Excess Electrons in Liquid Water: First Evidence of a Prehydrated State with Femtosecond Lifetime

A. Migus, Y. Gauduel, J. L. Martin, and A. Antonetti

Laboratoire d'Optique Appliquée, Ecole Polytechnique–Ecole Nationale Supérieure de Techniques Avancées,
91120 Palaiseau, France
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The localization and solvation of excess electrons in pure water have been resolved at the femtosecond time scale. Before it becomes solvated, the electron thermalizes and reaches in 110 fs a localized state absorbing in the infrared. This transient species with lifetime 240 fs has been postulated to exist but has not been observed previously in liquid water.

Since its discovery 25 years ago,[1] the hydrated electron continues to be of considerable theoretical and experimental interest, but neither the structure of the fully solvated state nor the dynamics of its formation is yet quantitatively known and understood. On the basis of experiments in alcohols,[2,3] it has been suggested that in polar liquids the electron solvation occurs through at least two stages. First comes localization: The electron goes from a quasifree extended state to some preexisting trapping sites or molecular clusters. This is then followed by a configurational relaxation of the medium in the field of the electron which deepens the trap. In principle a similar situation should be encountered in liquid water, but up to now this process has not been resolved. The best available measurement gave only an upper limit of 0.3 ps for electron solvation in water,[4] a value much shorter than the Debye relaxation time $\tau_D = 10$ ps attributed to the overall rotational motion in the pure liquid. This has led to the assumption of the existence of deep traps in which the electrons are directly captured. In this Letter we report experiments performed with femtosecond resolution in pure liquid water, which give clear evidence of a precursor of the fully solvated state and unique information on the dynamics of both trapping and solvation. This should provide experimental basis for the results yielded by the new escalation of computer simulation studies.[5-7]

The fully relaxed solvated electrons in liquid water at ambient temperature are characterized by an optical absorption band, which peaks near 1.7 eV. The band is asymmetric with a high-energy tail extending above 3 eV. The extinction coefficient is large $(1.85 \times 10^4$ cm^{-1} mol$^{-1})$ and corresponds to an oscillator strength of about 0.75.[8] It should be pointed out that there is no agreement on the nature of this transition: it has been argued to be a bound-state–to–bound-state transition on a single site, a transition between different sites, or a bound-state–to–continuum transition. An identical band shape is observed in low-temperature aqueous glasses and similar absorption extending into the visible have been found in liquid and solid alcohols. In all these

media, except in liquid water, an infrared (ir)-absorbing species is immediately present after electron injection and decays concurrently with the growth of the visible band. Conflicting conclusions have however been drawn as to whether or not these spectral changes originate from a continuous shift of the electron absorption band. This point is of prime importance for understanding the exact nature of solvation.

In this work we address the problem of resolving in time the absorption by electrons in liquid water starting from injection up to full solvation. To avoid any possible structure imposed on the liquid by the presence of guest molecules we have chosen to photoionize the water molecules directly. We used bideionized water doubly distilled in a quartz distillator with $KMnO_4$, and with oxygen removed by tonometry using pure nitrogen gas (at 296 K, $pH = 6.45$ and resistivity greater than 19 MΩ). Our experimental setup is based on a laser-amplifier system producing high–peak-power tunable pulses of typically 100 fs duration.[9] The initial pulse at 620 nm is split into two parts. One is focused into a 1.5-mm-long potassium dihydrogen phosphate (KDP) crystal to generate up to 10-μJ pulses at 310 nm (4 eV photon energy): This is the ionizing pump beam. The other part of the initial beam is focused into a 2-cm-long water cell to generate a white-light continuum. After probing the excited region of the sample this beam is directed toward a monochromator and a silicon or germanium diode. Precise dynamical measurements are obtained at selected wavelengths with a repetitive scanning of the delay between the ionizing and the probe pulses.[10] One key point in this experiment is the determination for each probe wavelength of both the instrumental instantaneous response and the zero time delay (coincidence) between the pump and probe pulses.[11] This has been done by observation of a very weak instantaneous induced absorption in a pure n-heptane solution excited at 310 nm in the same conditions as water.[12]

It is well-known that for low-intensity radiation, water is transparent in the uv spectral region up to 190 nm. However, since the two-photon absorption coefficient at
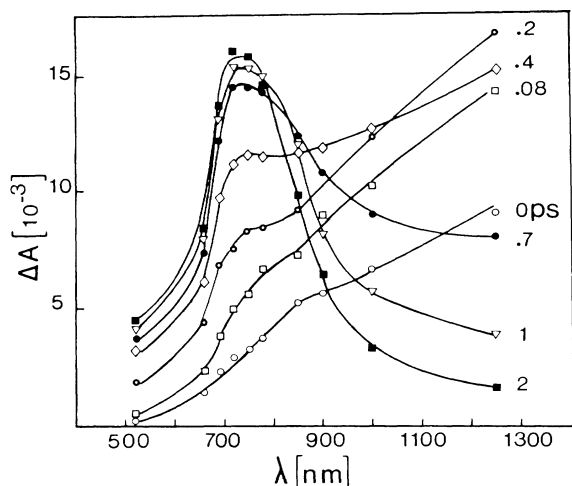
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FIG. 1. Absorption spectra of the electron at different delays after photoionization of liquid water at 21°C by two-photon uv excitation. The points are taken from the experimental kinetics. The lines were drawn through the points as a guide for the eye.

310 nm is about 4×10^{-13} m/W,[8] absorption through this process becomes nonnegligible when we deal with ultrashort pulses. The 8-eV two-photon excitation then falls above the ionization threshold for liquid water, estimated to lie around 6.5 eV.[8] The photoionization of water at 21 °C took place in a fixed-volume cell (2 mm path length) which is translated in a plane perpendicular to the propagation of the light beams, so that each pulse at a 10-Hz repetition rate excited a new region of the sample, producing a homogeneous solvated-electron con-

centration of about 5 μmol. Evidence that we generated solvated electrons has been obtained by scavenging experiments in an acetone (2M)-water mixture (results not shown here).

Experiments on pure water have been conducted by recording of the magnitude and kinetics of absorption changes probed in the range 0.5 to 1.25 μm. The transient spectra, shown in Fig. 1, are reconstructed from the different kinetics. The high-energy tail of an infrared band extending above 1.25 μm appears within the excitation and is fully developed after a delay of 0.2 ps. This band then decays concurrently with the rise of an absorption band which peaks around 720 nm. 2 ps after excitation the situation is stabilized: The infrared band has disappeared, leaving a broad absorption spectrum which coincides exactly with the known solvated electron one. This ir wing is strikingly similar to the one previously seen in liquid alcohols.[2] Note that to the best of our knowledge this Ref. 2 is the only experimental work on polar liquids whose results may imply the possibility of a continuous blue shift of the ir absorption, although this was far from being certain in view of the published data.

A careful analysis[10] of our kinetics data (Fig. 2) shows that they are mostly consistent with a model which assumes the existence of two species. The first one, absorbing in the ir, does not appear instantaneously but with a characteristic time T_1, and then relaxes with a constant time T_2 towards the solvated state. More precisely the calculated curves (continuous lines in Fig. 2) result from the convolution of the pulse shape with a linear combination of the population of the prehydrated species, $N_1(t) = A \exp(-t/T_1)$, and of the solvated one,

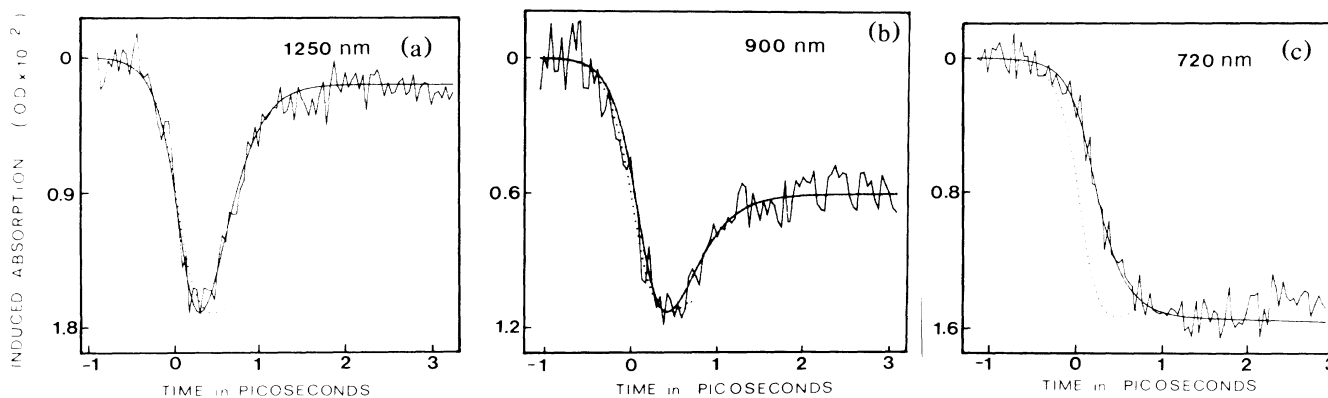$$N_2(t) = A\{1 - 1/(T_2 - T_1)[T_2 \exp(-t/T_2) - T_1 \exp(-t/T_1)]\},$$

FIG. 2. Typical kinetics of induced absorption vs time in liquid water, taken at different wavelengths. The instantaneous responses (dotted lines) have been recorded by exciting in the same conditions liquid n-heptane. The smooth lines represent the computed best fits assuming an appearance time $T_1 = 110$ fs for the ir species and its relaxation $T_2 = 240$ fs towards the solvated state. The kinetics at 1.25 μm (a) and 0.72 μm (c) reflects mostly the evolution of the ir and solvated species respectively, while the intermediate case at 0.9 μm (b) corresponds to a $\frac{2}{3}$ proportion of these species.

A being the final solvated population. Thus, the kinetics at 1.25 and 0.72 μm reflect mostly the evolution of the ir and solvated species, respectively, while the intermediate case at 0.9 μm corresponds to an almost equal contribution of both species; the best fits (continuous lines) assume $T_1 = 110$ fs and $T_2 = 240$ fs (or $T_1 = 240$ fs and $T_2 = 110$ fs because the solutions are symmetric in T_1 and T_2). A small discrepancy is, however, noticeable in the spectral region 800–850 nm (Fig. 1) since, following this interpretation, all the curves should cross at the same point at delays above 0.4 ps, as soon as the total electron population is established. While this may be due to the experimental uncertainty, we cannot completely preclude the existence of some small inhomogeneities in the rise of the solvated-electron spectrum, as seen previously in aqueous glasses.[13] Finally, our two-band analysis allows us to exact the absolute value of the ir absorption. Knowing the solvated-electron one and taking into account the lowering of the apparent signal due to the ultrashort lifetime, we find at 1.25 μm an extinction coefficient of either 6×10^4 mol^{-1} cm^{-1} if we adopt $T_1 = 110$ fs and $T_2 = 240$ fs, or 2×10^5 mol^{-1} cm^{-1} in the case $T_1 = 240$ fs, $T_2 = 110$ fs. This last value seems unrealistically high so that we suggest that the correct sequence is the first one. This choice may also be supported by the observation in small-chain alcohols of a relative correlation of the solvation times T_2 with the longitudinal dielectric relaxation time $\tau_L = \tau_D \epsilon_\infty / \epsilon_0$, where ϵ_∞ and ϵ_0 are respectively the high-frequency limit and the static value of the dielectric constant.[14] As demonstrated in the present work electrons behave in water just as they do in these alcohols. This would then also be consistent with a solvation time T_2 close to $\tau_L \sim 0.2$ ps in water.

Even more striking is the similarity of both the ir and the visible absorption bands in the solid and liquid phases. This suggests that the distribution of initial trapping sites in a solid is the frozen instantaneous one in the liquid, although these similarities must be handled with care because, as stated earlier, such spectral shapes do not permit us to distinguish among very different model potential; each of them related to a different structure for the localized electrons. In this respect it is recognized that these models, phenomenological in nature, can only be crude since the effects of short- and long-range forces felt by an electron in a fluid environment are not known. On the other hand *ab initio* studies of the stability of the electron as a function of the number of molecules in the cluster allow one to develop models independently of such an understanding.[15] Following the view that the initial preexisting trapping sites arise from statistical fluctuations and molecular clustering, a molecular dynamics simulation of pure water has recently attempted to identify favorable sites for electron localization.[7] The distribution of found sites is monotonically decaying in energy down to -1.4 eV, which may be compatible with our ir data. The rise T_1 of the ir spectrum would then include ionization, relaxation to the bottom of the conduction band and then trapping. Taking into account this density of states and assuming that the capture cross section is not strongly dependent on the site depth, we might expect trapping in the shallower sites the most significant. In this case it should take some time before the electrons reach the deeper traps, contributing therefore to the rise T_1.[16] Finally we may question whether the initial shallow localization is similar to the electron trapping on very small water clusters[17] observed with a supersonic nozzle since in this case only a very small binding energy is predicted and at very low temperature.[6]

Let us now turn toward the transition to the fully solvated state. It has been suggested that once the electron gets trapped, it evolves toward the solvated state via a configurational relaxation of the medium in the electronic field of the charge. Theories developed in such frameworks[18,19] predict that this system should relax with a characteristic time of the order of τ_L, which is in excellent agreement with the measured time T_2. But they also specifically predict that this evolution should be reflected by a continuous shift of the electron absorption spectrum, which is in contradiction with our observation of a stepwise process.

Nevertheless the correspondence between τ_L and T_2 may not be just fortuitous. The observation of a quite deep initial localization suggests only modest configurational changes[5] of the molecules around the electron during the liquid relaxation. This should have therefore little direct effect on the energy and absorption spectrum of the electron. However, as recently proposed in the ionization of lithium atoms immersed in liquid ammonia, solvent reorganization may favor the electron in a superposition of either localized and quasifree states[20] or bound states.[21] Our finding of a stepwise process may then be in agreement with the assumption that the initial localized and the final solvated electron are distinct electronic states, but that the transition between these two states is promoted by the reaction of the polar liquid to the charge. This interpretation implies that the structural relaxation of the surrounding molecules, which favors the electronic transition, is limited to an extremely small number of motions. This could be the librational motion of one single molecule.

In summary, localization and solvation of excess electrons in pure water have been resolved at the femtosecond time scale. The salient feature is the existence of a prehydrated state absorbing in the infrared. The following sequence is proposed: The initial electron induced by two-photon ionization of the solvent thermalizes in 110 fs within the conduction band and the tail of localized states, and from there relaxes in 240 fs towards the full solvated state. The unexpected absence of spectral shift during this evolution suggests that the solvation

process occurs through an electronic transition induced by the dielectric relaxation of the medium. An unambiguous identification of these states cannot be reached directly by spectroscopic data alone. Our observations provide, however, an experimental basis on which the new theoretical tools, such as molecular-dynamics and path-integral techniques, may be used to explore the dynamical behavior and the obvious quantum mechanical character of electron in polar solvents.

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