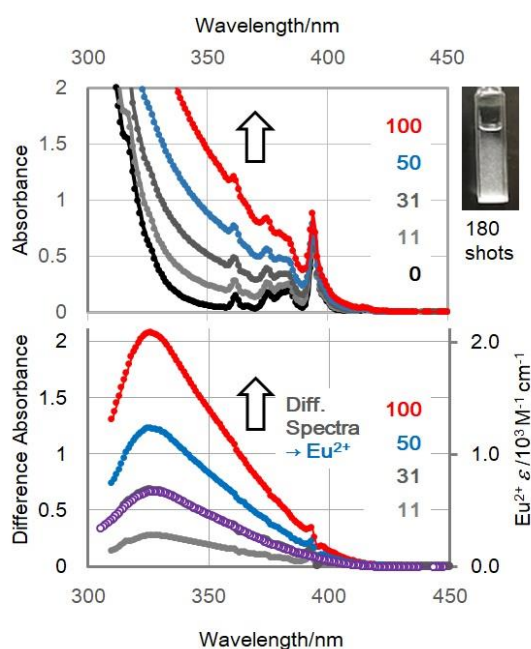


Fig. 1. Upper: UV absorption spectral changes are shown with irradiating laser pulses of 63 mJ from a 308 nm excimer laser, from 0, 11, 31, 50, and 100 shots. The initial concentration of Eu^{3+} was 0.42 M in EtOH. **Lower:** The difference spectra between

irradiated (11–100 shots) and the initial absorption (denoted 0 shot) spectra. The Eu^{2+} absorption spectrum is overlain on the difference spectrum at 31 shots by purple open circles as a reference. The molar extinction coefficients of the Eu^{2+} are on the right vertical axis. The sample solution became clouded after 180 shots as seen in the upper right inset.

In the upper panel in Fig. 1, Eu^{2+} was detected as a rise in absorption at wavelengths shorter than 410 nm with irradiation laser shots of 63 mJ/pulse at 308 nm laser. The structural absorption spectra between 350–400 nm were due to the familiar Eu^{3+} 4f-4f transitions. The lower panel shows difference spectra between 0 and 11, 31, 50, and 100 shots. It may be noted that the sample solution gradually became cloudy after 100 shots and white powder was visually seen as the inserted picture at 180 laser shots. The sample with the powder showed the characteristic strong luminescence around 420 nm. The EuCl_2 microcrystal has been known to show a blue emission [30]. The signal fluctuations around 394 nm in the difference spectra were attributed to artifacts because of lack of re-settability of the spectrometers around the sharp absorptions of Eu^{3+} .

To evaluate Eu^{2+} concentration, the molar extinction coefficient is $606 \text{ M}^{-1} \text{ cm}^{-1}$ at 350 nm of Eu^{2+} in EtOH was determined based on $414 \text{ M}^{-1} \text{ cm}^{-1}$ [29] in MeOH. The quantum yield of $\phi = 0.7$ for Reaction (2) was extrapolated back to the first shot from samples of a high Eu^{3+} concentration (in Fig.1) and from results at low Eu^{3+} concentrations. The single UV photon reaction showed a tendency toward saturation in the product absorbance of Eu^{2+} as the number of laser shots. This was simply because of the back photo-reaction of (2) and an approach to a photo-stationary equilibrium. The back reaction was in fact observed with a quantum yield of 0.35 at 308 nm laser irradiation starting from a fresh Eu^{2+} sample.

3.2 Eu^{2+} formation following femtosecond filamentation

Femtosecond pulses can reduce Eu^{3+} to Eu^{2+} . The femtosecond pulses are simply focused into a sample irradiated with an 80 fs negative chirp with typical 0.14 μJ pulse energy and 5 kHz at 800 nm. The sample of Eu^{3+} has no absorption at 800 nm excitation wavelength and is almost transparent in the visible region with weak 4f-4f transitions. The present irradiation energy/pulse can be regarded as the conditions which can generate a single filament without multiple refocusing. The filament conditions of single focusing in a single filament have been examined at 0.42 $\mu\text{J}/\text{pulse}$ ($\text{NA} = 0.015$) with 38 fs pulse [4, 5] in methanol.

The products were observed in the UV spectral changes. The spectral changes shown in Fig. 2 by femtosecond pulse excitation is similar to the nanosecond UV pulse results shown in Fig.1. The UV difference spectra clearly indicated the formation of Eu^{2+} .

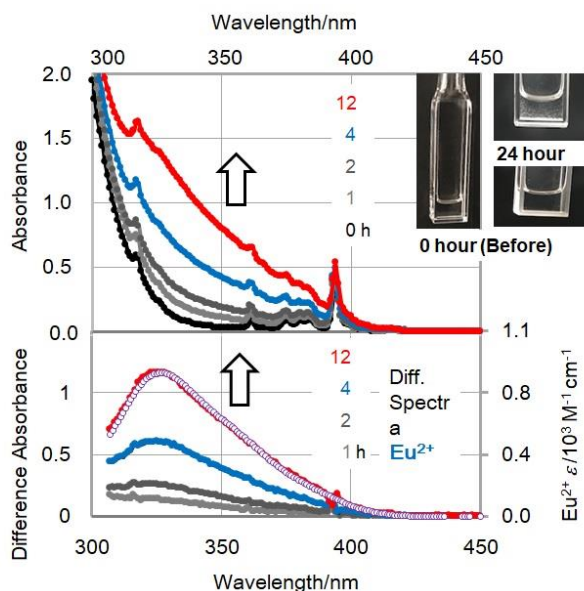


Fig. 2. Upper: The spectral changes by 800 nm fs pulse irradiation (0.14 $\mu\text{J}/\text{pulse}$, 5 kHz, 80 fs with a negative chirp focused through a 15 cm focal lens) were raised for 0–12 h. The spectrum before irradiation is shown as a black line (0.2 M EuCl_3 in EtOH); after 12

h of irradiation it was changed to the one indicated by the red line. **Lower:** The difference spectra between 0 and 1, 2, 4, and 12 h are shown. The purple open circles on the difference spectrum at 12 h are the UV absorption spectrum of Eu^{2+} normalized to the peak at 327 nm. Their molar extinction coefficients are on the right vertical axis. The inset pictures show a sample solution before irradiation (the left and lower ones, i.e., 0 hour) and after 24 h irradiation (the upper right).



From the Eu^{2+} absorption, an efficiency of $\phi = 0.021$ was obtained at 0.14 $\mu\text{J}/\text{pulse}$, where 13% energy was absorbed. The white continuum was seen throughout the irradiation, but a break in the continuum was sporadically seen at later time points, probably due to microcrystal of EuCl_2 formation. After 24 h the scattering became so strong, where the solution became a bit cloudy, then we stopped irradiation. The break and/or blinking were well suppressed either at low concentrations of Eu^{3+} or in MeOH, probably because of the high solubility of Eu^{2+} . The slightly cloudy solution sample after 24 hours shown in Fig. 2 would be attributed to EuCl_2 powder.

3.3 Efficiencies

The efficiencies for the one-photon formation reaction of Eu^{2+} (2) and that in a femtosecond filament (3) are summarized in Table 1.

Table 1. Efficiencies for the one-photon UV and IR femtosecond filament.

Reaction	Laser pulse energy E_0^0 , Hz, Laser WL, Pulse width ^a	ϕ (Q.Y.) (4) ^b	Y [$\mu\text{mol/J}$] (5) ^b	Ref. Fig.
$\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$	63 mJ, 1Hz, 308 nm, 20 ns	0.70	1.8	Fig.1
	0.14 μJ , 5 kHz, 800 nm, 80 fs negative	0.021	0.14	Fig.2

a) Irradiation energy E_0^0 on the cell surface with the repetition rate, the laser wavelength, and the pulse width).

b) The yield definition in parentheses. Probable errors estimated in ϕ and Y : $\pm 5\%$.

The definitions of the efficiency for the reactions (2) and (3) are represented by (4) and (5), respectively. The quantum yield ϕ in (4) is the most generally used index of the efficiency and is useful for one-photon chemistry. The yields for the one-photon Reaction (2) of 0.70 is in agreement with previously evaluated value of $\phi = 0.74 \pm 0.12$ in EtOH using nanosecond laser photolysis at a wavelength of 248 nm [27] obtained after the laser excitation (30 ns). The agreement means that the reaction is completed in the laser pulse, keeping the value for days without significant back reaction. An efficiency of $\phi = 0.021$ was obtained on the bases of absorbed photon number on Eq. (4).

$$\phi = \frac{\text{Products [mol]}}{\text{Absorbed photon [mol or Einstein]}} \quad (4).$$

$$Y = \frac{\text{Products [mol]}}{\text{Absorbed laser energy [micro J]}} \quad (5).$$

Another index, Y ($\mu\text{mol/J}$) (5), is introduced for one-photon reaction as well as femtosecond filament reaction, which is compared with the laser energy. One merit of the introduction of the definition Y is that it allows us to discuss efficiencies using a single reference based on absorbed laser energy. The femtosecond reaction (3), 0.14, showed about 8% of the one-photon reaction of (2) with 1.8 in the unit of efficiency Y .

3.4 Absorption efficiency: a contribution of chloride ions or chlorine atoms

The focused femtosecond laser pulse is absorbed by water, alcohols, and their solutions containing $\text{Cl}^\bullet/\text{Cl}^-$ and other halogenated salts as seen in Fig. 3. These measurements were indispensable to evaluate the efficiency in the above section 3.3. Furthermore, it was necessary to confirm whether or not EuCl_3 in alcohol specifically absorbs a focused 800 nm femtosecond pulse because the solution has a CT band peaked 275 nm, corresponding to three-photon energy of the laser wavelength. As shown in Fig. 3 **Right**, no specific absorption enhancement was observed for EuCl_3 in MeOH and EtOH, and YbCl_3 . Moreover, YbCl_3 in alcohol also has a CT absorption around the three-photon energy region. An increase of absorption by the halogenated atom and/or ions were considerably seen for NaCl , CaCl_2 , AlCl_3 , and CsCl . However, the salt solutions have no CT absorption in the UV region. We can deduce one smooth guideline as shown in Fig.3 **Right**. The results from the solutions of Eu and YbCl_3 can be plotted on the guideline. No clear specific absorption enhancements were seen, which might result from three-photon excitation to the CT level leading to Eu^{3+} reduction.

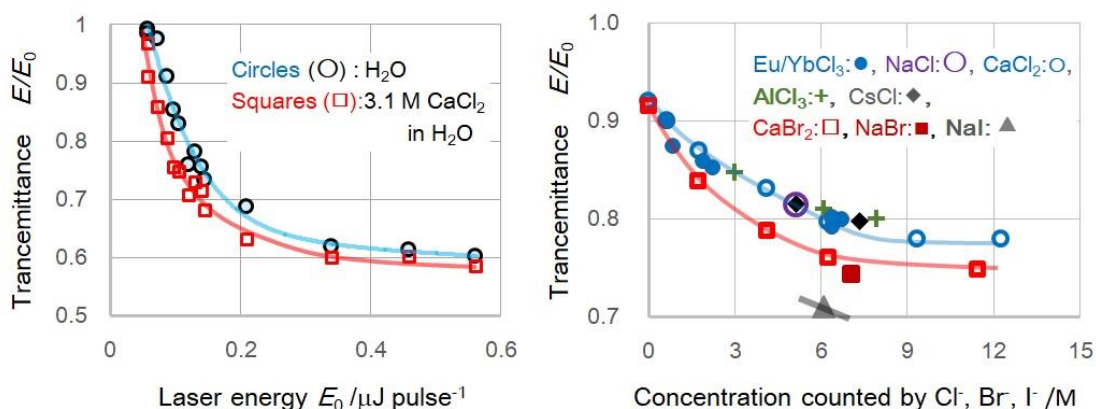


Fig. 3. Left: The transmittance of fs laser pulses for H_2O ($\circ$) and 3.1 M CaCl_2 aqueous ($\square$) (6.2 M as Cl^-) solutions. The laser pulse was 80 fs negative chirp and focused into the center of a 1 cm long cell through a 12 cm focus lens. **Right:** Transmittances of the same fs pulses with 0.09 μJ pulse energy for various salt solutions. The solid lines represent guides. The upper points on the blue guideline are for chloride metal salts.

Eu/YbCl₃ were dissolved in H₂O and also in alcohol (MeOH or EtOH). Various other salt solutions in H₂O are shown. The lower red guideline is for CaBr₂ (□) and NaBr in H₂O (■). The triangle indicates NaI in H₂O. (The E_0^0 , E_0 , and E are laser energies on the cell surface, transmission out of focus, and transmittance focused beam at the same optical arrangements as [12].)

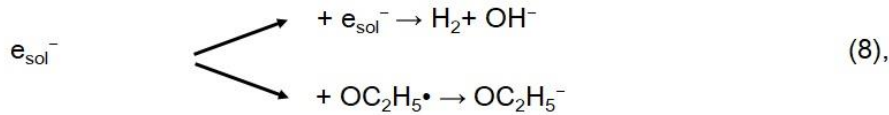
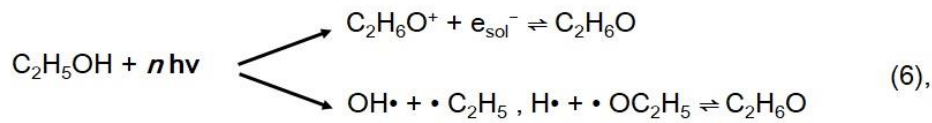
It was found that there is a level of enhancement in absorption by adding Cl•/Cl⁻ in the femtosecond filament. Figure 3 shows the laser energy transmittance of various halide salts in aqueous and/or alcohol solutions in the sub-μJ range. The absorptions are additionally increased by 15% or more with a solution of 6 M chlorine atom. The typical solution of 3.1 M CaCl₂ was counted as 6.2 M chlorine and 1.0 M AlCl₃ as 3.0 M chlorine concentrations. The transmittance can be plotted on one line versus the concentration of chlorine. The bromine complexes seem to have another transmittance line as shown in the right-hand panel of Fig. 3. No appreciable difference was observed between the various counter metals, such as Eu, Yb, Na, Cs, Ca, and Al. The enhancement tendency of Cl < Br < I has been recognized, although the data point for I is one. It would be reasonable on account of the order of the charge transfer to solvent (CTTS) levels of halogenated ions [31]. Several photons of 800 nm are required to overcome the water ionization potential as discussed in the next section. Four photons can reach the excited state of Cl⁻ and Br⁻ and three photons can reach the edge of the excited state for I⁻. Once their electronic levels are excited, electron ejection is expected as it been known to take place by one-photon excitation experiments [32]. The transmittance of solutions of H₂O, MeOH, and EtOH were similar, if any, the absorption efficiencies for MeOH, EtOH were only slightly higher than H₂O.

The present observations in Fig. 3 show that the major absorber of the femtosecond pulse is H₂O or alcohol containing Cl•/Cl⁻ and would achieve a few percentage-point enhancement in the range of chloride concentration of 1 M, in the present experiments. No specific absorption enhancement was observed for the present

EuCl₃ sample. They can be plotted on the blue line shown in Fig. 3. **Right.**

4. Discussion

The femtosecond filamentation schemes in EtOH can be rewritten in the next Reaction (1) and (6)–(9) on the basis of reactions in femtosecond filaments [12]. We attempt to estimate electron capture efficiency in the filament by the Reaction (1) of the generated electrons, which would be quenched by the radicals and itself with the Reaction (8). The parameters in the literature [7, 33, 34] in H₂O for ionization followed by relaxation and quenching in the filament were tentatively applied to the present EtOH system. One of the supports for this assumption is that absorption under the filament conditions were almost the same among water and alcohols as seen in the previous section 3.4; in addition to the facts that Eu³⁺ shows similar UV photochemical reactivities [27]. The femtosecond filament in water has a size of typical 0.2 mm length and 3 micron-meter in diameter and the initial electron density was measured to be $3 \times 10^{18} \text{ cm}^{-3}$ at 0.5 ps delay [7]. Because of the recombination as the subsequent events with a time of 1–12 ps [33], the density e_{sol}^- available for the present chemical reaction is approximately $1.5 \times 10^{18} \text{ cm}^{-3}$ ($2.5 \times 10^{-3} \text{ M}$). Another source of solvated electron e_{sol}^- would be added as seen in Reaction (7) in the reaction scheme. Although it has a little contribution, it may have to be considered in detail in future discussions.



Reaction (1) is a major reaction of the system and has been introduced since the first observation of Eu^{3+} to Eu^{2+} femtosecond reduction [10]. This reduction reaction of metal ions was applied for Au, Ag, and Pd particles formation [12]. The back reactions to the Eu^{3+} by oxidative species in (9) such as OH radicals (with a rate constant of $1.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [35]) would be negligible, because the OH radical would have been quenched by the solvent before Reaction (9).

An important suggestion for discussion has been given in regard to the ionization of water. The commonly used value was 6.5 eV [34] for the ionization limit of liquid water, but they suggested the effective ionization energy of 8.8 eV [36] and 8 eV [7] in femtosecond filament experiments, where 6 photons of 800 nm light are required to overcome the energy. The ionization of water has been significantly studied at 9.32 eV by two-photon absorption at 266 nm [37], which is close to the 6 photons (9.30 eV) of 800 nm. The electron (e_{sol}^-) yield was 0.26 after the solvent relaxation and geminate recombination processes [37]. The 40% of the e_{sol}^- is reported to be quenched by many active radicals in 1 ns [37].

The added Eu^{3+} of 0.2 M would capture electron by Reaction (1) and compete with the quenching Reactions (8). If we read the ionization yield of 0.26 with the reference (4) in unit of photon number, the yield at 800 nm would correspond to a value divided by

6 to 0.043. The present Eu^{2+} formation yield of 0.021 in Table 1 indicated that 48% of the initial e_{sol}^- is calculated to be captured by Eu^{3+} by Reaction (1). The estimation shows that about half of the initial e_{sol}^- would finally be converted to Eu^{2+} . The reduction by electron in water has been known to occur with a diffusion-controlled reaction rate constant (k_{diff}) of $6.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ [35]. The events would occur on the scale of nanoseconds for the case of the 0.2 M Eu^{3+} system ($t_r = k_{\text{diff}} [\text{Eu}^{3+}] = 1.2 \times 10^{10} \text{ s}^{-1}$ or the reaction time of 0.8 ns).

5. Conclusions

One of elementary reactions in femtosecond filamentation is an electron–capture. In this study, single focus conditions in a femtosecond filament [4] were generated by 80 femtosecond negative chirp 800 nm laser pulses. The reduction efficiency ϕ from Eu^{3+} to Eu^{2+} in ethanol was 0.021. In addition, the efficiency in unit of Y ($\mu\text{mol/J}$) corresponds to 0.14 and to 8% of the conventional one-photon photochemistry with a UV laser, where ϕ was 0.7. As a result, about half of the electrons that initially survived are estimated to be used for the reaction.

Halogen ions were found to enhance absorptions of input laser energy under femtosecond filament conditions.

Credit authorship contribution statement

Nobuaki Nakashima: Laser experiments, Writing, Conceptualization, Supervision. **Tomoyuki Yatsunashi:** Conceptualization, Supervision. **Kenji Sakota:** Nanosecond laser experiments. **Izumi Iwakura:** Femtosecond experiments. **Sena Hashimoto:** Femtosecond experiments. **Keiichi Yokoyama:** Conceptualization, nanosecond laser experiments. **Shohei Matsuda:** Nanosecond laser experiments.

Declaration of conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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