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One-Photon Ionization of Liquid Water upon 193 nm Laser Irradiation

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Water was photoionized through a one-photon process upon 193 nm laser irradiation. The quantum yield of photoionization was a few percent. Multiphoton ionization was not observed in this work, up to the laser fluence of 1.6 J / cm^2.

The photolysis of water has been investigated by several workers.[1-5] It is well known that water is photoionized by VUV irradiation and that the photoionization threshold is 6.5 eV.[1,2]

$$H_2O \xrightarrow{h\nu} H_2O^+ + e_{aq}^-$$

For 184.9 nm irradiation, the quantum yields of photoionization are ≤ 0.045[1] and 0.004.[2] On the other hand, water is photoionized by 266 nm laser irradiation through a two-photon process with a quantum yield of 0.15.[3,4] We have observed a one-photon ionization of water on 193 nm (6.4 eV) laser irradiation.

Water was produced by a superpure system (Super-Q, Milipore). The resistivity of water was 18 MΩ at 25 °C. Sample water in a fused silica cell was degassed by several freeze-pump-thaw cycles. The absorbance at 193 nm was 0.04 cm^{-1} at 25 °C, and this value is in agreement with the previous value of triply distilled water, within experimental error.[6] An excimer laser (EMG201MSC, Lambda Physik) with pulse width (FWHM) of 30 ns was used as the excitation laser. Absorption of hydrated electrons formed by photoionization was monitored using a He-Ne laser (632.8 nm).

No absorption other than hydrated electrons was observed in the visible region on UV irradiation.[2] Figure 1 shows the dependence of the absorbance at 632.8 nm on the 193 nm laser fluence. The slope of 1 was obtained

using 1 and 10 cm cells. If ionization occurs through a one-photon process, the straight line of the relationship between the laser fluence and the absorbance on a linear scale should pass through the origin.[7] It is confirmed that this consideration can be applied to our data. The results indicate that the photoionization occurs through a one-photon process and that the photoionization threshold is lower than 6.4 eV. One-photon ionization was observed in the region of 0.11-1.6 J / cm^2. The quantum yield of photoionization was a few percent. The laser power dependence for 248 nm laser irradiation is shown in Fig. 2. The slope of 2 was obtained in the region of low laser fluence, and this shows that two-photon ionization took place. Nikogosyan and co-workers also observed two-photon ionization for 266 nm laser irradiation.[3,4] Our result is consistent with these previous ones.

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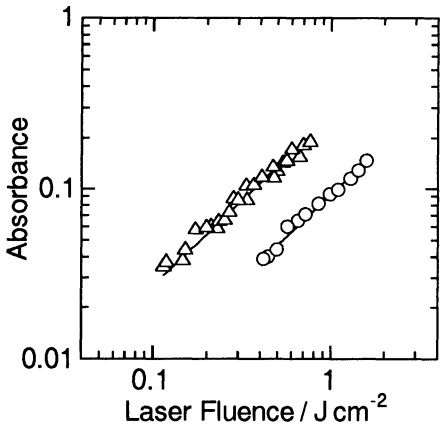

Fig. 1. Dependence of absorbance of hydrated electrons with optical length of 1 cm (○) and 10 cm (△) on laser fluence at 193 nm.

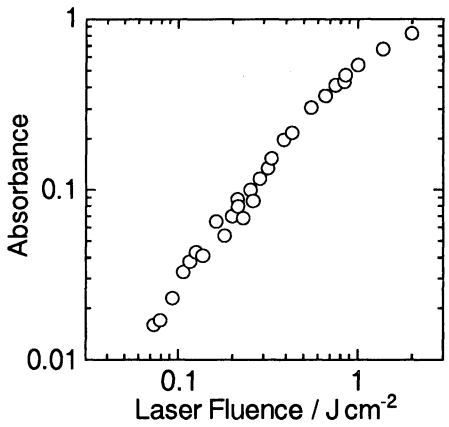

Fig. 2. Dependence of absorbance of hydrated electrons with optical length of 1 cm on laser fluence at 248 nm.

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