X-ray pulse emission from cesium chloride aqueous solutions when irradiated by double-pulsed femtosecond laser pulses

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The intensity of x-ray emission from the aqueous solutions irradiated with focused femtosecond laser pulses (main pulses and relatively low-intensity prepulses) was measured as a function of the delay time between the main pulses and prepulses. Four different x-ray intensity peaks were observed in the picosecond and nanosecond ranges. The prepulse irradiation caused an increase in the x-ray intensity by a factor of 10^3–10^4, as confirmed by x-ray emission spectroscopy. Time-resolved reflectance measurements and imaging revealed that the increase was caused by the solution surface dynamics such as the picosecond plasma formation and decay and the transient (nanoseconds) surface roughness. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2967882]

Intense femtosecond laser pulse irradiation onto condensed matter results in x-ray pulse emission in addition to various nonlinear phenomena such as plasma formation and laser ablation when the laser power at the focus exceeds about 10^{15} W/cm^2. Such ultrashort x-ray pulses have been applied to time-resolved x-ray diffraction[1] and x-ray absorption fine structure (XAFS) measurements[2] as probe pulses. When pulsed x-ray sources are applied to the above measurements, the x-ray intensity is an important parameter. There have been papers reporting techniques to increase the x-ray intensity by using metal targets comprising elements of various atomic numbers,[3] using solid materials with static surface roughness,[4–7] and applying double-pulsed laser irradiation.[8] However, the target materials employed thus far have mainly been limited to solid metal targets.

In contrast to solid metal targets, solution targets can be circulated by a pump and reused continuously as targets. Moreover, the x-ray emission spectra of aqueous solutions can be easily controlled by changing the solutes. These characteristics are advantageous for time-resolved XAFS measurements since long-time count accumulation is indispensable for such measurements and the characteristic x-ray lines of salt elements can be used as wavelength standards. We have reported hard x-ray emission from various aqueous solutions when irradiated by focused femtosecond laser pulses in air.[9–13] For an intensity increase due to double-pulsed laser irradiation, Berglund *et al.* reported an eight-times increase in the intensity of extreme-ultraviolet emission by using ethanol droplets as targets.[14] Recently, Anand *et al.* reported a 68-times increase in the intensity of hard x-ray emission from methanol droplets when irradiated by double-pulsed femtosecond laser pulses with a delay time of 10 ns.[15]

Prepulse irradiation induces various time-dependent phenomena on the solution surface such as the laser-induced plasma formation, transient surface roughness due to laser ablation, and furthermore solvated electron formation when the targets are aqueous solutions. However, the relation between various time-dependent phenomena and the x-ray intensity increase has not been elucidated. In this paper, the

x-ray intensity of aqueous solutions when irradiated by a double-pulsed femtosecond laser is measured by changing the time delay between two pulses in order to clarify the effect of various factors on the x-ray intensity increase.

The experimental setup is shown in Fig. 1. An aqueous solution of cesium chloride (4 mol/dm^3) was used as the sample solution. A vertically flowing flat solution film ($\sim$40 μm thick) was prepared using a titanium nozzle. Femtosecond laser pulses (260 fs, negatively chirped, 780 nm, 1 kHz, Clark-MXR, CPA2001, PositiveLight, EvolutionX) were divided into two beams using a half-wave plate and a polarization beam splitter. Here, vertically and horizontally polarized pulses are defined as a prepulse (0.02 or 0.06 mJ/pulse) and a main pulse (0.3 mJ/pulse), respectively. The delay time between the two pulses was controlled by using an optical delay line for the horizontally polarized main pulse. These pulses were combined coaxially using another polarization beam splitter and focused precisely onto the surface of the solution film by using an objective lens (NA=0.28, Mitutoyo, M Plan Apo 10×). The laser power of the main pulse at the focus was estimated to be approximately PW/cm^2. The incident angle of laser pulses was fixed at 30° to the solution film surface normal. The x-ray intensity was measured using a Geiger counter (Health Physics Instruments, model 5000) and the x-ray emission spectra were measured using a Si(Li) solid-state detector (Röntec, XFlash). Under these experimental conditions, no x-ray emission was detected when the solution film was irradiated by only the prepulse. All experiments were performed at atmospheric pressure and room temperature.
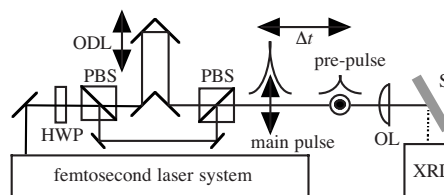

FIG. 1. Top view of the experimental setup for x-ray emission from aqueous solution when irradiated by double-pulsed femtosecond laser pulses. HWP: half wave plate. PBS: polarization beam splitter. ODL: optical delay line. OL: objective lens. S: sample solution. XRD: x-ray detector such as a Geiger counter or a solid-state detector.

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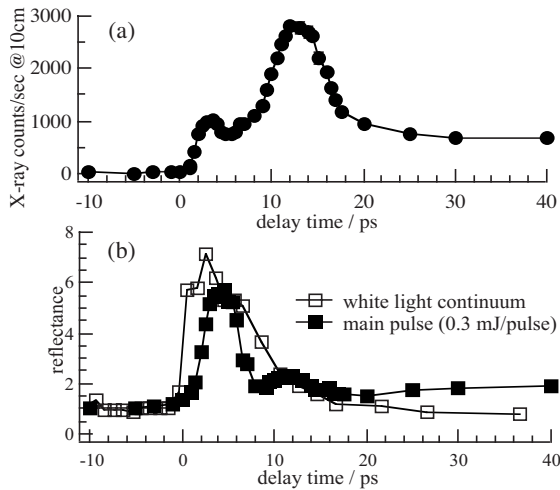
FIG. 2. (a) Time-dependent x-ray intensity and (b) transient reflectance of the main pulse and a white light continuum as a function of the delay time in the picosecond range. The sample solution is a cesium chloride aqueous solution (4 mol/dm^3). The prepulse intensity is 0.06 mJ/pulse.
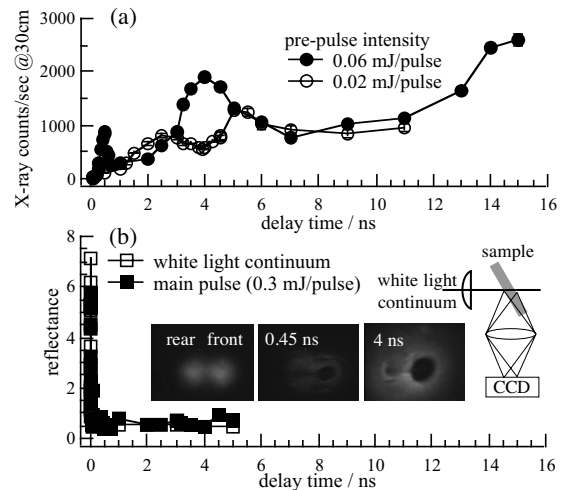

FIG. 3. (a) Time-dependent x-ray intensity and (b) transient reflectance of the main pulse and a white light continuum as a function of the delay time in the nanosecond range. The sample solution is a cesium chloride aqueous solution (4 mol/dm^3). The prepulse intensity is 0.06 mJ/pulse. Inserted images in (b) represent surface reflection images.

Figure 2 shows (a) the time-dependent x-ray intensity and (b) the transient specular reflectance of the main pulse and a probe pulse (695–705 nm) as a function of the delay time in the picosecond range. Two x-ray intensity peaks were clearly observed at 4 and 13 ps. Without the prepulse, the x-ray intensity was only 30 counts/s. Therefore, the x-ray intensity increases by a maximum of 100 times. The transient reflectance of the main pulse, which is normalized by the reflection intensity of the solution without the prepulse irradiation, also exhibits two peaks at the same delay times, while the reflectance of the probe pulse of a much lower intensity, as required by a reasonable probe, exhibits a unique peak at 3 ps, and not at the time origin.

Delayed increase in the reflectance under intense laser irradiation onto solutions such as water[16] and solids[17] has been reported by Fotakis and co-workers. The refractive index, which is related to the reflectivity, of plasma is a function of its electron density. On the other hand, the collision cross sections of high-energy electrons are smaller than those of low-energy electrons,[18] which indicates that low-energy electrons can ionize atoms more effectively than high-energy electrons in this energy region. The aqueous solution surface is originally an insulator; however, it transforms into a metal-like state due to the plasma formation by the prepulse irradiation. Since the vertically polarized prepulse laser power at the focus ($\sim 10^{14}$ W/cm^2) is sufficiently high for plasma formation (though not for hard x-ray emission), the conduction electron energy can be high, at least of the order of hundreds of eV. Even after the prepulse passes, high-energy conduction electrons collide with the surrounding atoms and ions in an aqueous solution, thereby inducing further impact ionization and losing their own energy. The electron density in the solution may increase, although this is a process that competes with the plasma expansion and electron-cation recombination.

In such plasma formation processes, until 4 ps after the prepulse irradiation, the delayed irradiation of the horizontally polarized (p-pol. to solution surface) main pulse onto the metal-like solution surface induces effective resonance absorption of the main pulse by the preformed plasma, resulting in intense x-ray emission. Similarly, in the decay processes of the preformed plasma after 4 ps, such as the

electron-cation recombination and the spatial expansion of the plasma, the incident main pulse can penetrate the plasma because of the low plasma density and induce further ionization in the temporally rising edge of the main pulse. As a result, another increase in the reflectance of the main (intense) pulse is observed again at 13 ps, while the reflectance of the probe pulse keeps decreasing, indicating another effective coupling between the main pulse and the plasma. This deliberation explains why two x-ray intensity peaks are observed in the picosecond range.

Figure 3 shows (a) the time-dependent x-ray intensity and (b) the transient reflectance of the main pulse and a probe pulse (695–705 nm) as a function of the delay time in the nanosecond range. Similar to the case in the picosecond range, two x-ray intensity peaks are observed at 2.5 and 5 ns when the prepulse intensity is 0.02 mJ/pulse, and these peaks appear to shift earlier to 0.45 and 4 ns when the prepulse intensity increases to 0.06 mJ/pulse. On the other hand, the specular reflectance of the main pulse and a probe pulse decreases to a value less than unity.

This decrease in the transient reflectance to a value less than unity in the nanosecond range indicates that the solution surface transiently becomes rough due to the laser ablation caused by a sufficiently high prepulse power at the focus. This hypothesis is supported by the results of time-resolved surface reflection imaging that are shown in Fig. 3(b). The reflection intensity from the front surface of the solution decreases and the area with low reflectivity becomes larger with the passage of time. Additionally, the optimum laser incident angles for the highest x-ray intensity are 35° and 30° for the delay times of 0.45 and 4 ns, respectively, as compared to the case of the single-pulse irradiation (60°) (not shown). This implies that the surface roughness grows as a function of time. Previously, we have reported such transiently formed rough surface due to laser ablation,[19,20] estimating the transient roughness to range from a few hundred nanometers at subnanoseconds to micrometers at nanoseconds when the surfaces of organic solutions were irradiated by intense (sub-TW/cm^2) femtosecond ultraviolet laser pulses. Furthermore, the roughness growth rates increase as the excitation laser intensity increases. On the basis of these
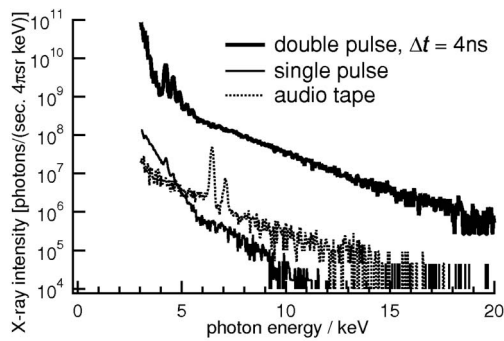
FIG. 4. X-ray emission spectra of cesium chloride aqueous solution (4 mol/dm^3) and an audio tape when irradiated by femtosecond laser pulses in air.

results and reports, the surfaces with the roughness in the submicrometer to the micrometer range can be formed under the prepulse irradiation.

The x-ray intensity increase under the femtosecond laser pulse irradiation onto statically rough surfaces has been reported as mentioned earlier. Recently, Rajeev *et al.* reported that the intensity of the x-ray emission in the region of 30–300 keV from the copper samples irradiated with femtosecond laser pulses (100 fs, 806 nm, 10^{15}–10^{16} W/cm^2) increased when the sample surfaces were nanostructured.[6] On the basis of the theory on surface plasmons, they also calculated the local increase in the laser field intensity due to the surface nanostructures and found that there was an optimum size of nanostructures for the laser field to be intensified most.[7] In the cases of solutions, another type of morphology-dependent x-ray intensity increase can be considered, that is, due to the focusing of the incident laser by droplets.[15,21]

On the basis of the explanations in those reports, the x-ray intensity peaks observed in the nanosecond range can be assigned to the following two processes. After the prepulse irradiation, a rough surface forms in subnanoseconds. The main pulse follows and irradiates the rough surface, inducing ionization in the temporally rising edge, which induces effective resonance absorption of the main pulse that results in an intense x-ray emission. In nanoseconds, the transient surface roughness grows to submicrometers to micrometers. Such rough and transparent solution surfaces can work as fly-eye lenses for the following main pulse.

Figure 4 shows the x-ray emission spectra (air-absorption effect corrected) under single (only the main pulse) and double-pulsed irradiation conditions. Here, the delay time between the prepulse (0.06 mJ/pulse) and the main pulse (0.3 mJ/pulse) is 4 ns. An x-ray emission spectrum of an audio-cassette tape is also shown in the figure. The characteristic x-ray lines of cesium ($L\alpha=4.3$ keV, $L\beta=4.6$ keV) and iron ($K\alpha=6.4$ keV, $K\beta=7.1$ keV) are clearly observed. The prepulse irradiation induces the x-ray intensity increase of three or four orders of magnitude. As for x-ray photon numbers in the double-pulsed excitation condition, 3.8×10^{10} photons s^{-1} 4π sr^{-1} at 3–20 keV and 1.4×10^{10} photons s^{-1} 4πsr^{-1} at 4.3 keV in 1 keV bandwidth can be calculated. As compared to the spectrum of the audio-cassette tape, the x-ray intensity of an aqueous solution when irradiated by the double pulse is comparable or even higher in a wide range of photon energies. If condition differences of irradiation laser pulses such as laser intensity, pulse width, and repetition rate are considered, these numbers are comparable to other cases using liquid mercury,[22,23] liquid gallium,[24] and liquid water.[25] As compared to the quasimonochromatic x-ray pulses from metal targets, the x-ray emission from aqueous solutions can be appropriate for the XAFS measurements and x-ray contrast imaging.

This paper describes the x-ray intensity increase in aqueous solutions when irradiated by double-pulsed femtosecond laser pulses. Plasma formation and decay are responsible for the x-ray intensity increase in picoseconds. In nanoseconds, the nanostructures transiently formed on the solution surface contribute to the local focusing of the incident main pulses, which results in the x-ray intensity increase.

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