Wave Packet Dynamics in Ultrafast Spectroscopy of the Hydrated Electron

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Hydrated-electron dynamics is examined by frequency-resolved pump−probe experiments using pulses of 13 fs centered at 780 nm. A recurrence at ~40 fs signifies a strong coupling of the electronic transition to underdamped solvent motions. Wave packet dynamics launched by the pump pulse produces an ultrafast red-shift of the electronic transition by approximately 6500 cm^{-1}. Gross features of the pump−probe experiments are analyzed using a two-level system.

1. Introduction

It is well-known that chemical reactivity in the liquid phase strongly depends on solvation dynamics, affecting state energies and potential energy surfaces and the dynamics of reactants and products near the transition state. Therefore, obtaining a better grasp of solvent and solvation dynamics has been high on the physical chemistry agenda for a long time.[1] In the past decade, molecular dynamics simulation studies and ultrafast experiments on dye solutions have unearthed the basic picture of the solvation process as well as the relevant time scales.[2−10] Important aspects of the early-time dynamics, however, remained questionable, because it was not clear how the intramolecular vibrational dynamics could be separated from the solvation dynamical process itself.[8,10] Recently it was shown that comparative studies on the same dye in different solvents can distinguish between the two processes. However, it would still be of paramount importance if a probe of solvation dynamics were used that had no internal degrees of freedom. In such a case all dynamics observed in the solvation process had to be assigned to the solute−solvent coupling.

Of all solvents in chemistry, water is the most important one, and henceforth solvent and solvation dynamics in water has been the subject of many theoretical and experimental studies. For instance, molecular dynamics simulation studies[11,12] and time-dependent Stokes shift experiments on a coumarin dye in water[13] both showed the initial solvation process to be exceedingly fast. However, because of lack of time resolution, the first 50 fs, where most of these dynamics is predicted to occur, was left unexplored.[13] Furthermore, as pointed out above, Stokes shift experiments include intramolecular dynamical effects, which are not easily separated from solvation dynamics.

In this paper we report on a solvation dynamical study of the electron in water. Because the electron is a bare particle, the observed dynamics must be due to coupling of the electron and the water-solvent motions. Besides the fact that the electron is a unique probe of solvation dynamics, hydrated-electron dynamics is, of course, an interesting topic in itself, because the electron is a key player in electron-transfer reactions and radiation chemistry.

The characteristic absorption band of the hydrated electron at 710 nm was first observed after injection of an electron beam into water.[13−19] About a decade ago the first grasp of subpicosecond solvation dynamics was gained by multiphoton ionization of neat water using intense pulses from an amplified CPM laser system.[20−24] A more thorough understanding of the ultrafast dynamics of the electron in water was acquired by subsequent experimental[24−49] and theoretical investigations.[50−76] The following picture has emerged from these studies. Upon photoexcitation the electron is ejected into a delocalized state before getting trapped within ~200 fs. Trapping does not proceed directly into an equilibrium state; at least this is generally considered a rare event.[45,49] Rather an intermediate state is observed, which is characterized by an absorption in the near infrared (peak at ~1300 nm). For this state a time scale for solvation of about 500 fs was reported. The well-separated spectral line shapes of the intermediate and the fully relaxed electron[38] strongly support a description in terms of three levels, in agreement with the interpretation of earlier experiments and model calculations.[20,58]

An alternative route to study the interaction of electrons with water is to perform pump−probe experiments on electrons that have already been equilibrated.[39] It has been argued that the dynamics observed in this type of experiment as, for instance, the relaxation from the excited state, can be fundamentally different, because the electron has substantially changed the local solvent structure in the initial equilibration process.[64,77] The clear advantage of using pre-equilibrated electrons is that the measured transients need not be corrected for geminate recombination.

In previous solvation studies of pre-equilibrated electrons, carried out by the Barbara group,[39−41] the time resolution was about 300 fs, which was not sufficient to cover the initial solvation dynamics.[42] In this paper, experiments with a substantially higher time resolution are reported. This allows for the first time the observation of wave packet dynamics. We show that the wave packet launched by optical excitation of the hydrated electron shifts the transition frequency by about 2000 cm^{-1} in the first 50 fs. A description of coherent effects taking place during pulse overlap are necessary to interpret the features in the pump−probe experiments on the hydrated electron. Although modeling in terms of a two-level system

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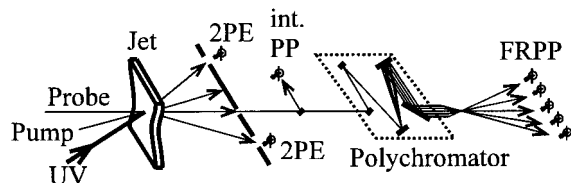*J. Phys. Chem. A, Vol. 102, No. 23, 1998* **4173**

Figure 1. Experimental layout to measure simultaneously spectrally integrated (int. PP) and frequency-resolved pump−probe signals (FRPP) and two-pulse photon echoes (2PE).
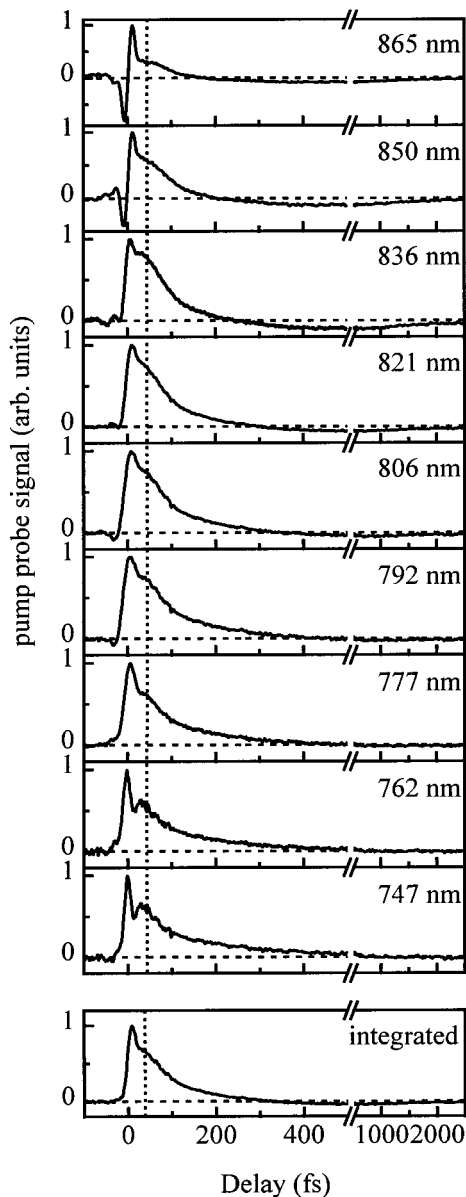

Figure 2. Frequency-resolved and integrated pump−probe signals of hydrated electrons. Positive signal corresponds to induced transmission. For frequency-resolved measurements, the wavelength settings of the polychromator (resolution ~2 nm) are indicated in the corresponding panels. Note the axis break at 500 fs.

nicely explains most of the features observed in pump−probe experiments at the earliest times, three-level effects are of substantial importance at longer delays.

2. Experiments

Electrons were generated by photodetachment in a free streaming jet (thickness ~100 μm) of an aqueous solution of $K_4[Fe(CN)_6]\cdot 3H_2O$ (4 g/L).[78] Excitation was performed with
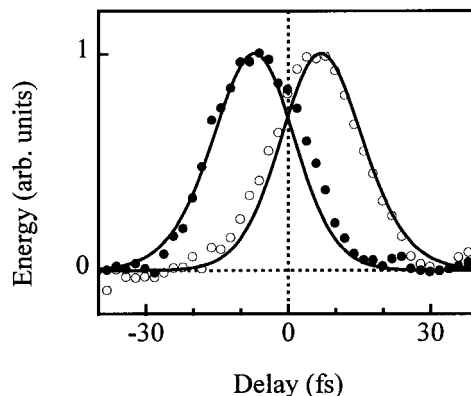

Figure 3. Two-pulse photon echoes measured in conjugate directions (circles). Solid lines result from calculations based on model II (see text).

a quadrupled Nd:YAG laser operating at 2 kHz repetition rate (Figure 1). UV synthesis pulses (pulse duration 70 ns, energy 5 μJ) were focused to a 100 μm spot into the solution generating an optical density of ~0.1. Pulses from a synchronously cavity dumped Ti:sapphire laser were split into parts of equal energy (13 fs, ~8 nJ). To perform the pump−probe experiments, two pulses were variably delayed before being overlapped with the UV beam. The infrared beams were focused to a spot size of ~50 μm. The arrival time of the Ti:sapphire pulses was chosen close to the peak of the UV pulse. The scavenging time of the electrons was measured separately to be about 60 ns at the concentration of $K_4[Fe(CN)_6]$ used.

The signals were picked up behind the jet after recollimating all beams. The probe beam was split behind the sample: The smaller part (10%) was used to measure the spectrally integrared pump−probe signal with an amplified photodiode. The rest of the pulse was dispersed in a polychromator, the output of which was optically mapped onto an array of 10 additional photodiodes to record the frequency-resolved pump−probe. All signals were recorded simultaneously with a digital lock-in amplifier for each photodiode.

Experimental results of the frequency-resolved pump−probe experiment are shown in Figure 2. A small background signal (less than 5%) was found at short delays when the UV beam was blocked. This signal was even detected in pure water and therefore assigned to Raman and nonresonant scattering by water molecules. The background was subsequently substracted from the pump−probe signals.

To accurately determine the zero delay point is crucial for the interpretation of our experiments. As internal reference, we used two-pulse photon echoes, picked up in conjugate directions (Figure 1).[79,80] Two-pulse echoes are useful here because the two coherent signals must lie symmetrically with respect to zero delay (Figure 3).

The actual zero point of the delay between pump and probe pulses was found to differ by ±10 fs from that inferred from conventially autocorrelation measurements made by replacing the sample with a second harmonic crystal.

3. Discussion

3.1. Features in Pump−Probe. Some of the experimental characteristics of our pump−probe experiment are well-known: The frequency-resolved pump−probe signals depicted in Figure 2 have an prominent oscillatory feature around zero delay between pump and probe pulses. These oscillations known as *coherent artifacts* arise from constructive and destructive interference between nonlinear polarizations generated by

different sequential orders of excitation pulses.[81,82] Our model calculations show that the coherent artifact is not very sensitive to the underlying dynamics of the polarization but is highly dependent on the temporal shape and phase (chirp) of the pulses. We note that the coherent artifact is automatically included in the simulations discussed below.

Next to the coherent artifact, a striking feature in the form of a recurrence is observed at a delay of 40 fs. This recurrence is observed at wavelengths below and above the central laser frequency. It also shows up as a bump in the decay of the integrated pump−probe signal (Figure 2, lowest panel). In experiments on dye molecules such a recurrence in pump−probe was attributed to intramolecular vibrations.[1,8,10] As the electron is a bare particle, the recurrence observed here points to a strongly coupled underdamped solvent motion.

On a longer time scale, the induced transparency turns into induced absorption. For delays exceeding 500 fs, the decay of the induced absorption can be fit to a single-exponential decay, with a time constant of ~0.5 ps. This time constant, most likely, reflects the excited state lifetime in accord with previous reports.[20,25,31,40,44,47,49] A single-exponential fit to the remainder of the signal yields a decay of ~110 fs. A rapidly decaying induced transparency and a slowly decaying induced absorption of hydrated electrons excited at 780 nm have been reported before.[40] Similar dynamics are observed here with considerably improved time resolution. Our experiments show that the relative amplitude of the rapid decay is larger and that its time constant is not spectrally dependent as in ref 40. Note, however, that the two experiments differ qualitatively in their excitation conditions: In the present paper short pulses were used for excitation *and* probing, whereas much longer but tunable pulses were used in ref 40. Therefore, in our experiments a coherent superposition of a larger number of states is generated by the pump pulse.

3.2. Model Calculations for the Pump−Probe. In our analysis of the pump−probe signals we concentrate primarily on the recurrence observed at ~40 fs. Because in the spectral region of our experiments excited-state absorption becomes dominant only after ~200 fs, a two-level model should suffice for a description of the early-time dynamics. This assumption is supported by the fact that in previous pump−probe experiments,[39−41] it has been established that the excited-state absorption shifts from the infrared (>1000 nm) to about 800 nm in ~400 fs.

Theoretical modeling of two-level system dynamics has been worked out in detail[1] and applied to a description of the hydrated electron dynamics. Taking the cumulant expansion approach, essentially all optical dynamics can be calculated from a spectral density $C(\omega)$, which is related to the correlation function $M''(t)$ of the energy gap by

$$C(\omega) = \frac{2\lambda\omega}{\pi} \int_0^\infty dt\, M''(t) \cos(\omega t) \quad (1)$$

where

$$\lambda = \int_0^\infty d\omega\, C(\omega)/\omega \quad (2)$$

is a normalization factor. In this model the Stokes shift (the gap between the first moments of emission and absorption) of the electronic transition is 2λ, provided that the excited-state lifetime is large compared to the solvation time.[8] This condition might not be fulfilled for the hydrated electron because of its extremely short excited-state lifetime. The calculations are rigorously carried out taking all possible time orderings and the finite pulse
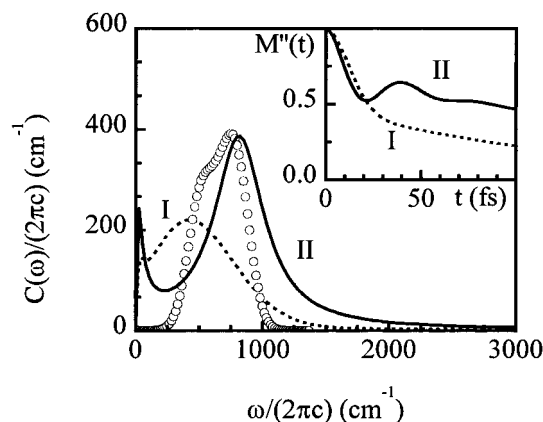

Figure 4. Spectral densities used in modeling of the optical dynamics of hydrated electrons (lines) compared to the librational spectrum of neat water measured by unpolarized Raman spectroscopy (multiplied by ω) plotted in arbitrary units (open circles[56]). The spectral densities are derived from the equilibrium response function calculated in ref 42 (model I) and for our response function (model II). The inset shows the corresponding correlation functions.

duration into account. The pulse was assumed to have a hyperbolic secant envelope with a 13 fs fwhm of the intensity profile.

We first consider a correlation function of the type calculated by Schwartz and Rossky[64] and Staib and Borgis[72] using molecular dynamics simulations (ref 11).

$$M''(t) = c_1 \exp(-0.5(t/\tau_1)^2) + c_2 \exp(-t/\tau_2) \quad (3)$$

Here we employ the parameters of ref 72: $c_1 = 0.465$, $c_2 = 0.544$, $\tau_1 = 12$ fs and $\tau_2 = 130$ fs. The resulting spectral density $C(\omega)$ is plotted in Figure 4 as model I. With the parameter set of ref 64 the calculations yield qualitatively the same results, although, of course, the details differ. The calculated frequency-resolved pump−probe transients are plotted in Figure 5, left panel. Apparently, this model does not produce a recurrence at 40 fs in the frequency-resolved pump−probe. This is not surprising because the correlation function (eq 3) is smoothly decaying and contains no oscillations (Figure 4, inset).

Clearly to generate a recurrence in the pump−probe signals one needs an oscillatory contribution to the correlation function, which is modeled here by an underdamped mode. The energy gap correlation function is therefore

$$M''(t) = c_1 \exp(-\gamma_0 t/2)[\cos(\Omega t) + (\gamma_0/2\Omega) \sin(\Omega t)] +$$
$$c_2 \exp(-\Lambda t) \quad (4)$$

where

$$\Omega = (\omega_0^2 - \gamma_0^2/4)^{1/2} \quad (5)$$

Figure 4 displays this correlation function and $C(\omega)$ (model II) using the following parameters: $\omega_0/2\pi c = 850$ cm^{-1}, $\gamma_0/2\pi c = 480$ cm^{-1}, $\lambda/2\pi c = 3380$ cm^{-1}, $\Lambda/2\pi c = 135$ cm^{-1}, $c_1 = 0.4$, and $c_2 = 0.6$. The normalization factor λ is 3380 cm^{-1}, chosen to reproduce the spectral width of the absorption subband expected for a single s $\rightarrow$ p transition.[53] With model II the recurrence at 40 fs (Figure 2) is well-reproduced (Figure 5, right panel). The two-pulse echoes are also fitted with this moddel (Figure 3, lines), showing that the normalization factor λ was chosen properly to describe the electron's absorption spectrum.

It has been argued that the spectral density relevant to solvation is identical to the neat solvent spectral density as
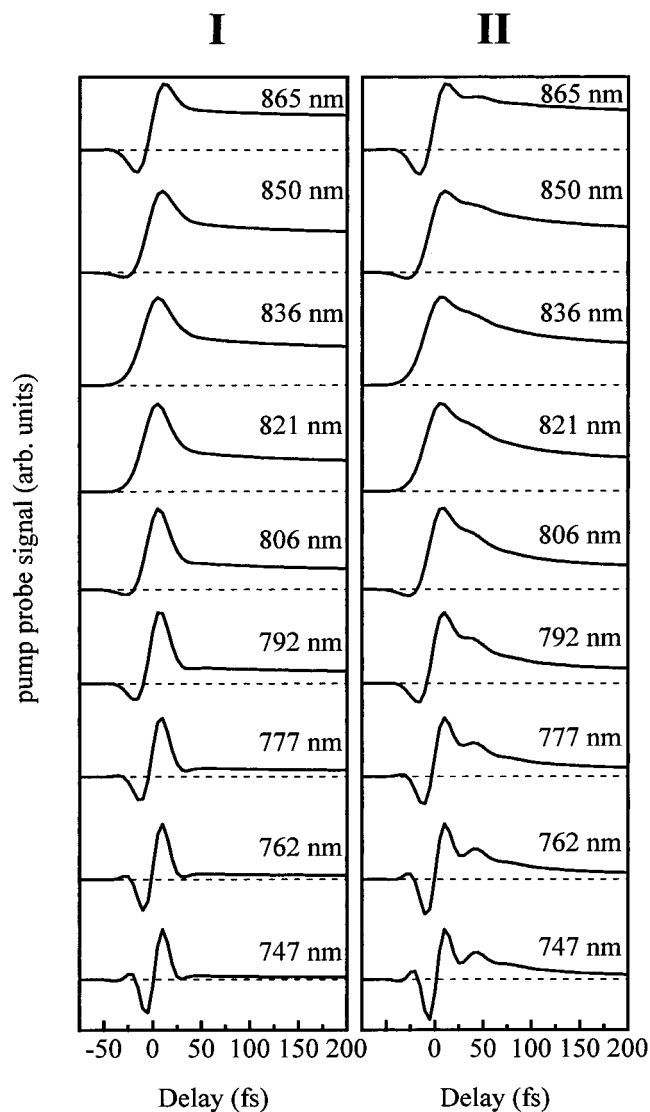
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Figure 5. Calculated frequency-resolved pump−probe traces (left, model I; right, model II).

4. Conclusions

Frequency-resolved pump−probe experiments with pulses as short as 13 fs have resolved wave packet dynamics in the coherent response of the hydrated electron. This new experimental feature in the solvation of electrons is explained using an electronic two-level system strongly coupled to a librational motion of water molecules. Full understanding of the results requires further work and modeling on the basis of a three-level system.

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probed, for instance, in an optical Kerr effect experiment.[83,85−87] Our previous experiments on dyes, however, showed this generally not to be the case.[8] Figure 4 shows that the spectral content of $C(\omega)$ agrees rather favorably with the unpolarized Raman spectrum of the highest frequency librational band of neat water[84,88,89] (note that the Raman spectrum of water in Figure 4 is multiplied by ω to allow a direct comparison with the spectral density[91]). We note that a librational mode of similar frequency was found in model calculations on solvation dynamics in water by Hsu et al.[12] We also note that the exponential part of our correlation function is identical to the one reported by Schwartz and Rossky.[64]

Our simulations of the pump−probe signals predict a spectral shift of ∼2000 cm^{-1} in the first 50 fs, caused by wave packet dynamics on the upper potential energy surface. Unfortunately, we were unable to determine directly the spectral position of the turning point of the wave packet. The 1500 cm^{-1} bandwidth covered by our 13 fs excitation pulses is still too small to determine fully the spectral shift. Our experiments also show that after 400 fs the excited-state absorption becomes overwhelming, giving rise to "negative" pump−probe signals. This induced absorption can only be modeled in a three-level system.[92]

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