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Hydrated-electron population dynamics

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Abstract

A detailed frequency-resolved pump–probe study of hydrated electron dynamics, performed with 5-fs pulses, is presented. We show that the experimental data can be successfully described with a model in which the excited state lifetime is ~ 50 fs in regular water and ~ 70 fs in heavy water. The deuteration effect on the lifetime strongly suggests that OH-vibrational modes in the first solvation shell act as accepting modes for energy relaxation.

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1. Introduction

Since the first observation of solvated electrons in liquid ammonia [1], the study of excess electrons in liquids has been an area of vast interest for both chemists and physicists. The existence of such electrons in aqueous solutions, known as *hydrated electrons*, was first postulated in 1952 [2,3] and discovered 10 years later by recording its absorption spectrum [4,5].

Excess electrons in condensed-phase media play a crucial role in the dynamics of chemical and biological processes. The hydrated electron is particularly interesting because many electron-transfer reactions in nature occur in a water environment. Electrons can also be used as an ideal probe for solvation dynamics since no internal energy redistribution is possible for a bare particle, such as the electron. Finally, the hydrated electron is perfectly suited as a model for quantum molecular dynamics (MD) simulations in the liquid phase. The unique possibility to compare directly the results of such computer simulation studies and femto-

second spectroscopy allows verification of the basic assumptions and calculation methods.

Computational studies on the hydrated electron in liquid water [6–8] have shown that the first solvation shell is composed of approximately six water molecules with their OH bonds directed toward the electron (the so-called Kevan geometry [9]). The localization of a hydrated electron in a water cavity gives rise to bound eigenstates: the lowest energy eigenstate is nearly spherical (1s state) and the first excited state consists of three p-like orbitals (2p state). The high sensitivity of the electronic states of the hydrated electron to the aqueous environment results in a broad absorption spectrum that peaks at ~ 720 nm and has a FWHM of ~ 350 nm. Very recently, MD simulations finally succeeded in an accurate portrayal of the hydrated electron absorption spectrum [10].

One of the unsolved questions surrounding the hydrated electron concerns its excited state lifetime. Despite the illusive simplicity of the system, the rate of electronic relaxation remains a heavily debated issue. So far MD simulations [11–16] have not been able to clarify the problem. The predicted lifetime ranges from ~ 120 fs to 1.1 ps depending on the particular choice of the electron–water pseudopotential and on the model chosen for water molecules. For instance, the initial assumption of ‘rigid’ water molecules and an electron–water pseudopotential [11] led to the prediction of a

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~ 1 -ps lifetime of the 2p state [12]. The implementation of the ‘flexible’ water potential reduced the radiationless relaxation times to ~ 120 and ~ 220 fs for the electron solvated in H_2O and D_2O , respectively [13]. Assuming a modified electron–water potential [14], the lifetime of the 2p state was inferred to be 1.1 ps, with electronic relaxation preceded by a 240-fs excited-state solvation process (i.e., rearrangement of the surrounding of the excited state) [15]. Finally, mixed quantum-classical MD methods yielded an excited-state survival time of ~ 1.5 ps [17] and an average decoherence parameter of ~ 6 fs [18].

Results from femtosecond spectroscopy [19–26] also remained inconclusive. According to one scenario [19,20,24,26], the excited state population relaxes with a time constant of ~ 200 fs; hereafter cooling back to the hot ground state with a 1-ps rate. In another scenario [22,23], the 2p-state solvation takes place on a 300-fs time scale, whereas the excited state decays predominantly with a time constant of 0.7–1.2 ps. Very recently, as shorter optical pulses became available, it was found that the 300-fs decay is preceded by dynamics on a ~ 50 -fs time scale, tentatively assigned to librational wave-packet dynamics [22,23,27,28] and/or non-Condon effects [27,29]. In addition, photon-echo and transient grating experiments revealed that the absorption spectrum is primarily homogeneously broadened and that the induced anisotropy decays within 5 fs [29] which seems consistent with recent MD simulations [18]. Evidently, extremely short pulses are required and experiments over a very broad spectral range need to be done to identify the earliest relaxation stage of the excited hydrated electron.

In this Letter, we present the results of femtosecond frequency-resolved pump–probe experiments on the hydrated electron, photo-excited from its equilibrated ground state. The use of broadband 5-fs pulses allows us to combine reliable acquisition of transient spectra in the range of 600–1050 nm with unprecedentedly high temporal resolution. Our data show that the depopulation of the excited state of the hydrated electron proceeds on a 50-fs time scale whereas in heavy water this lifetime increases by a factor $\sqrt{2}$. The proposed model for the hydrated electron dynamics successfully accounts for the observed experimental features.

The pump–probe experiments (Fig. 1) are carried out as follows: two replicas of a well-characterized 5-fs input pulse [30], separated in time by a delay τ , intersect in a 100- μm water jet containing the sample. Behind the sample, the probe beam is dispersed through a 1/8-m monochromator (CVI). The pump–probe signal ΔT (i.e., variations in the probe transmission with and without pump) is measured by a digital lock-in amplifier that is referenced to a mechanical chopper (~ 1 kHz) inserted in the pump beam. The differential absorption signal is computed as the $-\Delta T/T$ ratio, where T is the probe

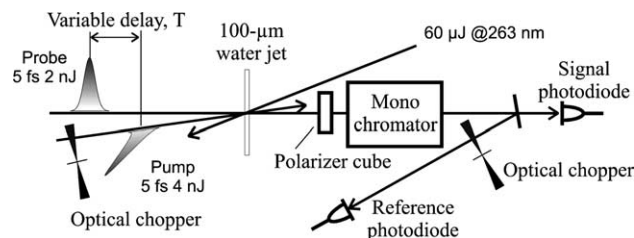


Fig. 1. Schematic of set-up for pump–probe on hydrated electron.

beam intensity. Orthogonal polarizations of pump and probe beams are used to avoid unwanted heterodyning of the signal by the light scattered from the pump pulse in the sample and to minimize coherent coupling between pulses at zero delay. Hydrated electrons are generated by photo-ionizing a small amount of potassium ferrocyanide (~ 2 g/l), added to the water, with the frequency-quadrupled output of a Nd:YLF laser (263 nm) [22,27]. All measurements are carried out at room temperature at a 5-kHz repetition rate. The contribution of pure solvent to the pump–probe signal ($< 10\%$ of the peak signal) is measured independently by blocking the UV preparation pulses and subtracted from the corresponding transient spectra of hydrated electrons.

Representative transient absorption spectra of hydrated electrons in water at different pump–probe delays are presented in Fig. 2b (solid dots). A dominant feature of the transient spectra in Fig. 2b at initial pump–probe delays is an absorption bleach contour (negative signal) that stretches through most of the covered spectral window. Around 720 nm, the bleach decreases by a factor of ~ 2 during the first 100 fs. The high-frequency wing (below 700 nm) of the bleaching contour becomes noticeably flatter in this time window. On the same time scale, a sharp rise of induced absorption (positive signal) at low frequencies is observed. All these processes are consistent with a rapid (within 100 fs) depopulation of the excited state, resulting in a loss of excited state emission/absorption and simultaneous development of hot-ground state absorption. No signature of p-state solvation or intra-band dynamics was found on this time scale, even with 5-fs resolution in the experiments. Had such processes existed on this time scale, they would manifest themselves through a red shift of the emission. However, no such red shift of the emission was observed. Hole-burning experiments with 18-fs pump and 5-fs probe pulses produced transients qualitatively similar to those in Fig. 2b with no indication of transient hole. This conclusion is corroborated by the previous pump–probe experiments [25] and is also in line with the finding that the absorption line shape of the hydrated electron is homogeneously broadened [29].

After ~ 100 fs, no drastic changes in the transient spectra are observed; the induced absorption contour move gradually towards the center of the steady-state absorption of the hydrated electron with characteristic

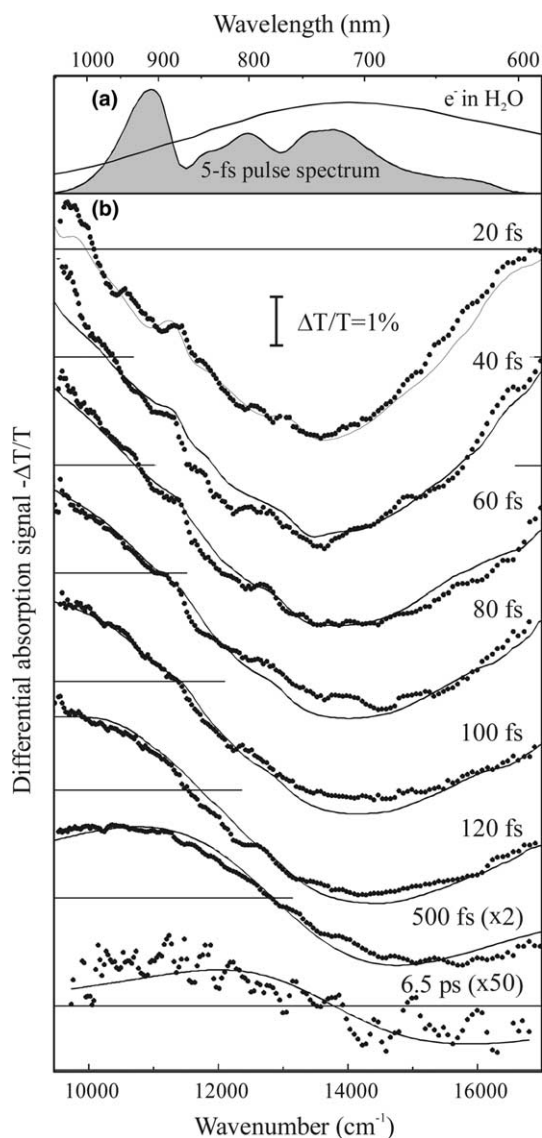


Fig. 2. Absorption spectrum of the hydrated electron (a) and differential absorption signals (b). Shaded contour in (a) depicts the spectrum of excitation 5-fs pulses. Experimental data and results of numerical simulations are depicted in (b) by solid dots and curves, respectively. Delay between pump and probe pulses is indicated in the right. Horizontal lines show the $\Delta T/T = 0$ level.

times of ~ 300 fs and 1.1 ps, corroborating previous reports [24–26].

Fig. 3a outlines a simple, yet realistic model to explain the experimental results of energy relaxation. The first pulse promotes the electron from the initial $1s$ to $2p$ state. The population relaxation of the $2p$ state occurs with the time constant T_1 after which the electron finds itself in the ‘hot’ ground state (denoted as $1s'$). The frequency of the ‘hot’ $1s'-2p'$ is red-shifted [31] with respect to the frequency of the original $1s-2p$ transition as a result of the local temperature rise due to the energy release after the population relaxation. Subsequently, the contribution from the red-shifted induced absorption builds up while the contributions from the $2p$ -state

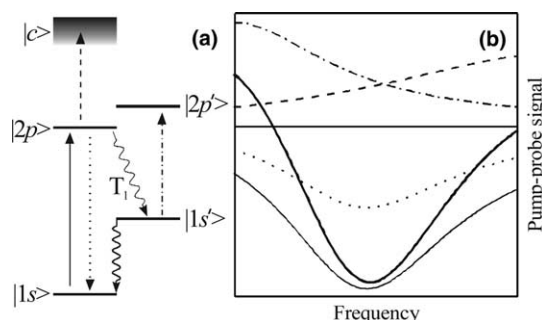


Fig. 3. Model of hydrated-electron dynamics (a) and processes (b) that contribute to the pump–probe signal (thick solid curve): bleaching of the $1s$ state (thin solid curve), emission from the $2p$ state (dotted line), absorption from the $2p$ state to continuum states (dashed curve), absorption from the ‘hot’ $1s'$ state (dash-dotted line). T_1 denotes the lifetime of the $2p$ state.

fluorescence and absorption decrease correspondingly (Fig. 3b). The latter flattens the blue flank of the pump–probe signal (Fig. 2b). Finally, the energy flows from the first solvation shell further into water bath leading to thermalization of the hydrated electron.

The pump–probe signal is therefore a sum of four terms [32], which originate from bleaching of the $1s$ state, induced absorption from the $1s'$ state, and fluorescence and induced absorption from the $2p$ state, respectively (Fig. 3b):

$$\begin{aligned}
 -\Delta T/T(\Omega) \propto & -\sigma_{sp}(\Omega, \Gamma_{sp}, \omega_{sp}) \\
 & + a_{s'}(\tau)\sigma_{s'p'}(\Omega, \Gamma_{s'p'}(\tau), \omega_{s'p'}(\tau)) \\
 & - a_p(\tau)\sigma_{sp}(\Omega, \Gamma_{sp}, \omega_{sp}) \\
 & + a_p(\tau)a_{pc}\sigma_{pc}(\Omega, \Gamma_{pc}, \omega_{pc}), \quad (1)
 \end{aligned}$$

where $a_p(\tau)$ and $a_{s'}(\tau)$ are the respective populations of the $2p$ and $1s'$ states, a_{pc} is the absorption cross-section of the $2p-c$ transition, and σ_s denote the transition spectral shapes. The condition of population conservation dictates that $a_p(\tau) + a_{s'}(\tau) = 1$. The crucial difference between the current model and the previous ones [24,26] is that solvation and/or intra-p-band dynamics play no role.

In general, expressions for σ_s are quite complex and include a 2-fold integral over the applied electric fields and the third-order susceptibility [29]. To highlight the main features of the pump–probe signal, we derived a simplified expression that is valid when the pump/probe pulse duration is much shorter than the population relaxation time:

$$\sigma(\Omega, \Gamma, \omega) = \left[\frac{\Gamma_{sp}}{\Gamma} \right] \frac{4\Omega^2\Gamma^2}{(\omega^2 - \Omega^2)^2 + 4\Omega^2\Gamma^2}. \quad (2)$$

Note that upon deriving Eq. (2) one *cannot* invoke the rotating-wave approximation because the central frequency ω is of the same order of magnitude as the characteristic half-width Γ [29]. As follows from Eq. (1),

the total pump–probe signal is proportional to a linear combination of line shapes of the form given by Eq. (2) (Fig. 3b). Remarkably, it does not depend on the particular shape or chirp of the excitation pulses as long as these pulses remain much shorter than the population relaxation time T_1 of the 2p state.

The fit to the data proceeds as follows. The width Γ_{sp} is set at 3300 cm^{-1} , which corresponds to dephasing time $T_2 = 1.7\text{ fs}$ as measured in photon-echo experiments [29]. The width, the central frequency and the time-dependent amplitude of the $1s'$ -p' contour are treated as local fitting parameters (i.e., specific for each delay time), while the rest of variables are global (i.e., common for all delays). For the pump–probe spectra measured at short time-delays ($\leq 100\text{ fs}$), we used the full expressions for the line-shape functions [29] to be able to account for the actual amplitude and phase properties of the laser pulse. The fits of individual pump–probe spectra, obtained using the model, are depicted as solid curves in Fig. 2b. Clearly, the overall fit quality is excellent, which supports the proposed model.

Fig. 4 shows the populations of 2p and $1s'$ states as a function of the pump–probe delay time as derived from the global fit. The mono-exponential fit of the 2p-state population yields an $\sim 50\text{-fs}$ lifetime. Correspondingly, the population of the $1s'$ state increases with a 50-fs time constant. After the initial build-up, $a_s(\tau)$ stays reasonably close to unity (Fig. 4, inset), which is fully consistent with the overall population conservation. This feature originates solely from the fit and is not assumed a priori and, therefore, presents a powerful check of the correctness of the model. It must be noted that the extraction of a 50-fs lifetime was not possible from the data obtained in the previous pump–probe studies [19,20,22,24–26], due to the lack of adequate temporal resolution (typically $\sim 150\text{ fs}$).

To gain more insight into the physical processes underlying the hydrated-electron dynamics, we examine the impact of deuteration on the spectro-temporal

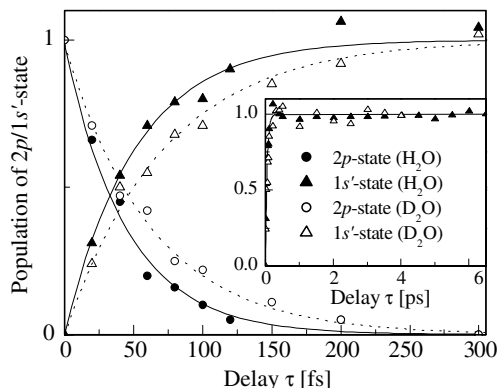


Fig. 4. Population of the 2p state (circles) and $1s'$ states (triangles) as deduced from the fit to experimental data (Fig 2). Exponential fits with time of 50 and 70 fs are shown for water (solid curve) and heavy water (dashed curve), respectively.

behavior of the pump–probe signal (Fig. 4, open symbols). The lifetime of the 2p state and, accordingly, the build-up time of the $1s'$ state of the electron in heavy water is $\sim 70\text{ fs}$ which is by a factor of $\approx \sqrt{2}$ longer than found in H_2O . The subsequent dynamics, however, are nearly identical in both solvents [27,29].

The extremely short excited-state lifetime allows the following interpretation of the results of transient-grating (TG) experiments [27,29] on the hydrated electron (Fig. 5). The signal peak delayed by $\sim 40\text{ fs}$ in H_2O and $\sim 60\text{ fs}$ in D_2O has been assigned before to librational wave-packet dynamics [23,27,28] and/or non-Condon (i.e., time-dependent variations of a transition dipole moment) effects [29]. In the framework of the proposed model, the retarded TG response receives a perfectly natural explanation as interplay between different contributions to the TG signal. At the early times, the loss in 2p-state fluorescence due to population relaxation is counteracted by a simultaneous drop in 2p-state absorption. On the other hand, induced $1s'$ -state absorption does not substantially contribute to the total TG signal as it is being developed mostly outside the spectral region of the pulses and detector. The combined effect of all these factors leads to the *increase* in the TG signal with time. It is only after $\sim 50\text{ fs}$ when the contribution from $1s'$ -state absorption begins to dominate which results in a sharp decrease of the TG signal. However, after $\sim 100\text{ fs}$ the 2p state is almost depopulated, and only two contributions ($1s'$ -state bleaching and hot $1s'$ -absorption) donate to the TG signal. This results in leveling of the signal which further decays with a time constant of $\sim 150\text{ fs}$ (300-fs relaxation time as TG signal is homodyne) within the dynamic range of detection.

The TG signals on the electron solvated in heavy water (Fig. 5) are quite similar to those for normal water but the maximum is delayed to longer times ($\sim 60\text{ fs}$).

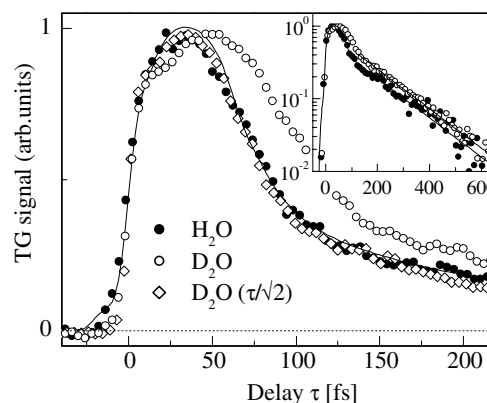


Fig. 5. Comparison of the transient grating signals obtained from electrons hydrated in H_2O (solid dots) and D_2O (open circles). All data are given for perpendicular polarizations of excitation pulses. The delay axis for D_2O has been compressed by a factor of $\sqrt{2}$ to highlight the isotopic effect (diamonds). Solid line shows the result of simulations according to the model described in the text. The inset shows the same data in the logarithmic scale.

However, if the time scale of the D₂O TG data is compressed by $\sqrt{2}$, the TG signal becomes virtually indistinguishable from that for H₂O (Fig. 5, diamonds). As we discussed, this is a direct consequence of the 2p-state lifetime that changes by a factor of $\sqrt{2}$ in H₂O and D₂O. The fact that both TG signals behave similarly at the long time scale indicates that librational motions of water molecules are overtaken by those that exhibit no isotopic effect (e.g., translations).

From the fits to the pump–probe data we extract that $\sim 8500 \text{ cm}^{-1}$ of the energy deposited by photo-excitation is dissipated with a time constant of 50 fs due to population relaxation from the initially excited 2p state. Such a fast relaxation process can only be explained by assuming a conical intersection to exist between the excited and ground state coupled to several vibrational modes [33]. For the latter, the most likely candidates are the OH-stretching vibrational modes of the six nearest water molecules in the Kevan geometry [9]. Upon electron excitation to the p state, the combined system ‘electron coupled to six OH modes’ tends to lower its energy by elongating the octahedral structure (Jahn–Teller-like instability). Our estimations show that the energy gain due to the cavity elongation can be as high as 1 eV, in good agreement with the measured value. After cavity deformation, a non-Born–Oppenheimer transition [33] takes place from the 2p to the 1s state within several vibrational periods (~ 10 fs). The observed $\sqrt{2}$ -dependence of the lifetime points at a dominant role of the OH-stretching mode in the radiationless relaxation process of the excited state which is consistent with the recent resonance Raman experiments on the hydrated electron [34].

The relaxation processes following the excited state depopulation, occur at time scales of ~ 300 fs and ~ 1 ps and do not exhibit any appreciable isotopic effect. The former time is reasonably closed to the population relaxation time of the OH-stretching mode of ~ 250 fs [35]. Approximately after 300 fs, the energy is released in the form of local heating (i.e., raise of the local temperature) and spreads further away from the electron. It is likely that the existing hydrogen bond network helps to speed up the energy transfer.

In summary, optical pulses of extremely short duration (< 5 fs) and with a large spectral width (> 450 nm) have been applied to uncover the initial dynamics of the hydrated electron. From the fit of the pump–probe spectra, we inferred a ~ 50 -fs lifetime of the first excited state. This lifetime increases by $\sqrt{2}$ in heavy water. This fast relaxation process is suggested to be associated with a conical intersection between the ground and excited state caused by the strong coupling between the electron and OH-vibrational modes of water molecules in the first solvation shell.

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