Relative quantum yield in laser-induced desolvation of hydrated electrons observed in a water jet immersed in a low-pressure plasma

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Abstract: We detect hydrated electrons by laser-induced desolvation in a micrometer-size water jet immersed in a low-pressure plasma. The relative quantum yield of laser-induced desolvation was examined at the wavelengths of the 2nd, 3rd and 4th harmonics of Nd:YAG laser pulses. The relationship between the photon energy and the quantum yield suggests the possibility that hydrated electrons produced by plasma-liquid interaction have lower hydration energies than well-known hydrated electrons.
Keywords: hydrated electron, laser-induced desolvation, plasma-liquid interaction

1. Introduction

Hydrated electrons are generated by plasma-liquid interaction. However, there have been limited reports on the detection of hydrated electrons in liquids interacting with plasmas [1]. The difficulty is caused by the fact that hydrated electrons generated by the plasma irradiation are localized in a narrow region with a thickness of several nanometers below the plasma-liquid interface. To overcome the difficulty, we have developed a method to detect hydrated electrons in the interfacial region [2]. Hydrated electrons in the interfacial region are converted to free electrons when they are irradiated with laser beam having a photon energy exceeding the solvation energy. Free electrons produced by the desolvation are transported to the gas phase. In a previous work, we used an atmospheric-pressure helium dc glow discharge with the liquid cathode and observed the pulsed increase in the discharge current when the liquid cathode was irradiated with the laser pulse. The pulsed current represented the transport of free electrons produced from hydrated electrons. In the present work, we tried to detect hydrated electrons in a micrometer-size water jet immersed in a low-pressure plasma.

2. Experimental method

Figure 1 shows a schematic of the experimental setup. A NaOH aqueous solution was squirted through a plastic (polyetheretherketone: PEEK) tube into a vacuum chamber at a flow rate of 1.2 mL/min. The length of the PEEK tube was 1.5 cm, and the inner diameter φ of the PEEK tube was 75 μm. The concentration of the NaOH solution was 10%. The conductivity of the solution was 35 S/m, resulting in a resistance of $r_w =$ 65 kΩ/cm in the PEEK tube. The water jet had a filament-like shape with a length of approximately 2 cm in vacuum, and it was dispersed into droplets in the downstream. The droplets were caught on the bottom of the chamber which was cooled with liquid nitrogen. The pressure of water vapor in the chamber was 7-9 mTorr. We added helium into water vapor, and the total pressure was 100 mTorr. An inductivity coupled plasma was generated using a spiral antenna which was connected to a rf power supply with a power of 150 W. The water jet was irradiated with the 2nd, 3rd and 4th harmonics of Nd:YAG laser pulses. The durations of the laser pulses were 8 ns. A dc voltage was applied between the electrical ground and the solution in the reservoir. The dc voltage was adjusted between -150 and +200 V. The resistance between the reservoir and the nozzle was negligible in comparison with the resistance in the PEEK tube. A coaxial cable was connected to the stainless-steel joint, and the pulsed current through the water jet was determined from the voltage across the resistor of 50 Ω.

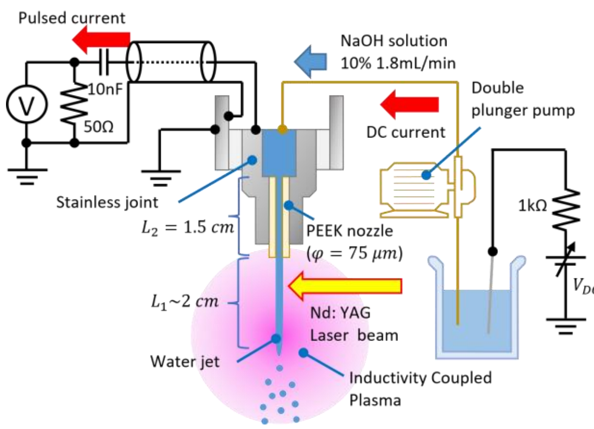

Figure 1. A schematic of experimental setup.

3. Simulation method

We estimated the relative quantum yield of the electron release. Figure 2 shows an energy diagram regarding the release of an electron in the experimental situation. The quantum yield of the electron release is given by the product of the quantum yield of laser-induced desolvation and the transport efficiency of free electrons to the gas phase. According to the work by Suzuki and coworkers [3], the solvation energy of hydrated electrons has a Gaussian distribution given by

$$f(E) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left\{-\frac{(E - E_c)^2}{2\sigma^2}\right\},$$

where $E_c = -3.76$ eV and $\sigma = 0.43$ eV. As shown in Fig. 2, hydrated electron is desolvated if $E + E_p \geq E_0$, where E_0 is the bottom energy of the conduction band. We employed $E_0 = -1.2$ eV. Hence, the quantum yield of laser-induced desolvation is given by

$$q(E_p) = \int_{E_0}^{\infty} f(E - E_p) dE$$
$$= \frac{1}{2}\left\{1 - \mathrm{erf}\left(\frac{E_0 - (E_c + E_p)}{\sqrt{2\pi}\sigma}\right)\right\}.$$

To obtain the transport efficiency of free electrons, that were produced by laser-induced desolvation, to the gas phase, we carried out Monte Carlo simulation by using the Particle and Heavy Ion Transport code System (PHITS) [4]. An electron source was placed in water at a depth between 0.1 and 9 nm from the liquid surface, and the transport efficiency was defined as the fraction of electrons that passed through a surface in the gas phase at a distance of 0.5 nm from the liquid surface. The distribution of the kinetic energy of free electron just after desolvation was assumed to be

$$f_K(E) = f\left(E - \left(E_p - E_0\right)\right).$$

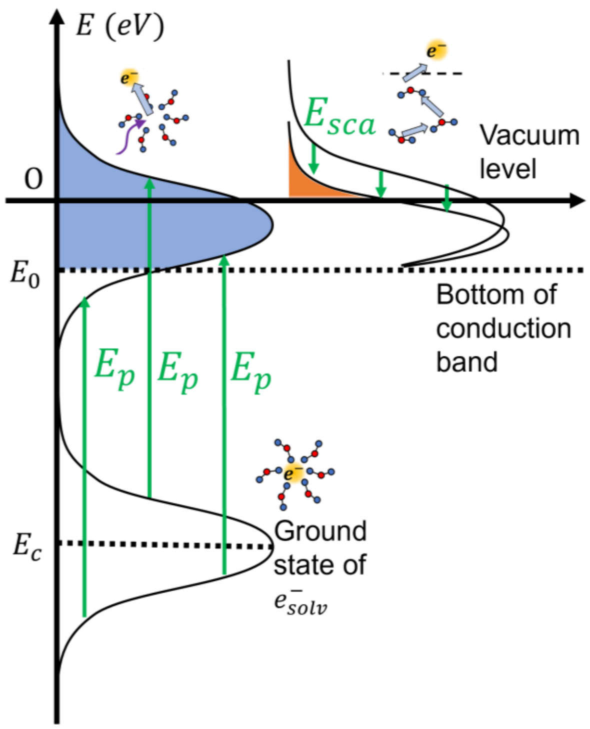

Figure 2. Energy diagram of laser-induced desolvation.

4. Results and Discussion

Figure 3 shows the waveform of the pulsed current observed at the timing of the Nd:YAG laser irradiation. The laser energy and the wavelength were 30 mJ/pulse and 266 nm, respectively. We observed the pulse current at the timing of the pulsed laser irradiation. The positive current means the flow of electrons from the water jet to the plasma. This direction is consistent with the transport of free electrons produced by laser-induced desolvation.

The effect of the photon energy on the amplitude of the pulsed current is shown in Fig. 4. In this experiment, we applied voltages between -100 and +150 V to the NaCl solution in the reservoir. The laser energies were adjusted to 12, 9, and 6 mJ/pulse at the wavelength of 266, 355, and 532 nm, respectively, which enabled us to carry out the experiments with the same photon flux at the different wavelengths. We plotted our previous data observed in an atmospheric-pressure dc glow discharge (APGD), where the plasma-liquid interface worked as the cathode of the discharge (the plasma-liquid interface was bombarded by positive ions) [2]. The solid curves show the relative quantum yield estimated by the simulation. The plots and the curves are normalized at the photon energy of 4.66 eV. As shown in Fig. 4, higher quantum yields were observed in the present experiment using the water jet and the low-pressure plasma than the previous one using APGD in the low photon energy region. In addition, the experimental quantum yield was much higher than that estimated by the simulation, even if we assumed that the location of solvated electrons is very close to the real gas-liquid interface (0.1 nm). This means that the result of the present experiment cannot be explained by the solvation energy reported by Suzuki and coworkers [3]. Siefermann and coworkers have suggested the existence of partially hydrated electrons in the vicinity of the gas-water interface [5]. Since solvation

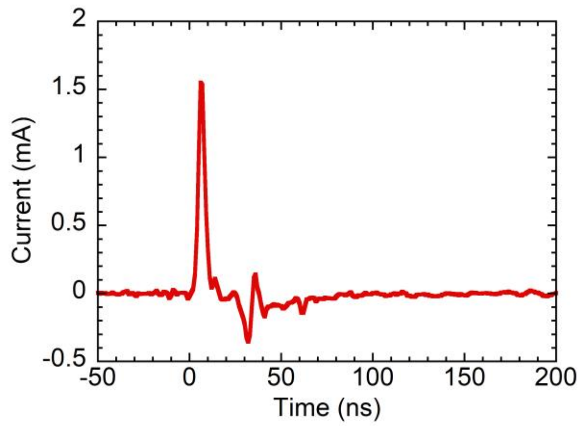

Figure 3. Temporally change in the current from the water jet.

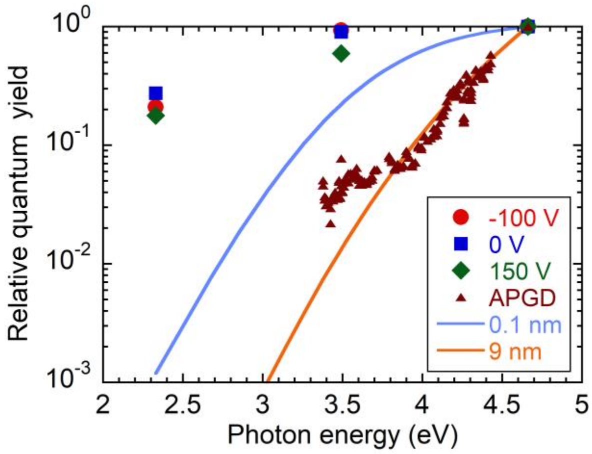

Figure 4. Comparison among the present experimental results at various bias voltages, our previous results observed in atmospheric-pressure dc glow discharge (APGD) [2], and quantum yields estimated by the Monte Carlo simulation. We assumed two locations (0.1 and 9 nm from the gas-water interface) for hydrated electrons in the simulation.

energies of partially hydrated electrons are lower than those of fully hydrated electrons, a higher quantum yield of laser-induced desolvation is expected for partially hydrated electrons at a low photon energy. The present experimental result would possibly be explained if we detected partially hydrated electrons.

5. References

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