PICOSECOND LASER STUDIES OF ELECTRON SOLVATION IN ALCOHOLS

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We report the direct measurement of electron solvation times in methanol and ethanol. A picosecond technique utilizing a laser-triggered flash lamp and a streak camera is used to monitor the solvation process. The relationship of the solvation dynamics to dielectric relaxation, local heating, and pulse-radiolysis results are presented

1. Introduction

When low-energy excess electrons are injected into a polar fluid [1,2], they become rapidly thermalized. These thermalized electrons are initially localized in shallow potential wells formed by the surrounding solvent molecules. They are called trapped electrons, e_t^-, and are characterized by absorption spectra with maxima in the infrared, a narrow ESR line, and a sudden drop in mobility. In the absence of a reactive chemical channel, the surrounding solvent dipoles reorient themselves about the electron, deepening the potential well and leading to the formation of the solvated electron, e_s^-. Solvated electrons are characterized by absorption spectra with maxima in the visible and a broadened ESR line.

The absorption spectral changes taking place during the solvation process have been followed experimentally by pulse radiolysis [3–5]. It was first observed [3] in cold alcohols that an initial IR absorption gradually shifted into the characteristic visible e_s^- absorption band. Subsequent room-temperature picosecond pulse-radiolysis data [4,5] shows that the decay of the trapped electron at 1300 nm correlates with the growth of the solvated electron at 600 nm. The solvation rate decreases as the alcohol viscosity increases since the molecular motions involved in the solvation process slow down.

In this communication we report preliminary results

of the direct measurement of electron solvation in methanol and ethanol, the relationship of the solvation dynamics to dielectric relaxation, and a comparison of our work with pulse-radiolysis results. In the work reported here the electrons are generated in the liquids by the method of laser two-photon ionization of the solute molecules. Although picosecond laser spectroscopy has been used to measure the electron solvation rate in water [6], it was found in that pioneering study that the solvation process was completed within the laser pulse width. The work reported here is the first picosecond laser study on electron solvation in liquids which is not pulse-width limited and thereby enables us to extract the solvation rate constants.

The formation of the solvated electron is monitored by the use of a laser-triggered flash lamp and picosecond streak camera. This technique is quite different from the variable delay and transmission echelon techniques which utilize one or more laser probe pulses [6]. These latter techniques require many laser shots in order to yield the time-dependent absorption profile, whereas in our method the continuous time absorption is obtained in one laser shot. In addition, complications due to coherent interactions [7] between laser pulses at early times do not occur. It is also worthwhile to note the potential use of this system to obtain both time and wavelength dependences of the transient absorption signal in one laser shot.

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2. Experimental

The schematic of the experimental apparatus is shown in fig. 1. A mode-locked Nd^{3+}—phosphate glass oscillator generates a pulse train from which a single TEM_{00} pulse is extracted and amplified to an energy of ≈ 15 mJ. The amplified 1054 nm pulse is then frequency doubled in a KD^*P crystal to generate a green pulse at 527 nm. Further mixing of the 1054 nm and 527 nm pulses in an ADP crystal generates a UV pulse at 351 nm. In this work the UV pulse is used for excitation and the green pulse is used both to monitor the pulse width, generally 6—8 ps and as a signal averaging marker. The relative delay of the two pulses is adjusted so that the green pulse is ahead of the UV pulse by about 50 ps.

The Imacon streak camera is coupled to an intensifier. The signal is digitized by a PAR optical multichannel analyzer which is interfaced to a Digital Minc computer and a Kennedy 9000 tape drive. Time resolution of the streak camera—OMA system is 5 ps. Streak speed is calibrated with an etalon. Linearity of the intensity response is checked in every experiment and

the curvature introduced by the streak camera—OMA response function is corrected in each shot.

The transient absorption is monitored by a laser-triggered flash lamp. This flash lamp is a modified version of the laser-triggered spark gap previously used for electro-optic switching [8,9]. The output flash has a fwhm of about 100 ns and a rise time of 10 ns. This probe pulse is collimated and focused onto the sample cell overlapping with the excitation UV pulse. After the sample cell the probe pulse, now containing information about the transient absorption change, is collimated again and focused into the streak camera. The probe wavelength is selected with a monochromator or narrow-band filters. The timing between the triggering of the flash lamp and the streak camera is adjusted so that the streak camera starts sweeping after the probe flash reaches its plateau. The construction details and performance data of this flash lamp will appear elsewhere.

The observed absorption signal is the convolution of the absorption signal, the laser pulse width, and the resolution function of the streak camera—OMA system. The solvation time is extracted by an iterative convolu-
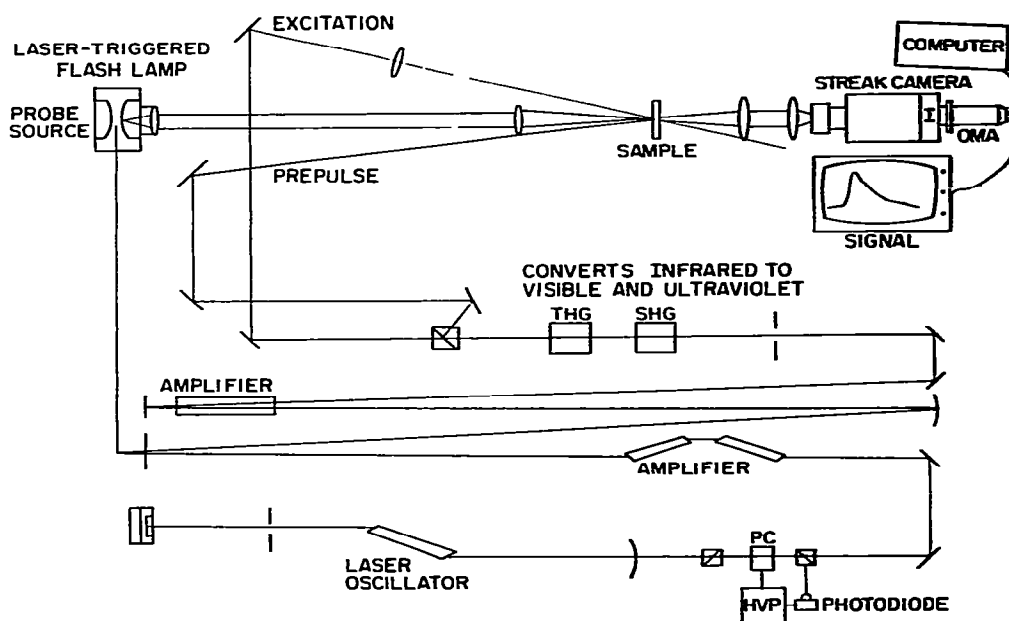

Fig 1. Schematic of experimental apparatus PC: Pockells cell. SHG. second-harmonic generating crystal. THG: third-harmonic generating crystal.

tion yielding the best least-squares fit of theoretical curve with experimental points.

All experiments were carried out at 20°C. The pyrene (Aldrich Chemical Co.) was purified by recrystallization and vacuum sublimation. The alcohols were distilled before each experiment.

3. Results and discussion

Solutions of pyrene in methanol and ethanol (2 5 X 10^{-2} M) are irradiated by a 351 nm picosecond laser pulse. Electrons are produced in the alcohols through the two-photon ionization process [10]

$$Py + 2h\nu \rightarrow Py^+ + e^-. \tag{1}$$

Subsequently the electrons are trapped in the potential wells formed by the surrounding solvent molecules and ultimately become solvated electrons

$$e^- \rightarrow e_t^- \rightarrow e_s^-. \tag{2}$$
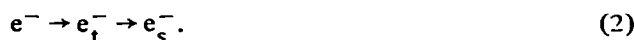
Since the trapping step is much faster than the solvation step [4] the formation of e_s^- should be exponential in time. In fig. 2 we show the growth of solvated

electrons monitored at 600 nm in methanol. The growth curves are best fit with exponentials having rise times of 17 ps in methanol and 26 ps in ethanol. The standard deviation of the theoretical from the experimental curves is 4% in methanol and 6% in ethanol. There is also a 5% maximum variation in sweep speed at the screen center of the streak camera. The overall uncertainty in our solvation times can therefore be safely estimated as being less than the 20% listed in table 1.

Control experiments were done to make sure that pyrene excimer fluorescence (emission maximum ≈ 500 nm [11]) was not mixed with the absorption signal. Pyrene radical cation, the other product of photoionization, has an absorption maximum at 450 nm [12] and does not show significant absorption at 600 nm. The $S_1 \rightarrow S_n$ transitions of the pyrene excited singlet state are known to lie above 360 nm [13]. Although the trapped electron has a rather broad absorption spectrum centered in the near IR, it does not extend into the 600 nm regions significantly [4,14]. In conclusion, the absorption signal we observed at 600 nm is due to the solvated electron.

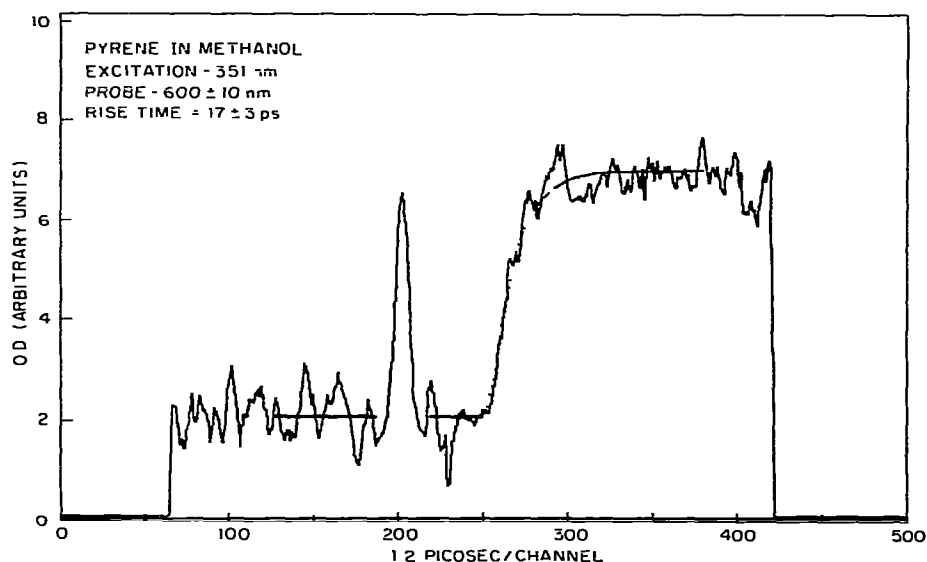In attempting to correlate the electron solvation

PYRENE IN METHANOL
EXCITATION - 351 nm
PROBE - 600 ± 10 nm
RISE TIME = 17 ± 3 ps

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Fig 2. The formation of solvated electron in methanol. Solid curve represents experimental points and broken curve represents theoretical points. The pre-pulse (fwhm is 8 channels) is ahead of the excitation pulse (not shown in the plot) by 52 channels. The data shown here is the average of 10 shots.

Table 1
Picosecond formation times of solvated electrons in alcohols at 293 K

	Solvation times (ps)			Dielectric relaxation times (ps) [a]				
	picosecond laser (this work)	pulse radiolysis		τ_1	τ_2	τ_3	τ'_1	τ'_2
		ref. [4]	ref. [5]					
methanol	17 ± 3	10.7 ± 1		52	13	1.4	9.4	10
ethanol	26 ± 5	23 ± 2	18 ± 2	191	17	1.6	30	13

[a] τ_1, τ_2 and τ_3 are the dielectric relaxation times under constant external field. τ'_1 and τ'_2 are the corrected values of τ_1 and τ_2 according to $\tau'_i = \tau_i \epsilon_{i\infty}/\epsilon_{i0}$. Values of $\epsilon_{i\infty}$ and ϵ_{i0} are either obtained or extrapolated from ref. [16].

times with the dielectric relaxation times of the neat solvent one must consider the possibility that the introduction of an electron into the solvent alters the dielectric relaxation processes [4,15]. Dielectric relaxation times are generally obtained by measuring the response of the system to a weak electric field. In the presence of an electron the dielectric relaxation rate of the solvent can be increased [15]. The corrected dielectric relaxation time, τ', under the constant-charge approximation is given by [15]

$$\tau'_i = \tau_i \epsilon_{i\infty}/\epsilon_{i0}, \qquad i = 1, 2, 3, \tag{3}$$

where τ_i is the ith dielectric relaxation time of the neat liquid in a weak constant field, $\epsilon_{i\infty}$ is the limiting high-frequency dielectric constant of the ith dispersion region [16], and ϵ_{i0} is the limiting low-frequency dielectric constant of the ith dispersion region. In alcohols the τ_i are interpreted as follows: τ_1 is the time required for the breaking of intermolecular hydrogen bonds followed by reorientation of the molecule, τ_2 is the reorientation time of a free monomer, and τ_3 is the reorientation time of OH dipoles [16].

It can be seen that our results (table 1) do not closely agree with any of the dielectric relaxation times, whether constant-field or constant-charge approximation. With our preliminary results we are unable to attribute the solvation process to any one motion, and in fact cannot be certain the process is the same for both ethanol and methanol. Interestingly, the methanol result seems close to τ_2 while the ethanol result is similar to τ'_1. However, the point of the comparison is that electron solvation may not be interpretable in terms of simple dielectric relaxation times. The ranges of validity for the constant-charge and constant-field approximations are not experimentally or theo-

retically clear insofar as electron solvation is concerned. The solvation process may involve rotational motions, translational motions and local structural changes. The relative importance of these processes remains unclear, at least for the alcohols considered here. For a thorough discussion of various models of electron solvation the reader is referred to refs. [1,2,17—22].

At this point the question arises as to why the pulse-radiolysis and laser-photoionization results differ. One clear difference between the two methods is the very large local energy deposition in pulse radiolysis. In this latter method the secondary electrons generated by the incident high-energy electron beam dissipate their energy very rapidly through ionizations and excitations (electronic, vibrational and rotational). The thermalization process typically occurs within 1 ps after the initial ionization [23]. This sudden transfer of electron kinetic energy to vibrational and rotational energy of the surrounding molecules in a sufficiently small region (spur) can cause a jump in the local temperature, accelerate the molecular motions, and thus increase the solvation rate of the electron. The faster solvation rates obtained in pulse radiolysis compared with our results are thus consistent with this local heating model of pulse radiolysis.

By comparing the pulse-radiolysis data with the picosecond-laser data we can make an estimate of the spur temperature. It is found that the pulse-radiolysis data at 261 K in methanol and 277 K in ethanol have the same solvation rates as the corresponding rates measured in our study at 293 K. This implies an "effective" temperature jump of 32 K for methanol and 16 K for ethanol in the pulse-radiolysis experiments. Thus these preliminary studies support the existence of a significant temperature jump in the spur, a point of

lively contention [22,23]. (The result of Kenney-Wallace for ethanol was not used in the comparison since she did not report a temperature-dependence study. Her value, however, implies a greater temperature jump than does that of Chase and Hunt.)

It is interesting to compare our temperature esti-mate to that given by theory. According to Mozumder [23], the initial temperature jump in the pulse-radioly-sis experiment, assuming a spherical spur, relaxes in time and space according to

$$T(r, t) = T_0(1 + 4\delta t/r_0^2)^{-1.5} \exp[-r^2/(r_0^2 + 4\delta t)], \quad (4)$$

where r_0 is the initial spur radius and T_0 is the initial (maximum) temperature jump at the center of the spur. The quantity δ is the thermal diffusivity, defined by

$$\delta = k/\rho C_V, \quad (5)$$

where k is the thermal conductivity, ρ is the density, and C_V is the specific heat at constant volume. The half-life time for the temperature decay at the center of the spur is

$$t_{1/2} = 0.147 r_0^2/\delta, \quad (6)$$

which for methanol is about 11 ps. Therefore processes occurring within 50 ps could be affected considerably.

In order to extract an "effective" temperature jump from the Mozumder theory (to compare with our ex-perimental estimate) we average $T(r, t)$ at the spur cen-ter over the time required for roughly 90% of the solva-tion dynamics to be completed. Assuming the total en-ergy deposited into a 20 Å radius spur to be 30 eV based on the estimates of Magee [24,25] and Mozumder [23] one obtains an "effective" tempera-ture jump of 28 K for methanol and 16 K for ethanol. Our estimates are consistent with these theoretical pre-dictions. However, we emphasize that these theoretical results depend upon the values which one chooses for the spur radius and the amount of energy deposited per spur. The agreement we have obtained thus quali-tatively supports a model of small spur size and signifi-cant temperature rise.

It should be noted that the effects of a local tem-perature jump should be most pronounced for the faster solvation process. This is expected since the local temperature jump relaxes rapidly to the ambient temperature and thus slower processes only experience the higher temperature for a smaller fraction of their

lifetimes. Since theory indicates [eq. (3)] that both T_0 and $t_{1/2}$ are very close for methanol and ethanol we expect a larger effect for methanol, as observed. Using the same arguments we can predict that as the alcohol chain length increases, the solvation times measured by pulse radiolysis and laser photoionization should converge.

We are presently extending our measurements to the longer-chain alcohols as well as to different tem-peratures in order to achieve a better understanding of electron solvation in polar liquids.

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