Ultrafast Librational Dynamics of the Hydrated Electron

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Photon echo and resonant transient grating experiments on the equilibrated aqueous electron are reported, using 15 fs excitation pulses. Both experiments exhibit clear signatures of wave packet dynamics, attributed to an underdamped solvent motion of about 850 cm^{-1}. Experiments in D_2O expose the librational nature of this mode. The overall agreement between experiment and quantum-molecular dynamics simulations is good, except for the initial oscillatory dynamics, which have not been predicted.   [S0031-9007(98)06199-7]

Since its discovery about 35 years ago [1], the hydrated electron has captured the imagination of experimentalists and theoreticians alike. It seems one of the simplest physical systems to study, with an s-like ground state and three near degenerate p-type excited states confined in a water cavity [2,3]. Yet, even after decades of intensive experimentation and calculations on the hydrated electron, understanding of its solvation and nonadiabatic relaxation dynamics is far from being complete.

As a quantum system, the electron in water presents a unique opportunity to test the validity of various mixed quantum-classical theories. The ultimate test of these theories is, of course, whether or not they can describe the experiments correctly. Next to an important theoretical challenge for quantum-molecular dynamics simulations, grasp of the electron dynamics is essential from a chemical point of view, as the electron is a ubiquitous transient species in many chemical reactions, and water is the most important solvent in chemistry.

Pioneering optical studies on the hydrated electron started about ten years ago [4,5], when 100-fs pulses became available in the wavelength region where the equilibrated aqueous electron has an intense absorption band. From these early experiments, it became clear that the excess electron, when generated in a multiphoton process, is born in a quasifree extended state. From there, it localizes into a preexisting trap, from which it further relaxes to a deeper well on a time scale of $\sim 250-500$ fs. But then the electron has reached an electronically excited state (formerly known as the wet electron [5]), from which it decays on a picosecond time scale to the electronic ground state.

Stimulated by these experiments, mixed quantum-molecular dynamics simulations [6–13] and path-integral Monte Carlo methods [3,14] were used to explore the energetics and dynamics of the aqueous electron. Not surprisingly, the results proved quite sensitive to details of the electron-water interaction. It was shown, for instance, that many-body polarization contributions were essential

to simulate the absorption spectrum [14], which comprises three overlapping s-p transitions, split by ~ 0.2 eV. However, irrespective of the force field, all calculations predict a bimodal solvent response function for the equilibrated electron, with the ultrafast part ($\sim 10-20$ fs) assigned to librational [7,12], or translational-mechanical dynamics [11,15,16], and the slower part, on a time scale of 130–240 fs, to diffusive solvent motion.

These calculations in turn provided a strong stimulus for new optical experiments. The Barbara group, for instance, made detailed pump-probe investigations of the hydrated electron [17,18], showing solvation dynamics, nonadiabatic relaxation, and excited state absorption to be strongly intertwined. From these experiments, it was concluded that solvation dynamics is complete within 300 fs and that the excited state lifetime is between 0.5 and 1 ps [13,17,18]. However, because of the limited time resolution (~ 100 fs), the crucial part of the solvation process, predicted to proceed on a 10-fs time scale [6–14], could not be resolved. Clearly, much shorter optical pulses are needed to capture the early time dynamics of the solvated electron [19–21].

In this Letter, we report and discuss results of photon echo and resonant transient grating experiments on the solvated electron, using 15-fs pulses. The key experiment is the so-called echo-peak shift measurement, which shows the energy-gap correlation function to exhibit oscillatory dynamics, implying a particular solvent motion to be strongly coupled to the electronic transition. Interestingly enough, this phenomenon has not been predicted by quantum-molecular dynamics simulations. Transient grating experiments on the electron in normal and deuterated water suggest that this strongly coupled water motion is a libration. Our analysis, based on the Brownian oscillator model [22], provides a system-bath correlation function that determines the first few hundred femtoseconds of the hydrated electron dynamics.

The pulse sequence and phase-matching geometry of the experiments are sketched in Fig. 1. The hydrated electron

is generated by photoionizing potassium ferrocyanide dissolved in water (concentration ~ 5 mM) using the quadrupled output of a Q-switched Nd:YAG laser, operating at 1 kHz [17,18]. The 70-ns, 35-μJ photoionizing pulse is focused to a spot of ~ 50 μm which yields a peak optical density of the electron's absorption of ~ 0.1 over a 100-μm-thick water jet. The Nd:YAG laser triggers a cavity-dumped Tr:sapphire laser [23], whose output is split in three equally intense beams. These beams, after suitable delays, are focused to a spot of about 50 μm in the sample jet. The wavelength of the excitation pulses is centered at the red flank (~ 795 nm) of the equilibrated electron's absorption spectrum. Various photon echo signals, generated in different phase-matching directions Fig. 1(b), are detected using photodiodes and lock-in amplifiers. By blocking the UV beam, we verified that the solvent contribution to the coherent response is less than 5% of that from the hydrated electron and thus can be disregarded.

Figure 2 shows a series of stimulated photon echoes measured at a fixed waiting time between the second and third pulse (t_{23}), while scanning the delay between the first two excitation pulses (t_{12}). The two signals symmetrically displaced with respect to $t_{12} = 0$ are photon echoes launched into different conjugate directions [24]. The time $t_{23} = 0$ was determined by comparison of the profiles of the stimulated photon echo and the two-pulse echo signals, for which $t_{23} = 0$. The shift of the echo maximum with respect to $t_{12} = 0$ constitutes the observable, denoted as echo-peak shift (EPS), whose waiting-time dependence will be referred to as EPS function. Recently it was shown [25–27] that for an electronic two-level system the EPS function tracks the overall solvation correlation function remarkably well, except at very early times. Moreover, this even holds for excitation pulses that have durations comparable to the fastest relaxation time.

At this point the problem should be addressed whether modeling of the hydrated electron by a two-level system,

comprised of an s-ground state and a single p-excited state, is physically meaningful. The validity of this approach at early times is based on the following considerations: First, it has been shown [17,18] that for excitation and probing near 800 nm at short times (≤ 50 fs), continuum states are not significantly involved in the spectral dynamics and therefore can be discarded. Second, taking only a single p state into account is also justified because the bandwidth of the optical pulses is not large enough to coherently excite two $s \rightarrow p$ transitions. Third, by exciting at the red flank of the electron's absorption spectrum only one p-state is involved. We emphasize that a two-level model presents only a first-order approximation to the electron's dynamics (*vide infra*).

The echo maxima were determined from a Gaussian fit to the profiles of the signals (Fig. 2) and used to generate the EPS function displayed in Fig. 3. To demonstrate the precision of the experiment, the two-pulse echo peak shift—which is waiting-time independent—is also displayed in Fig. 3. Clearly, the EPS function exhibits extremely fast decay and oscillatory dynamics. Recalling the fact that the EPS function mimics the energy-gap correlation function, we conclude that the short-time solvation response of the electron is dominated by a high-frequency strongly coupled solvent mode. The underdamped nature of the energy-gap correlation function is also evident from Fig. 4, which presents the transient grating (TG) signal of the aqueous electron. Here wave-packet-like dynamics is observed corresponding to a mode of about 850 cm^1, in reasonable agreement with the observed maximum in the
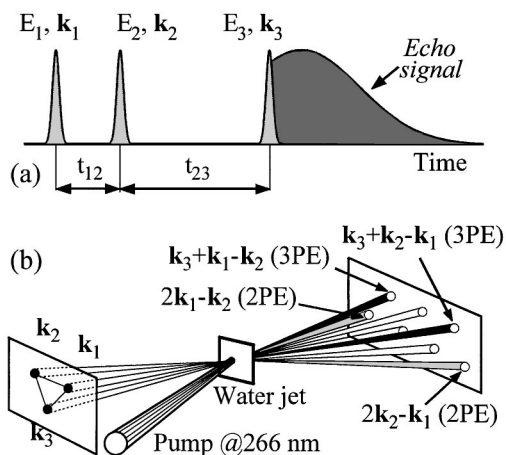

FIG. 1. Pulse sequence (a) and layout of experimental geometry (b). Stimulated photon echoes are generated into phase-matching directions $\mathbf{k}_3 + \mathbf{k}_2 - \mathbf{k}_1$ and $\mathbf{k}_3 + \mathbf{k}_1 - \mathbf{k}_2$ (black beams) while two-pulse echoes (2PE) are emitted into $2\mathbf{k}_2 - \mathbf{k}_1$ and $2\mathbf{k}_1 - \mathbf{k}_2$ directions (shaded beams).
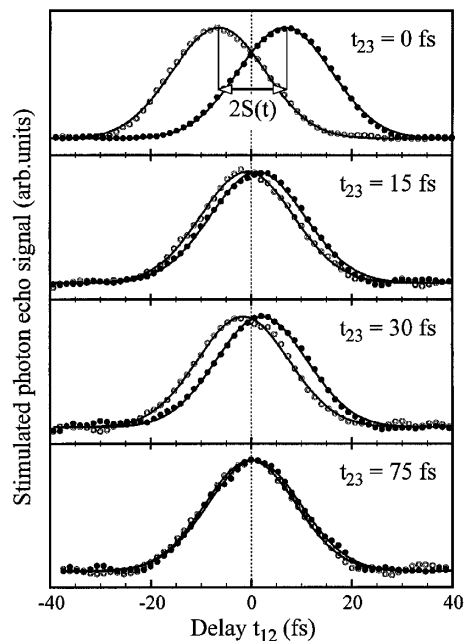

FIG. 2. Stimulated photon echo signals detected for the directions $\mathbf{k}_3 + \mathbf{k}_2 - \mathbf{k}_1$ (close circles) and $\mathbf{k}_3 + \mathbf{k}_1 - \mathbf{k}_2$ (open circles) for different waiting times t_{23}. $S(t)$ denotes the echo-peak shift. Solid lines are Gaussian fits to experimental profiles. Note that the echo-peak shift approaches a minimum at $t_{23} = 15$ fs.

EPS function at $\sim$30 fs. To determine the physical nature of this mode, we performed TG experiments on heavy water (inset of Fig. 4). In D_2O, the recurrence occurs at a time $\sim\sqrt{2}$ larger than that for normal water, which is a strong indication that the coupled solvent motion is a water libration [7,28,29], because librational frequencies are inversely proportional to the square root of the moments of inertia. The overall decay of the TG signal is multi-exponential with the major component decaying at a time scale of $\sim$75 fs. When the time axis is scaled by $\sqrt{2}$, the TG response in D_2O is identical, suggesting that librational motions play a dominant role here as well.

To make the connection between the spectroscopic observables and solvation dynamics, we employ the multimode Brownian oscillator (MBO) [22]. The central element in the MBO model is the correlation function $M(t)$ [22] of the transition's energy gap, which can be equated to the solvation correlation function [30]. The correlation function itself comprises a normalized sum of correlation functions of Brownian oscillators, which represent generalized solute or solvent motions that are coupled to the electronic transition. Once the correlation function is known, all spectroscopic observables can be calculated using well-known expressions for the various nonlinear optical signals [22,26]. Since in our experiments the pulse duration is of the same order as the fastest solvation time scale, it was essential to account explicitly for the excitation pulse shape in the calculations.

A first-order estimate of the correlation function can be made by inspection of the EPS function in Fig. 3 and TG signal in Fig. 4. Evidently, an underdamped oscillator with a frequency of $\sim$850 cm^{-1} is an important element of $M(t)$. It is also clear from the residual EPS at $t_{23} > 100$ fs that the correlation function has a substantial part decaying on a longer time scale. To simulate these longer time dynamics, a single overdamped Brownian oscillator wi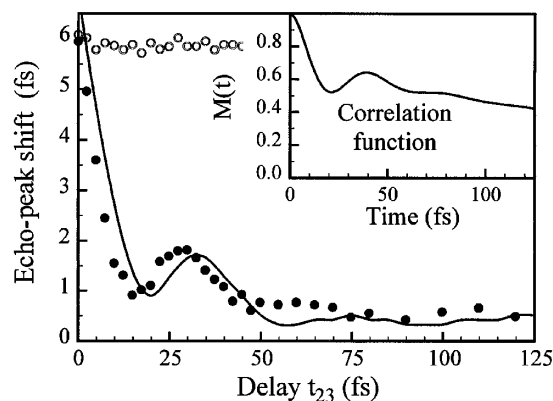th a lifetime of 250 fs was taken. Figure 3 compares the measured EPS function with the one calculated on the basis of the correlation function displayed in the inset of Fig. 3. Because of the reasonably good agreement between experiment and simulation, the given interpretation of the early-time solvation response of the electron as being due solvent librational motion stands on firm grounds. The prominent role of water molecular librations in the solvation process, however, has not been predicted by quantum-classical molecular dynamics simulations, which find the energy gap of the solvated electron to be modulated by translational-type [13,15,16] solvent motion. It is worth mentioning that a calculation based on a dielectric continuum mode [29] exposes the important role of librational effects in the solvation response of the hydrated electron.

We have also performed preliminary simulations of the TG signal (Fig. 4). While the predicted wave-packet dynamics is in qualitative agreement with experiment, the overall decay of the signals cannot be reproduced, even when solvent motion at a time scale of 150–250 fs is taken into account. Clearly, at time scales beyond 50 fs, the continuum states play a significant role in the spectral dynamics. Yet, these simulations bring out a peculiar aspect of the observed wave-packet dynamics, namely, that the recurrences in the TG signals are broader than predicted by calculations based on the correlation function in Fig. 3. An explanation for this anomaly may be that the librational density-of-states function exposes substantial asymmetry.

Another possible cause is the breakdown of the Condon approximation, which may occur for the following reason: Upon optical excitation of the p state, the solvent response proceeds according to the quadrupolar symmetry of the charge distribution in the excited state. Under this modified local symmetry, the s ground state rapidly destabilizes and mixes with d-like orbitals, while the nonoccupied p-states mix with f-like orbitals. This mixing of basis-set functions in the Hilbert space

FIG. 3. Experimental (solid dots) and computer simulated (solid line) echo-peak shift function. The t_{23}-independent two-pulse echo shift is also shown (open circles), demonstrating the ±0.2-fs experimental accuracy in the echo-peak shift determination. The correlation function used in simulations is shown in the inset.
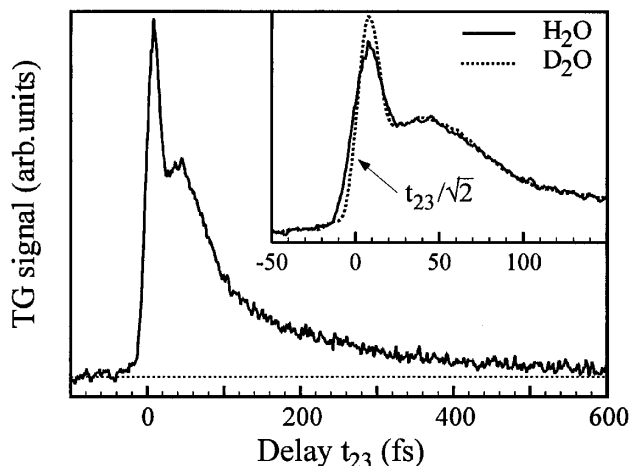

FIG. 4. Transient grating (TG) signal ($t_{12} = 0$) of the aqueous electron. The inset displays the initial decay for normal (solid line) and heavy (dashed line) water. For D_2O, the time scale is compressed by $\sqrt{2}$.

belonging to the ground state solvation symmetry generates a time-dependent transition dipole moment that tracks the solvation correlation function. A clear signature of this effect was observed in the simulations of Barnett *et al.* [7]. This non-Condon effect will be reflected in the TG experiment as a smeared-out wave-packet feature, caused by a time-varying transition dipole moment that reaches its maximum at the outer turning point. A non-Condon effect will have little impact on the EPS, since it mainly affects the amplitude of the coherent signal and not its timing. The non-Condon effect may also be the reason of some mismatch between the EPS function and simulation thereof in Fig. 3, which used a librational frequency deduced from the TG experiment.

Irrespective of the possible presence of non-Condon effects, the conclusion from our experiments and simulations is that the initial solvation dynamics of the electron is dominated by librational motion. Its frequency (~ 850 cm^{-1}) points to a libration around an axis parallel to the H-H direction [31]. Although recent calculations found oscillations with the same frequency in the fluctuations of both the ground and excited state energies [13], the energy gap fluctuations were not affected by this motion. In contrast, librational motion is found to be of major importance in the aqueous solvation response of a solute undergoing a charge jump [32,33].

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