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Ultrafast dynamics of solvated electrons in polar liquids

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Abstract. The temporal evolution of the optical absorption of solvated electrons in a pure water jet between 5 and 70 °C has been investigated in two pulse femtosecond experiments. A 60 fs (FWHM) UV pulse at 270 nm directly ionized pure water and the subsequent absorption was probed by a white light continuum at 12 different wavelengths in the range between 450 and 1000 nm. Due to the thickness of the water jet the time resolution is limited to about 150 fs. The transient absorption contains not only information on the temporal evolution of the absorption spectrum but also data on the time dependence of the concentration of the solvated electrons. We have used the optical sum rules to separate the temporal evolution of the absorption spectrum from the concentration of the electrons in the time interval between 300 fs and 100 ps. At ultra-short times the absorption spectra are displaced to the red and undergo a substantial blue-shift during the first few picoseconds. After about 5 ps the absorption spectrum of thermally equilibrated solvated electrons is recovered. Within our time resolution the data show no evidence of transient electronically excited states of solvated electrons. We interpret the temporal evolution of the absorption spectrum using the optical sum rules and deduce the time dependent decrease of the mean squared dispersion in position, $\langle \Delta r^2(t) \rangle$, of the electrons. Certainly, $\langle \Delta r^2(t) \rangle$ is related to the solvation process of electrons in polar fluids and therefore contains information on the solvation dynamics.

1. Introduction

Electrons in polar fluids and the process of their localization have extensively been studied in the past both experimentally and theoretically [1–8]. In liquid water, solvated electrons play a particularly important role as they essentially contribute to the photochemistry, photoelectrochemistry and radiation chemistry in aqueous solutions. Due to their short lifetime in liquid water, they were first observed in pulse radiolysis experiments [2] by their broad, intensive and featureless absorption spectrum peaking at room temperature near 720 nm [9].

First subpicosecond experiments by Wiesenfeld and Ippen [10] revealed the absorption of the solvated electron to appear less than 300 fs after photolysis of aqueous ferrocyanide solutions. First theoretical simulations favoured a mechanism involving pre-existing trapping sites. These ideas have been picked up by various subpicosecond experiments by Gauduel *et al* [11, 12], Eisenthal *et al* [13] and Laubereau *et al* [14], who generated electrons by a direct multi-photon process in pure water using ultrashort laser pulses at 310 or 282 nm, respectively.

Barbara *et al* [15, 16] used a three-pulse sequence where the first pulse photodetaches electrons from suitable anions (iodide or ferrocyanide) in aqueous solutions. After a delay time of a few nanoseconds allowing the electrons to equilibrate pump–probe experiments were performed. The very fast relaxation of the excitation of about 5 ps was interpreted by a two-state electronic relaxation combined with ground-state relaxation dynamics as supported by molecular dynamics simulations by Rossky *et al* [17, 18] and by Bratos *et al* [19, 20]. Although fast transients are predicted to appear on a femtosecond timescale, the thermalized asymmetric optical absorption spectrum could not be successfully described. In particular, the red shift of the absorption spectrum with increasing temperature under conservation of the profile could not be reproduced [21]. However, the solvated anion complex model (SAC-model) by Tuttle and Golden [5] can explain the asymmetry and the shape stability of the spectrum as well as the optical absorption spectra of solvated electrons in binary mixtures of polar solvents.

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In this paper, we present our experimental results and an alternative interpretation of the dynamics of transient absorptions of solvated electrons in water without incorporating transient electronically excited states.

2. Experiment

The laser system consists of an entirely home-built Ti:sapphire oscillator and regenerative amplifier described elsewhere [22, 23]. Briefly, a prism-compensated oscillator is pumped by an argon-ion laser (Coherent, Innova 310) and produces 15 fs pulses at 90 MHz repetition rate and a cw power of 350 mW. The pulses are amplified by a regenerative amplifier which is pumped by a 1 kHz intracavity-frequency-doubled 10 W Nd:YAG-laser (Clark-MXR, ORC-1000). Our system produces nearly transform-limited 60 fs pulses centred at 800 nm with pulse energies up to 1 mJ. The pulses are split into two parts. The most intense part is used to generate frequency-tripled pulses at 266 nm. The less intense part of the 800 nm pulses is focused on a thin sapphire plate (1 mm) to generate a white light continuum ranging from 400 to 1000 nm. The UV pulses are focused into a water jet to generate the electrons. The thickness of the water jet was estimated as about 200 μm which is somewhat less than the aperture of 300 μm of the sapphire nozzle (Spectra Physics). The white light pulses are used to probe the transient absorption of the sample. For this purpose we placed identical interference filters directly in front of two photodiodes (Hamamatsu) measuring the incident and transmitted light intensities I_0 and $I(t)$, respectively. Thus we directly determined the transient absorbances $A(t)$ as

$$A(t) = \log(I_0/I(t)). \tag{1}$$

The time delay (t) between the pump and the probe pulse was controlled by a translation stage (Melles Griot; Nanomover) with a resolution of 0.33 fs. We varied the actual delay steps from 6 to 500 fs and covered a total delay of up to 100 ps. Due to the different group velocities of the pump and probe pulses in the water sample we achieved a time resolution of only about 150 fs. Measurements were performed in a temperature range from 5 to 70 °C. We achieved stable performance over many hours by an accurate alignment of all parts. Quenching of the transient absorption signal by impurities such as ions or O_2 is negligible on our timescale [15, 16].

We exclusively prepared electrons in pure water using direct UV photoionization. The detailed mechanism of the ionization has not yet been understood and many alternative direct or delayed ionization mechanisms have been postulated in the literature [24]. However, there is agreement that electrons are produced in a two-UV-photon process [25].

$$\mathrm{H_2O(aq)} + 2\hbar\omega \rightarrow (\mathrm{H^+} + \mathrm{OH} + \mathrm{e^-})_{aq}. \tag{2}$$

After the charges are separated the three fragments will be solvated by the surrounding water molecules.

$$(\mathrm{H^+} + \mathrm{OH} + \mathrm{e^-})_{aq} \rightarrow \mathrm{H^+(aq)} + \mathrm{OH(aq)} + \mathrm{e^-(aq)}. \tag{3}$$

Simultaneously, the solvated electrons disappear in a geminate recombination process which occurs in two parallel reactions either with the OH radical

$$e^-(aq) + OH(aq) \rightarrow OH^-(aq) \tag{4}$$

or with the solvated proton

$$e^-(aq) + H^+(aq) \rightarrow H(aq). \tag{5}$$

3. Results

We have recently confirmed [23] that on the long time-scale (>5 ps) the relative loss of absorbance is identical at all wavelengths within our range of observation between 400 and 1000 nm. This phenomenon has been interpreted as being due to geminate recombination of the solvated electrons [14, 26, 27]. In addition, we have found [23] that in the temperature range between 5 and 70 °C the rate of geminate recombination is almost temperature independent within the experimental uncertainties. The kinetics of the geminate recombination has been analysed in the literature and although different analytical expressions have been reported the temporal behaviours all agree reasonably well after 5 ps. A comparison of the different experimental results is given in figure 1.

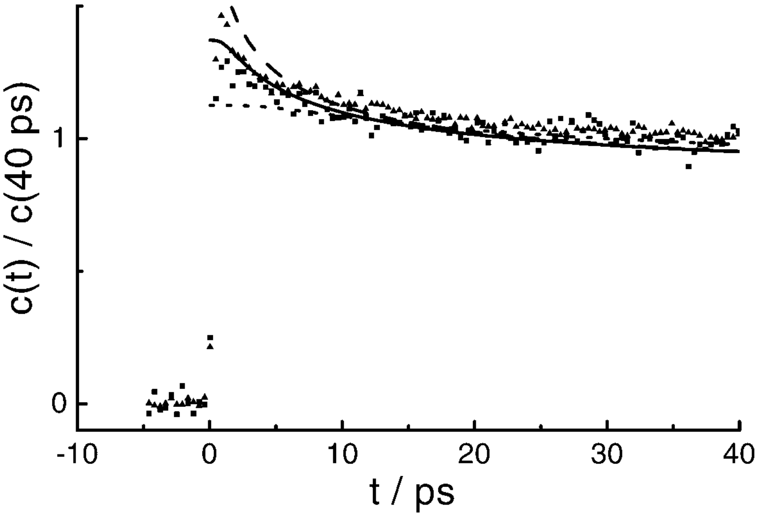

Figure 1. Long-time behaviour of the concentration of solvated electrons in water after photolytic preparation. The concentrations are scaled to their value at 40 ps (▲: this work ($T = 28\,^\circ$C; $\lambda = 740$ nm); ■: this work ($T = 70\,^\circ$C; $\lambda = 650$ nm); dotted line: reference [24]; dashed line: reference [25]; full line: reference [13]).

However, at early times and in the sub-ps regime the transient absorbance depends strongly on the observation wavelength and also on the temperature. In figure 2 we present the ultra-short-time behaviour of the transient absorbance at 28 °C for four representative wavelengths of 452, 692, 741 and 1000 nm, respectively. All absorbances are given in the following reduced form

$$A_{red}(\lambda, t) = \frac{A(\lambda, t)}{A(\lambda, 40\ \mathrm{ps})} \frac{\varepsilon_\infty(\lambda)}{\varepsilon_\infty(\lambda_{max})} \tag{6}$$

where $A(\lambda, t)$ and $A(\lambda, 40\ \mathrm{ps})$ are the experimentally measured absorbances at the wavelength λ after the delay times t and 40 ps, respectively. The decadic molar absorption coefficients of

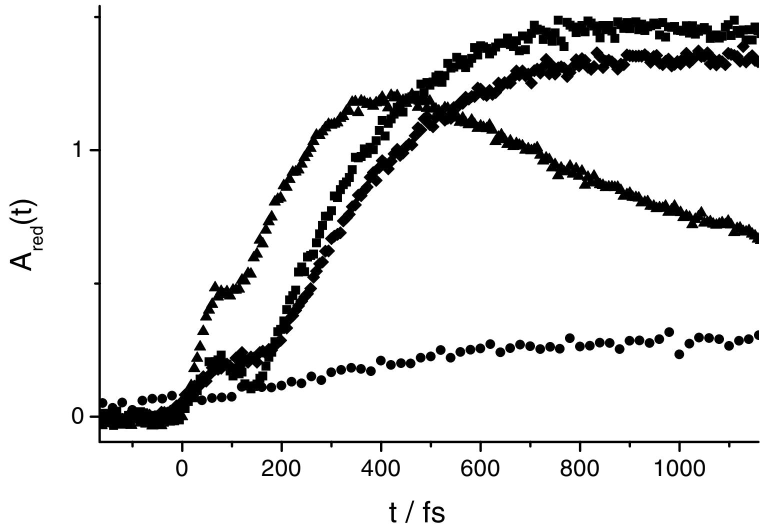

Figure 2. Ultra-short-time response of the transient absorbance of solvated electrons after 266 nm photolytic preparation in a water jet at $T = 28\,^{\circ}\mathrm{C}$. The signals are scaled to the absorbance at 725 nm after 40 ps representing the position of the maximum absorption of the thermally relaxed spectrum (▲: $\lambda = 1000$ nm; ■: $\lambda = 741$ nm; ◆; $\lambda = 692$ nm nm; ●: $\lambda = 452$ nm).

the thermalized solvated electron and its maximum value are denoted as $\varepsilon_\infty(\lambda)$ and $\varepsilon_\infty(\lambda_{max})$. In this way the relative absorption spectrum of the thermalized solvated electrons is reproduced after 40 ps.

At early delay times (up to 500 fs) the reduced absorbance at 1000 nm is larger than at shorter wavelengths. The maximum absorbance at 1000 nm has been reached about 300 fs earlier than for 741 nm while at 452 nm the absorbance is continuously increasing during the first picosecond. We attribute this different behaviour essentially to thermalization of the excess electrons where the absorption spectrum of initially ‘hot solvated electrons’, as prepared by the UV pulse, is located in the infrared beyond 1000 nm. As time evolves the spectrum shifts to the blue due to relaxation into thermal equilibrium. Consequently, the maximum absorption at longer wavelengths is always reached earlier than at shorter wavelengths. However, the relaxation of the solvated electrons into thermal equilibrium [23] is temporally overlapped by the geminate recombination. This relaxation is completed after about 5 ps and the geminate recombination persists for about another 100 ps.

4. Discussion

For a quantitative analysis of the temporal evolution of the absorption spectrum of solvated electrons the knowledge of zero delay time between the pump pulse and the probe pulse at each wavelength is crucial. In this particular case, the water system itself can be used to determine the maximum temporal overlap between the pump and the probe pulse. At very early delay times when pump and probe pulse overlap in the water jet the transient absorptions at all probe wavelengths showed a distinct local maximum or at least a marked plateau (see figure 2). This phenomenon is not well understood but it may be interpreted as a cross phase modulation or Raman-induced change of absorption occurring when pump and probe pulses temporarily overlap [28, 29].

Knowing the absolute zero points for the transient absorptions at different wavelengths we can reconstruct the temporal evolution of the absorption spectrum. It turns out that the location of the maximum absorption $\hbar\omega_{max}$ shifts with time from the infrared to the visible while the width of the spectrum essentially does not change. The shape stability and the spectral shift of the absorption spectra of solvated electrons in polar fluids are well known and have been repeatedly pointed out in review articles by Tuttle and Golden [5]. The temperature shift of the absorption spectrum was first mentioned by Jou and Freeman [9] and a linear shift of -2.4 meV K^{-1} has been reported in water.

In figure 3 we represent the temporal shift of $\hbar\omega_{max}$. At early times of about 300 fs the absorption spectrum is red shifted by about 0.5 eV with respect to the thermally relaxed spectrum. After about 1 ps the red shift has reduced to about 0.1 eV and after about 4 ps the spectrum has almost completely relaxed into its thermal equilibrium. On the basis of the temperature shift of the spectrum these shifts correlate with temperatures of about 500 and 340 K at 300 fs and 1 ps, respectively.

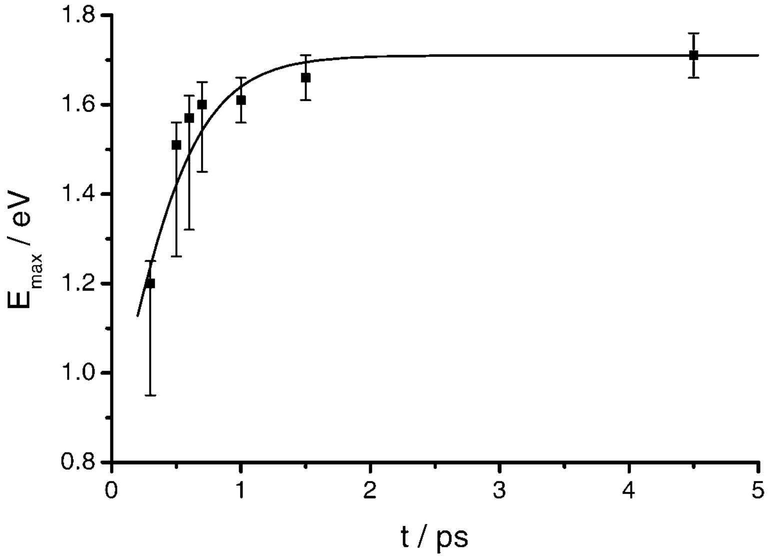

Figure 3. Ultra-short-time response of the position of maximum transient absorption $\hbar\omega_{max}$ of solvated electrons after 266 nm photolytic preparation in a water jet. A relaxation time constant of $\tau = (300 \pm 50)$ fs is extracted from a first order fit.

The temporal evolution of the absorption spectrum contains important information on the dynamical behaviour of solvated electrons on a very early time scale. Previously, this has been interpreted mainly in terms of transient electronic states [10–16, 27, 30]. We suggest an alternative and much simpler interpretation which takes into account only the well known properties of the absorption spectrum of solvated electrons such as shape stability and temperature shift. These characteristics of the spectrum can be used to extract important information on the electronic ground state of solvated electrons. For this purpose, we apply the optical sum rules [31–35] and accordingly interpret the relaxation of the optical absorption spectrum. In particular, the mean squared dispersion in position $\langle \Delta r^2 \rangle$ of the electronic ground state and the oscillator strength f are given by the following moments of the absorption spectrum:

$$S(-1) = n_0 \frac{\hbar c}{C_0 e^2} \int_0^\infty \varepsilon(\omega)\omega^{-1}\,\mathrm{d}\omega = \frac{2}{3}\langle \Delta r^2 \rangle \tag{7}$$

$$S(0) = n_0 \frac{m_e c}{C_0 e^2} \int_0^\infty \varepsilon(\omega)\,\mathrm{d}\omega = f \tag{8}$$

with $\varepsilon(\omega)$ = molar decadic absorption coefficient, $\omega = 2\pi c/\lambda$ (c/λ = frequency of the probe light), n_0 = refractive index and $C_0 = 2\pi^2 N_A/\ln 10$.

For thermally equilibrated solvated electrons in a variety of polar fluids an oscillator strength of $f \approx 1$ [5] has been found. Equation (8) therefore represents the Thomas–Reiche–Kuhn sum rule [31] confirming that all possible transitions from the ground electronic state are included in the observed absorption spectrum. In the following we infer that during the relaxation into thermal equilibrium the oscillator strength of $f = 1$ is conserved as well as the shape stability of the spectrum. This will be discussed in more details in a forthcoming paper [36].

The determination of $\langle \Delta r^2 \rangle$ of the electronic ground state is straightforward. The shape stability of the spectrum facilitates the integration of equation (7) and $\langle \Delta r^2(t) \rangle$ can be obtained from the position of the optical absorption spectrum. A simple correlation between $\langle \Delta r^2 \rangle$ and the location of the maximum absorption cross section $\hbar\omega_{max}$ has been elaborated recently by Krebs *et al* [37].

$$\langle \Delta r^2 \rangle = (10.09 \pm 0.26)\ \text{Å}^2\ \text{eV}/(\hbar\omega_{max}). \tag{9}$$

The correlation is excellent and valid for solvated electrons in many different polar solvents and mixtures over wide temperature ranges. We interpret the time dependence of the mean squared dispersion in position $\langle \Delta r^2(t) \rangle$ of the electronic ground state as the solvation process of the solvated electron, i.e. the solvation dynamics. For the position of the optical absorption spectrum a relaxation time constant of (300 ± 50) fs can be extracted from figure 3. According to equation (9) this time constant must be identified as the time constant for the relaxation of $\langle \Delta r^2(t) \rangle$ and thus the solvation process itself.

5. Conclusions

We could clearly show that in the femtosecond domain the transient spectra of solvated electrons are due to thermalization of the initially 'hot solvated electrons'. According to our interpretation the thermalization process of electrons is identical to the solvation process. In water this process is extremely fast and proceeds with a time constant of about (300 ± 50) fs.

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