Chapter 7
Ground State Recovery of the Photo-Excited Hydrated Electron

Abstract
In this Chapter, we present a detailed frequency-resolved pump–probe study of the hydrated electron dynamics, which was performed with 5-fs pulses. We analyze the difference in the behavior of the pump–probe signal obtained from a two- and a three-electronic-level system. This provides the guidelines to resolve a long-standing dilemma of the two contradicting models that are used to describe the dynamics of the hydrated electron. The first model predicts a rapid, whereas the second one implies a slow electronic relaxation of the excited state. The dynamics of the blue shift in the measured transient spectra is shown to correspond perfectly to the behavior of the transients at various detection wavelengths. This provides strong support for the short-lived excited state model. Next, the pump–probe spectra at all delays are successfully fitted on the basis of this model, yielding the excited state lifetime of ~50 fs. Also, the equilibration of the ground state is shown to proceed with a predominant time constant of ~1 ps. In accordance with our previous findings, the shortest decay time is dominated by the librations of water molecules. Other decay components that exhibit no isotopic effect are assigned to the translational motions of water molecules. To clarify the structure of the potential surfaces at the long pump–probe decays, the time-domain dependence of the energy gap is converted into the function of a generalized solvent coordinate. Finally, a multidimensional model of the hydrated electron solvation is proposed.
7.1 Introduction

In Chapter 6 we have studied the earliest steps of the energy relaxation that take place within the first 100 fs following the optical excitation of the $s-p$ transition in the hydrated electron. In this Chapter, we broaden the studied time window to include the picosecond delay range. Here we attempt to account for the whole complex scheme of photo-excitation and relaxation, which includes different stages. Next to examining the initial rapid relaxation components, we now turn our attention to the subsequent, slower processes. The exploration of these contributing pathways of the photo-excitation energy dissipation is important in two ways. First, it should provide the answers about the mechanisms of the solvent response dominating each particular stage of the relaxation. Second, by reconstructing all subsequent steps, we will be able to verify our ideas about the initial energy relaxation process that occurs within just a few tens of femtoseconds.

Based on the observation of the isotopic effect in the transient grating signal, we concluded that inertial motion of water molecules is responsible for the initial step of energy dissipation. According to the dynamical model proposed in Section 6.3.4, librations of water molecules in the first solvation shell dominate the overall solvent response within approximately the first 50-100 fs, following the excitation. This is a reasonable conclusion, considering the instantaneous character of the expansion that the spatial extent of the electron charge distribution undergoes upon photo-excitation. Obviously, in that case, librations of the O-H (O-D) bonds of H$_2$O (or D$_2$O) molecules can proceed much faster than the translation motion of the entire molecules away from the electron to accommodate the change in the size of the latter. It is evident, therefore, that another, slower time-scale of energy relaxation must set in, reflecting the change from initially predominantly librational to later predominantly translational movement. Because of the almost unidirectional expansion of the side lobes of the electron excited-state $p$-wavefunction [1,2], uneven forces propel the molecules surrounding the electron from different sides. It is justified, therefore, to expect different time constants to be responsible for the positional adjustment of the “on-axis” and “off-axis” water molecules, which has been recently predicted in computer simulations [3]. Furthermore, the slowest time scale of energy relaxation must be identified with the typical diffusional motion of the solvent molecules in and out of the shell surrounding the electron. The indication of the radical change in the relaxation rate can be also found in the computer simulations [2], where a transition from a rapid 25-fs component to an ~300-fs one has been predicted.

The extraction of the excess energy from the photo-excited electron to the surrounding liquid water results in an electron transition back to the ground state that is now altered, compared with the pre-excitation situation [2,4]. Numerical calculations [2] predict that the return to the modified $s$-state, which is more compact than the previously occupied $p$-state, creates a void in the solvent, which corresponds to the sudden “implosion” of the electron. Unlike in the case of the instantaneous expansion of the photo-excited electron, which forcibly drives the water molecules to rapidly reorient and give room, the closing of the
solvent void in the wake of the “collapsed” electron is supposed to proceed at a much slower, diffusion-governed pace.

Summarizing the ideas presented above, we expect to see several time-scales determining the later stages of energy relaxation, which take over the initial, libration-dominated part. Accordingly, the goal that we pursue in this Chapter is to create a self-consistent model explaining all stages of the photo-excitation relaxation cycle. To this end we have to find the energies released at each particular step of the energy relaxation, as well as to determine the time scales and molecular dynamics behind these events. The capital questions that must be answered concern 1) the thermalisation time of the excited $p$-state, 2) its lifetime, and 3) the time of the modified ground state evolution from the configuration directly after the $p$–s transition to that of the equilibrated ground state.

So far, the experimental evidence provided by the time-resolved transient absorption spectroscopy on the equilibrated hydrated electron [5-11] remains, at large, inconclusive. For reasons, which will be addressed later in this Chapter, the pump–probe data can be interpreted using two contradicting models. According to one possible scenario [5,7,10,11] the lifetime of the excited state is very short, in the order of 200 fs, and the “cooling off” process of the modified (hot) ground state back to the equilibrium proceeds with a ps time constant. In the opposite interpretation [2,6,9,12], after the thermalisation that takes place on a 200-300 fs time scale, the excited state (nonadiabatically) decays with a predominant time-constant in the range from 700 fs to 1.2 ps. As it followed from molecular dynamic simulations for this model, upon the $p$–s transition, the initial equilibrated ground state is rapidly recovered in <100 fs [2,9]. Because the latter process is superimposed over a slower, picosecond decay component, it cannot be experimentally resolved.

The schematic qualitative representation of the above-described controversy is given in Fig.7.1. Based on the librational nature of the initial solvent response, established in Chapter 6, the first relaxation step is identical to the one in Fig.6.12. Despite the initial similarity of the two scenarios, they correspond to substantially different dynamical behavior at the later energy relaxation stages. In the short-lifetime model, the energy involved in the water cavity readjustment, accompanying the sudden increase in the size of the electron charge distribution, is sufficient to cover the modified $s$–$p$ energy gap. The remaining excess energy that corresponds to the picosecond cooling of the ground state is then dissipated once the water molecules close the void in the solvent, which has formed after the “burst” of the excited state. On the contrary, the long–lifetime model implies that the energy involved in the rearrangement of the first solvation shell is considerably smaller than the frequency of the $s$–$p$ gap. Therefore, the $p$-state remains conserved for a substantially longer (picosecond) time. In this model, as opposed to the other one, the energy transfer from the electron to the solvent proceeds in a reversed fashion. This means that the main part of the excess energy, corresponding to the transition from the $p$- to the modified $s$-state is transported on the slow (picosecond) time-scale, while the remainder is quickly dissipated within 100 fs or so. A possible explanation of why this last step is so fast was put forward by Schwartz and Rossky
[4] who suggested that the free rotation of the water molecules, which becomes possible due to the formation of the void in the solvent, constitutes a rapid and efficient solvation channel.

The resolution of the conflict outlined above, i.e. a short-lived $p$-state vs. a long-lived $p$-state model, forms the core of this Chapter.

It is essential to realize the great importance of determining the lifetime of the excited state. Indeed, a short-lived $p$-state means that a very substantial part of the excitation photon energy is rapidly transferred to the surrounding water molecules and, therefore, this great
amount of energy is further absorbed by different-level solvation shells. To provide a channel for such a fast and efficient initial dissipation of the excess energy, there must be a very strong coupling of the hydrated electron to water molecules. In the opposite, long-lived \( p \)-state scenario, a longer survival of the \( p \)-state signifies a more “autonomous” status (i.e. a higher level of adiabaticity) of the electron whose ties with the surrounding water molecules appear to be weaker. Therefore, the probability of the excited state depopulation is substantially smaller. The eventual \( p \rightarrow s \) transition in this case is triggered by much slower events such as, for example, the rearrangement of the first solvation shell as a consequence of the diffusional relocation of the water molecules from the outer shells.

The experimental differentiation between these two controversial models should have a profound impact on choosing the right approach to the molecular dynamics simulations of the hydrated electron in particular, and of the aqueous environment in general. The main “sticking point” of the computer studies performed to this date [1,2,4,12-24] is the use of a quantum mechanical description for the electron and a classical one for the water molecules. While an oscillator in a classical flexible molecule can accept any quantity of energy, in a quantum-mechanical one it is capable of receiving only a limited amount [15,23,25]. The quantized disposal of a large excess energy from the relaxing electron to real molecules must, therefore, be slower than in the case classical flexible molecules. In the (semi-)classical approach, the use of which is justified because of the high computational efficiency, the results of any calculation are predetermined by the built-in assumption of how much energy a water molecule is allowed to accept. Thus, a widespread range of predictions for the lifetime of the excited state has emerged from the computer simulations of different authors.

For instance, the initial use of “rigid” water molecules in the calculation of Rossky and coworkers resulted in the lifetime of the \( p \)-state in the order of 1 ps [22]. The implementation of the “flexible” water potential [26] and the electron–water pseudopotential [27] in the work of Neria et al. produced an \(~120\)-fs and \(~220\)-fs radiationless transition times for \( \text{H}_2\text{O} \) and \( \text{D}_2\text{O} \), respectively, in a mixed classical–quantum-dynamical treatment [28]. These figures subsequently rose to \(~220\) fs for \( \text{H}_2\text{O} \) and \(~800\) fs for \( \text{D}_2\text{O} \) in a semi-classical simulation [24]. The electronic relaxation time of 230 – 250 fs has also been found in other simulations [25,29]. A different, also “flexible” potential [30] was assumed in the work of the Rossky group. Initially, the lifetime of the excited state of \(~160\) fs was inferred [23]. The following attempts of Rossky et al. to restrict the over-flexibility of the water molecules yielded a steady increase of the lifetime. This resulted, first, in the lifetime figure of \(~250\) fs [15], which subsequently was nearly doubled, to produce an average nonadiabatic \( p \rightarrow s \) passage rate of \(~450\) fs [2]. The latter value has been refined later [17], claiming a 240-fs and a \(~300\)-fs time of the excited state solvation for \( \text{H}_2\text{O} \) and \( \text{D}_2\text{O} \), respectively, and a 1.1-ps lifetime of the equilibrated \( p \)-state.

It should be expected, therefore, that with such a great reliance on \textit{a priori} assumptions, the above cited results of numerical simulations present, at best, the attempts to reconcile the times seen in the femtosecond experiments [5,7,8,11,31-33] with the computed results. This
but once more signifies the importance of resolving the issue of the $p$–$s$ relaxation experimentally.

In this Chapter, we explore the transient absorption dynamics of the hydrated electron, photo-excited from its equilibrated ground state. This type of experiment, which involves hydrated electron preparation by a UV pulse preceding the femtosecond pump–probe pulse sequence, was first demonstrated by the group of Barbara [5,7,8,11]. Their measurements had a relatively poor, 300-fs time resolution. The latter was substantially improved in subsequent studies of the hydrated electron by the same group [6,9], in which much shorter, ~25-fs pulses were used. Similar pump–probe experiments were also reported by Laubereau and coworkers [10] who, however, employed considerably longer, 170-fs pulses. Also, in our previous pump–probe measurements of the hydrated electrons [34], we used 15-fs pulses, concentrating primarily on the measurements of the initial, librational dynamics.

Compared with the experimental work of other researchers, this study presents several important advancements. First, the use of 5-fs excitation and probe pulses provides an unprecedented time resolution. Second, the adequately short duration of the excitation pulse prevents distortion of the pump–probe signal as a consequence of the rapid energy loss in the excited state. Third, the spectral dynamics in the range of 600 - 1050 nm is covered at once by the spectrum of the 5-fs pulses. This removes the need to tune the wavelength of the probe pulses and to synchronize them each time with the pump pulse. Therefore, it became possible to record accurate transient spectra with a high density of data points. Fourth, a considerably enhanced dynamic range of our measurements, up to 4 decades, allowed a highly precise study of the kinetic as well as the spectral behavior in the pump–probe delay interval up to several picoseconds. Finally, we successfully employed a modeling procedure that enabled us to unravel the contributions of the excited and (hot) ground states in the overall shape of the transient spectra. Consequently, based on our fit of the experimental results we prove the validity of the short-lived $p$-state model and conclude that the electronic depopulation of the excited state proceeds on a 50-fs time scale.

This Chapter is organized as follows. In Section 7.2, we discuss the difference in the pump–probe signals obtained if the system is modeled 1) in a three-electronic-level model with a long-lived first excited state, and 2) in a two-electronic-level model with a rapid electronic relaxation and a subsequent ground state solvation. We produce practical guidelines for the experimental discrimination between the two models. Section 7.3 provides the details on the experimental procedure. In Section 7.4, the results of the 5-fs pump–probe measurements are presented and fitted according to the short-lived $p$-state model. Finally, in Section 7.5 we summarize the findings of our investigation.

### 7.2 Short-lived vs. long-lived $p$-state: Manifestation in pump–probe

In the previous Section, we outlined the basic controversy related to the rate of electronic relaxation from the excited $p$-like state back to the $s$-like state. Another aspect of this problem lies in the necessity to explain how many electronic states contribute to the transient
absorption picture. Indeed, it is well known that, before its localization in a polar solvent, a quasi-free electron is initially released into the conduction band, or continuum. Subsequently, in the process of localization, the electron occupies bound states of the liquid cavity, until it finally solvates to the bottom of the lowest electronic state. Obviously, the transient dynamics seen in an optical pump–probe experiment will depend on the number of bound electronic states involved, on their position in frequency with respect to each other and to the continuum, and on the dipole moment strength of each transition. Below we address separately the views on the structure of the electronic energy levels, which emerged from numerical simulations, experiments probing electron trapping and solvation in water, and from interpretation of the earlier pump–probe measurements on the equilibrated hydrated electron.

Molecular dynamics simulations [1] predict the existence of several bound states with the strongly allowed transitions to the lowest three of them, i.e. the $p$-states (see Fig.1.2), from the ground state. Individual bands corresponding to weaker-bound electronic states comprise the blue tail of the absorption spectrum of the hydrated electron. With the occasional exception of the fourth excited state, all higher excited states (nine in total) [1] lie in the positive energy (continuum) region, i.e. they are delocalized, or unbound. In the same simulation [1], the energy gap, separating the $p$-states from the edge of the continuum, was estimated to be less than 1 eV.

Several important remarks can be made about such level structure. First, as it has been argued in Chapter 6, the difference of energy levels associated with the three $p$-states in the discussed simulation [1] was created artificially in these simulations due to the applied energy sorting. Without this sorting, the variation of the frequency gap between the $s$- and each of the $p$-states covers the whole absorption band. Therefore, because the different $p$-levels overlap in energy, it would be impossible to discriminate among them in a pump–probe experiment. Second, the general overestimation of the transition energies by $\sim 1$ eV in this calculation [1] misplaced the position of the excited states to a higher energy value. Consequently, practically all excited states above the $p$-states reach into the continuum band. However, if the correct size of the $s$–$p$ energy gap is taken into account, it leaves room for speculation that some higher than $p$ excited states may still be bound. Hence, in a pump–probe spectrum, this would manifest itself as an excited state absorption contour centered at the corresponding transition frequency. In short, from the cited molecular dynamics simulations it is impossible to conclude to which extent, if at all, the continuum and high excited-state absorption will contribute to the pump–probe signals. Consequently, experimental answers should be sought.

The first indirect probing of the electronic level evolution of the hydrated electron was realized in the experiments on the trapping of a photo-ionized electron and its subsequent equilibration (solvation) to the bottom of the potential well formed by the solvent cavity. In the measurements of this kind [31,32,35-40] a UV electron photo-detachment- and an IR probe- pulses are applied. These experiments monitor the onset and evolution of the
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absorption band of the electrons as it changes into the steady-state absorption spectrum, such as in Fig.6.7. Some of the transient spectra recorded in these studies revealed the presence of an isosbestic point \cite{31,32,35,36}. This was interpreted as a presence of a distinct step-wise electronic transition between the two fixed states, the so-called “weakly-bound” and the “strongly-bound” states, which the electron occupies during different stages of the trapping and solvation process. Recent, most elaborate and exhaustive studies (e.g. Ref. \cite{41}) of the equilibration of the photo-detached electrons in heavy water, however, have convincingly demonstrated a continuous spectral blue shift that accompanies the evolution of the electron absorption band associated with the electron in the lower, “strongly-bound” state. The characteristic time of \textasciitilde0.52 ps attributed to this shift must, therefore, describe the solvation rate of the final (ground) state of the electron hydration. In brief, these experiments generally point at the existence of two distinct bound or semi-bound electronic levels, at least one of which (the bottom one) undergoes a complex evolution.

The just mentioned UV-pump–NIR-probe studies of electron photo-detachment provide a valuable insight into the electronic level structure and the time scales of electron solvation. An advantage of this method lies in the relative experimental simplicity (only two laser pulses are involved) and in the fact that the equilibrated ground state of the hydrated electron is not populated in the beginning. As a result, there are no contributions of the ground state bleach in the measured evolution. In contrast to the UV-pump–NIR-probe method, the presence of the latter contributions in the pump–probe signal from equilibrated hydrated electrons (\textit{vide infra}) significantly complicates the data interpretation.

Despite the mentioned advantages, the photo-ionization–probe experiments have severe limitations. One of these, namely geminate recombination \cite{39,42-45} makes the studies in the picosecond delay-time range particularly difficult. In absence of electron recombination, kinetics measured in this experiment would reach a plateau that could be used as a background line. Because of the geminate recombination, which is the fastest process reducing the numbers of surviving hydrated electrons, the background of such kinetics shifts in time. This strongly affects the precision with which the hydrated electron solvation can be measured.

Most crucially, however, such experiments have an intrinsically low time resolution, because of the large phase mismatch between the UV and NIR pulses in the water sample. For instance, despite the use of 90-fs pulses at 267 nm, the obtained time resolution of the experiments described in Ref. \cite{40} was about 150 fs due to the finite thickness of the sample. This is the best time resolution of this type of experiments to the date. However, even this value is not entirely sufficient to study the initial event of electron localization. The times of trapping in the “weakly-bound” state reported in the literature on the issue are in the range of 100 to 300 fs \cite{31,32,35,46}, which is in all cases very close to the time resolution used in the experiments. In fact, on the basis of one UV-pump–NIR-probe study, it has been suggested recently \cite{40} that the electronic level structure of the hydrated electron may consist of a single weakly-bound state. Obviously, the insufficient time resolution, limited by the duration
of the UV pulse and the phase mismatch with the probe pulse, can affect the interpretation of the measured results. It is important to note that possibly some intermediate short-lived electronic states may be overlooked in this type of experiments. The problem of the low time resolution can be more easily solved in an all-NIR-pulse pump–probe on equilibrated hydrated electrons. Therefore, the latter variety of pump–probe, which is also employed in the present work, is a powerful method to disclose both the structure of the electronic levels as well as the rates of passage to the bottom of the ground state.

Unlike the UV-pump–NIR-probe method, which investigates the formation of the hydrated electron and its absorption band, the pump–probe measurements on the already equilibrated species [5-7,9-11,34,47] study the changes in the absorption spectrum upon photo-excitation of the \( s-p \) transition. Technically, this experiment involves a sequence of three laser pulses. First, a UV preparation pulse produces hydrated electrons. Subsequently, upon equilibration of the electrons, the NIR pump and probe pulses are applied. Therefore, the time resolution is not affected by the phase mismatch between the UV and the NIR pulses, nor does it depend on the duration of the preparation pulse. The fundamental features of the transient absorption dynamics of the equilibrated hydrated electron became clear after the pioneering experiments of the Barbara group [5,7,8,11], despite a relatively poor, 300-fs time resolution. The kinetic data showed bleach recovery for the wavelength region below the peak of the steady state absorption (720 nm) and appearance of a red-shifted positive transient absorption signal superceding the initial bleach on a sub-ps time scale. The decay of the pump–probe kinetics was found to be essentially bimodal. The average time constant at different probe wavelength lay within the 0.3 – 0.8 ps interval. The variation in the time scales of the pump–probe dynamics and the absence of an isosbestic point evidenced strongly against a simple two-state model, where the energy levels of each state remain fixed.

Despite the clear advantages of this experimental route, the data interpretation, however, is not straightforward. While in the UV-pump and NIR-probe spectroscopy, for the delays outside the pulse overlap, the measured data consists of a pure absorption contribution, in the equilibrated electron pump–probe one should discriminate between different components of the transient spectra. As has been mentioned above, transient absorption bleach and stimulated emission dynamics add to, and can be superimposed on transient absorption from previously unpopulated states. In the case of the hydrated electron, the excitation of the \( s-p \) transition creates a “hole” in the population of the \( s \)-state. The “hole” gives rise to the bleach component in the transient spectrum, which initially has the same spectral position as the stimulated emission from the \( p \)-state that is now occupied. This complicates the assignment of the contributions from different electronic states to the overall observed pump–probe spectrum.

The latter difficulty is illustrated in Fig.7.2. The solid contour in Fig.7.2 schematically shows a typical pump–probe spectrum of equilibrated hydrated electrons, which is well known from the experiments [6,7,10,11]. This spectrum can be decomposed into the negative contributions of the ground-state bleach and stimulated excited emission and a positive
component due to excited state absorption. In principle, the resulting “butterfly” shape, can have any wanted ratio of the negative vs. positive peak amplitude and can cross zero at an arbitrary wavelength, depending on the strengths of the transition dipole moment, the energy gap between the two excited states, and their mutual curvature.

Fig. 7.2: Schematic shape of pump–probe spectrum of hydrated electron in presence of the occupied $p$- or, alternatively, hot $s$-state.

The complication outlined above brings us to the fundamental issue of this Section, – finding the criteria that will make it possible to differentiate between the short-lived $p$-state model vs. the long-lived one in pump–probe on the equilibrated hydrated electrons. First, we notice that the decay of the induced transparency might be, in general, explained by both the recovery of the hole in the ground state and by the depopulation of the excited state. Second, the positive transient absorption changes correspond to a transition from a now occupied but previously unpopulated state to another electronic state. As has been already mentioned, these positive changes above the central wavelength of the steady-state absorption have been observed in all pump–probe experiments on the equilibrated hydrated electrons [5-8,10,11]. Two explanations of these pump–probe features correspond to different involvement of various electronic states, which is outlined in two models depicted in Fig. 7.3. The first one (Fig. 7.3.a) complies with the short-lived $p$-state scenario, while the second one (Fig. 7.3.b) becomes necessary to explain a picosecond lifetime of the excited state.

In the short-lived $p$-state scenario, the transient component of the positive sign arises due to induced absorption from the hot ground state (Fig. 7.3a). Consequently, the essential evolution of the pump–probe dynamics at long pump–probe delay times takes place only on two potential energy surfaces, that of the $s$- and of the $p$-state. Contrary to it, in the long-lived $p$-state model (Fig. 7.3b) another, higher lying excited state must be involved to explain the presence of the positive transient absorption.
Both these models have been applied to interpret experimental pump–probe results. The initial explanation of the kinetic behavior observed in the early studies by the group of Barbara [5,7,8] was given in accordance with the above-presented short-lived excited state model. However, in view of a short, <100 fs ground state equilibration time and a long ~1 ps p-state lifetime predicted in the Rossky et al. simulations, the interpretation of the experimental data was modified [17] in favor of the second, long-lived p-state model. The following pump–probe measurements conducted in the Barbara group with a much-improved resolution were also interpreted along these lines [6,9]. Conversely, the model of a rapid nonadiabatic electronic relaxation and a subsequent long vibrational cooling of the ground state was upheld for solvated electrons in alcohols [17,48]. The scheme that involves a rapid p–s relaxation and a ps equilibration of the s-state in the hydrated electron has re-appeared recently in the study by the group of Laubereau [10]. Despite the use of inadequately long, ~170-fs pulses, these researches inferred from the fit routine an ~190-fs lifetime of the excited state and an ~1.2 ps time constant of the ground state recovery. Moreover, sub-100-fs dynamics in the excited state was concluded, which is significantly faster than the limit imposed by the temporal resolution of the experiments.

Evaluating the properties of one relaxation model against another, one can easily see that the long-lifetime scheme, which involves three different electronic states with arbitrary parameters, can describe virtually any dynamics within a limited spectral window of the experiment. Therefore, the success of such a three-level model (Fig.7.3b) in explaining the numerous pump–probe data is to be expected.

Exactly the same pump–probe features, depicted in Fig.7.2 can be observed upon the excited state relaxation in the two-electronic-state model that includes the ground state solvation (Fig.7.2a). Consequently, neither the transient spectrum shape, nor the decay of the kinetic traces can directly betray the underlying system of electronic potentials. Therefore, a

Fig.7.3: Two models of photo-excitation relaxation in hydrated electron. (a) short-lived p-state (Refs. [5,7,10]). (b) long-lived p-state (Refs. [2,6,9,12]).
challenge remains to differentiate between the two models on the basis of more subtle features of the transient spectral dynamics.

To this end, we notice that there are two ways, in which the evolution of the transient absorption spectrum proceeds in the three-level (i.e. long $p$-state lifetime) model. The first way is the excited state solvation that causes the modification of the transition frequency between the first and the second excited states and also decreased the $p$-$s$ energy gap. As a result, the contour of the stimulated excited state emission moves to the red and the spectrum of the induced absorption shifts as well (typically, to the blue). The second way lies in the nonadiabatic character of the excited state depopulation [17,18]. This basically means that the probability of relaxation is related to the actual size of the $s$–$p$ gap, i.e. the rate of depopulation is higher for lower transition frequencies. While the first way (solvation) introduces the overall shift, the second one (nonadiabatic relaxation) changes the shape of the spectral contour of each excited state contribution. Upon completion of the solvation process, which is faster than the electronic relaxation, the spectral position of both the excited state absorption and stimulated emission further remains fixed. Subsequently, the overall transient absorption spectrum decays with the given rate of the nonadiabatic relaxation for the given wavelength. A useful quantity here becomes the frequency, at which the “butterfly” shape of the pump–probe spectrum (Fig.7.2) crosses zero. In the three-level system, this frequency changes during the excited state solvation and remains “frozen” afterwards. Schematically, this is shown in Fig.7.4. Therefore, tracing the position of this frequency from the experimental data allows discriminating between the faster rate of solvation and a much slower rate of electronic relaxation (Fig.7.4, right panel).

![Diagram](image_url)

**Fig.7.4:** Evolution of zero-crossing frequency (top row) and kinetic traces (bottom row) in two different models. Horizontal dashed line indicates the frequency of the $s$–$p$ transition. See text for details.
Despite the external similarity of the pump–probe spectra predicted by a three-level and a two-level (or short-lived $p$-state) models, the behavior of the zero-crossing frequency in the latter is entirely different. The reason for that is a continuous blue shift of the hot ground-state absorption contour, which moves towards the initial size of $s$–$p$ transition frequency corresponding to an equilibrated hydrated electron. The decay of the pump–probe kinetic traces in this model is a direct consequence of the shifting population of the hot ground state as it overlaps and “fills in” the hole in the population created by the excitation pulse. Consequently, the continuous spectral blue shift (e.g. monitored by the evolution of the zero-crossing frequency) and the decay of the kinetic traces must have identical rates (Fig.7.4, left panel).

An additional virtue of the zero-crossing as a model “sensor” lies in its asymptotic frequency at very long pump–probe delays. While the short-lived $p$-state model automatically predicts the arrival of zero-crossing to the center of the steady-state absorption spectrum, the asymptotic frequency in the long-lived $p$-state model depends on the interplay of the individual state parameters. Therefore, in the latter case, a sheer coincidence would result in the absorption peak being the asymptotic value.

Last but not least, the sliding of the hot ground state population downhill to recombine with the “hole” has one more profound impact on the pump–probe spectra. Based on the considerations of electronic population conservation, we evaluate yet another helpful difference between the two models. In the three-electronic-level model, at least three signal contributions have to be considered at any pump–probe delay, namely, 1) the ground state bleach (“hole”), 2) excited state absorption, and 3) stimulated emission. One of them, the transient absorption, can, in principle, have considerably different transition strength and, consequently, a much stronger or weaker contribution to the transient spectrum. Therefore, the integral of the pump–probe spectrum along the frequency axis can produce a finite value. A value of zero in this case signifies that, by coincidence, the excited state absorption contribution to the overall signal exactly cancels the combined weight of the ground state bleach and the stimulated emission put together.

The situation in the two-level model is completely different. Here, upon the transfer of the entire displaced population to the hot ground state, only two contributions, the “hole” and the hot ground state absorption, form the pump–probe spectrum. Close to the bottom of the $s$-state potential well, both the transition dipole moment and the shape of the transient absorption must automatically match those of the “hole”. Therefore, the integral over the whole frequencies of the pump–probe spectrum should produce exactly zero, which signifies a perfect balance between the “hole” and transient absorption. The straightforward implementation of this last criterion on experimental data maybe not easy, considering the limited window of the laser spectrum and the breadth of the hydrated electron spectral features. We will, however, put this stringent criterion to use in our fit procedure.

In closing to this Section, we have identified several useful features that allow discriminating in practice between a short-lived and a long-lived $p$-state model. These are: 1)
the comparison of the zero-crossing dynamics with the decay of kinetic traces, 2) the asymptotic value of zero-crossing, and 3) the ratio of the positive vs. negative contributions to the transient spectra. These recipes for model identification will be subsequently applied in this Chapter on the measured results.

7.3 Experimental

In this Section we briefly outline the practical aspects of measuring pump–probe kinetics and spectra of the hydrated electron, using 5-fs optical pulses. The basic elements of the femtosecond spectrometer and the sample preparation have been discussed already in Section 6.2. Therefore, here we only address the necessary changes in the set-up.

The schematic of the pump–probe spectrometer is presented in Fig.7.5. The difference with the self-diffraction geometry implemented here is in the orthogonal polarizations of pump and probe beams. The reason for this is to avoid unwanted heterodyning of the weak nonlinear polarization by the scattering from the pump pulse, which takes place in the sample. Because of the ultrafast dephasing in the hydrated electron, the use of orthogonal polarizations for the pump and probe does not decrease the amount of useful signal. This measure is necessary, since it is impossible to screen off the scattered pump light, which spectrally exactly overlaps with the probe radiation, by any means of spectral selection. To further protect the measured signal from the pump scatter contamination, a polarizer cube was installed in front of the detection scheme. The probe beam was subsequently focussed into a 1/8-m monochromator (CVI) and split behind it into two channels by a metal beam-splitter with a calibrated reflection/transmission ratio over the spectral range of interest. The two channels served for the measurement of the pump–probe signal (i.e. modulation of the probe beam intensity, $I_{pr}$) and the reference (i.e. the probe beam intensity, $I_{pr}$). Two separate optical choppers set at different chopping frequencies served to modulate the excitation and the reference beams. Accordingly, the pump–probe signal and the reference intensity were registered by two separate digital lock-in amplifiers (SRS) and fed to the computer. The difference absorption signal was then computed as the $\Delta I_{pr}/I_{pr}$ ratio. The

![Fig.7.5: Schematic of set-up for pump–probe on hydrated electron. (Also see Fig.6.1).](image)
measurements consisted of recording sets of transient spectra and sets of kinetic traces at different probe wavelengths.

The spatial overlap of the 5-fs pump- and probe- beams, and of the UV-preparation beam from the YLF laser was verified through an aperture \( \varnothing 25 \mu m \). The optical delay was subsequently aligned so that no noticeable deterioration of the beam overlap was present for the large scans of the pump–probe delay in excess of 200 ps.

![Normalized Pump-Probe Signal](image)

**Fig.7.6:** A long delay-range pump–probe trace of hydrated electron in water at the detection wavelength of 650 nm.

The contribution of pure solvent to the pump–probe signal was measured by blocking the UV preparation pulses from the sample. The amplitude of this contribution comprised about 10-15% of the peak signal from the hydrated electron. The response from water quickly disappears outside the pump–probe overlap. Transient spectra in absence of UV radiation were taken for each pump–probe delay in the delay region of ±50 fs and subtracted from the corresponding spectra of hydrated electrons.

A typical long-range kinetic trace is presented in Fig.7.6. Identical large-delay scans (not shown) at different wavelengths all resulted in a slight remaining bleach component, the decay time of which is in the order of 100 ps or longer. The amplitude of this component is very small, only about 0.002 of the peak amplitude, to have any effect on the results of the ultrafast part of the pump–probe studied here. Therefore, it has been subtracted from all relevant data. The presence of this scanty component is an interesting fact in itself, signifying that the system has not returned to the original state even after 100 ps. One of the plausible explanations of this effect might be direct photo-ionization of a small percentage of the hydrated electrons back to a quasi-free state. These electrons have higher chances of
recombination and may never return to a bound state. Hence, the “escaped” particles can no longer be accounted for in the pump–probe measurement. Also, similar “non-conservation” of the pump–probe traces has been reported in the recent study of Laubereau and coworkers [10], although they did not comment on this fact.

7.4 Results and discussion

7.4.1 The measured traces

The representative transient absorption spectra of hydrated electrons in water at different pump–probe delays are presented in Fig.7.7 (solid dots). The large spectral width of the 5-fs pulses allowed reliable acquisition of the pump–probe data in the range of 600 – 1050 nm. The depicted dependencies are the averages of multiple scans. To provide an adequate signal-to-noise ratio at all pump–probe delays, the number of scans was gradually increased in accordance with the drop in the amplitude of the signal. Consequently, while only 5 scans needed to be accumulated for the spectra in the delay range below 100 fs, more than 100 spectral scans were required for the delays above 5 ps.

![Transient spectra of the hydrated electron obtained at different delays (solid dots). Solid curves represent best fits to experimental data, which consist of the ground-state bleach and hot-ground state absorption contributions, as described in Section 7.3.2. Note different scaling of the vertical axis.](image)

One measurement cycle of transient spectra in the delay range up to 7 ps took, on average, ~30 hrs, demonstrating extraordinary stability of the set-up. The pump–probe data showed
excellent reproducibility, with the main source of experimental error attributed to the drop of spectral amplitude in the wings of the probe pulse spectrum. Similar transient spectra have been recorded on the hydrated electron in heavy water (not shown).

Fig. 7.8: Zero-crossing point as a function of pump and probe delay of hydrated electrons in water (solid circles) and heavy water (solid squares). Note that the asymptotic value in each case approaches the position of the absorption maximum of the fully equilibrated electron (indicated by the dashed horizontal lines). Solid curves show biexponential fits. The fit parameters are $\tau_1=205\pm30$ fs, $A_1=0.56\pm0.03$ and $\tau_2=1\pm0.1$ ps, $A_2=0.44\pm0.03$ for water, and $\tau_1=215\pm20$ fs, $A_1=0.64\pm0.03$ and $\tau_2=1\pm0.1$ ps, $A_2=0.36\pm0.03$ for heavy water. (The combined amplitude of $A_1$ and $A_2$ is normalized to unity). Inset shows the isotopic effect at early pump–probe delays. Vertical arrow indicates the end of overlap between the data for $\mathrm{H}_2\mathrm{O}$ and, on the compressed by a factor of $\sqrt{2}$ time scale, data for $\mathrm{D}_2\mathrm{O}$.

A dominating feature of the spectra in Fig. 7.7 at initial pump–probe delays is an absorption bleach contour, which stretches through most of the covered spectral window. Another peculiarity is the rise and blue shift of the induced absorption. It corresponds to the contour of positive amplitude, which appears in the infrared and progresses towards the center of the steady-state absorption. This spectral evolution is easily traceable by the position of zero-crossing that corresponds to the frequency where the strength of the induced absorption equals the amplitude of the ground-state bleach. Dashed vertical lines in Fig. 7.7 denote the spectral evolution of the zero-crossing as the latter shifts toward the center of the steady state absorption peak (720 nm). The values for the zero-crossing wavelength were extracted from a linear fit of each measured contour in the adjacent to the crossing interval. The size of the interval was set at 50 – 80 nm. The intersection of the resulting straight line with the x-axis was subsequently taken as a zero-crossing point. Compared with the direct use of a single data point, in which the measured pump–probe spectrum intersects with the
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horizontal axis, the outlined procedure is more trustworthy with respect to experimental noise.

To exploit the model-identification criteria, put forward in Section 7.2, we now plot the zero-crossing wavelength, traced from each transient spectrum as described above, as a function of the pump–probe delay. The corresponding dependence for hydrated electrons in water and heavy water is depicted in Fig.7.8. It is clear that both cases exhibit a continuous blue shift over the whole range of measured delays. The picosecond tails of both data sets asymptotically arrive at the position of each respective peak of the steady-state absorption. The solid curves in Fig.7.8 depict biexponential fits starting from 100-fs delay.

![Graph showing zero-crossing wavelength as a function of pump–probe delay.](image)

Fig.7.9: Pump–probe kinetics of hydrated electron in water at detection wavelengths of 650 nm and 900 nm. Circles depict measured data points, while curves represent biexponential fits (see text for details). The kinetic traces are scaled so the picosecond tails overlap. The parameters of the fits are $\tau_1=1.04\pm0.08$ ps, $A_1=-0.975\pm0.05$ and $\tau_2=4.9\pm0.3$ fs, $A_2=-0.025\pm0.02$ for 650 nm, and $\tau_1=1.18\pm0.1$ fs, $A_1=0.94\pm0.06$ and $\tau_2=5.1\pm0.4$ fs, $A_2=0.06\pm0.02$ for 900 nm. (The combined amplitude of $A_1$ and $A_2$ is normalized to unity. In the case of the 650-nm trace $A_1+A_2$ accounts for 1/17 of the total amplitude of decay.) Inset shows the full extent of the measured transients.

We now turn our attention to the decay of pump–probe traces, which, according to the model recognition recipe in Section 7.2, must provide the answer whether the time constants of the spectral evolution and of pump probe decay are identical or not. The typical transients at two different probe wavelengths, corresponding to the bleach recovery ($\lambda=650$ nm), and to the build-up and subsequent recovery of induced positive absorption ($\lambda=900$ nm), are
presented in Fig. 7.9. The behavior of the kinetic tails in the delay range above 2 ps is clearly bimodal. The biexponential fits for the detection wavelength of 650 nm and 900 nm, starting from a 1.7-ps value of delay, are shown by a dashed and by a solid curve, respectively. The presence of the 1.1±0.1-ps component is thoroughly documented in the previous experimental work of other groups [5-7,10], as has been discussed in the previous two Sections.

Two facts become apparent from the inspection of the dynamics of zero-crossing (Fig. 7.8) and the recovery of the transient kinetics (Fig. 7.9). First, the dynamics of the blue shift clearly matches the picosecond rate in the tail of kinetic trace recovery. The presence of the additional 3–5% 5-ps component in the observed transients does not affect this conclusion, since the dynamic range of the kinetic measurement is significantly higher compared to the experimental precision, with which we can estimate the evolution of zero-crossing. Therefore, in the available zero-crossing data, a 5-ps tail, if present at all, would manifest itself merely as a raised background. This precludes the possibility to observe this rate in the reported here experiment. Second, the asymptotic value of the blue shift in zero-crossing invariably arrives at the peak of the equilibrated absorption spectrum for both water and heavy water. In their combination, these two observations support, with a great certainty, the short-lived $p$-state model. A general fit of the pump–probe spectra, consistent with such a scenario, will be presented in the following Section.

We now discuss several other issues surrounding the pump–probe measurements described in this Section.

Next to the well-known ~1-ps absorption recovery time, another, previously unreported, 5-ps component is seen in our pump–probe data. As is apparent from the fit parameters, the relative contribution of this exponential tail to the overall pump–probe trace is nearly 20 times smaller than that of the 1-ps component. Therefore, due to the sheer weight of numbers, the 5-ps component cannot represent any substantial population relaxation of the excited state. The fact that this decay rate has not been reported previously may be explained in a number of ways.

As has been pointed out above, the dynamic range of our measurements presented here is much higher than the one in the past experiments [5-7,10]. Therefore, this small component could not have been resolved previously and the reported rates might have comprised the weighed average of a faster and this slower component. A plausible explanation of the presence of a slower rate in the pump–probe kinetics can be found in the recent visco-elastic continuum simulations of the hydrated electron by Berg [3]. These simulations predicted a small 5-ps relaxation component caused by the expansion and subsequent contraction of the water cavity surrounding the electron in the direction perpendicular to the principal axis of its $p$-wavefunction side-lobes.

Another explanation may be given considering the fact that the solvated electrons in our experiments are produced by photo-ionization of potassium ferrocyanide ions. It cannot be excluded that for some photo-ionized ferrocyanide molecules the released electron stays in
the direct vicinity of its parent ion. Consequently, the electron can be trapped in a cavity that has a ferrocyanide ion in the vicinity. This inevitably leads to an increase in the time constants of the transient absorption decay. For instance, for the electron in liquid methanol, which has less mobile, and twice as heavy molecules compared with water, the relaxation rates slow down nearly by an order of magnitude [48,49]. Therefore, it is possible that in our pump–probe experiments we detect a statistical contribution from the electrons with different environments.

Several important issues have to be addressed in connection with the spectral dynamics at early delays. As is easy to notice in Fig.7.7 (top panel), the transient spectra in the delay range up to 100 fs clearly show some modulation, which subsequently disappears (Fig.7.7, middle panel). This phenomenon is addressed in Appendix I, where we relate it to the temporal and spectral overlap of the pump and probe pulses and to a short lifetime of the excited state.

Another aspect of the transient spectra in the sub-100-fs delay region is a large amount of spectral shift (Fig.7.7, top panel). This suggests a great speed of population rearrangement, either within the same electronic state due to rapid solvation or between two different electronic states. Therefore, the use of extremely short excitation pulses is essential to “freeze” the nuclear motions of the solvent molecules [50] for the duration of pump. Indeed, in our experiments with an 18-fs 800-nm excitation pulse and a 5-fs probe we observed some deviations from the transient behavior shown in Fig.7.7, although the overall pattern remained quite similar. With the longer excitation pulse duration, the negative absorption changes were proportionally smaller, while the zero-crossing point was a few nanometers offset to the red. A very logical explanation of this observation is the rapid population movement on the excited state potential, which covers a noticeable energy distance on the 18-fs duration of the pump. This results in a red shift of the contour of absorption bleaching.

We now more closely examine the impact of deuteration on the spectro-temporal behavior of the pump–probe signal. The impact of isotope substitution on the early delays is illustrated in the inset to Fig.7.8, which presents the results of two identical measurements, carried out on hydrated electrons in water and in heavy water. To ensure that the conditions, i.e. the pulse and beam characteristics, stay exactly identical, the experiments with these two solvents in the 0 – 500 fs delay part were performed back-to-back. Like in the case of transient grating (Fig.6.11), the scaling of the delay axis for D2O by a factor of \( \sqrt{2} \) reveals a perfect overlap of the zero-crossing shift in water and heavy water in the initial part. The subsequent rate of the blue shift, however, is nearly identical for both solvents, as is readily seen from the parallel tails of the unscaled dependencies and nearly identical, 200-fs time constants obtained in the biexponential fit (Fig.7.8). Consistently with our previous conclusions (Chapter 6), the observed results of the isotopic effect again show that the initial solvent response within the first 100 fs in water and ~140 fs in heavy water is predominantly of librational nature.
As is clearly seen in Fig. 7.8 (inset), the initial behavior of the zero-crossing shift is highly non-exponential. Indeed, the measured dependence for water shows a “bump” around a 50-fs delay. The fact that the same bump but on the time scales different by a factor of \( \sqrt{2} \), is observed in both H\(_2\)O and D\(_2\)O rules out a possibility of the measurement artifact related to the properties of the laser pulses. Observation of a similar bump in the transient grating experiments (see Chapter 6) led us to a hypothesis about a strong influence of a non-Condon effect. The presence of a bump in the spectral position of the zero-crossing point indicates that if the dipole-moment variation were caused by a non-Condon behavior, it should be wavelength-dependent. A possible alternative view on the origin of the bump can be given by implying a short-lived excited-state absorption, which causes a delay in the transient signal growth. We will return to the discussion about the role of the excited-state absorption in the following Section.

### 7.4.2 The fit of transient spectra

In the previous Section, we have established that the observed pump–probe behavior is consistent with a two-level model. We now perform a fit procedure of the transient spectra, which allows us to decompose the overall response into separate contributions of each involved state. The approach undertaken here relies on the same formalism and assumptions that brought us to Eq.(6.8). The only difference is that the pump–probe signal is linearly proportional to induced polarization (See Section 5.5), while in transient grating this dependence is squared. Therefore, we are interested in the direct sum of the various states’ contributions. Consequently, for each transient spectrum \( S_{pp}(\Omega) \) at the delay time \( T \), we obtain:

\[
S_{pp}(\Omega) = -a_{gr}\sigma_{gr}(\Omega, \Gamma_{gr}, \omega_{eg}) + a_{hot-gr}\sigma_{hot-gr}(\Omega, \Gamma_{hot-gr}, \omega_{hot-gr})
\]

(7.1)

where \( a_{gr} \) and \( a_{hot-gr} \) are the corresponding amplitudes of the contributions formed by the population “hole” in the ground state and by the “hot” ground state, and \( \sigma \)’s denote the spectral shapes that are defined similarly to Eq.(6.2), i.e:

\[
\sigma(\Omega, \Gamma, \omega_0) = \left[ \frac{\Gamma_{gr}}{\Gamma} \right] \frac{4\Omega^2 \Gamma^2}{(\omega_0^2 - \Omega^2)^2 + 4\Omega^2 \Gamma^2}, \quad \ \ (7.2)
\]

where \( \omega_0 \) stands for the central frequency, and \( \Gamma \) is the characteristic half-width of each contour. For the “hole” contribution \( \sigma_{gr}(\Omega, \Gamma_{gr}, \omega_{eg}) \equiv \sigma_A(\Omega) \) and \( \Gamma = T_2^{-1} \), where \( \sigma_A(\Omega) \) is the steady-state absorption spectrum given by Eq.(6.2). The contributions of the stimulated emission and of the hot ground-state absorption are denoted by \( \sigma_{ex} \) and \( \sigma_{hot-gr} \), respectively.
To fulfill the condition of population conservation, the amplitude of the excited state contribution (which is proportional to $p$-state population) in Eq.(7.1) equals to the difference of the total number of excited electrons and the amount that has already returned to the hot-ground state, i.e. $a_{gr} - a_{hot-gr}$. Additionally, the scaling factor in the square brackets in Eq.(7.2) ensures that each normalized $\sigma$-contour retains its area regardless of the size of $\Gamma$.

The fit procedure runs as follows. The width $\Gamma_{gr}$ is set at 3250 cm$^{-1}$, which corresponds to the best fit of the steady-state absorption at room temperature in Fig.6.7. Then the value of $a_{gr}$, that is identical for all contours, is fixed. Subsequently, the widths and the central frequencies of the stimulated emission contour, $\sigma_{ex}$, and the hot-ground-state induced absorption, $\sigma_{hot-gr}$, and the amplitude $a_{hot-gr}$, are globally fitted as free parameters. A Levenberg–Marquardt routine was used for minimization [51]. The freedom in allowing the stimulated emission to have a somewhat different central transition frequency is provided deliberately to account for the fact that a nonadiabatic electronic relaxation [17] is faster at narrower energy gaps. The nonadiabatic relaxation shifts the position of $\sigma_{hot-gr}$ to the red with respect to $\sigma_{ex}$. The fits of individual pump–probe spectra, obtained in this model, are depicted in Fig.7.7 as solid curves. As can be seen from the overlap with the experimental points, the overall fit quality is very high.

The summary of the fit parameters as a function of pump–probe delay is shown in Fig.7.10. As is evident from Fig.7.10a (the initial delay part is shown enlarged in the inset), the amplitude of the stimulated emission rapidly drops within the first 100 fs. The mono-exponential fit of this amplitude yields an $\sim$55-fs time constant of the lifetime of the $p$-state. The negligible amount of the excited state population, left after $\sim$120 fs, allows taking away the $\sigma_{ex}$-contour from the fit of further spectra. Therefore, the solid curves presented in the middle and the bottom rows of Fig.7.7 correspond to the three fit parameters, i.e. the width, amplitude, and position of $\sigma_{hot-gr}$. Keeping $a_{hot-gr}$ as a free parameter is necessary to account for the gradual population build-up of this state. As can be seen from Fig.7.10a and c, at large pump–probe delays, when the population of the hot ground state approaches the equilibrium region, both the amplitude and the width of the $\sigma_{hot-gr}$ converge into those of the $\sigma_{gr}$-contour. Except for the initial 100 fs, corresponding to the build-up of the hot ground state population, the ratio of $a_{hot-gr}/a_{gr}$ stays reasonably close to unity, which is consistent with the overall population conservation. The fact that this follows from the fit and is not assumed $a$ priori is a powerful check of the right model choice. Note that the small deviations of the $a_{hot-gr}/a_{gr}$ ratio from unity in the delay region of 0.5–4 ps are related to the simultaneously occurring change in the spectral width $\Gamma_{hot-gr}$. The latter influences the magnitude of the amplitude $a_{hot-gr}$ via the normalization factor scaling in Eq.(7.2).

The initial relatively small width of the $\sigma_{hot-gr}$ (Fig.7.10b) is an indication of the rapid funneling of the $p$-state population through a relatively narrow photochemical “sink” [52], i.e. a region of the excited state potential with the highest probability of crossing back to the ground state potential. The width of $\sigma_{hot-gr}$, $\Gamma_{hot-gr}$, subsequently broadens during the
downhill slide on the hot ground state. A more detailed explanation of this will be provided in the following Section. The blue shift of the central position of the $\sigma_{\text{hot-gr}}$ exhibits the familiar, $\sim1.2$-ps predominantly exponential evolution (Fig. 7.10c). This rate is slightly different from the one inferred from the evolution of the zero-frequency shift, which was estimated to be $1\pm0.1$ ps. The small discrepancy can be explained by the fact that the location of the zero-frequency point is determined by the overlap of two asymmetric contours, i.e. $\sigma_{\text{hot-gr}}$ and $\sigma_{\text{gr}}$, which somewhat speeds up the rate of zero-frequency shift.

---

**Fig. 7.10**: Summary of fit parameters as a function of pump-probe delay. (a) Relative amplitudes of the hot ground state (solid circles) and excited state (open circles). Solid curve in the inset shows a mono-exponential fit with a time constant of 55 fs. (b) Relative width of the hot ground state absorption spectrum. (c) Spectral shift of the peak of the hot ground state absorption with respect to the initial transition frequency.

The frequency of the $p-s$ gap, where the population of the excited state crosses back to the ground state is around 9500 cm$^{-1}$. This value corresponds to a substantial portion of the
initial transition frequency, i.e. \( \sim 14000 \text{ cm}^{-1} \). Therefore, a large amount of energy deposited on the hydrated electron is rapidly absorbed by the solvent with a characteristic transfer time of \( \sim 50 \text{ fs} \).

Clearly, it was impossible to extract such a short, 50-fs lifetime of the excited state from previous pump–probe studies [5-7,10], due to the lack of adequate temporal resolution. The values of the lifetime as short as 120 fs did emerge, however, from numerical simulations [23,28]. These figures, nonetheless, are still higher by a factor of two than the lifetime of the \( p \)-state that resulted from the fit of our pump–probe data. We suggest that the discrepancy between the simulations and the interpretation of the experimental data maybe \textit{a priori} “built in” into the computed results. Set aside the fact that the electron–water interaction is typically simulated by a “pseudopotential” [27,53], there is a distinct problem with representing water molecules by a model potential [26,30] in general. For instance, it has been realized for the simple point charge potential [30] that the effective stretch force constant is different for an isolated water molecule, and for the one that has its OH bond aligned with the oxygen of the neighboring molecule. There is every reason to believe that, unlike in the case of a partly screened oxygen atom, in the case of the hydrated electron, the hydrogen bond formation might be even stronger. As an indication of this one should recall the predominant OH bond alignment in the direction of the electron in the first solvation cavity, revealed by the electron spin resonance study of glassy water [54] (see Fig.1.1). Therefore, the description of the first solvation shell by a potential, which is identical to the one used to describe the bulk solvent, should result in an underestimation of the coupling forces and the energy involved in the electron–water interaction. Accordingly, this must be reflected in the lengthening of the computed electronic relaxation time. Even though the energy deficit can be made up for by the addition of the interaction “pseudopotential”, the fundamental properties, such as oscillation frequencies, of the neighboring to the electron molecules will be accounted for incorrectly.

A closer inspection of the fit quality at the 0–100 fs delays (Fig.7.7, top row) reveals a deficit of positive transient absorption in the blue wing, which rapidly traverses the spectral window of observation on the same time scale as the excited state depopulation. This, together with the calculations of the pump–probe spectra during the pulse overlap (see Appendix I), and with the bump around 50-fs delay in the spectral shift of zero-crossing (see previous Section), can be explained by excited state absorption to the continuum (\( c \)-state) [1] (Fig.7.3a). The rapid blue shift and the subsequent total disappearance of this absorption correspond to depopulation of the excited state. The inclusion of this transient absorption into the overall fit was not attempted yet for two reasons. These are: 1) the shape of the \( p–c \) absorption is unknown. Assuming, that the coupling strength between the \( p \)- and the various states comprising the continuum manifold stays identical, the spectral shape of the corresponding absorption would be described by a sigmoidal function, rising towards the high frequencies. 2) The lack of information on the strength of the \( p–c \) transition and on its evolution in time extremely complicates any sensible fit with not-too-many parameters.
Anyhow, because the population lifetime of the excited state is ~50 fs, the \( p-c \) contribution to the pump–probe can be disregarded for the delays longer than 80 fs.

The \( p-c \) transient absorption presents an alternative view to the hypothesis proposed in the previous Chapter, which involved a non-Condon effect. To what extent the first or the second, or both these processes together dominate the initial dynamics of the hydrated electron energy relaxation remains to be clarified. Hopefully, measurements in an even broader spectral window, than the one provided by the spectrum of 5-fs pulses, would give an answer to this question.

In summary to this Section, from the fit of the pump–probe spectra we have inferred a very short, ~55-fs lifetime of the first excited state and obtained time dependencies of the spectral width of the hot-ground state absorption and the corresponding size of the modified-\( s-p \) energy gap. In the following Section, we perform an inversion of the time-domain picture, observed at the longer delays, into the generalized solvent coordinate.

### 7.4.3 The inversion of temporal data to potential surfaces at long times

The desired goal of the pump–probe experiment, besides estimating the energy relaxation rates, is to clarify the structure of the potential energy surfaces. Therefore, a transition should be made from the measured time-dependence to the actual (spatial) solvent coordinate(s). It has been shown by Zewail and coworkers [55-57] that such inversion is a relatively straightforward task for the photo-dissociation experiments in molecular beams where quasi-free fragments reach, after some time, terminal velocity and retain their kinetic energy. In this case, because of the linear dependency of the covered distance on the time, the inversion involves a simple scaling of the coordinate space. The situation, however, is substantially different in condensed media. Here, because of the strong interactions with the surroundings, the kinetic energy of a photo-excited particle is rapidly lost. Consequently, velocity along any of the solvent coordinate undergoes a substantial and nonlinear decrease as a function of time. Clearly, the inversion method of Zewail \textit{et al.} is not applicable to the situation of the hydrated electron.

Here we utilize a different approach to reconstruct the difference between the ground and excited state potentials of the hydrated electron. To do this, the temporal behavior of the hot ground state absorption, obtained from the general fit of the transient spectra, is exploited. The concept is illustrated in Fig.7.11. We apply a classical treatment to the downhill movement of the hot-ground-state population. Our assumption relays the width of the \( \sigma_{hot-gr} \) to the combined curvature of the ground and excited state potentials that are denoted, respectively, as \( V_{gr} \) and \( V_{ex} \). According to this scheme, the recovered from the spectral fit central frequency of \( \sigma_{hot-gr} \) as a function of delay, \( \omega_{hot-gr}(t) \), provides the size of the current gap energy gap, i.e. \( V_{ex} - V_{gr} \). At the same time the spectral contour width, \( \Gamma_{hot-gr}(t) \) is related to the shape of \( V_{ex}(q) - V_{gr}(q) \) as:
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\[ \Gamma_{\text{hot-gr}}(t) \propto \frac{\partial V_{\text{ex}}}{\partial q} \bigg|_t - \frac{\partial V_{\text{ex}}}{\partial q} \bigg|_t \propto \frac{\partial \omega_{\text{hot-gr}}}{\partial t} \frac{1}{\Phi}, \]  

(7.3)

where \( q \) is the generalized solvent coordinate, and \( \Phi \) is velocity. The expression (7.3) is exact in the case of a Brownian oscillator model [58], which considers two identical harmonic potentials that are displaced along the solvation coordinate. The spatial extent of the wavepacket in this scenario remains constant [59]. Consequently, it is the curvature of the potentials, which determines the width of the corresponding transient absorption. However, in general Eq.7.3 presents only a first-order approximation that breaks down, for instance, in the case of not-displaced potentials, with non-identical frequencies.

Fig.7.11: Concept of hydrated electron potential surface inversion from the width and spectral position of the hot-ground-state absorption.

According to Eq.7.3, the \( q \rightarrow t \) transition can be readily realized by computing the following integral:

\[ q(t) = \int_0^t \frac{\partial \omega_{\text{hot-gr}}}{\partial t} \frac{1}{\Gamma_{\text{hot-gr}}(t)} \, dt + \text{const} \]  

(7.4)
Because the function $q(t)$ is unambiguously defined for each delay instance, the inverted function, $t(q)$, can be directly obtained.

The result of this procedure, applied to the fit parameters from Fig.7.10, is shown in Fig.7.12. This picture corresponds to a strongly damped motion. Indeed, while about $2/3$ of the distance, separating the point of population return to the (hot) ground state and the Frank-Condon region, are covered within the first picosecond, the subsequent change of location is very slow.

![Fig.7.12: Time to solvent coordinate inversion of the data in Fig.7.10. The abscissa value of -1 corresponds to the initial position of hot-ground state population after radiationless $p$–$s$ transition. Zero stands for the coordinate of $s$–$p$ transition of the equilibrated hydrated electron.](image)

First, the linear dependence of the energy gap on the coordinate is consistent with the picture of two identical harmonic potentials that are displaced. This *a posteriori* justifies the application of Eq.(7.3) for the long times in the case of the hydrated electron. Second, the change of the behavior of the gap towards a linear coordinate dependence suggests that a certain type of nuclear motion becomes dominant. Note, that that Eq.(7.3) has been obtained for the one-dimensional case. In the multidimensional scheme with involvement of several solvent coordinates, which is typical in chemistry, the inversion problem does not have a simple solution, such as the one given by Eq.(7.4). However, we can still rely on this approach if the energy relaxation has distinct phases, associated with different types of molecular motions. One, nonetheless, should bear in mind that at different locations this coordinate could, in principle, represent very different nuclear degrees of freedom. A
confirmation of the latter idea can be found in the reconstruction of the $s-p$ energy gap as a function of a single generalized solvent coordinate $q$ presented in Fig.7.13. Indeed, the observed picture can be readily understood by stepping from a single coordinate $q$ to a multidimensional space, which separates different degrees of freedom of the water molecules. In the following Section, we further elaborate on the relaxation pathways on the basis of a multi-coordinate representation.

![Graph showing $s-p$ gap as a function of generalized solvent coordinate. Solid and open circles show the values of $\omega_{hot-gr}$ and $\Gamma_{hot-gr}$, respectively, obtained from the fit (see Fig.7.10). Solid curve computed by numerical integration of $\Gamma_{hot-gr}$ over $q$ (see text for details).](image)

**Fig.7.13:** $s-p$ gap as a function of generalized solvent coordinate. Solid and open circles show the values of $\omega_{hot-gr}$ and $\Gamma_{hot-gr}$, respectively, obtained from the fit (see Fig.7.10). Solid curve computed by numerical integration of $\Gamma_{hot-gr}$ over $q$ (see text for details).

It is important to realize that it is impossible to assign the actual shape and curvature of each potential, since the pump–probe experiment measures a gap between the excited states. Therefore, an additional input from Raman or other-kind vibrational spectroscopy is required in order to obtain information on the curvature of the ground-state potential.

Before closing this Section, we point out an interesting aspect of the applied procedure. It concerns the relation between the temporal and spatial evolution of the width and position of $\sigma_{hot-gr}$, which are independent in the time domain but are connected in the $q$-space by definition in Eq.(7.3). To verify that the numerical calculation of the temporal derivative of the discrete array of $\omega_{hot-gr}$ did not introduce any distortions in application of Eq.(7.4), we can compute the function $\omega(q) \propto \int_{0}^{q} \Gamma_{hot-gr}(q)dq + const$, which follows from integration of Eq.(7.3). The result of this validity check is plotted in Fig.7.13 as a solid curve. The good
overlap of this dependency with the values $\omega_{\text{hot-gr}}$ indicates that there are no significant inconsistencies in our calculations.

In summary of this Section, we have demonstrated a practical method of inversion of the pump–probe data, which allows reconstructing the energy gap between the ground- and excited-state potential surfaces of the hydrated electron.

### 7.4.4 The multidimensional relaxation model

In Section 7.4.2 we have established the time scales and the sequence of the basic steps in the energy relaxation process of the hydrated electron. According to the results of the global fit of the pump–probe data, approximately 2/3 of the deposited by photo-excitation excess energy is dissipated with a time constant of 50 fs due to population relaxation from the excited state. This process is deuteration-dependent and, therefore, is likely to be dominated by the librational motion of the water molecules. The relaxation process following the excited state depopulation is attributed to the cooling of the ground state. Contrary to the population decay, no clear-cut dependence of this process on deuteration has been observed. Therefore, we assume that collective translational motion of the water molecules takes over in this time range. Subsequently, in Section 7.4.2 we have mapped the energy loss of the photo-excited hydrated electron onto the generalized solvent coordinate. This provided further indication that more than one characteristic motion of the water molecules participates in the process of energy dissipation. In this Section, we attempt to tentatively disentangle the contributions associated with the evolution of different solvent coordinates from the overall response. In other words, we aim at recreating a multidimensional trajectory of energy relaxation.

Our idea is based on the clear separation of the time scales associated with a predominantly librational and, subsequently, with a predominantly translational response of the water molecules. Obviously, within 50 fs the translational motion cannot be substantial in comparison with the more rapid librations. This is also proved by the observed strong dependence on the isotopic effect. On the other hand, Fig.7.13 suggests that after 300 fs practically only translations determine the process of energy relaxation. This conclusion is based on the linear dependence of the energy gap on the coordinate $q$. As has been pointed out in Section 7.4.3, this is consistent with a picture of two displaced harmonic potentials with identical frequency along this coordinate. As a result of the time scale separation, we can consider that for the short (<50 fs) times the electron “propagates” mostly along the librational generalized coordinate while for longer (>0.3 ps) times – along the translational one. It is also clear that there should be an intermediate region where both coordinates change simultaneously. This interval corresponds to the intermediate decay rates observed in all transients. Although there are no conclusive data available on the actual behavior of each coordinate in the intermediate time, we can, nonetheless, take a very good guess, since the amount of energy released to the solvent during this interval is known from the potential inversion (Fig.7.13).
The deduced trajectory of the relaxing hydrated electron is given in Fig.7.14. Upon optical excitation the electron undergoes the $s \rightarrow p$ electronic transition. The initial excess energy supplied by the photon is approximately 14000 cm$^{-1}$. As we have established, the first stage of the solvation process starts with an ultrafast energy loss to the librations of the water molecules. The concept of librations should be understood in a broad sense, i.e. as hindered rotations of water molecules, and bending and stretching of the O-H bonds. According to the results of the global fit in Section 7.4.2, the change of the energy in the initial step is $\sim$9500 cm$^{-1}$. This is remarkably close to the triple frequency of the O-H stretching mode in liquid water ($\sim$3400 cm$^{-1}$). However, since the electron in the excited state basically undergoes a one-dimensional expansion, it is expected that only 2 out of 6 water molecules (Fig.1.1) can efficiently take up the energy of $\sim$6800 cm$^{-1}$. The rest is either absorbed by an O-H stretch with a lower efficiency, or by one of the other four molecules in the first solvation shell. Alternatively, it is distributed among several lower-frequency modes. The deduced lifetime of $\sim$50 fs compares very well with the time needed to transport energy to multiple O-H bonds. Indeed, as determined by the inverse frequency, an excitation of a single
O-H bond roughly takes place in 10 fs. Accordingly, the required time increases by a factor of $\sqrt{2}$ in the case of D$_2$O.

As revealed by the fit results of the pump–probe data (Fig.7.10), by approximately 100 fs after the excitation most of the electrons have already returned to the (hot) ground state. This corresponds to the “collapse” of the size of the hydrated electron, which now occupies a more compact hot $s$-state, leaving a void in the solvent. The more compact configuration of the electron changes the character of the librational motion from forcibly driven by the electron expansion to a more random one. Accordingly, the “distance” covered by the electron along the librational coordinate stops increasing while the “propagation” along the translational coordinate begins. During this phase, the water molecules in the first solvation shell deploy the accumulated excess energy into a collective-type translational motion. It is likely that the existing hydrogen-bond network [60,61] helps to speed up the energy transfer that occurs on an ~250-fs time scale.

The kinetic traces on the intermediate time scale do not exhibit any appreciable isotopic effect. This can be explained by the fact that the excess energy received from the electron by the librational modes of water molecules is subsequently released (passed on to further solvation shells) through translational motion. Only after dissipating this extra energy, the molecules of the first solvation shell can close the void that has formed after the crossing from the $p$-to the $s$-state.

**Fig.7.15**: Local heating effect as a function of time since the photo-excitation. Solid circles show the temperature calculated from the spectral position of the hot-ground state absorption. Solid curve depicts a biexponential fit with the parameters $A_1=135$ K, $\tau_1=0.3$ ps and $A_2=120$ K, $\tau_2=1.1$ ps. Inset shows peak position of hydrated electron absorption from the data in Ref. [62] (hollow circles). Solid line is given by expression $v_{eg} = 20730 - 20.75T$, were $T$ is the temperature in K.
Approximately after 300 fs, the librational coordinate returns to its initial value before the excitation while the translational one reaches the maximum. This means that the librational energy has already been transferred into translational motions of the first and the next solvation shells. From now on the energy is released in the form of local heating (i.e. the local temperature is substantial raised) and spreads further away from the electron. Finally, by about 5 ps practically full equilibration of the hydrated electron is achieved.

The local temperature can be evaluated from the spectral position of the hot ground state absorption. The change of the local temperature as a function of time is estimated in Fig.7.15. Here we extrapolated the known linear dependence of the hydrated electron absorption peak on temperature [62] and took the position of the hot-ground state absorption in time from the fit results depicted in Fig.7.10c. Although the resulting value of the local temperature exceeds 500 K, one should bear in mind that up to the times of ~300 fs the excess energy is accumulated primarily in the (collective) librational modes of the water molecules. Therefore, the change of the temperature, viewing the latter as a measure of the mean kinetic energy of the water molecules, is unlikely to exceed ~100 K. Nevertheless, this value is substantially higher than the one reported before [11].

In summary to this Section, we have proposed a complete multidimensional model of the energy relaxation in the hydrated electron. We distinguish three main phases in this process. The first stage is a librational relaxation, which is responsible for an energy loss of ~9500 cm\(^{-1}\) with a time constant of ~50 fs. The second, an intermediate phase takes place during 100-300 fs following the excitation and accounts for the energy release in the order of 1000 cm\(^{-1}\). Collective translational modes are being excited during this time. The last step is a purely translational relaxation, which proceeds with a time constant of ~1 ps and is responsible for the further release of the remaining 3000 cm\(^{-1}\) of the excess energy. The local heating of the hydrated electron environment is estimated to be around 100 K.

### 7.5 Conclusions

Frequency-resolved pump–probe measurements with 5-fs laser pulses rendered a comprehensive picture of the energy relaxation pathways that a hydrated electron undergoes upon photo-excitation of the \(s\rightarrow p\) transition. This work clarified several issues that have posed a challenge for the ultrafast laser spectroscopy of this species, despite a decade of intense efforts. For the first time, pulses of an adequately short duration and broad bandwidth were applied to uncover the initial spectral dynamics that rapidly evolves within a few tens of femtoseconds. Additionally, a significant breakthrough in describing the energy relaxation process on the picosecond time scale was achieved due to the unprecedented dynamic range of the measurements. Importantly, the correct understanding of the picosecond time scale also appears to be vitally linked to the use of as short as possible excitation pulses, ensuring that no substantial population relaxation occurs for the duration of the excitation pulse. In all, the use of 5-fs pulses, employed in this study, has resulted in a considerable progress in the research of the hydrated electron dynamics.
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The fundamental difficulty that has been solved in order to enable a correct pump–probe data interpretation is the delineation of various contributions comprising the observed signal. Namely, two different models of electronic relaxation can be used to account for the transient spectral dynamics seen through the frequency window that is limited by the pulse spectrum. To resolve the issue, in this Chapter we have developed the guidelines for recognition of a “short-lived $p$-state + slow ground state solvation” vs. a “long-lived $p$-state + fast ground solvation” models of the hydrated electron. The resulting recipes for the level scheme identification are based on the combined analysis of the spectral as well as kinetic dynamics and, in general, are very reliable in determining the right relaxation scenario.

The application of the derived criteria to the experimental data provided strong support for the “short-lived $p$-state + slow ground state solvation” relaxation model. Subsequently, a global fit according to this model has been performed on the transient spectra and revealed an ~50-fs lifetime of the excited state. Indirect evidence of such a fast electronic relaxation has also been provided by numerical simulations of the transient spectra in which the actual amplitude and phase of the pump and probe pulses have been used.

According to our current understanding, the relaxation dynamics of the hydrated electron consists of three stages: 1) a rapid, 50-fs depopulation of the excited state, which corresponds to transfer of the energy of ~9500 cm$^{-1}$ to the surrounding water molecules; 2) a slow, 1-ps equilibration of the ground state; and 3) an intermediate phase between the first two phases. Similarly to the behavior of the transient grating signals, reported in Chapter 6, the early delay region of up to about 100 fs is dominated by librational motions of the water molecules, which is manifested by an $\sim \sqrt{2}$ difference in the time scales for H$_2$O and D$_2$O. The energy released to the solvent by the ground state thermalisation amounts to ~1/3 of the initial $s$–$p$ transition energy. The features of pump–probe spectra in the range of delays from zero to 60 fs suggest the presence of a short-lived excited state absorption to a higher lying state or to the continuum band. The disappearance of this contribution at delays longer than 60 fs is fully consistent with the rapid depopulation of the first excited state.

A practical method for the inversion of the potential energy gap between the ground- and the excited- state potential has been proposed and applied to the experimental data. This procedure resulted in the reconstruction of the $s$–$p$ energy gap as a function of the generalized solvent coordinate. As has been suggested in the interpretation of our kinetic data, this generalized coordinate represents a passage between, at first, a mostly librational to a mostly translational coordinate later on. This enabled us to produce a tentative multidimensional picture of the energy relaxation that takes place upon a photo-excitation of the hydrated electron. In the proposed model, a gradual transition between the two modes of the electron-to-solvent energy transfer has been put forward. The first mode determined by the collective librations of the water molecules, accounts for the highest excess energy loss on a sub-100-fs time scale. It is progressively superceded by the second mode, described by collective translations of the water molecules, which is responsible for the dissipation of the accumulated local heat. In the proposed explanation, the return of the hydrated electron to its
equilibrium state at times longer than 300 fs can be described almost purely by a propagation along the translational coordinate. The model consistently accounts for all time scales and transition frequency changes observed in the pump–probe (Chapter 7) and transient-grating (Chapter 6) experiments.

Appendix I: Modulation of pump–probe spectra

The pump–probe spectra in Fig.7.7 at early delays (up to 120 fs) exhibit a certain amount of modulation, which subsequently disappears. Here, to explain this phenomenon, we perform a calculation of the transient spectra according to the complete expressions given by Eqs.(5.6) and (5.21, 5.22). To avoid the problem with the evolution of the excited state contribution after excitation, we now consider the transient spectrum at zero pump–probe delay (Fig.7.16, solid points). In this particular case, the contribution of the ground state bleach and stimulated emission from the excited state are exactly identical. Thereupon, we utilize the expression of the third-order susceptibility, given by Eq.(5.17) to describe both the “hole” in of the ground state and the “particle” in the excited state. We further employ the value of $T_2=1.6$ fs, derived in Section 6.3.2, and $T_1=50$ fs, which follows from the fit of transient spectra in Section 7.3.2. The difference absorption contour computed, using the actual spectrum and the phase of the 5-fs pulses, is depicted in Fig.7.16 by solid curve.

A good overlap with the measured data (solid points) is achieved upon shifting the computed spectrum by the amount shown by the dashed line. The reason for this discrepancy lies, most probably, in the excited state absorption to the continuum band (or another higher-lying excited state). A similar deficit of the positive absorption component that rapidly shifts to the blue causes apparent deviation of the measured transient spectra from their fits, reformed in the two-electronic-state model (Fig.7.7, top panel). Despite the need to account for an additional transient absorption to a higher excited state, our calculations, which employed the $\chi^{(3)}$ of a homogeneously broadened transition, successfully reproduce the fine features of the measured signal.

A modulation of the pump–probe spectrum in the region of pump and probe spectral overlap potentially may, in general, have an entirely different origin, e.g. the one associated with hole-burning of inhomogeneously broadened absorption spectra. Our present simulation of the pump–probe signal in a homogeneously broadened system, however, dismisses this idea. In fact, as has been discussed in Section 5.5, the spectral modulation pattern in our experiments is caused by a very short population lifetime, i.e. $T_1$. 

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**Fig. 7.16**: Simulation of transient spectrum at delay $T=0$ for hydrated electron in heavy water. Solid points show the measured spectrum, while the solid curve presents calculated results shifted up by the level of dashed line. Shaded contour depicts the spectral intensity of the laser pulses.

**Fig. 7.17**: (a) Simulation of transient bleach at delay $T=50$ fs for a homogeneously broadened system with $T_2=50$ fs (solid curve) and $T_2=500$ fs (dashed curve). Shaded contour shows steady-state absorption, or, in other words, the transient bleach spectrum in the case of $\delta$-pulse excitation. (b) Enlarged detail of pump–probe modulation.

To deepen our understanding of the role of $T_1$ in the pump–probe spectra modulation we next perform calculations at a delay where the main bodies of the two pulses are already well separated in time. For the sake of demonstration, we only consider the contribution of the “hole” in the ground state and do not include the input of the excited state. This is
legitimate, since the transient spectra consist of a linear superposition of various contributions. Therefore, the conclusions made on the basis of one selected contribution are applicable to the whole combination as well. The results at the delay value of 50 fs, which corresponds to a homogeneously broadened transition with $T_2=1.6$ fs and with $T_2=50$ fs and $T_2=500$ fs are depicted in Fig. 7.17.

As can be seen from this simulation, the relative size of the surviving modulation in comparison with the magnitude of the overall signal is considerably larger for a short-lived system. Consequently, the modulation seen in the pump–probe spectra of the hydrated electron in Fig. 7.7 at short delays is a direct outcome of the short value of $T_1$. 
References

Ground State Recovery of the Photo-Excited Hydrated Electron

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