Chapter 6

Early-Time Dynamics of the Photo-Excited Hydrated Electron

Abstract

Employing photon-echo techniques, we investigate the early relaxation dynamics of the equilibrated hydrated electron within the first 200 fs upon photo-excitation. The use of 5-fs laser pulses provided unprecedented temporal resolution of our measurements. We conclude that the absorption spectrum of the hydrated electrons is primarily homogeneously broadened. The comparison of two pulse photon echo experiments on pure water and hydrated electrons allows us to measure the pure dephasing time of ~1.6 fs. The shape of the absorption spectrum is described excellently by an extended Lorentzian contour with a spectral width fully determined by the pure dephasing time. From the polarization-dependent transient grating experiments we establish that the polarization anisotropy of the hydrated electron falls to the zero value within 5 fs after initial excitation. A prominent role of a non-Condon effect due to strong coupling of the electron to neighboring water molecules is suggested. Based on the observed isotopic effect we conclude that the initial relaxation dynamics are determined by the inertial response of the water molecules which is librational in its origin. A microscopic picture of the early dynamics of the hydrated electron based on the experimental results is presented. Finally, we develop a theoretical model based on wavepacket dynamics, which is capable of capturing the subtle features of the experimental data.
6.1 Introduction

Upon injection into a fluid, an electron can be captured in a potential energy well formed by neighboring molecules of the liquid. The first observation of such an electron, known nowadays as the solvated electron, dates back to 1864, when Weyl reported a blue color of solutions of metals in ammonia [1]. However, it took more than half a century until Kraus [2] suggested that the blue color was caused by bound species: electrons trapped among the ammonia molecules. The solvated electron has been the subject of numerous investigations ever since. In the sixties the electron solvated in water, called the hydrated electron, was discovered through the observation of the extraordinarily broad absorption spectrum spanning from 500 to 1000 nm which appeared upon injection of electrons [3,4].

The vast interest in the hydrated electron from both theoretical and experimental points of view is by no means accidental. The hydrated electron is a transient species in charge-transfer reactions in biology, non-silicon solar-cell technology [5-8], and chemistry. Important examples are photosynthesis [9], charge transport through biomembranes [10], and long-distance charge transport in nerves [11]. The hydrated electron is also a key intermediate in radiation chemistry [4] and electrochemistry [5-8]. Next to this, the hydrated electron is a perfect test-ground for various theories of complex quantum–mechanical systems. The three-dimensional confinement of the single electron by the surrounding water molecules gives rise to discrete quantum states. This closely resembles a quantum dot [12], an entity that has raised immense attention in recent years as a model system for atoms [13-15] and molecules [16], and holds a great promise for the use in optical devices [17]. However, the important difference between the quantum dot and the hydrated electron is that in the former case the potential giving rise to the confinement is static whereas in the latter case it changes rapidly in time due to dynamical fluctuations of the liquid surrounding.

Numerous computational studies have been performed to investigate the quantum-mechanical status of the hydrated electron and the microscopic structure of its surroundings. It became clear that the first shell of water around the electron is composed of approximately six molecules with their OH-bonds oriented toward the electron [18,19]. (See Fig.1.1.) A similar result was also found in electron-spin echo measurement on the electron solvated in glassy water [20,21]. When the molecular dynamics simulations matured, they succeeded in reproducing the general features of the absorption band shape, such as its breadth and asymmetry [18,22-25], although the transition energies were somewhat overestimated. After being shifted toward lower frequencies, the simulated spectra closely resembled the experimental data. According to the extensive computational modeling performed by the group of Rossky [18,22,23], the absorption spectrum of solvated electrons is primarily caused by a strongly allowed transition from a roughly spherical localized s-like ground state to a triple of p-like states that are also bound and localized. The existence of the s-state indicates that on average the potential energy well, created by the molecules surrounding the electron, is close to spherical. However, because of the asymmetries caused
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by the dynamical nature of liquid water, the potential energy surface does not have a perfect spherical shape, which results in three non-degenerate $p$-states.

The question about homogeneous vs. inhomogeneous broadening in the optical absorption spectrum of the excess electron in water and other fluids, as well as the explanation of its asymmetry and extraordinary spectral width, has remained a standing problem for over three decades. Numerous attempts have been made to fit the experimental data by various line shapes [26-30] and superposition of lines [31-33]. In the computer simulations [22], by imposing an ordering of the $p$-states according to their energy, the resulting absorption contour was decomposed into a superposition of the contributions from separate $s$–$p$ transitions. Each of the obtained three bands is claimed to be substantially inhomogeneously broadened by different structures of the solvent surroundings. The energy splitting between two adjacent $s$–$p$ transitions found in these simulations is ~0.4 eV, which nearly constitutes the width of the bands associated with each separate transition.

The dynamical behavior of the hydrated electron, i.e., the energy relaxation after an instantaneous $s$–$p$ excitation has been thoroughly modeled as well [18,19,25,34-41]. All computer simulations predict that the solvation dynamics are essentially bimodal. The initial decay is responsible for ~50% of the total energy relaxation and occurs at a 10–25 fs time scale which is followed by a slower 130-250 fs decay. It is generally agreed that the latter time scale results from the diffusional motion of water molecules into and out of the first solvation shell.

However, the microscopic nature of the fast initial decay is still under considerable debate. By comparing the frequencies from the power spectrum of the correlation function of the $s$–$p$ energy gap with the Raman spectrum of water, Staib et al [25] concluded that the accelerated decay was determined by coupling to hindered rotations of water molecules, generally called librations. Based on the dependence of the most rapid time scale in ordinary and deuterated water, Barnett et al. found that the initial dynamics of the hydrated electron is caused by free rotational diffusion of water molecules [34]. Conversely, Berg [41] and the group of Rossky [36,37,40] revealed no isotope effect in the first 25 fs of the solvation dynamics of the hydrated electron. They accordingly inferred that the origin of the initial dynamics is translational. Park et al. concluded that the motions of the water molecules in the first solvation shell of the hydrated electron are dominantly rotational through repulsion of hydrogen-bonded hydrogen atoms and attraction of dangling hydrogen atoms [19].

The past decade has witnessed numerous studies of the hydrated electron with an ~200-fs time resolution [32,42-50]. The femtosecond time-resolved studies of hydrated electrons were pioneered by Migus et al. [43]. The electrons were generated by multiphoton ionization of neat water and studied by transient absorption of a super-continuum probe. Later similar experiments were carried out by several groups evidencing the importance of geminate recombination and pump-probe cross phase modulation in the recorded transients [32,42,44-48].
In another approach, the already-equilibrated hydrated electron is excited from the ground $s$-state to the $p$-state using a short pulse, and the resulting solvation dynamics is probed as a function of time with another, delayed, pulse. Following this route, the group of Barbara found decays of $\sim 300$ fs and $\sim 1.1$ ps in a pump-probe experiment [51]. The results were explained using a three-state model, where the fastest decay is caused by the relaxation down to the ground state, giving rise to a not yet-equilibrated “hot” ground state. Recently Assel et al. refined this model by including excited state solvation that took place before relaxation back to the ground state [32].

More recently, experiments carried out with a substantially improved time resolution revealed that the early solvation dynamics occur on a much shorter time scale [52-55]. In these experiments, it was found that the $\sim 300$ fs decay is preceded by the dynamics on a timescale of less than 50 fs. Interestingly, both the experiments with 35-fs-pulses [52,53] and with 13-fs pulses [54,55] pointed to the librational nature of this initial solvation dynamics. It became evident, however, that even shorter pulses are required to match the large spectral width of the hydrated electron absorption. The rapid progress of state-of-the-art laser technology in the last years has made such pulses available for spectroscopic experiments [56-60].

In this Chapter, we report the latest results on the early dynamics of the hydrated electron obtained with an unprecedented time resolution of 5-fs pulses. Based on the comparison of photon echo signals from hydrated electrons and from water alone, we derive a 1.6-fs pure dephasing time of the hydrated electrons. This value is fully consistent with the line-shape of the absorption spectrum, which is shown to be overwhelmingly homogeneously broadened. We demonstrate that the optical response of the hydrated electron is substantially delayed with respect to the excitation pulses. This unexpected effect is explained using a model in which the transition dipole moment of the electron increases after the excitation due the strong coupling to the solvent molecules. Furthermore, it is shown that the effect is librational in nature. Finally, we demonstrate that a simple model based on wavepacket dynamics can account for the experimental results.

This paper is organized as follows. In Section 6.2, we describe the experimental set-up for the ultrafast photon-echo spectroscopy and give a detailed account on the preparation of equilibrated hydrated electrons. In Section 6.3, the results of two- and three-pulse transient nonlinear spectroscopy on electrons in ordinary and deuterated water are presented. Subsequently, a model is presented that satisfactorily explains the observed behavior. Finally, in Section 6.4, we summarize our findings.

### 6.2 Experimental

#### 6.2.1 Femtosecond laser system

The femtosecond spectrometer is based on a home-built cavity-dumped Ti:sapphire laser, that has been described in detail in Chapter 2. The schematics of the set-up are presented in Fig.6.1. Briefly, the cavity-dumped laser is a standard Ti:sapphire oscillator that incorporates
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a Bragg cell inside the cavity. This allows us to produce 15-fs pulses at the central wavelength of 790 nm at a desired repetition rate. The energy of the dumped pulses reaches up to 35 nJ and is adjustable by setting a level of RF power applied to the Bragg cell.

![Diagram](image-url)

**Fig.6.1:** Schematics of the femtosecond photon-echo spectrometer. BS1 is an R=30% beamsplitter, BS2 is a 50% beamsplitter. CP’s are compensating plates, and PD1-4 are silicon light detectors. $E_1, E_2,$ and $E_3$ are femtosecond excitation pulses. $t_{12}$ and $t_{23}$ are the delays between pulses $E_1-E_2,$ and $E_2-E_3,$ respectively. The bottom-left inset shows the image of the signal and excitation beam arrangement on the recollimating mirror. The bottom-right inset shows the profiles of two-pulse photon echoes measured in two conjugate directions by PD1 and PD2.

To provide adequate time resolution for the study of the ultrafast dynamics of the hydrated electron and broaden the spectral window of our measurements, the output of the cavity-dumped laser is externally compressed to the pulse duration below 5 fs. The 15-fs laser pulses, precompressed by a pair of fused silica prisms, are injected into a single-mode quartz fiber through a microscope objective lens. The white-light continuum resulting from the combined action of the self-phase modulation and dispersion in the fiber core is collimated by an off-axis parabolic mirror to avoid chromatic aberrations and bulk dispersion of a collimating lens. A portion of the white-light in the spectral range of 580-1060 nm
(shaded contour in Fig.6.2) is then compressed in a state-of-the-art three-stage pulse compressor that includes a pair of 45° quartz prisms, specially designed chirped dielectric mirrors, and thin-film dielectric Gires-Tournois interferometers.

Immediately before performing photon echo spectroscopy on hydrated electrons, the compressor is adjusted to yield the shortest duration of the pulses, which are characterized by second-harmonic frequency-resolved gating (SHG FROG), as has been described in Chapter 4. Because dispersive broadening easily affects the 5-fs pulses even as they propagate through air, the FROG characterization is carried out directly at the location of the spectroscopic sample by replacing it with a very thin (10 µm) second-harmonic BBO crystal (EKSM).

6.2.2 Transient grating and photon echo experiments

The experimental arrangement used for the photon echo spectroscopy is depicted in Fig.6.1. The beam carrying 6-nJ, 5-fs pulses is split into three channels of approximately equal intensity by the 0.5-mm-thick beamsplitters BS1 and BS2 (pulses $E_1$, $E_2$, and $E_3$ in Figure 6.1). Compensating plates (CP) of the same thickness are inserted into the beams to equalize dispersion in all three channels. To minimize distortions in the pulse duration and preserve its spectral content, silver mirrors overcoated by a thin protective layer are used throughout. To match the reflectivity of the beamsplitters, the initial horizontal polarization of the laser beam is turned 90° by a mirror periscope. The optical polarization of one of the pulses, $E_3$ is further turned by 45° with respect to the polarization of the pulses $E_1$ and $E_2$ by another periscope to facilitate photo echo measurements in the parallel and orthogonal polarization directions. Two independent optical delay lines, $t_{12}$ and $t_{23}$ are employed to fabricate desired sequences of the three pulses.

The beams are focused into a 100-µm water jet, in which the hydrated electrons are generated, and recollimated behind it by spherical mirrors with the radii of curvature R=-250-mm. A small incidence angle on the spherical mirror is chosen to prevent astigmatism of the beams within the intersection region. The intersection angles between the incident beams are kept at ~4°. The waist of the focused beam is ~ 30 µm in diameter. The phase-matching geometry of the laser beams is explained in the bottom-left inset to Fig.6.1, presenting the enlarged image of the beam configuration on the recollimating mirror. The advantages of employing such a beam arrangement have been discussed by de Boeij et al. [61].

The two- and three-pulse stimulated echo signals are detected simultaneously behind the sample by silicon photodiodes PD1–4 equipped with built-in amplifiers. The photodiode signals are processed by lock-in amplifiers, digitized, and stored in the computer memory.

The ability to determine the exact overlap of the pulses $E_1$–$E_3$ in time with a high degree of precision presents a considerable experimental challenge and is vital for the photon echo measurements with 5-fs pulses that occupy merely 1.5 µm in space. Fortunately, the overall symmetry of the employed configuration makes it possible to accurately find $t_{12}=0$ and $t_{23}=0$ without employing additional means.
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The two-pulse photon echo traces are measured as a function of delay between the pulses $E_1$ and $E_2$. A typical result of a $t_{12}$ scan is depicted in the bottom-right inset to Fig. 6.1. Here the solid and the dashed curves represent the contours obtained in the two conjugate directions, monitored by the photodiodes PD1 and PD2, respectively. Since these two-pulse photon echo traces are intrinsically symmetric around $t_{12}=0$, such a scan allows finding the precise overlap of the pulses $E_1$ and $E_2$. Similarly, the precise location of $t_{23}=0$, i.e. the overlap between the pulses $E_2$ and $E_3$, can be verified by a $t_{12}$ scan of the three-pulse echo signals, which in the case of coinciding pulses $E_2$ and $E_3$ correspond to the signals depicted in the inset to Fig. 6.1.

The transient grating scans, a variety of three-pulse photon echo spectroscopy, are performed by scanning the delay $t_{23}$ between the time-coincident pair of excitation pulses $E_1-E_2$ and the third (probe) pulse $E_3$. The symmetry of the incident beam arrangement implies that in this case two exactly identical signals are emitted in $k_3+k_2-k_1$ and $k_3-k_2+k_1$ directions. This also serves as a sensitive indicator to continuously monitor the perfect time overlap of the excitation pulses. By rotating polarizing cubes in front of PD3-4, we record the components of the transient grating signal parallel and perpendicular to the polarization of the pulses $E_1$ and $E_2$.

### 6.2.3 Generation of hydrated electrons

The technique of hydrated electron generation through electron photo-detachment from various types of anions [62] has been introduced almost immediately following the observation of hydrated electron formation by the action of intense electron beams on water [3,4]. The former production method offers a clear advantage, since it typically requires merely one-photon ionization and, therefore, is employed in our experiments. Among different complex ions, studied for the electron photo-detachment [62-65], ferrocyanide (hexacyanoferrate(II), $\text{Fe(CN)}_6^{4-}$) was found to have the highest quantum yield reaching the value of 0.9 for 228-nm irradiation [66]. In the case when a ferrocyanide ion is photolyzed to yield a hydrated electron, a $\text{Fe(CN)}_6^{3-}$ ion, hexacyanoferrate(III), forms in the solution which gives rise to an absorption band at 415 nm [63,67]. The important fact that the absorption of this photoproduct clearly lies outside the spectral range of our femtosecond experiment, is an additional favorable aspect of employing ferrocyanide rather than another negative ion.

Hydrated electrons are generated by photo-ionizing a small amount of potassium ferrocyanide [52,62,66,68] added to water, with the quadrupled output of a Nd:YLF laser (263 nm). Potassium ferrocyanide was obtained from Merck. Water and heavy water of HPLC grade were purchased from Aldrich and used without further purification. The polished sapphire nozzle (Kiburtz) ensured good quality of the jet and, therefore, no addition to the solution of the chemical substances stabilizing the jet surfaces [52] was needed. All measurements were carried out at the room temperature.

The repetition rate of the YLF laser and, consequently, the repetition rate of the entire spectrometer was set at 4 kHz. The UV pulses are focused directly into the intersection region
of the pulses $E_1$, $E_2$, and $E_3$ in the water jet. To avoid noticeable variation of electron concentration within the interaction area of the femtosecond pulses, the spot size of the UV beam on the water jet is approximately two times larger than the waist of the three other beams. The triggering of the Nd:YLF laser is synchronized with the cavity-dumping of the Ti:sapphire laser so that the UV pulse precedes the femtosecond pulse by ~200 ns. The absorption spectrum of hydrated electrons has been measured in the spectral region 480–1100 nm with uncompressed white-light pulses and obtained as a difference in optical density of the water jet in presence of, and without UV radiation. The typical absorption spectrum (Fig.6.2, open circles) has the peak value of O.D.≈0.2 around 720 nm. The data of our absorption measurement coincide very well with the known from the literature [33] absorption spectrum of hydrated electrons (Fig.6.2, solid line) that have been directly injected into a volume of water.

![Absorption spectrum of electrons in water. The solid line is the absorption of hydrated electrons produced by electron beams in bulk water (adopted from Ref. [33]). The solid dots are measured with the femtosecond white-light continuum upon photo-ionization of potassium ferrocyanide with 263-nm pulses. The shaded contour shows the spectrum of the 5-fs pulses.](Fig.6.2)

Unlike the injected electrons which reportedly in water have a lifetime of ~10 µs [3], the electrons released through photo-ionization generally have a shorter recombination time. The mechanism responsible for this shortening is a so-called scavenging process, whereby an electron recombines with one of the ions of the donor molecules or other scavengers introduced to the solution [64]. Thus, the variation of the concentration of ferrocyanide in the solution has a two-side effect. On one hand, the increase of the concentration is directly proportional to the amount of the electrons generated by photo-ionization. On the other hand, it increases the rate of electron recombination with the ferrocyanide ions because of the scavenging. To measure the recombination time, we recorded the change in absorption of the hydrated electrons as a function of delay between the photo-ionizing UV pulse and the white-light pulse. The normalized kinetics at 720 nm obtained at two different concentrations of ferrocyanide are depicted in Fig.6.3 as circles. The intensity profile of the 120-ns UV pulse
shown alongside (shaded contour) was detected with a fast solar-blind photo-multiplier tube (Hamamatsu) and recorded with a 1-GHz sampling oscilloscope (Hewlett Packard). The delay between the two pulses was set electronically by varying the triggering time of the Ti:sapphire and the Nd:YLF lasers in steps of 24 ns.

The photo-ionization process, countered by the electron scavenging, was modeled by a simple balance equation similar to the one derived in Ref. [64] in which we included the scavenging term and explicit pulse shape:

\[
\frac{dN(t)}{dt} = -\frac{N(t)}{\tau} + \alpha I_{UV}(t),
\]

here \(N(t)\) is a concentration of equilibrated hydrated electrons, \(\tau\) is the time constant of electron-ion scavenging, \(I_{UV}(t)\) is the intensity of the UV pulse, and \(\alpha\) is a constant reflecting the quantum efficiency of photo-ionized electron generation. In Eq.(6.1) we assumed that the hydrated electrons are formed instantaneously. Since the spectrum of the hydrated electrons is formed with a time constant of 0.3–0.5 ps [67,69], this assumption is fair on the much slower time scale of our experiment.

Equation 6.1 was solved numerically to fit the data presented by circles in Fig.6.3. Digitized pulse shape (Fig.6.3, shaded contour) was used as the parameter \(I_{UV}(t)\), and \(\tau\) was a fitting parameter to match the experimental dependence. The respective fits of the two data sets are depicted in Fig.6.3 by solid lines. The decay time \(\tau\) obtained for the ferrocyanide concentration \(C=0.4\) g/l is 115 ns, while for \(C=4.0\) g/l \(\tau=45\) ns. Therefore, a tenfold increase
of the ferrocyanide concentration results in an about twofold acceleration of the rate of electron–ion recombination, while the absorption of hydrated electrons at its peak increases by a factor of 5.

The femtosecond photon-echo spectroscopy on the hydrated electrons was performed in the time window indicated on the falling edge of the absorption change traces in Fig.6.3 as a vertical bar. While the concentration of the electrons is still near its peak at this delay, the UV pulse is already largely over and, therefore, predominantly equilibrated hydrated electrons are present in the solution at this time.

6.3 Results and Discussion

6.3.1 Intensity-dependence measurements

To verify the order of the nonlinearity contributing to the transient grating signal from the hydrated electrons, we measured the dependence of this signal on the intensity of femtosecond pulses. Since tuning the 5-fs pulse intensity is not feasible without destroying the pulse duration or its spectral content, we employed for this purpose 15-fs pulses directly from the cavity-dumped laser. The energy of the 15-fs pulses was changed by varying the RF power of the cavity-dumper driver in the interval 5—30 nJ. This corresponds to the combined intensity of the three pulses in the sample ranging from $0.6 \times 10^{11}$ to $4.0 \times 10^{11}$ W/cm$^2$. The power dependencies of the TG signal (i.e., $t_{23}=0$) from electrons in water measured at two different values of $t_{23}$ delay are depicted in Fig.6.4 (dots). Solid lines shown alongside the experimental data represent the cubic power dependence that is expected from nonlinearity based on the third-order response. Clearly, no noticeable deviation from the third-power law is reached with the intensities used.

![Fig.6.4: Intensity dependence of the transient grating signal from hydrated electrons. Close and open circles show data measured at delays between the excitation pulse-pair and the probe pulse of $t_{23}=0$ fs and 50 fs, respectively. The solid lines depict third-power dependencies expected for the third-order nonlinearity.](image)
Previous intensity-dependence measurements of the pump–probe signal from hydrated electrons revealed departure from a purely third-order nonlinear response for the intensities of the excitation pulse in excess of $\sim 3.0 \times 10^{11}$ W/cm$^2$ [52]. For higher intensities, leveling-off of the signal was reported. Since the pulse intensities applied in our measurement did not exceed $4.0 \times 10^{11}$ W/cm$^2$, the saturation regime has not been reached yet.

The total intensity of the excitation pulses in the 5-fs experiments amounted to $2 \times 10^{11}$ W/cm$^2$. Therefore, the contribution of higher-order nonlinearities or saturation effects is not expected in the experiments reported below.

The contribution of the pure water to the total nonlinear optical response of the sample was checked by recording the photon echo traces in absence of UV pulses. This contamination of the signal did not exceed $\sim 5\%$ of the signal peak value obtained in the presence of the hydrated electrons and was confined to the region of delays within the overlap of the 5-fs excitation pulses.

6.3.2 Pure dephasing time of hydrated electrons

The employed method for the generation of hydrated electrons provides us with a unique opportunity to compare the photon echo signal from the hydrated electrons with the one measured in pure water, that is in absence of photo-ionizing radiation. Since electronic hyperpolarizability [70-72] heavily dominates the overall water response [73,74], it is well justified to treat the nonlinearity as nearly instantaneous on the time scale of our pulses. Therefore, the signals obtained from pure water correspond to the ultimate instrument response of the spectrometer. This instrument function, among its other merits, automatically accounts for the pulse duration, mode size, and spatial as well as spectral filtering in the detection. Therefore, the differences in the shape of photon echo traces recorded in the presence and without the UV radiation provide us with direct information on electronic dephasing of the hydrated electrons.

The two-pulse photon echo signals from the water and hydrated electrons are shown as solid circles in Fig.6.5a and 6.5b, respectively. A minute difference in the widths of these two traces suggests that the electronic dephasing of the photo-excited hydrated electrons is extremely fast. To fit to the experimental data (solid curves in Fig.6.5a and 6.5b), we used the formalism developed in Chapter 5. The precise pulse parameters were obtained from independent FROG characterization as described in Section 6.2.1. For water (Fig.6.5a), we assumed an instantaneous response function (Eq.(5.15)) $R(t_1,t_2,t_3) \propto \delta(t_1)\delta(t_2)\delta(t_3)$ or, in other words, the frequency-independent third-order susceptibility. In the case of the hydrated electron (Fig.6.5a), complete Eq.(5.15) was used with the dephasing time $T_2$ being the fitting parameter. The population lifetime $T_1$ was considered to be much longer than any relevant experimental time scale, including pulse duration. Experimental evidence [52,53] supports the idea that the excited state lifetime can be as large as hundreds of femtoseconds. Therefore, the difference between the full electronic dephasing time, $T_2$, and the pure dephasing time, $T_2^*$, which are connected by Eq.5.16, is negligible.
Fig. 6.5: Results of two-pulse photon echo experiments on water alone (a) and hydrated electrons (b). Circles represent experimental data points and solid curves show fits obtained according to the procedure described in the text.

The finite population lifetime of the electrons in the excited state causes the delay of the echo trace in Fig. 6.5b (its shift of further away from $t_{12}=0$ compared to the data in Fig. 6.5a). The best fit to the experimental data yields the dephasing time of $T_2 = 1.6$ fs. Note that this value is reasonably close to theoretical estimations derived from a model based on the Gaussian wave packet approximation for the bath [39, 75, 76]. The addition of any appreciable amount of inhomogeneity immediately results in pulling the echo maximum away from zero and appearance of noticeable asymmetry of the trace.

Evidently, such a 1.6-fs dephasing time should manifest itself in the absorption line shape, which has to be substantially homogeneously broadened [77]. Here we stress that the use of a standard Lorentzian line shape is not warranted for the spectra with the widths comparable to the central frequencies. Instead, a more general relation should be used [78-80]:

$$
\sigma_A(\omega) \propto \omega \text{Im}[\chi^{(2)}(\omega)] \propto \omega \text{Im}\left[\frac{1}{(\omega_{eg} - \omega) - iT_2^{-1}} + \frac{1}{(\omega_{eg} + \omega) + iT_2^{-1}}\right]
$$

$$
\propto \frac{4\omega^2 T_2^{-2}}{(\omega_{eg} - \omega^2)^2 + 4\omega^2 T_2^{-2}}
$$

(For example, see Eq.(3.5.25) in Ref. [78]). In Eq.(6.2) $\sigma_A$ is the absorption cross-section and $\omega_{eg}$ is the transition frequency. In the case of a narrow absorption band, i.e. $T_2^{-1} \ll \omega_{eg}$, one can make use of the approximation $\omega \equiv \omega_{eg}$, which immediately gives the conventional Lorentzian contour:

$$
\sigma_A(\omega) \propto \frac{T_2^{-2}}{(\omega_{eg} - \omega)^2 + T_2^{-2}}
$$

(6.3)
In fact, the rejection of the second term of the sum in Eq.(6.2), resulting in Eq.(6.3), amounts to application of the so-called rotating-wave approximation (RWA) [77,78,81].

The difference between the two line-shapes, given by Eq.(6.2) and Eq.(6.3), mostly affects the asymptotic behavior in the spectral wings. Unlike the pure Lorentz function Eq.(6.3), which produces a centro-symmetric contour, the line shape described by Eq.(6.2) is essentially asymmetric. The latter contour has a more abrupt red wing and a prolonged blue wing. The difference between the two line-shapes is plain to see in Fig.6.6. The need to account for the experimentally observed asymmetry precluded the use of a single Lorentzian line-shape in the past attempts to model the absorption spectrum of hydrated electrons. Consequently, a collection of spectral lines [26,31,32] or a combined line-shape [27-30,33] was required for a reasonable fit.

Employing the more general relation for a homogeneously broadened line-shape given by Eq.(6.2), we obtained fits (solid curves in Fig.6.7) to the absorption spectra of electrons injected into bulk water and heavy water at various temperatures. Solid circles in Fig.6.7a and Fig.6.7b represent experimental data from Ref. [33] for water and heavy water, respectively, at different temperatures. Evidently, the whole absorption spectrum can be excellently reproduced by a homogeneously broadened line-shape. The dephasing time $T_2=1.7$ fs, deduced from the fit of the spectrum of solvated electrons in water at 298 K, perfectly agrees with the one obtained from the photon-echo experiment. This leaves no room for doubts about the homogeneous nature of spectral broadening of the hydrated electron absorption band.

Having established that the absorption spectrum of the hydrated electron is homogeneously-broadened, we address the results of MD simulations from which the conclusion of inhomogeneous broadening of each $s–p$ bands was made [18,22,23]. It is clear...
that the stipulated non-degeneracy of the $p$-states is a direct and natural consequence of the not entirely spherically symmetric solvent cavity. However, the decomposition of the absorption spectrum into three bands seems to be somewhat artificial. Indeed, as the energy of a given $p$-state fluctuates in time as a result of the rearrangement of the surrounding solvent molecules, this state might well become the highest or the lowest among the three $p$-states.

![Fig.6.7](image)

Fig.6.7: Fit of absorption spectrum of electrons in H$_2$O (a) and D$_2$O (b). The circles show measured absorption of hydrated electrons produced by electron beams in bulk water (adopted from Ref. [33]). The solid curve shows the fit by homogeneously broadened line-shape calculated according to Eq.(6.2). The insets present the value of $1/T_2$ resulting from the fit. Temperatures are indicated with the respective absorption spectra. The artificial offset of 0.2 along the vertical axis between each two adjacent curves is applied for better viewing.

According to the proposed ordering of the excited states by energy, one should then reassign the transition to this $p$-state as belonging to a different absorption sub-band. As a consequence of this artificial reassignment, the width of the Gaussian-like sub-bands revealed by these simulations becomes nearly equal to the separation of the band centers (*vide supra*). If the energy-dependent order were dropped, the absorption band associated with each $s$–$p$ transition eventually would have the same width as the whole absorption spectrum of the solvated electron. This means that, depending on the current precise solvent surroundings, the optical transition to a designated $p$-state can take place anywhere across the whole absorption spectrum. The dynamic fluctuations of the solvent cavity cause constant “migration” of the respective $s$–$p$ absorption bands within the common envelope.

We state that the seeming confusion with the assignment of the three absorption sub-bands arose from the averaging over an ensemble of solvent configurations (Ref. [18,22,23]) rather than averaging of the same configuration evolving in time. The same averaging of multiple static cavity “snapshots” led to the conclusion of the inhomogeneous broadening of each absorption line [18,22,23].
To the best of our knowledge, there has been no experimental evidence supporting the hypothesis of the inhomogeneous nature of the line broadening in the absorption of an electron in a fluid. Both picosecond [82] and femtosecond [32] transient pump–probe spectra revealed no presence of hole-burning behavior. Our recent attempts to imprint a spectral hole in the hydrated-electron absorption line employing a 15-fs excitation pulse centered around 800 nm and a broadband 5-fs readout pulse likewise resulted in a uniform and immediate bleaching of the whole absorption contour, suggesting that the latter is overwhelmingly homogeneously broadened. The lack of asymmetry in the two-pulse photon-echo signal (Fig.6.5b) is another strong evidence in favor of overwhelming homogeneous broadening. Besides, in the TG experiments we observed no quantum beats which are usually associated with the coherent excitation of several transitions (vide infra).

Therefore, based on the current and previously accumulated experimental data we conclude that the absorption spectrum of the hydrated electron is predominantly homogeneously broadened. An important question now should be raised about the physical origin of a very rapid dephasing associated with a very broad absorption band. Indeed, hardly any nuclear motion on such a short time-scale should be expected. However, the electronic dephasing is not necessarily the consequence of the rapid fluctuation of local structures, nor does it mean that a large amount of energy has to be dissipated by the bath within a few femtoseconds. It is well known that the difference in the frequencies of (harmonic) ground and excited state potentials influences electronic dephasing through the so-called quadratic electron–phonon coupling [83-87]. This mechanism also has been shown to lead to prevalently homogeneous broadening of absorption lines [88]. Since multiphonon interactions are involved in nonlinear electron–phonon coupling, the latter explains large breadths of absorption spectra in the case of a relatively modest width of the spectral density of the solute–solvent fluctuations [77].

To conclude this Section, we suggest that the absorption band of equilibrated hydrated electrons is primarily homogeneously broadened with the corresponding dephasing time $T_2 \approx 1.6$ fs. The asymmetry of the spectrum is explained by the frequently neglected dependence of the optical absorption cross-section on frequency. A mechanism responsible for the extraordinary width of the absorption spectrum is most probably the quadratic electron–phonon coupling due to appreciable difference in the steepness of the ground– and

### 6.3.3 Transient grating spectroscopy

The early part of TG transients of the hydrated electron is shown in Fig.6.8a for parallel polarizations of the excitation pulse pair and the probe pulse. The signal has a sharp peak around zero which is followed by a prominent recurrence at ~40 fs. Subsequently, the signal decays on an ~200 fs timescale.
Fig. 6.8: Transient grating signals obtained from the hydrated electron in H$_2$O (a) and their difference (b). Solid dots and open circles in (a) represent experimental data measured with the parallel and perpendicular polarization of excitation pulses, respectively. Solid curves in (a) depict the fits calculated as described in Section 6.3.5. The difference between the two signals is shown in (b) by filled diamonds while solid curve gives the two-pulse echo signal from Fig. 6.5b for comparison. Note that the non-zero difference is confined in the region where the pulses overlap in time.

Although the 5-fs pulses have enough spectral bandwidth to excite more than one of the $p$-states at once, there is no indication of quantum beats that are associated with the presence of several transitions [77]. From the calculated splitting between the different $s$-$p$ subbands [18,22,23] one expects the quantum beats with an ~10-fs period. This raises the question about the exact meaning of the three $p$-states found in the quantum molecular dynamics simulations. The separate bands arise from the following procedure: in each snapshot corresponding to one time step in the simulation (1 fs), the three $p$-states were ordered by energy, and the spectrum is subsequently decomposed into contributions from each of the three transitions. This procedure does not incorporate the important factor of the time scale at which the energy of each of the $p$-states changes in time. As was shown above, the electronic dephasing for the $s$-$p$ transition is exceptionally fast, giving rise to an extremely broad homogeneous absorption line-shape. This means that every $s$-$p$ transition rapidly samples all possible energy differences within the absorption spectrum. Therefore, we cannot assign to the latter three separate bands with each of them corresponding to a separate $s$-$p$ transition.
As a matter of fact, the total spectrum consists of the sum of three bands with approximately the same width as the total spectrum and the nearly identical central frequencies. As a result, no quantum beats can be observed under these circumstances.

Next we focus on the origin of the narrow peak around zero and the subsequent recurrence in the TG signal. In the earlier papers on experiments with a 15-fs time resolution [54,55], we suggested that a similar shape of TG transients were caused by librational motions of water molecules in the first solvation shell. Upon excitation a coherent wavepacket is created, that undergoes underdamped oscillatory motion on the excited-state potential surface. The return of the wavepacket to the inner turning point gives rise to the recurrence in time-resolved optical signals. The signal amplitude near $t_{23}=0$ is indeed higher than that of the recurrence due to two main reasons: the damping of the wavepacket and additional coupling between interaction pulses near zero-delay known as coherent artifact [89-91]. The latter is a manifestation of extra contributions to the TG signal originating from irregular time ordering of the excitation pulses. For example, around zero delays the second pulse $E_2$ is scattered from the grating imprinted by pulses $E_1$ and $E_3$ thus leading to the increased signal.

However, if the polarization of the excitation pulse pair and the probe pulse is orthogonal (Fig.6.8a, solid dots), the peak around zero vanishes. The second intriguing feature of the transient is that its amplitude is precisely equal to the one obtained with the collinear polarizations. This is highlighted in Fig.6.8b, where the difference between the two signals is shown. For comparison, we also depicted the two-pulse photon echo signal from Fig.6.5b. Obviously, the non-zero part of the difference between the TG signals with parallel and orthogonal polarizations is confined to the region of the pulse overlap. Note that this is highly uncommon because usually the signal obtained with parallel polarizations is stronger than the one obtained with orthogonal polarizations because of polarization anisotropy [92]. The amplitudes of the two signals become equal only after some time as a consequence of rotational diffusion processes, which randomize the preferential orientation of dipole moments induced by the first pulse(s).

Clearly, the situation in the case of the hydrated electron is entirely different. As we have shown in Section 6.3.2, the absorption spectrum of the hydrated electron is primarily homogeneously broadened. The underlying mechanism is that the charge distribution in the ground state rapidly samples many configurations with different orientations. The time scale at which the sampling takes place is shorter than the duration of 5-fs excitation pulses. The hydrated electron experiences a variety of possible orientations of the neighboring water molecules during the excitation process. Therefore, the orientations of the excited $p$-state are completely randomized by the time the excitation is completed. As a result, no anisotropy can be observed after the excitation pulse pair ends.

We conclude that, in the case of the aqueous electron, the transient anisotropy disappears in less than 5 fs. The important consequence is that when the polarizations of the pump pulses and the probe pulse are perpendicular, the coherent coupling between them is
extremely ineffective. Therefore, if the contributions with irregular time ordering (as, for instance, $E_1-E_3-E_2$) are omitted, the total number of permutations is decreased by a factor of two [61]. Hence, the TG signal near $t_{23}=0$ for perpendicular polarizations is expected to be approximately one fourth of the signal with parallel polarizations. This is value is very close to the one observed in the experiment (Fig.6.8a).

![Figure 6.9](image.png)

**Fig.6.9**: Two pulse photon echo signals from hydrated electrons in H$_2$O. Solid dots and open circles show the signals obtained, respectively, with parallel and perpendicular polarizations of the laser pulses. In order to ensure identical pulse intensities and focusing conditions, these measurements were performed with 15-fs laser pulses. Note that virtually no signal is detected in the case of perpendicular polarizations.

To verify this finding, we performed a two-photon echo spectroscopy with parallel and perpendicular polarizations of two pulses. In this experiment, the time ordering is essentially identical to the irregular time ordering around zero delay in the TG scan. The use of 15-fs pulses directly from the cavity-dumped laser allowed us to easily control the polarizations while maintaining constant energy of the pulses. For this purpose, a zero-order $\lambda/2$-plate (Karl Lambrecht) was introduced in one of the spectrometer arms. Note that this is hardly possible in the case of 5-fs pulses since the $\lambda/2$-plate cannot equally rotate the polarization of spectral components in the 600–1100 nm range. The results of the experiments are presented in Fig.6.9. The signal in the case of perpendicular polarizations (solid circles) is suppressed by a factor of ~30 compared to the signal with parallel polarizations (open circles). This proves our conclusion that the efficiency of the excitation of the hydrated electron with two pulses having orthogonal polarizations, is extremely low.

Based on the data obtained in polarization-dependent photon echo and TG spectroscopy, we reach a conclusion that the signal at short delays is substantially weaker than that at ~40 fs. Therefore, there is no recurrence but rather a delayed response in the TG signal. The TG data for the orthogonal polarizations clearly indicate that the delayed response
cannot be explained by underdamped wave packet dynamics. In that case, the signal would always be the largest at $t_{23}=0$ due to inevitable damping of coherent motions.

The mechanism we suggest to explain the delayed response is that the transition dipole moment of the hydrated electron increases as a function of time after the initial excitation. Since the amplitude of the TG signal depends on the transition dipole moment (consult Eqs.(5.9) and (5.17)), the signal increases before falling due to irreversible energy relaxation. The rise in the transition dipole moment should be directly connected to the strong coupling between the hydrated electron and water molecules that begin to readjust their positions after the excitation to minimize the total free energy of the system. The dependence of the transition dipole moment on nuclear degrees of freedom is known in molecular spectroscopy as the non-Condon effect [93].

We next determine the microscopic motions of water molecules underlying the non-Condon effect. For this, we performed the TG experiment on the electron solvated in heavy water (Fig.6.10). The TG signals are quite similar to those for normal water (Fig.6.8a) but the maximum is delayed to longer times (~60 fs). However, if the time scale of the D$_2$O TG data is compressed by $\sqrt{2}$, the TG signal becomes virtually indistinguishable from that for H$_2$O (Fig.6.11).

The difference in time scale can be explained by the fact that the moments of inertia of H$_2$O and D$_2$O differ precisely by a factor of 2. This immediately leads us to the conclusion that the maximum in the TG signals is caused by an overdamped librational motion of the water molecules. The specific dependence on deuteration rules out translations because the total mass of a water molecule changes only by a factor of 18/20. Another mechanism for the $\sqrt{2}$ dependence proposed by Barnett et al. [34] is free rotational diffusion of water molecules surrounding the electron. However, this explanation is not very likely. Rotations of molecules in a liquid can hardly be called free, especially in the case of a strongly hydrogen-bonding
liquid like water. Furthermore, there is no signature of free rotations in the Raman spectrum of water [94].

![Fig.6.11: Comparison of the transient grating signals obtained from electrons hydrated in H\textsubscript{2}O (solid dots) and D\textsubscript{2}O (open circles). All data are given for perpendicular polarizations of excitation pulses. The delay-axis for D\textsubscript{2}O has been compressed by a factor of $\sqrt{2}$ to highlight the isotopic effect.

6.3.4 Early-time dynamics: the microscopic picture

The microscopic picture underlying the early-time dynamics of the hydrated electron that has emerged from our experiments is schematically presented in Fig.6.12. In this cartoon, only four of the approximately six water molecules in the first solvation shell around the electron are depicted for the sake of simplicity. The dark contour in the left panel shows the charge distribution (i.e., squared modulus of the wavefunction) of the hydrated electron. We assumed that the latter is confined in a harmonic potential formed by the neighboring water molecules (right panel). The use of, for example, square-shaped potential does not change the main conclusions. The relevant mean size of the electron cloud in the ground $|g\rangle$ state was matched to value reported by the group of Rossky (1.9 Å) [23] while the distances between the electron and the water molecules were taken from Ref. [20].

Before excitation, the electron finds itself in the $s$-like ground state in equilibrium with surrounding water molecules (Fig.6.12a, left panel). Upon excitation, the electron makes a transition to the excited $p$-state wavefunction that is elongated in a particular direction (Fig.6.12b, left panel). Since the excitation pulses are very short, the water molecules have no time to react and, therefore, they still preserve their compact geometry. However, as time progresses, the water molecules in the first solvation shell are being pushed away by the expanded charge distribution of the electron (Fig.6.12c, left panel). We have already concluded from the TG experiments that the underlying microscopic processes at this stage are the librations of water molecules schematically shown by curved arrows in Fig.6.12c. This reorientational motion makes the potential energy well in which the electron is confined,
shallower as shown in Fig.6.12c, right panel. Subsequently, the charge distribution of the electron expands even further (Fig.6.12d), and so on.

**Fig.6.12:** Artist’s impression of the early-time dynamics of the hydrated electron. Left panel: configuration of the charge distribution of the electron (dark contour plot) and surrounding water molecules. Right panel: the potential-energy well in which the electron is confined (red curve) and the wavefunctions in the ground $\langle g \rangle$ and excited $\langle e \rangle$ states. The wavefunction of the currently occupied level is shaded. The delay time after the initial excitation is shown in the right bottom corner of the right panel. The thickness of the arrow corresponds to the magnitude of the transition dipole moment.
Expansion of the cavity occupied by the electron has a profound effect on the wavefunction of the unoccupied ground-state as well. As the water molecules in the first solvation shell are readjusting their orientations, the ground-state wavefunction is elongating in the same direction as the excited-state wavefunction (Fig.6.12, right panel). Therefore, the dipole moment of the electronic $p-s$ transition, $\mu_{eg}$, becomes larger due to the increased overlap between the probability densities of the ground and excited states. For instance, in the case of a harmonic potential the transition dipole moment increases inversely proportional to the square root of the oscillation frequency $\omega_0$.

The amplitude of the TG signal depends on the fourth power of the transition dipole moment that changes in time. Hence, a very moderate extension of the electron cloud leads to a substantial increase of the TG signal as was observed experimentally (Fig.6.8 and 6.10).

The position of the maximum in the TG signal gives us an estimate for the time scale of the expansion of the first solvation shell: ~50 fs. The frequencies that correspond to this time coincide reasonably well with librational band of water which span the range ~300-900 cm$^{-1}$, and which also scales with $\sqrt{2}$ upon deuteration [94]. The decay following the maximum in the signal is most probably caused by relaxation down to the ground state at the 125-fs time scale [32]. The stimulated emission is rapidly diminished due to the decreasing population on the excited state while at the same time the equilibrating ground state gives rise to induced absorption.

6.3.5 Theoretical model

In order to put the microscopic picture of the solvation of the hydrated electron developed in the previous Section on a more quantitative ground, we next introduce a simple model based on wavepacket dynamics on the ground and the excited states (Fig.6.13). In this picture, we assume that prior to the photo-excitation the ground state of the hydrated electron is equilibrated. The excitation pulse pair creates a hole in the ground state distribution (Fig.6.13a) and a wavepacket in the excited state (Fig.6.13b). This gives rise to a bleach of the ground–state absorption and to a stimulated emission from the excited state. Assuming that no population relaxation takes place yet on the duration of the applied laser pulses and the optical transition is primarily homogeneously broadened, both the bleach and the stimulated emission contours have approximately the same spectral shape as the steady-state absorption band.

Immediately after the excitation, the contours of the bleach and the stimulated emission are exactly identical. Subsequently, the downhill movement of the wavepacket on the excited state potential takes place, which reflects the gradual expansion of the water cavity. Because the energy gap between the two potentials decreases as the wavepacket moves on the excited state surface, the stimulated emission band becomes increasingly red-shifted with respect to the ground state bleach whose spectral position remains fixed (Fig.6.13a,b).
The expression for the observed TG signal can be easily calculated in the slow diffusion limit [77,95]. Based on the finding of predominantly homogeneous dephasing in Section 4.1, we assume the nonlinear response function of the ground state, \( R_{gr}(t_1,t_2,t_3) \), in the form given by Eq.(5.15). The nonlinear response function associated with the populated excited state is then given by [95]:

\[
R_{ex}(t_1,t_2,t_3) = R_{gr}(t_1,t_2,t_3) \exp[i\Delta \omega t_3 [1 - M(t_{23})]] ,
\]

where \( \Delta \omega \) is the Stokes shift, i.e. the spectral shift of absorption (fluorescence) due to energy reorganization, and \( M(t) \) is the electronic bandgap correlation function [77]. Here we assumed that \( M(t) \) changes slowly on the time of electronic dephasing characterized by \( T_2 \). Adapting the model of an overdamped vibration [77], \( M(t) \) then can be expressed as:

\[
M(t) = \exp\left(-\frac{t}{t_{ex}}\right) , \quad t_{ex} >> T_2
\]

To obtain the spectral shape of the ground- and excited-state contributions we now Fourier-transform \( R_{gr}(t_1,t_2,t_3) \) and \( R_{ex}(t_1,t_2,t_3) \). The resulting third-order susceptibility for the ground-state contribution to the nonlinear signal is given by Eq.(5.17) while the contribution of the populated excited state is expressed by:
As described in the previous Section, the expansion of the solvent cavity forced by the photo-excitation leads to the increase of the transient dipole moment magnitude as a function of time, which gives rise to the non-Condon effect. Therefore, it is assumed that the change of the transition dipole moment strength occurs on the same time scale as the motion of the excited state wavepacket. This change does not influence the magnitude of the absorption bleach band since the latter is caused by a static hole in the ground state. On the other hand, the magnitude of the spectral contribution caused by the traveling wavepacket is dependent on the changing strength of the transition dipole moment. Therefore, \( \mu_{eg} \) in Eq.(6.6) should be considered as a function of time, i.e.:

\[
\mu_{eg}(t) = \mu^0 F_{NC}(t),
\]

where \( \mu^0 \) is the initial dipole moment, and the non-Condon parameter, \( F_{NC}(t) \), is a slowly changing function compared with the pulse duration.

After about 200 fs, the excited state wavepacket reaches the region where the potentials of the ground and the excited states cross [32]. In this region, the wavepacket "leaks" from one potential surface to another. However, the crossing occurs to a modified (hot) ground state that has to "cool" before reaching the equilibrated steady state. Therefore, the hot ground state wavepacket gives rise to an induced absorption band that shifts from the red to the blue and eventually cancels the ground state bleach (Fig.6.13c). In the model, this crossing process is taken into account by assuming that the excited state stimulated emission vanishes with the same rate as the hot ground state absorption builds up.

We next calculate the TG signal according to the formalism developed in Section 2.1. If the population relaxation time \( T_1 \) is long compared to the pulse duration, in Eq.(5.17) and Eq.(6.6) one can assume \( \tilde{\chi}^{<3b} \propto \delta(\omega''-\omega') \). Then, integrating Eq.(5.9) over frequency \( \Omega \) and making use of Eqs.(5.7), (5.17) and (6.6), and accounting for the hot-ground state contribution, we arrive at:

\[
\tilde{\chi}_{ex}^{<3b}(t_{23}, \omega_{eg} - \omega', \omega'' - \omega_{eg} + \Omega) = -\frac{\mu_{eg}^4 N}{h^4} \frac{1}{T_1^{-1} - i(\omega'' - \omega')}
\]

\[
\times \left[ \frac{1}{T_1^{-1} - i(\omega_{eg} - \omega')} + \frac{1}{T_2^{-1} - i(\omega'' - \omega_{eg})} \right]
\]

\[
\times \frac{1}{T_2^{-1} + i(\omega_{eg} - \Delta \omega) \left[ 1 - \exp \left( -\frac{t_{23}}{t_{es}} \right) \right] - \Omega}.
\]
Here, \( I(\Omega) \) is the spectrum of excitation pulses and the contributions from the ground, excited, and hot ground state potentials are respectively written as

\[
\sigma_{gr}(\Omega) = \sigma_A(\Omega) \\
\sigma_{ex}(\Omega) = F_{NC}^4(t_{23}) \exp(-\gamma_{c} t_{23}) \sigma_A(\Omega + \Delta \omega [1 - \exp(-\gamma_{ex} t_{23})]) \\
\sigma_{hot-gr}(\Omega) = F_{NC}^4(t_{23}) [1 - \exp(-\gamma_{c} t_{23})] \sigma_A(\Omega + \Delta \omega \exp(-\gamma_{gr} t_{23}))
\]

where \( \sigma_A(\Omega) \) is the steady-state absorption spectrum, \( \Delta \omega \) is the Stokes shift, \( \gamma_{ex} \) and \( \gamma_{gr} \) are the rates at which the wavepacket moves on the excited and the ground states, respectively, and \( \gamma_c \) is the crossing rate from the excited state to the ground state.

The expressions given by Eqs.(6.9–11) represent Lorentzian line shapes described by Eq.(6.3). These constituent terms of the TG signal are schematically depicted in Fig.6.13a-c in their respective order. The first term is static and stands for the hole in the ground state (Fig.6.13a). The second and the third ones account for the moving wavepacket in the excited (Fig.6.13b) and hot ground (Fig.6.13c) states, respectively. The use of RWA [78] [77] in derivation of Eqs.(5.17) and (6.6) leads to symmetric Lorentzian contours, rather than the asymmetric extended line-shape given by Eq.(6.2) employed to explain the absorption spectrum in Section 6.3.2 The spectrally-integrated TG signal, however, is insensitive to such a minute difference in the spectral contours, which justifies the use of centro-symmetric line-shape in our calculations.

The physical meaning of the movement of the Lorentzian wavepacket can be explained as follows: The difference in curvature of the ground and excited state potentials implies a strong quadratic electron-vibration coupling that is responsible for the extraordinary amount of homogeneous spectral broadening. On the other hand, linear electron-vibration coupling determines, at large, the presence of the wavepacket dynamics. This is due to predominantly linear change of the energy gap with nuclear coordinate between the ground and excited states as a result of the displacement of their potentials with respect to each other.

The time-dependent non-Condon parameter is assumed to be equal to

\[
F_{NC}(t_{23}) = 1 + f_{NC} [1 - \exp(-\gamma_{c} t_{23})]
\]

where \( f_{NC} \) is a measure of the strength of the non-Condon effect or, in other words, the ratio of the magnitudes of the initial and maximal dipole moments. The influence of the non-Condon effect on the TG signal is illustrated in Fig.6.14. With a constant transition dipole moment (\( f_{NC} = 0 \)), the TG signal peaks close to zero (Fig.6.14a). If the non-Condon strength is chosen to be 0.5, the dipole moment grows as a function of time, and reach a maximum
after ~100 fs (Fig.6.14b). Subsequently, it balances the drop in the TG signal due to population relaxation, which results in a maximum that is significantly shifted away from zero (Fig.6.14c).

Fig.6.14: Simulated transient grating signals for perpendicular polarization of excitation pulses. (a) Signal without non-Condon effect \((f_{NC} = 0)\). (b) Transition dipole moment as a function of time with a non-Condon effect present. (c) The transient grating signal from (a) when the non-Condon effect is taken into account.

In order to incorporate the fact that we are dealing with the pulses of finite duration, we convoluted the polarization of Eq.(6.5) with the instrument response function. The following parameters are taken for water: \(1/\gamma_{ex} = 33\) fs; \(1/\gamma_{gr} = 300\) fs; \(1/\gamma_{c} = 125\) fs; \(\Delta \omega = 0.50\) PHz; \(f_{NC} = 0.5\). For heavy water, all rates are decreased by a factor \(\sqrt{2}\) in accord to the established fact that underlying microscopic dynamics are determined by librations. The calculated TG signals for H\(_2\)O and D\(_2\)O are depicted in Figs.6.8a and 6.10, respectively. Evidently, by inclusion of the non-Condon effect we are well able to reproduce the delayed maximum in the TG signals, even though the rate of increase of the transition dipole moment is not an independent variable. As can be seen from Eqs.(6.10) and (6.12), we ascribed a single common rate, \(\gamma_{ex}\), to the evolution of both the transition dipole moment strength and the
dynamic Stokes shift. The fact that we can fit the experimentally observed dependencies reflects the common microscopic origin of the dynamic Stokes shift and the non-Condon effect: the unidirectional expansion of the solvent cavity caused by librational reorientation of the water molecules.

We predict that the time constant of populating the hot ground state is faster than 100 fs for H₂O. Careful inspection of the measured TG traces (Figs.6.8a) shows that at this point there is a slight bend in the curvature. Apparently, this is a signature of the interplay between stimulated emission from the excited state that is being diminished and the induced hot ground state absorption that is being increased simultaneously. After this, the induced ground state absorption shift to the blue on a time scale of 300 fs. This shows up as the slower decay in the transient grating. These points will be further addressed in Chapter 7.

6.4 Conclusions

Photon echo and transient grating spectroscopy on the hydrated electron performed with the best time resolution available to date has provided a powerful insight in the microscopic processes that underlie solvation dynamics.

Both two-pulse photon echo and TG experiments, involving two and three femtosecond pulses, respectively, have been performed on equilibrated hydrated electrons. By comparing two-pulse echo signals from hydrated electrons and from water alone, we have derived the pure dephasing time of ~1.6 fs. We have shown that the absorption band of equilibrated solvated electrons in water is predominantly homogeneously broadened and succeeded in modeling the whole absorption spectrum of the hydrated electrons by a single homogeneous line shape. The typically employed symmetric Lorentzian line shape has been abandoned in favor of a more general expression for a homogeneously broadened line. Importantly, in the line shape used in our fit, the long-puzzling issue of the asymmetry of the absorption spectrum found a natural explanation. Further proof for the homogeneous nature of the absorption spectrum comes from the absence of quantum beats on the 10-fs time scale in the TG signal, pointing to the fact that the absorption spectrum does not consist of three separate absorption bands.

The TG experiments on the hydrated electron with perpendicular polarizations of excitation pulses have revealed a delayed response never observed before due to limited time resolution. We have suggested that the delayed response is due to a non-Condon effect, caused by librational motions of the water molecules surrounding the electron. The large magnitude of the non-Condon effect is a direct consequence of the fact that the Hamiltonian of the hydrated electron is fully determined by the configuration of the neighboring water molecules. This renders the hydrated electron a convenient probe for the local structure of water, the most-important-for-life but still mysterious liquid [21]. We have also shown that a numerical model including the non-Condon effect which is due to initial librational motion of water molecules, and subsequent population relaxation and ground state cooling can reproduce the essential features of the observed signals, putting our ideas on solid grounds.
Electron in polar liquids continues to be a vast experimental and theoretical field in which many intriguing questions remain to be answered. There are still many conflicting and not well understood issues concerning electron equilibration [47,96], energy relaxation of the photo-excited electrons in fluids [32,52], the nature and the number of the bound localized and unbound states of the electron trapped in the solvent cavity [22,50], etc. In the current paper, we have addressed only the earliest part of the energy dissipation that directly follows photo-excitations. The subsequent relaxation processes, albeit taking place on a slower time scale, are no less interesting or less controversial. In particular, the questions about the lifetime of the bound excited state and the involvement of the quasi-continuum states, predicted by quantum molecular dynamics simulations [23], have to be addressed.
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References

Chapter 6

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6308 (1994).