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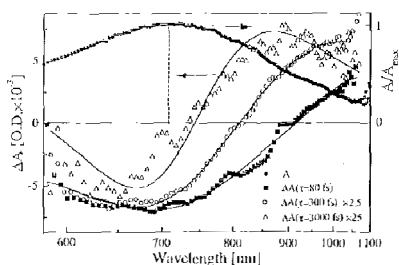
Relaxation dynamics of the hydrated electron studied with 5-fs pulses

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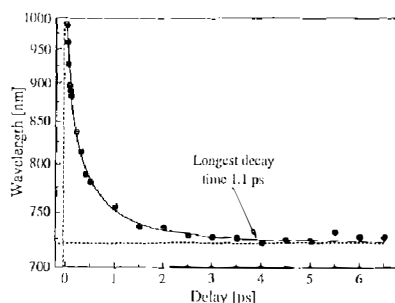
Since its discovery in the early sixties,¹ the hydrated electron has received a continued interest from chemists and physicists alike. Basically, the hydrated electron is an excess electron trapped in a potential well formed by surrounding water molecules, with an *s*-like ground state and three non-degenerate *p*-type excited states.² The electron surrounded by the oriented water molecules is a chemical reactant with an unusually high electron donor capacity as its characteristic chemical feature. On the other hand, it seems to be one of the simplest physical systems to study solvation dynamics and to test mixed quantum-classical theories experimentally. Yet, even after decades of intensive experimentation and calculations on the hydrated electron, understanding of its relaxation dynamics is far from being complete. One of the most important questions is the explanation of an ~ 1 -ps relaxation rate of the photo-excited hydrated electron. This rate has been controversially attributed to the population lifetime of the *p*-state³ or cooling of the ground state after rapid relaxation from the *p*-state.⁴

In this Contribution we present the experimental study of the energy relaxation of the photo-excited hydrated electron. The results of frequency-resolved pump-probe with 5-fs pulses provide sufficient evidence in favor of the hot-ground-state model, outlined above. The initial ultrafast energy relaxation of the photo-excited electron, controlled by the librations of the surrounding water molecules,⁵ takes place during the ~ 50 fs upon the excitation. We show that after the first 100 fs almost the entire population of the *p*-state is transferred to the hot ground state that subsequently cools down on a ps time scale.

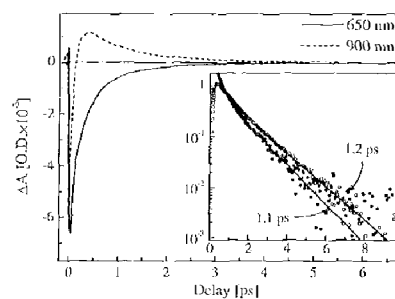
The evolution of the transient absorption spectrum at different pump-probe delays is depicted in Fig. 1. A substantial positive contribution that corresponds to the induced absorption appears at early times. However, this fact alone does not favor any model since the induced absorption may be caused by transitions from the excited *p*-state to continuum. We propose the following method to distinguish the models: One follows the evolution of the wavelength for which $\Delta A = 0$ (zero-crossing point) as a function time (Fig. 2). The longest decay time of this dependence is compared to the longest decays of frequency-resolved transients (Fig. 3). If the former is shorter than the later, then the solvation in the excited state is followed by the population re-



QFB2 Fig. 1. Transient spectra of the hydrated electron obtained at 80 fs (squares), 300 fs (open circles), and 3 ps (open triangles). Solid circles show the absorption spectrum of the equilibrated hydrated electron. Solid curves represent best fits to experimental data, which consists of the ground-state bleach and hot-ground state absorption contributions.



QFB2 Fig. 2. Zero-crossing point as a function of probe and pump delay. Note that its asymptotic value approaches the position of the absorption maximum of fully equilibrated electron (indicated by the dashed horizontal line).



QFB2 Fig. 3. Pump-probe transients at the detection wavelength of 650 nm and 900 nm.

laxation. However, if the two processes have identical decays, we should conclude that the population relaxation is much faster than solvation that takes place in the nonequilibrated ground state.

Our experimental data indicate that the shift of the zero-crossing point in the ΔA signal occurs precisely at the same time scale as detected in the frequency-resolved transients. This corresponds to the movement of the wavepacket down the ground state potential surface with the time of ~ 1 ps. The continuous spectral shift rules out the possibility of a long-lived excited state. Also, the position of zero-crossing in ΔA spectra asymptotically approaches the position of steady-state absorption maximum (Fig. 2). This is a direct prediction by the hot-ground-state model while

in the case of long population lifetime it would be a pure coincidence.

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QFB3

8:30 am

Competition of different ionisation pathways in K_2 investigated by fs pump&probe spectroscopy: experiment and theory

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During the last decade both, experimentalists and theoreticians, began extensively to investigate ultrafast phenomena as wave packet propagation, coherent control, internal vibrational redistribution, structural relaxation and photodissociation in physical, chemical and biological systems. In particular, the wave packet propagation of small molecules as the potassium dimer are studied in great detail.^{1,2} Recent studies of this molecule focused on the ionisation step in ultrafast pump&probe experiments, applying fs-multiphoton ionisation spectroscopy. In these schemes the pump pulse prepares a wave packet in both the $A^1\Sigma_u^+$ and $(2)^1\Pi_g$ state at the inner turning point by means of a one or two-photon process. The delayed probe pulse can transfer the wave packet to an ion state by another two or one-photon process. The generated ions are detected mass-selectively.

We will show, that it is possible to control the transition of the wave packet by changing the applied wavelength of the probe pulse. Two features appear in this context: First the transition pathway can be shifted within the same potential energy surface or, second, in such a way that the ionisation proceeds via different electronic surfaces.

In our investigations on the potassium dimer we used fs-pump&probe spectroscopy in the spectral range of 837 nm and 779 nm. A variety of structures observed (see Fig. 1) reflects the complicated interplay of nuclear dynamics and ionisation processes we will discuss in our report. For the wavelength of 837 nm we find a clear oscillatory structure with a period of ~ 500 fs. The maximum occurs after half a period as was shown in previous experiments at this wavelength.² This indicates an ionisation at the outer turning point. Decreasing the laser wavelength below 816 nm, we find that the peaks of increased ionisation begin to split to form a double peak structure with a slight difference in peak height. This trend is continuous and eventually leads to a frequency