Evidence for Resonance-Enhanced Multiphoton Ionization of Liquid Water Using 2-eV Laser Light: Variation of Hydrated Electron Absorbance with Femtosecond Pulse Intensity

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The multiphoton ionization of liquid water that occurs in femtosecond laser photolysis is investigated with an experimental setup in which 2-eV photons are sent into the sample. Hydrated electrons are identified as the generated absorbing species and their absorbance A is measured as a function of the laser irradiance E. The power law $A \propto E^{1.8}$ which is found differs markedly from that expected from energetic considerations. This is explained in terms of a resonant four-photon absorption involving the $\tilde{A}\,{}^1B_1$ electronic state of water which, in the liquid phase, is partly autoionizing.

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In recent decades, pulsed laser and radiolysis techniques have been used to study the ionization of various polar liquids as well as the formation and early reactions of transient species such as the solvated electron in those media [1-6]. With the advent of femtosecond pulsed lasers, those phenomena could become directly observable in water [3-6], a liquid in which orientational relaxation of the molecules occurs very rapidly [7]. In contrast to the considerable experimental [2-6] and theoretical [8] effort devoted to electron hydration, the actual process of water photoionization has received little attention, despite the likelihood that the large laser intensities that result from using ultrashort pulses perturb this process. In fact, a variety of high-intensity effects, involving the excited states of the atoms or the molecules to be ionized, have been observed and well characterized in the gas phase [9-11], and could also occur in liquids.

In experiments where femtosecond pulses of 310-nm (4 eV) UV light are used to generate hydrated electrons (e_{aq}^-) in pure water, considerations on the energetics and on the e_{aq}^- recombination kinetics strongly suggest that photoionization occurs mainly through biphotonic absorption [3,6,12]. However, no intensity-dependent e_{aq}^- yield measurements have been done in the femtosecond experiments to understand the nature of this absorption. The only related study is that of Nikogosyan, Oraevsky, and Ruposov [13] who used picosecond laser pulses in the 266–316-nm wavelength range, and irradiances E [14] at least 10^3 times smaller than those typically used in femtosecond photolysis experiments. These authors measured e_{aq}^- yields that varied as E^x, with $x=2$ in their lowest-intensity regime ($E<10^9$ W/cm^2), but also found that for $10^9<E<10^{10}$ W/cm^2, x became ~ 1. Their first observation confirms that the absorption was indeed biphotonic. Their second observation, which was not understood at the time, indicates that electronic states could be involved in the photoionization process.

In this study, we use 620-nm (2 eV) femtosecond light pulses, with $E\sim 10^{13}$ W/cm^2 to investigate the role played by the excited electronic states of liquid water in its multiphoton ionization. In order to do so, we vary the laser irradiance in the sample and monitor the resulting change of e_{aq}^- absorbance. Since this constitutes the first attempt to generate hydrated electrons in pure water with visible light, we identify unequivocally the observed absorbing species by a detailed study of its spectrum.

The experimental setup is similar to that used in Refs. [3] and [6] and shown schematically in Ref. [15]. In essence, an ultrashort pulse (620 nm, 60 fs, 1 nJ) is extracted at the output of a colliding pulse mode-locked dye laser (CPM). It is then amplified in a chain consisting of a Kiton red and three sulforhodamine dye cells which are optically pumped by a frequency-doubled Q-switched Nd:YAG at a repetition rate of 10 Hz. Water used in the experiment is at room temperature and is purified by a Milli-Q Plus system (ZD40 115 95) to a resistivity >19 MΩcm. It circulates through a 2-mm quartz suprasil cell. In spite of the large irradiances involved in our experiments ($\sim 10^{13}$ W/cm^2), no dielectric breakdown of liquid water was observed because of the very short duration of our pulses which hinders the occurrence of this phenomenon [16,17].

In contrast to previous setups, two cells are used in parallel to amplify the pulse in the fourth stage, just after its temporal compression with grating pairs. The energy which arises from first-order diffraction on both sides of the grating normal is used to send two pulses on separate paths. One of them serves as the pump pulse while the other generates a white-light continuum from which probing wavelengths are selected with interference filters. This modification allows a near doubling of the pulse irradiance available at the output which becomes as large as 0.5 mJ for each path. The most significant change to the usual procedure consists of sending 2-eV photons directly into the sample by not using a frequency doubler.

Figure 1 shows the kinetic trace obtained at a probe wavelength of 720 nm. As one can see, an absorbing species appears in less than 1 ps and decays slowly afterwards. This species can be clearly identified by scanning its absorbance over a range of wavelengths while keeping

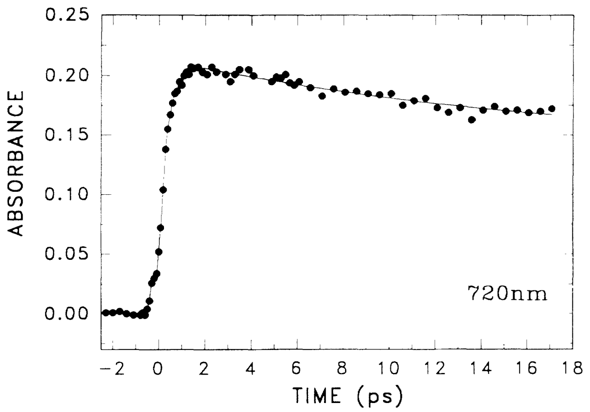

FIG. 1. Variation of the observed absorbance with time for a probe wavelength of 720 nm. Time zero corresponds to the best superposition of the pump and the probe pulses. The solid line, which consists of a polynomial function, is simply drawn here to show the general trend of the experimental points.

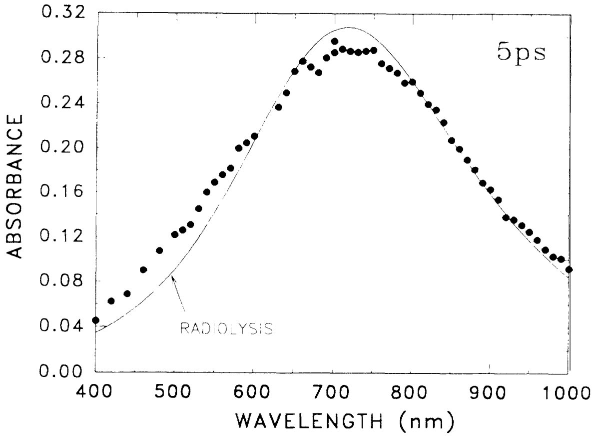

FIG. 2. Absorption spectrum of the hydrated electrons measured with a constant time delay of 5 ps between the pump and the probe pulses. The solid line is the corresponding absorption spectrum obtained from radiolysis experiments (see Ref. [18]).

a fixed time delay Δt between the pump and probe pulses. This is what is shown in Fig. 2 for $\Delta t = 5$ ps. Comparison of this absorption spectrum to that found at longer time for e_{aq}^- by radiolysis techniques [18] establishes that it is indeed the hydrated electron that is observed. This is further confirmed by the fact that the formation kinetics of the absorbing species is consistent with those of previous e_{aq}^- femtosecond studies [3,6]. It is worth noting here that the measured absorbances (up to 0.3) are the largest reported so far. The fact that we can generate e_{aq}^- more easily with 2-eV photons than with 4-eV ones can be explained by the loss of intensity that results, in the latter case, from the conversion in the frequency doubler.

Owing to the large laser intensities that we have and to the good efficiency of e_{aq}^- formation with 2-eV photons, we can attenuate the pump pulse and study the variation of the e_{aq}^- absorbance A with E. Figure 3 shows this variation on a log-log scale in the case where $\Delta t = 6$ ps. As one can see, a straight line can be drawn through the first nine experimental points, thus indicating that the simple power law $A \propto E^x$ holds over a wide range of laser irradiances. The exponent x which is given by the slope is ~ 1.8. A saturation effect is observed for $E/E_{\max} > 0.5$.

The power law we obtain, with $x = 1.8$, differs from that expected since, with an e_{aq}^- generation threshold of ~ 6.5 eV [13], at least four 2-eV photons are needed to ionize. The lowering of x does not mean that the ionization involves less than four photons. It can be attributed to the fact that, with 8 eV of excitation energy, a resonance occurs with the $\tilde{A}\,{}^1B_1$ excited electronic state of water which extends from ~ 7.4 to ~ 9.4 eV in the liquid phase [19], and which is known to be dissociative and partly autoionizing [20]. It is indeed well established from experiments on gases [9–11] that, with large laser intensities and in the presence of such a resonance, the exponent x can be significantly affected by the ac Stark effect which brings about upward shifts and broadenings of the electronic states when they become sufficiently "dressed" with photons. The increase of the electronic transition energy with increasing irradiance degrades or improves the quality of the resonance, depending on whether the multiphoton energy is originally lower or higher than the transition energy. In the case under consideration here, the energy of the four photons (8 eV) is below the maximum of the transition energy (~ 8.4 eV). The Stark shift is thus expected to degrade the resonance and, in turn, to hinder the expected increase of A with E. This last phenomenon is generally referred to as "dynamic detuning" [10]. Interestingly, recent studies on the ionization of rare gases have shown that, with subpicosecond 620-nm laser pulses in the irradiance range

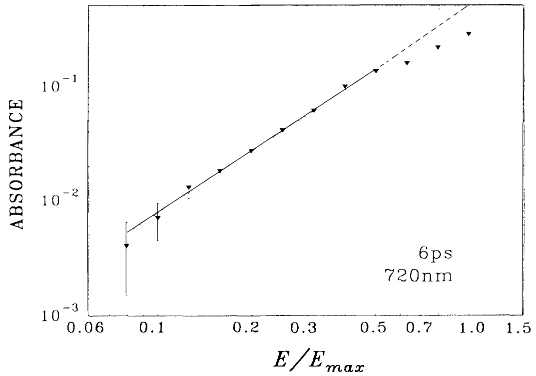

FIG. 3. Variation of the e_{aq}^- absorbance with the normalized irradiance of the pump pulse in the sample. The absorbance is measured at a probe wavelength of 720 nm and with a time delay of 6 ps between the pulses. The maximum irradiance is estimated to be $\sim 0.5 \times 10^{14}$ W/cm^2. The solid line, which is fitted through the first nine data points, reveals that $\log A = 1.79 \log(E/E_{\max}) - 0.315$ for $E/E_{\max} \leq 0.5$. The dashed line is simply an extrapolation of the solid line to larger laser irradiances.

10^{13}-10^{14} W/cm^2, the Stark shift can be as large as a few tenths of an electronvolt [21,22], and thus comparable to the half-width of the $\tilde{A}\,{}^1B_1$ state of water.

We could also consider the possibility that the ionization of water proceeds via a biphotonic absorption of water molecules that are highly excited vibrationally. In that case, the first two photons are absorbed sequentially and the rate limiting step of the ionization consists of the subsequent biphotonic absorption that brings the water molecule into an excited electronic state. However, our observations make that mechanism unlikely since we do not detect the stimulated emission that would result from the passage of the probe pulse through a medium in which specific vibrational overtones (at 2 and 4 eV) are populated [23].

The saturation of A that is observed at high E values should not originate, as is sometimes the case in the gas phase, from a local depletion of molecules to be ionized [9,11]. Considering the e_{aq}^- concentrations present in the experiment ($\sim 10^{-3}M$), it is more likely that it would come from early recombinations of e_{aq}^- with $H\cdot$ and $\cdot$OH radicals which are formed in large numbers in the solution through the swift and efficient dissociation of the $\tilde{A}\,{}^1B_1$ state [13,20].

Preliminary results indicate that the exponent x obtained with $\Delta t > 6$ ps is slightly larger than that reported above. This would imply that the e_{aq}^- decay, which is due to the geminate recombination of e_{aq}^- with $\cdot$OH and H_3O^+ (Refs. [4], [5], and [24]), is also dependent on E. This, in fact, is expected since, as E increases, the proportion of H_2O molecules that absorb a fifth photon increases as well. This leads to a larger proportion of electrons generated with substantial initial excess energy and thus to larger thermalization distances and to a slower e_{aq}^- recombination. A similar variation of the recombination with intensity has been reported with 4-eV photons and was attributed to a mixture of two- and three-photon absorption [25].

In summary, the large e_{aq}^- absorption coefficient and its well-characterized kinetics allowed us to investigate the nature of liquid water multiphoton ionization and to show that the high-intensity effects observed in the gas phase can occur in the liquid as well. The power law we obtain, namely, $A \propto E^{1.8}$, differs markedly from that expected from purely energetic considerations. We interpret this result as an indication of the essential role played by the first excited state ($\tilde{A}\,{}^1B_1$) of liquid water in the multiphotonic absorption via Stark broadening and shifting of the electronic states. We thus conclude that the overall e_{aq}^- generation with 620-nm (2 eV) light occurs through a resonant four-photon ionization process involving a dissociative and partly autoionizing state. Since we expect this resonance to influence also the A vs E relation in experiments where 4-eV photons are absorbed, we suggest that intensity-dependent measurements of e_{aq}^- absorbance be taken in those conditions as well.

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[1] For recent reviews, see, for example, J. C. Mialocq, J. Chim. Phys. **85**, 31 (1988); J.-P. Jay-Gerin and C. Ferradini, in *Excess Electrons in Dielectric Media*, edited by C. Ferradini and J.-P. Jay-Gerin (CRC, Boca Raton, 1991), Chap. 8, p. 259.

[2] J. M. Wiesenfeld and E. P. Ippen, Chem. Phys. Lett. **73**, 47 (1980).

[3] A. Migus, Y. Gauduel, J. L. Martin, and A. Antonetti, Phys. Rev. Lett. **58**, 1559 (1987).

[4] H. Lu, F. H. Long, R. M. Bowman, and K. B. Eisenthal, J. Phys. Chem. **93**, 27 (1989).

[5] Y. Gauduel, S. Pommeret, A. Migus, and A. Antonetti, J. Phys. Chem. **93**, 3880 (1989).

[6] F. H. Long, H. Lu, and K. B. Eisenthal, Phys. Rev. Lett. **64**, 1469 (1990).

[7] See, for example, R. Schiller, in *Excess Electrons in Dielectric Media* (Ref. [1]), Chap. 4, p. 105.

[8] For a recent review, see, for example, P. J. Rossky, J. Opt. Soc. Am. B **7**, 1727 (1990).

[9] P. Lambropoulos, in *Advances in Atomic and Molecular Physics*, edited by D. Bates and B. Bederson (Academic, New York, 1976), Vol. 12, p. 87.

[10] J. Morellec, D. Normand, and G. Petite, Phys. Rev. A **14**, 300 (1976).

[11] N. B. Delone and M. V. Fedorov, Usp. Fiz. Nauk **158**, 215 (1989) [Sov. Phys. Usp. **32**, 500 (1989)]; M. V. Fedorov and A. E. Kazakov, Prog. Quantum Electron. **13**, 1 (1989).

[12] T. Goulet, A. Bernas, C. Ferradini, and J.-P. Jay-Gerin, Chem. Phys. Lett. **170**, 492 (1990).

[13] D. N. Nikogosyan, A. A. Oraevsky, and V. I. Rupasov, Chem. Phys. **77**, 131 (1983).

[14] The terms irradiance and intensity are equivalent but the latter one is left for qualitative descriptions. The symbol recommended for irradiance is E and its usual units are W/cm^2 [see, for example, EPA (European Photo-chemistry Association) Newsletter No. 25, November 1985, p. 28]. It should not be confused here with the amplitude of an electric field which is never referred to in the present work.

[15] A. Migus, A. Antonetti, J. Etchepare, D. Hulin, and A. Orszag, J. Opt. Soc. Am. B **2**, 584 (1985).

[16] A. Penzkofer, Opt. Commun. **11**, 265 (1974).

[17] C. A. Sacchi, J. Opt. Soc. Am. B **8**, 337 (1991).

[18] J. P. Keene, Radiat. Res. **22**, 1 (1964); B. D. Michael, E. J. Hart, and K. H. Schmidt, J. Phys. Chem. **75**, 2798 (1971); F.-Y. Jou and G. R. Freeman, J. Phys. Chem. **83**, 2383 (1979).

[19] J. M. Heller, Jr., R. N. Hamm, R. D. Birkhoff, and L. R. Painter, J. Chem. Phys. **60**, 3483 (1974); G. J. Kutcher and A. E. S. Green, Radiat. Res. **67**, 408 (1976).

[20] P. Han and D. M. Bartels, J. Phys. Chem. **94**, 5824

(1990).

[21] R. R. Freeman, P. H. Bucksbaum, H. Milchberg, S. Darack, D. Schumacher, and M. E. Geusic, Phys. Rev. Lett. **59**, 1092 (1987).

[22] S. L. Chin, C. Rolland, P. B. Corkum, and P. Kelly, Phys. Rev. Lett. **61**, 153 (1988).

[23] C. Pépin, D. Houde, H. Remita, T. Goulet, and J.-P. Jay-Gerin (to be published).

[24] S. M. Pimblott, J. Phys. Chem. **95**, 6946 (1991); T. Goulet and J.-P. Jay-Gerin, J. Chem. Phys. **96**, 5076 (1992).

[25] F. H. Long, H. Lu, X. Shi, and K. B. Eisenthal, Chem. Phys. Lett. **185**, 47 (1991).