Electron Solvation in Neat Alcohols

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We have performed femtosecond studies of electron solvation in a series of neat linear alcohols. The measured formation time of the solvated electron is consistent with previous studies using solutes. The major character of electron solvation, i.e. the two-state character, is evidenced by the finding of an approximate isosbestic wavelength for methanol at 750 nm. Isotope effects for CH_3OH, CH_3OD, and CD_3OD as well as chain length effects in slowing the solvation dynamics are attributed to hydroxyl librational and translational motions of the alcohol molecules that form the electron cavity. A slower process was also observed, which is attributed to the cooling of the solvated electron as it "vibrationally" relaxes in the ground electron state. In addition to electrons, an ultrafast transient at early times is clearly resolved, this transient species is attributed to either the neutral excited state or the cation of the alcohol.

I. Introduction

The understanding of electron localization and solvation in liquids is a fundamental problem in the chemistry and physics of condensed phases.[1] The solvation dynamics of electrons in water has been the subject of considerable theoretical and experimental interest in the last few years.[2–14] These studies have revealed the importance of nonadiabatic relaxation in the electron solvation process in water, where the observed electron solvation dynamics can be viewed as transitions from the lowest p-like excited state to the s-like ground state of the electron. To examine the universality of these characteristics of electron solvation, it is important to compare the electron solvation dynamics in water with the dynamics in other liquids such as alcohols.

Early studies on electron solvation in alcohols were done using picosecond time-resolved techniques.[15–17] The studies have evoked much controversy about the real nature of electron solvation in alcohols. Results showing the correlation between the electron solvation time τ_s and the monomer alcohol molecule rotation time τ_{D2} have led to the dielectric relaxation picture of electron solvation.[18,19] On the other hand, the similarity between the formation time of the equilibrium visible absorption band and the decay time of the initial near IR absorption band has been considered as evidence of a stepwise two-state process in the electron solvation dynamics. These two mechanisms are qualitatively different.

The experiments presented here are a femtosecond study of electron solvation in neat alcohols. The results show that the wet electron, i.e. the precursor species of the solvated electron, is similar to the wet electron found in water.[2] The two-state character of electron solvation is established by the presence of an approximate isosbestic wavelength in methanol at 750 nm. In addition to the major stepwise feature of electron solvation, a slower relaxation process, which may be ground state cooling, is also suggested by our data. The existence of this slow component in the solvation dynamics is consistent with the interpretations of the experiments using a 625 nm pump done by C. Pepin et al.[20] and the three pulse experiments of Barbara and co-workers.[21] The dependence of solvation times on the alcohol chain length and isotope substitutions has also been examined to explore possible effects of hydroxyl librational motions and translational motions on the dynamics. A transient species, which is attributed to either an alcohol cation or an excited state of the neutral alcohol molecule, was observed in our experiments.

II. Experimental Section

The experiments reported here were transient absorption measurements using an amplified colliding pulse mode-locked dye laser operating at 10 Hz, 625 nm, and 300 μJ/pulse. The 312.5 nm pump pulses were generated by frequency doubling the 625 nm fundamental light with a 200 μm BBO crystal. The probe beam was either a small fraction of the fundamental beam or part of a continuum pulse produced in a 1 cm path length cell of D_2O. The fundamental pulse width was found to be 80 fs from autocorrelation measurements; the UV pump pulse width and the probe pulse width other than 625 nm were 150 fs and 170 fs, respectively, as determined from cross correlation measurements. The UV pump intensity in the sample cell was 4×10^{12} W/cm^2. In order to minimize group velocity dispersion between the pump and the probe, a 200 μm cuvette was used in the experiments. A long sample cell, for sample 5 mm,[20] will make the system response significantly slower and distort the system response function from the original shape of the laser pulse.

Alcohols were purchased from Aldrich (HPLC grade). Before use, the alcohols were distilled over Mg and were stored over cleaned and activated 4 Å molecular sieves. The experiments were performed at ambient room temperature, 21 °C.

III. Results and Discussion

A. Electron Solvation Dynamics in Methanol. Previous studies in alcohols have suggested that the solvation dynamics involved two states.[15] However the evidence for the two-state mechanism of electron solvation in alcohols is not conclusive and the solvation mechanism remains in controversy. A simple way to test the validity of this model is to search for an isosbestic wavelength, as was done in studies of electron solvation in neat water.[2] The isosbestic wavelength is the wavelength where the

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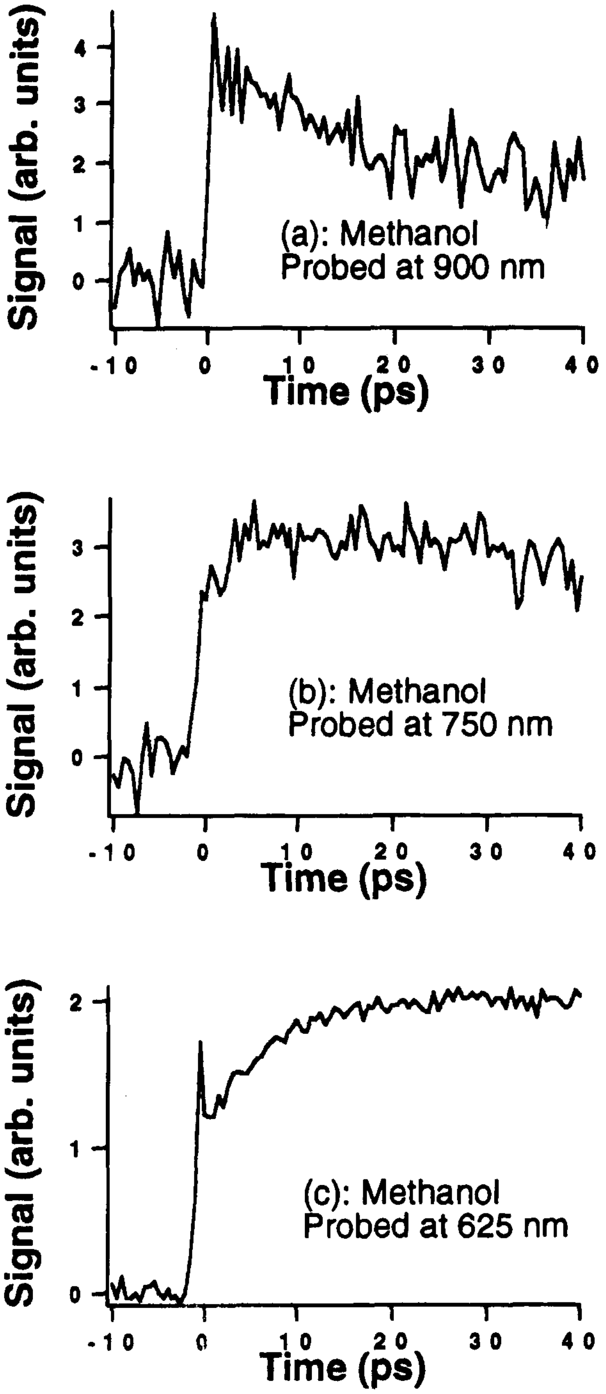

Figure 1. Wavelength dependence of the electron solvation dynamics in methanol.

wet and the solvated electron hae the same absorption coefficients. At the isosbestic wavelength, the time dependent absorption is only related to the total number of wet electrons and solvated electrons, which is conserved if other dynamic processes such as geminate recombination are not taking place on the same time scale. Therefore at the isosbestic wavelength, the absorption appears constant in time after the formation of the wet electrons.

Representative data at different probe wavelengths for the electron solvation dynamics in neat methanol are shown in Figure 1. At wavelengths shorter than 750 nm, an increase in the signal is observed due to the formation of the solvated electron, while the signal decreases at longer probe wavelengths due to the decay of the wet electron population. This behavior is a consequence of the fact that the wet electron absorbs more strongly than the solvated electron in the IR region. At 750 nm, the absorption signal appears flat for about 10 ps after the formation of wet electrons, which implies that the absorption coefficients of the wet electron and the newly formed solvated electron are equal at this probe wavelength. This is an indication of an isosbestic wavelength. The successful observation of this isosbestic wavelength relies on the fact that there is a good time scale separation between electron solvation and other dynamic processes such as geminate recombination and possible ground state relaxation. In addition to the observation of dynamics that shows isosbestic wavelength characteristics at 750 nm, a slow decay of the absorption signal at longer times is also observed. This slow decay cannot be due to geminate recombination because it is not observed at 625 or 550 nm probe wavelengths. Imperfect location of the isosbestic wavelength at 750 nm cannot account for it either, since similar decay is observed at the 720 nm probe wavelength after the slow rise of the absorption due to the formation of the solvated electron. In analogy to electronic and vibrational relaxation of molecules in liquids, one of the possible mechanisms which can account for this slow decay is the "vibrational cooling" of the solvent.[22] For the electron, either a dielectric relaxation or a solvent cooling would produce a blue shift in the absorption spectra as the solvent relaxes, similar to what is suggested in other experimental results.[20,21] Whether the slow component of ground state cooling can be observed depends on the probe wavelength used. If the probe wavelength is at the far red end of the solvated electron absorption maximum, both the formation of solvated electrons and the cooling of the ground state result in a decrease of absorption. In contrast, if the probe wavelength is at the blue end of the solvated electron absorption maximum, then both the formation of solvated electrons and the cooling of the electron in the ground state lead to an increase of absorption. Therefore, it is hard to resolve the slow component for these two cases, because the formation of the solvated electron dominates the change of signal and obscures the slow component. However when the probe wavelength lies between the isosbestic wavelength and the solvated electron absorption maximum, we have the situation where the formation of solvated electrons causes an increase of absorption and the cooling of the ground state causes a decrease of absorption, thereby allowing the slow component to be more readily observed. To satisfy this requirement, we have measured the kinetics at 720 nm, which is between the isosbestic wavelength at 750 nm and the maximum of the equilibrium solvated electron absorption at 630 nm.[23] Simple data fitting gives the decay rate of the slow component to be $(40 \pm 8)^{-1}$ ps^{-1}, which is on the time scale for the cooling of vibrationally hot molecules in liquids.[22] The spike at $t = 0$ is an ultrafast transient species, which will be discussed in section C.

In a strict sense, the observed isosbestic wavelength at 750 nm is only an approximate isosbestic wavelength because of the ground state cooling. However, the existence of this approximate isosbestic wavelength in the dynamics is significant in that it provides strong experimental evidence that the transition between the wet electron and the solvated electron involves only two electronic states. The cooling on the ground state surface corresponds to the "vibrational" relaxation of the solvated electron. It is important that no significant geminate recombination of the solvated electron is seen in methanol on this time scale with the 312.5 nm pump at an intenstiy level of 4×10^{12} W/cm^2. With the longer wavelength pump, the approximate isosbestic wavelength may be obscured due to a decrease in the electron separation from the methanol cation and consequently an increase in the geminate recombination rate.[20] The dependence of electron geminate recombination on the excitation wavelength originates from different electron generation mechanisms. The recent experiments of Zhang et al. showed that geminate recombination of electrons produced through direct ionization of water molecules was extremely slow,[24] in contrast to previously observed much faster geminate recombination of electrons which were partly produced through excited water molecules.[2] In methanol, the threshold for electron generation is 4.7 eV,[25] and the theoretically estimated vertical ionization potential is about 7.6 eV.[25,26] Therefore, electrons produced by a two-photon process or a three-photon process using a 4.0 eV laser pulse can go directly to the conduction band of the solvent, while electrons produced a three-photon process using a 2.0 eV laser pulse are generated indirectly through the excited states of methanol molecules. Because the kinetic energy available to the indirectly generated electron is less than that from the direct photoionization pathway, due to the involvement of nuclear motions of the excited molecules during the electron generation process, the injected electrons are closer to their parent fragments and thus undergo faster geminate recombination similar to what we have observed in water. Within our experimental error, the signal decay rate observed at 900 nm is found to be the same as the signal rise rate at 625 or 550 nm after an initial transient absorption. This observation supports the description of electron solvation dynamics as being essentially two-state. The formation time of the wet electron cannot be accurately determined from our experiments because of the interference from the transient species at early times; it can only be estimated to be 1 ps or less.

The absorption spectra of the solvated electron in methanol are well-characterized.[23] When the signal at early times at each wavelength is compared to the absorption at longer times, which is totally due to the solvated electron, it can be seen that the wet electron spectrum will have a blue tail extending out past 2.5 eV. This indicates the presence of a very localized electron at early times. The accurate absorption spectrum of the wet electron is difficult to obtain because of the interference from the transient species at early times and possible direct formation of the solvated electron from electron states that lie above the wet electron state.[10]

It is worth mentioning the recent experimental results of Barbara et al. on electron solvation in water and alcohols using a three-pulse scheme.[21,27] In their experiments, a UV "synthesis pulse" first generates solvated electrons by multiphoton processes, followed by a near IR pulse which is delayed by several nanoseconds to allow for equilibration. The near infrared pump pulse excites the electrons from the s-like ground state to the p-like excited state, followed in time by a third probe pulse to monitor the spectral dynamics. The results of their three-pulse experiments are consistent with our observations in two-pulse experiments in water and alcohols.[2] Of course, the detailed dynamics observed in two-pulse and three-pulse experiments can be different due to different physical situations. In two-pulse experiments, the newly generated electrons see a "natural" solvent molecular organization as its initial environment, and the following dynamics carry the information on how the created nonequilibrium electron−solvent configurations relax to the final equilibrium electron−solvent configurations. In three-pulse experiments, the p-like excited state electrons see a solvent configuration which is optimized for the equilibrium ground state. In other words, the created wet electrons experience more nuclear polarization at the creation instant in three-pulse experiments than those produced in two-pulse experiments. Although the adiabatic relaxation of electrons on the wet electron potential can be very fast, as indicated in simulations which put an electron in a natural water structure initially to simulate the two-pulse experiments,[9] the adiabatic relaxation of wet electrons on the wet electron potential in three-pulse experiments could differ, because the initial position of the wet electron on the potential curve is different. This possibility was suggested in a recent simulation of Rossky et al., which put an electron in a solvent configuration optimized for solvated electrons.[28] In addition, the observed dynamics in three-pulse experiments can be complicated by the relaxation on the ground state surface as well as the excited state surface.

B. Electron Solvation Dynamics in Isotope-Substituted Methanols and Other Alcohols. To further understand the electron solvation process and in particular identify important molecular motions in the nonradiative transition process,[9,10,12,13] we have done experiments on electron solvation on isotope-substituted methanols. The intermolecular vibrational modes (translations) of the alcohol molecules making up the electron cavity and the librational modes of the OH groups of the cavity alcohol molecules can contribute to the change in cavity size and shape associated with achieving the optimum solvent configuration for the transition from the excited to the ground electronic surface of the solvated electron. Recent simulations of nonadiabatic relaxation of electrons in water using both rigid water and flexible water suggest the possible importance of these motions in the solvation process.[10,12,28] In these simulations, it was found that the excited state lifetime is about 1 ps for the rigid water solvent and 120−240 fs for the flexible water solvent. By isotopically substituting the OH group, we can probe OH librational motions, and by changing the mass of the CH_3 group, we can examine the contribution of translational modes to the electron solvation dynamics (Figure 2). From the kinetic experiments we found that the solvation time increases from 7.1 ± 0.3 ps for CH_3OH to 8.8 ± 0.3 ps for CH_3OD, pointing to the participation of librational modes in the relaxation process. We also observed a small but real increase in solvation time in going from CH_3OD, 8.8 ± 0.3 ps, to CD_3OD, 9.4 ± 0.3 ps. This result indicates that there is a methyl mass effect, which alters the translational motions of the alcohol molecules comprising the electron cavity. The data analysis was based on a standard two-state kinetic model of electron solvation.[2] The rates of solvation were obtained by fitting the data using a single exponential function starting at about 2 ps. A convolution procedure is not necessary in these cases because the solvation times are much longer than our system response times (about 230 fs at fwhm). Since the wet electron formation time is short, the dynamics after 2 ps are essentially the solvated electron formation dynamics from the wet electron. This fact suggests that the observed rate difference in isotope-substituted methanols is due to a kinetic effect rather than a spectral effect. The spectral effect on the rise time is expected to come into play only when the wet electron formation dynamics and the solvated electron formation dynamics cannot be well separated, as it is for the water case. The effects of deuteration can be viewed as slowing the librational and translational motions of the deuterated methanols, thereby increasing the time it takes to achieve those solvent configurations for which the transition from the p-like wet electron state to the s-like ground solvated electron state is most probable. The importance of solvent translational motions in electron relaxation in water was demonstrated recently in simulations by Rossky et al.[29]

In addition to probing the effects of mass on the dynamics, as we have just discussed for the deuterated methanols, we have investigated the dependence of solvation on alcohol chain length by carrying out measurements in the linear alcohols ethanol and

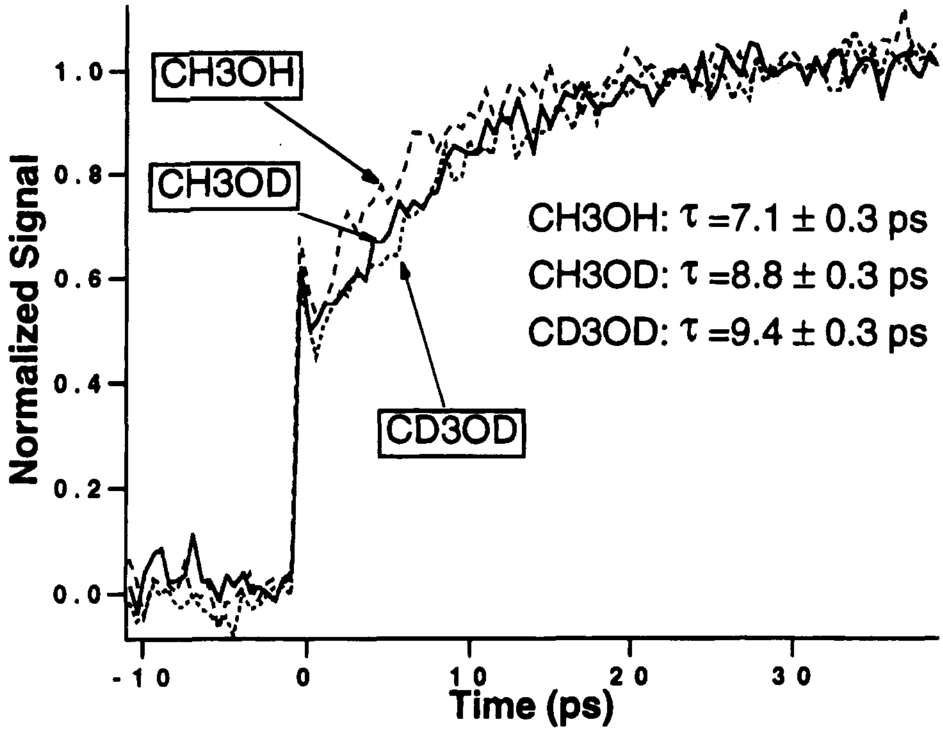

Figure 2. Isotope dependence of the electron solvation dynamics in methanol probed at 625 nm: dashed line, CH_3OH; solid line, CH_3OD; dotted line, CD_3OD.

butanol (Figure 3). The formation times of the solvated electron in the three linear alcohols were obtained at 625 nm and found to be 7.1 ± 0.3 ps in methanol, 15 ± 1 ps in ethanol, and 33 ± 3 ps in butanol. We attribute the reduction of solvation rates in the longer chain linear alcohols to the decreased frequencies of intermolecular vibrational modes due to the increase in the mass and the moments of inertia of the cavity molecules. Because of these slower cavity motions for the heavier alcohols, it takes longer to achieve those solvent configurations for which the transition is most probable from the wet electron state (excited state) to the solvated electron state (ground state). The solvation time obtained is consistent with previous measurements of electron solvation in alcohols using other methods of electron generation such as photoionization of a solute molecule.[15-17] The agreement obtained using a solute molecule in an alcohol solvent and the neat solvent used in the present study is significant because it suggests that perturbations of the solvent by a solute are not very important in the formation of the solvated electron. This is also consistent with the lack of geminate recombination seen in methanol and ethanol on this time scale. Since no geminate recombination is observed, the thermalization distance of the electron is most likely much greater than the Onsager distance, at which the electron cation interaction energy is equal to kT. The Onsager distance in methanol is approximately 16 Å, assuming a dielectric constant of 33. At these distances, which are large on the length scale of molecules, no strong local solvent perturbations due to a solute or cation would be expected.

C. Ultrafast Transient in Neat Methanol. In Figure 4, typical absorption data with a 625 nm probe from neat methanol are shown. The appearance of an ultrafast transient signal is obvious. This species is prominent at probe wavelengths to the blue of 750 nm. The ultrafast component could be an excited state of neutral methanol or the methanol cation. Both species are expected to be produced by the UV pump pulse. Since the alcohols do not absorb at the pump photon energy of 4.0 eV, we conclude that the photoproduced species are formed by multiphoton processes. From gas phase studies, methanol cations are expected to undergo ultrafast proton transfer reaction with neutral methanols.[30] Analogous to water, excited states of methanol directly dissociate into fragments.[31] Thus both the excited methanol and the methyl cation, if produced, would have very short lifetimes. We note that this transient species was not found to be isotopically sensitive and is also seen in ethanol and butanol. Due to the presence of this transient species, it is difficult to obtain any detailed information about the electron solvation dynamics or spectra change at the very early times. More work is needed before a more positive spectral identification of this transient species can be made.

IV. Summary

We have performed femtosecond time-resolved studies of electrons in neat alcohols using a 4.0 eV pump and a continuum-generated visible probe source. We find that the electron solvation can be characterized by a stepwise transition from an excited state of the electron in its solvent cavity, commonly referred to as the wet electron, to the ground state of the electron, commonly referred to as the solvated electron. The evidence for an essentially two-state solvation process was the demonstration of an isosbestic wavelength at 750 nm in methanol. Following the nonadiabatic transition from the lowest excited state to the ground state, the newly formed solvated electron undergoes a ground state cooling process. In methanol the transition from the excited state surface to the ground state surface occurs in 7.1 ± 0.3 ps followed by a "vibrational" cooling relaxation in the ground electronic state of 40 ± 8 ps. From deuteration experiments on methanol we have obtained evidence for the participation of hydroxyl librational modes in the wet to solvated electron transition. The dynamics for CH_3-OD was 8.8 ± 0.3 ps, compared with 7.1 ± 0.3 ps for CH_3OH. We also found an increase in solvation time in going from CH_3-OD (8.8 ± 03 ps) to CD_3OD (9.4 ± 0.3 ps), indicating that there is a methyl mass effect, which alters the translational motions of the cavity alcohol molecules. An increase in the solvation time was also found for the longer chain alcohols,

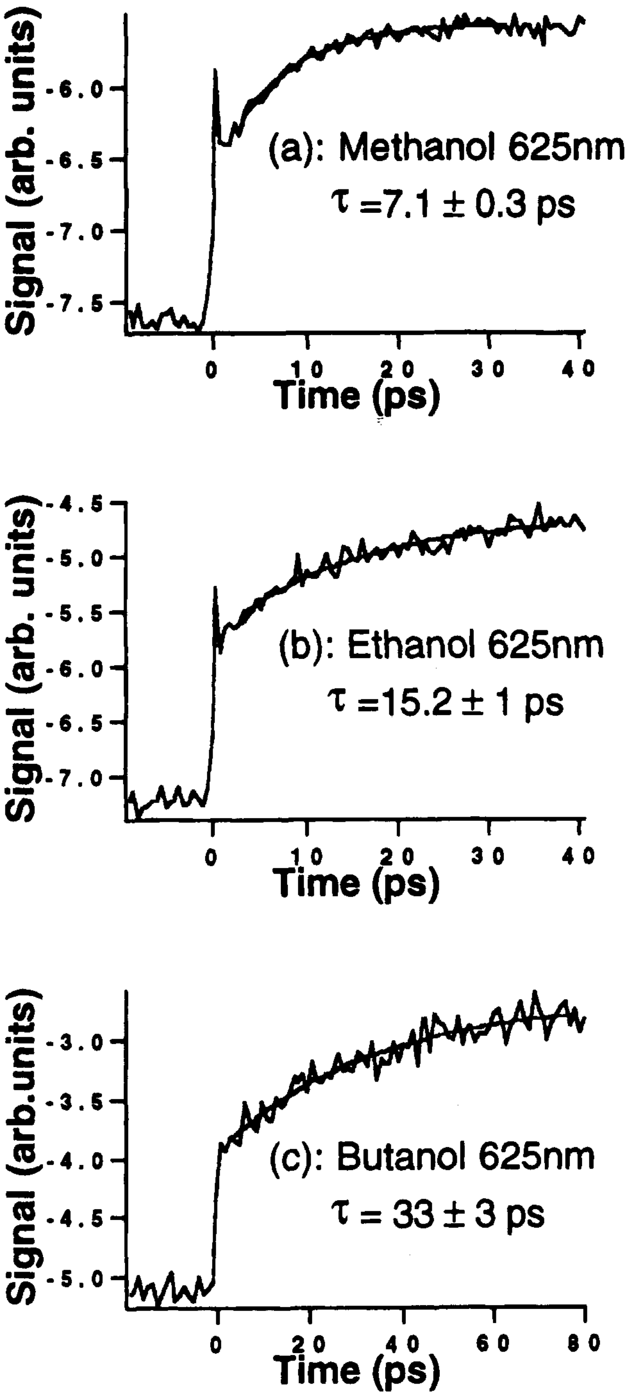

Figure 3. (a) Electron solvation dynamics in neat methanol, probed at 625 nm. (b and c) Electron solvation in ethanol and butanol, probed at 625 nm. The ultrafast transient is not seen in butanol because the time step used was too large to capture the transient signal. It can be resolved using a smaller time step.

ethanol (15 ± 1 ps) and butanol (33 ± 3 ps). The effects of deuteration and the increased mass of the longer chain alcohols can be viewed as slowing the librational and translational motions of the alcohol cavity molecules, which increases the time it takes for them to achieve those configurations for which the nonadiabatic transition is most probable.

In addition to the electron absorption, an ultrafast transient absorption is seen with a visible probe. This species could be the alcohol cation or the neutral excited state of the alcohol, both of which are expected to have very short lifetimes. No geminate recombination of the solvated electron was observed in methanol and ethanol on the electron solvation time scale.

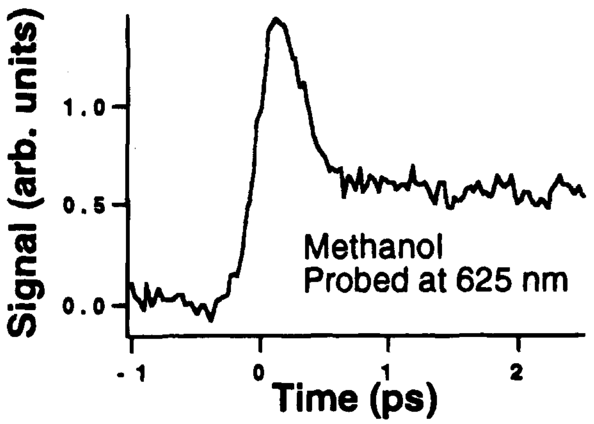

Figure 4. Ultrafast transient in neat methanol measured at 625 nm.

A further result of interest was the observation that the formation time of the solvated electron obtained in this study on neat alcohols was quantitatively consistent with previous studies of electron solvation using low ionization potential organic solutes or highly energy electron beams. This result suggests that the final step in the solvation process is not strongly influenced by different initial conditions of the quasi-free electron.

From these time dependent experiments on alcohols and earlier experiments and calculations on water, we conclude that the model of electron solvation dynamics as an internal conversion process from the first excited state surface to the ground state surface may be quite general for hydrogen-bonding liquids and perhaps for polar liquids in general.

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