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Laser Photolysis Studies on the Structure and
Photoexcited States of Solvated Electrons

Final Report

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Abstract

We have completed the assembly of a high powered, Q-switched Ruby laser-dye laser photolysis system in order to make measurements of the solvation times and excited state lifetimes of solvated electrons in alcohols, employing laser saturation spectroscopy.

Preliminary results are reported from laser saturation studies at 694 nm of solvated electrons in ethanol and 2-propanol. The solvated electrons (e_s^-) were generated via the two-photon ionization of selected arenes (such as pyrene) in alcohol at 347 nm. The results are interpreted in terms of a two level saturable absorber and upper limits on the excited state lifetimes of e_s^- are calculated.

Solvation times of e_s^- in long chain alcohols, measured independently in picosecond pulse radiolysis, showed that the time taken for the electron population to reach a fully relaxed, solvated ground state increased as the length of the alcohol chain increased, each e_s^- spectrum exhibiting a significant blue shift during the initial 10^{-10} s.

The implications of the excited state lifetime data, solvation measurements, and trends in the relative G_e values at times $\ll 10^{-9}$ s, will be discussed in the context of electron models. Qualitative conclusions may be drawn on the nature of the electron trapping site and the solvation process in long chain alcohols.

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Introduction

In this research project we set out to investigate the electronic and molecular structure of solvated electrons (e_s^-) with particular reference to excess electrons stabilized in liquid alcohols. Employing the techniques of laser saturation spectroscopy we have attempted to measure excited state lifetimes and have looked for photobleaching effects across the optical absorption band of e_s^- . In addition we have measured the solvation times of electrons localized in long-chain alcohols and some of their isomers. By monitoring the appearance and time-dependent spectral shifts of the characteristic e_s^- optical absorption, observed when electrons are "injected" into the alcohol (either by optical photo-ionization of a solute molecule, or by picosecond pulse radiolysis of the pure solvent), we have obtained data pertinent to both the solvation process and the solvation site.

This final report is divided into four parts, three of which deal with the various stages of experimental progress and new data, including an evaluation of these optical saturation techniques and the implications for future studies in this area, while the fourth and final part presents relevant details on the scientific personnel involved.

The discovery of the hydrated electron in 1962 opened a decade of tremendous theoretical and experimental interest in these new chemical species that gained momentum as excess electrons were found to be stable in a wide range of protic and aprotic solvents. The optical absorption spectra of solvated or trapped electrons share remarkably similar features, and yet the nature of the electronic transitions, the origin of the line broadening and the spectral line shape are issues still to be resolved (1,2,3). Recently we presented evidence (4) for the predominance of short-range, charge-dipole interactions in determining the binding and transition energies of electrons solvated in a series of alcohols and their isomers. This again focused attention on the topographical features of the molecular

solvation site, and so it was in this context that I proposed to examine the electronic and molecular structure of electrons localised in alcohols, for which the spectral data were readily available. Optical saturation techniques, employing pulsed lasers, were chosen as a unique way in which to follow both the rapid solvation of the excess electron, and its' ultrafast; radiationless transitions to the ground solvated state following photoexcitation. Complimentary picosecond pulse radiolysis experiments were conducted to follow the solvation process independently, and to measure the initial solvated electron yields as a function of the "local" dielectric relaxation properties of these liquids.

These solvation time and excited state lifetime data are of great significance to various theoretical models (1,2,3,5,6) of excess electron states, in which the molecular dynamics of the discrete, microscopic trapping sites are now seen to play an important role. These experiments are a strong test of such models, and although at the present stage such an evaluation is by no means complete, these data reveal most interesting trends. It is with this background that we now turn to the details of the project, and to the experimental results that have been achieved so far.

(1) Design and Construction of Laser Systems

The design and construction of this laser saturation spectroscopy apparatus built upon the basic KORAD K1 Q-switched Ruby oscillator. For optical saturation studies, in which relaxation times rather than spectral linewidths are the principal measurements, the four main technical objectives are (1) laser stability, (2) high laser pulse power, (3) high detection sensitivity (signal-to-noise ratio), and (4) a fast time response for the total optoelectronic detection system. I shall cover briefly our experience in reaching each of these objectives. The final layout of the apparatus is shown in Figure 1.

In a well-aligned laser, with a good quality rod, the two main sources of instability arise from fluctuations in the ambient temperature and in the pumping power. The stability or pulse-to-pulse reproducibility of our laser was improved by maintaining the water cooled ruby rod at constant temperature by means of a small heat exchanger, and filtering the water. Charging capacitors, on reaching maximum operating charge usually leak charge (≥ 100 V) in a matter of seconds. Since the energy going to the pumping flash lamps is proportional to $1/2 CV^2$, a drop to 3.85 KV from the operating voltage 4.00 KV leads to a 7% drop in energy, which results in turn in a further non-linear decrease in the power output from the pumping lamp. Thus careful attention to the timing of the charging and firing sequences led to a noticeable improvement in the reproducibility of consecutive pulses, and less drift over extended periods of time. The $\pm 5\%$ pulse reproducibility quoted here refers to the saturation pulse at the end of the delay line. The incident laser pulse was stable to within 5%. We also introduced a sapphire mirror in a micrometer precision mount as the front reflector to increase the alignment sensitivity. All optical components were similarly mounted.

Having optimised the performance of this ruby laser, we obtained 2.1 Joules in a 15 nanosecond (full width half maximum, fwhm) pulse from a 4" x 3/8" rod in a 19" resonant cavity. This represents a peak power output of ~ 140 M Watts. This is a rather high power density (~ 197 M Watts. cm^{-2}) to use safely on a routine basis from this small rod and thus typical operating parameters were chosen as: laser pulse energy of 1.5 Joules yielding 100 M Watts peak power, and a power density of ~ 140 M Watts. cm^{-2} .

Frequency doubling was accomplished initially with a KDP crystal, angle tuned and mounted to our own design; however stability considerations led us to incorporate both index matching fluid and a temperature control into the final device. Under the latter circumstances we obtained typically 100 mJ of light at 347 nm giving doubling efficiencies from 5 to 8% in a 16 mm cube crystal. The frequency-doubling efficiency depends on the power density, the spatial homogeneity and divergence of the fundamental beam, and the length of the non-linear crystal; therefore these efficiencies are quite satisfactory from this minimal length of crystal. Perhaps more relevant is the fact we were able to initiate an adequate number of detectable two-photon ionization events with 100 mJ of 347 nm laser radiation impinging on the liquid sample.

It is instructive, at this point, to look for ways in which the second harmonic power might be increased and thus yield a higher number density of excited or ionised states in these experiments. The second harmonic power $P_{2\omega}$, generated by a single mode, gaussian beam of radius R , power P_ω , and angular frequency ω , incident on a nonlinear crystal of thickness l and second-order, nonlinear susceptibility $X_{2\omega}$, is given by (1):

$$P_{2\omega} = J P_\omega^2 l^2 X_{2\omega}^2 \sin^2 \theta \frac{1}{R} \left\{ \sin\left(\frac{\Delta k l}{2}\right) \right\}^2 \quad (1)$$

where J is constant of the crystal, and θ is the angle between the crystal optic axis and the fundamental beam under phase matching conditions. The latter are met when $\Delta k = 0$, that is

when the refractive indices for the fundamental and harmonic waves are the same. Inspection of equation (1) indicates that, if phase matching is optimized, $P_{2\omega}$ can only be increased by (a) raising the power density in the fundamental beam, either by reducing the beam diameter R (by focusing) or increasing the pumping power to the ruby rod, (b) by using a longer nonlinear crystal, or (c) by exploiting favourable $X_{2\omega}$ values in new classes of crystals, such as CDA. The maximum practical doubling efficiency at room temperature appears to be $\sim 25\%$ for a rubidium dihydrogen phosphate crystal, and this can only be achieved with a pulse from a single-mode, high intensity, diffraction-limited laser beam.

A dye laser was constructed, the design for which is shown in Figure 1, to permit us to monitor photobleaching effects throughout the visible and near infra-red region, and to probe the possible spectral inhomogeneity of the absorption band through intracavity techniques. The dye can be pumped longitudinally or transversely in this dye cell design, and either Brewster-angled or normal optics can be employed. A small telescope was inserted into the resonant cavity in front of the $\lambda/20$ aluminized rear reflector (or holographic grating), and ensured that the power density was well below damage threshold for those optical surfaces. In this way we also attained narrower linewidths, an important requirement for the laser saturation intracavity experiments. The front reflector was a sapphire ($\lambda/10$) window. A flow system was employed to recirculate the dyes. Peak powers (untuned) were from 0.1 to 5 M Watts.

A simple calculation shows that the photon flux in both the fundamental ruby beam and in the output from the dye laser is more than adequate for saturation experiments, for which the photon density must be greater than, or equal to, the density of saturable absorbers. A 15 nanosecond (fwhm) ruby laser pulse of 1.5 J energy in a $3/8$ " diameter beam is equivalent to a flux of $\sim 5 \times 10^{26}$ photons $\text{cm}^{-2} \text{sec}^{-1}$. This is $\sim 5 \times 10^{18}$ photons per pulse and means that we can reach a number density of absorbing species up to $\sim 10^{18} \text{cm}^{-3}$ before any uncertainty arises about

saturation conditions. A concentration of solvated electrons of 10^{-5} M yields $\sim 6 \times 10^{15}$ molecules. cm^{-2} of absorbing species along a 1 cm pathlength cell, and thus we will have an approximate ratio photon/ e_s^- of 1000:1, which ensures each absorber will be photoexcited many times during the pulse. However, this is an idealized and maximum value, since it does not take into account reflection and transmission losses along the optical delay lines. The flux at the sample position was 2×10^{26} photons. $\text{cm}^2.\text{sec}^{-1}$. This represents about a 40% transmission efficiency since, in this particular case, the initial pulse energy was 1.24 J, as measured after the ruby laser pulse had passed through the KDP crystal. In the experiments reported here in section (2), the average saturation photon flux was $\geq 10^{26}$ photons. $\text{cm}^{-2}.\text{sec}^{-1}$ and the photon/ e_s^- ratios ranged from 10^3 to 10.

The optical delay line initially comprised three quartz prisms at positions a, b and c; however in later experiments two coated spherical mirrors were introduced at b and c to attempt to increase the transmission efficiency of the line and counteract the beam divergence. Figure 2(a) shows two clearly resolved laser pulses, the first is ruby light scattered at the sample position during the initial photolysis of the sample, the second is the arrival of the saturating pulse some 30 nanoseconds later. Only the time separation of the peaks (not their relative amplitudes) is important as a calibration, and this can be varied by changing the length of the optical delay line.

The detection system comprised an ITT (S20) biplanar photodiode biased at 1 KV and coupled through 50Ω to a Tektronix 475 ($>200 \text{ MHz}$) oscilloscope. The limiting response time of ≤ 2 nanoseconds was governed by the oscilloscope which was triggered externally by scattered light picked up by a HP 4207 photodiode close to the front reflector. A second HP 4207 photodiode measured the attenuated laser output from the rear reflector of the laser cavity and fed this information

into a second channel on the oscilloscope for simultaneous display. In this way we monitored the pulse-to-pulse reproducibility for each experiment. The detection system was checked for linearity of response and scattered light reduced to a minimum by employing a J-Y holographic monochromator and narrow band pass filters where appropriate. The fundamental laser beam was attenuated by placing saturated solutions of CuSO_4 in 1 cm quartz cells in the laser beam. These chemical attenuators were checked for spurious photobleaching effects, but proved quite reliable under the highest photon fluxes we could generate from the ruby laser.

The formation and decay of e_s^- was monitored at 632.8 nm by passing a He-Ne (CW) laser beam through the sample cell and onto the slits of the monochromator. A RCA 1P28 photomultiplier was employed on occasion for continuous monitoring of this beam while the ITT simultaneously sampled the ruby laser pulse. As a consequence of this double monitoring technique the self-absorption effects (see section (2)) were finally understood.

(2) Results from Laser Saturation Experiments

The preliminary photoexcitation measurements were carried out on the hydrated electron generated by two photon photoionization of 5×10^{-4} M pyrene (at 347 nm) in 0.05M aqueous sodium dodecylsulphate solution. The absorbance of e_{aq}^- in a 1 cm cell was 0.63 at 694.3nm. The half-life of the e_{aq}^- decay was ~ 200 nsecs and so there would be no loss of e_{aq}^- by virtue of reaction during the laser pulse. The $[e_{aq}^-]$ of 2.8×10^{-5} M was equivalent to a number density of $1.7 \times 10^{16} \text{ cm}^{-2}$, and thus the photon/ e_s^- ratio was approximately 10^2 .

(a) Initial Observations

Under a low photon flux the linear absorbance of the solution was 0.6 at the ruby wavelength. Under a saturating photon flux the absorbance increased to 0.8. This effect was entirely reproducible in the experimental design shown in Fig. 1, and implies that under saturating conditions more ground state species are available to absorb - in contrast to the anticipated depletion of the ground state and hence decreased absorbance of the sample. These observations puzzled us for some time and could not be assigned to any optical misalignment or detection artifact. However the origin of the effect became clear when it was noted that, in the presence of a saturable absorber in the sample cell, the saturation laser pulse was already significantly diminished before it was transmitted along the optical delay line.

The explanation of our observations is as follows, and is an important point for the design of future saturation experiments. The fundamental (694 nm) and frequency doubled (347 nm) laser pulses emerge coaxially from the KDP crystal and simultaneously traverse the absorbing sample of pyrene/solvent. The leading edge of the 347 nm pulse induces two-photon photoionization events in the pyrene from which e_s^- are created rapidly in the solvent. Solvation of a "free" electron occurs on the time scale 10^{-11} to 10^{-10} s for the solvents in

question. Those e_s^- generated during the early part of the "photoionization" pulse now undergo photoexcitation and conceivably saturation during the remainder of the 694 nm pulse to which they are being simultaneously exposed. Hence the fundamental pulse emerging from the sample (and entering the optical delay line) will be markedly reduced in amplitude due to absorption by e_s^- created by the 347 nm pulse.

Since there is a sharp time-dependent concentration of e_s^- due to the sensitive dependence of the two-photon cross section on the incident (347 nm) light intensity, there is also a time-dependent absorbance of the solution of e_s^- at 694 nm. It is not necessarily the case that the criteria for saturation and the photostationary state approximation are valid throughout the pulse duration. Of course some 347 nm light will also be reabsorbed by long-lived e_s^- .

The 694 nm pulse emerging from the sample is thus a convolution of several time-dependent processes, electron solvation, photoexcitation, saturation and relaxation back to the ground electronic state, at that wavelength.

(b) Optical Saturation Results

Presumably attempts could be made to deconvolute the above pulse shape by developing a set of coupled differential equations, each describing the relevant process and varying parameters to fit the experimental pulse shape. However, since the rate of relaxation is the unknown parameter we are attempting to measure in these experiments, but is not the only unknown in this "reabsorption" phenomenon, it seemed more constructive to redesign the saturation experiments. (This effect could be exploited perhaps in alternative experiments.) A quartz flat, transmitting at 347 nm but coated for maximum reflectance at 694.3 nm (for a 45° incident wave, s polarization), was inserted at a 45° angle between the KDP crystal and the sample. The fundamental beam bypassed the sample and was then redirected along the optical delay line as usual, while the 347 nm pulse travelled along its normal path. Distilled-in-glass

solvents (Burdick and Jackson) were employed and the long lifetime (μsec) of the solvated electron at low pyrene concentrations was taken as a measure of the purity level.

A comparison of linear (low flux) and non-linear (high flux) absorptions of e_{aq}^- at 694 nm led to a $\leq 10\%$ change in absorbance induced by laser saturation. Typical waveforms are presented in Figure 2(b). The reproducibility of the saturating pulse imposed this limit within which more accurate measurements were not possible. In the case of ethanol and 2-propanol, we also failed to detect photobleaching, where the sensitivity of the measurement was again restricted by a $\pm 5\%$ variation in the saturating laser pulse.

(c) Treatment and Interpretation of Data

In an n level saturable absorber under a radiant flux I one may describe the time-dependent population N_i in any set of quantum states ($i = 1, 2, 3, \dots, n$) as shown below (7,8):

$$\frac{dN_i}{dt} = -\sum_j \sigma_{ij} (N_i - N_j) I + \sum_{j>i} k_{ji} N_j - \sum_{j<i} k_{ij} N_i$$

where σ_{ij} is the absorption or emission cross-section to a given level, and k is a first order rate constant describing nonintensity dependent relaxations between the levels. This equation encompasses all radiative and non-radiative transitions, and assumes molecular diffusion processes and reaction can be ignored on the time scale of the laser pulse, and thus $\sum_i N_i$ is constant. Multiphoton processes can be included by adding higher order terms. Furthermore, in using this equation, it is assumed that the laser-illuminated volume has cylindrical geometry due to the relatively insignificant divergence of the laser beam through a 1 cm optical path (x).

Since $\frac{dI}{dx} = \sum_{i>j} \sigma_{ij} (N_i - N_j) I$, and $\frac{dN_j}{dt} = 0$ (as a consequence of the photostationary state approximation (9), valid when the laser pulse width $\ll 1/k_{ji}$) we have shown (10) that for a

2 level system the rate (k) of relaxation back to the ground state is given by:

$$k_{21} = \frac{2\sigma_{12} I 10^3 (1 - 10^{-A})}{(A^0 - A) 2.303}$$

where $\sigma_{12} = 3.81 \times 10^{-21} \alpha_{12}$ (the molar absorption coefficient); A^0 , A are the absorbances at low and high fluxes respectively, and I is the saturating flux.

From this model, a value of $k \geq 1.09 \times 10^{11} \text{ sec}^{-1}$ was determined for e_{aq}^- , for e_s^- in ethanol $k \geq 7.4 \times 10^{10} \text{ sec}^{-1}$, and for e_s^- in 2-propanol $k \geq 6.9 \times 10^{10} \text{ sec}^{-1}$.

What are the implications of these measurements? The rate of relaxation to the ground state can be interpreted as an excited (electronic) state lifetime (τ^*) if indeed the final quantum state to which e_s^- is excited at 694 nm is a bound state. From this perspective we may say that $\tau^* = 0.69 \text{ k}^{-1}$, and the excited state lifetimes, following photoexcitation at 694 nm, are

$$\tau_{694}^* \leq 6 \text{ psec for } e_s^- \text{ in water}$$

$$\tau_{694}^* \leq 9 \text{ psec for } e_s^- \text{ in ethanol}$$

$$\tau_{694}^* \leq 10 \text{ psec for } e_s^- \text{ in 2-propanol}$$

This value for e_{aq}^- is in fact identical to an earlier upper limit of $< 6 \text{ ps}$, measured in a different experiment 10.

If we have a distribution of molecular traps, then the lifetimes are much shorter for we have only saturated (and possibly removed) one selected electron population whose transitions correspond to the laser wavelength; so the actual photon/ e_s^- ratio is much higher. Alternatively, k could be a measure of the cross-relaxation between the discrete molecular sites in resuming equilibrium. Finally, we may consider the

final state (following photoexcitation on the high energy side of the absorption maximum each case) as a continuum state or autoionizing state; that is, the electron has been photoreleased from its trap by incident radiation of 1.8 eV. From this viewpoint, k is the time taken to resoluate the electron and is a measure of the quasi-free bound relaxation time (τ_s). If this is a more accurate representation of the events at this wavelength, then the τ^* measured should bear some relationship to τ_s as measured in pulse radiolysis, since presumably solvation or resolution will entail the same molecular rotational reorganization about the electron, once it has been captured.

Inspection of the τ^* and τ values from this and previous work (10-13) show that, for the limited cases investigated, the τ^* measurements in laser saturation techniques are of the same order of magnitude as the τ_s data from picosecond pulse radiolysis taken at a similar wavelength.

<u>Solvent</u>	<u>τ^*, excited state lifetime</u>	<u>τ_s, solvation period</u>
water	$\tau_{694}^* \leq 6 \text{ ps}$;	$\tau_{600} \leq 2 \text{ ps}^{11}$ $\sim 4-6 \text{ ps}^{12}$
ethanol	$\tau_{694}^* \leq 9 \text{ ps}$;	$\tau_{600} = 10 \pm 2 \text{ ps}^{11}$
2-propanol	$\tau_{694}^* \leq 10 \text{ ps}$;	$\tau_{600} = 13 \pm 2 \text{ ps}^{11}$

This is not as strong a test of the correlation as the identical measurements in long chain alcohols would be, where τ_s is $\geq 5 \times 10^{-10}$ secs and thus well above the limit of the present limiting sensitivity of the laser saturation technique. (The sensitivity, can be improved by eliminating reflection losses in the delay line.) Furthermore, these measurements should be made at various wavelengths throughout the e_s^- absorption band, as originally we had intended, with the dye laser. Since evidence clearly indicates that short-range charge-dipole interactions in a discrete solvation structure govern the binding and transition energies of e_s^- in ROH, regardless of the electronic

states, we still should anticipate a distribution of molecular traps coexisting in thermal equilibrium. Thus τ^* (or k) may vary with wavelength in the same manner as τ_s have been shown to do; indeed, for e_{aq}^- the same wavelength dependence for τ^* and τ_s has already been observed.

In summary we may say that, from the limited data available, there appears to be a correlation between τ^* and τ_s , but further measurements at different wavelengths and in higher alcohols need to be performed before any unequivocal conclusions may be drawn about the electronic transitions of e_s^- .

(3) Summary of Picosecond Pulse Radiolysis Data

The preliminary work in this area is summarized in the enclosed paper, presented to the 5th International Congress of Radiation Research, 1974. The equipment has been recently described (14).

The latest data and results on C_3 to C_{10} alcohols are represented in Figures 3, 4 and Table 1. A summary of the most notable points is as follows, and should be read with reference to the figures. All absorptions have been normalised to the signal in ethanol as a control, since the formation time there is ~ 10 ps (11).

(a) The solvation process appears to occur in two steps; a fast step that, within our experimental resolution of ~ 45 ps (14), appears to be common to all the alcohols, and a slower step that varies from solvent to solvent. This discontinuity in the growth kinetics appears real.

(b) The longer the alcohol chain, the longer the average time taken for the electron population to reach a fully relaxed, solvated ground state, at a given wavelength. The lag in the absorption signals for e_s^- in a higher alcohol versus ethanol is seen in Figures 3 and 4.

(c) For a given alcohol this relaxation period is longer at shorter ("blue") wavelengths. In other words, significant blue shifts are exhibited over long times, up to 10^{-9} s in 1-decanol.

(d) There is significant decay at early times, particularly in the "red" portion of the spectrum, but insufficient data are available to correlate the kinetics in the "red" and "blue" regions, or to locate isobestic points in the time-dependent spectra.

(e) The early relative G_e values for solvated electrons in the long chain alcohols are fairly high and all the same, close to 35 or 40% of the water values. Rapid decay ($>35\%$) in the initial 30 ns questions some of the predictions of the spur-diffusion model. Further statements must await μs yields to establish free-ion values.

In view of the uncertainty in the kinetic picture, only τ_s values for 514 nm are tabulated at this stage, since least decay is expected from these "deep" traps. Without selecting a kinetic model, it is unrealistic to deconvolute the present data to obtain rates for the very rapid, first formation step of e_s^- . The jump in τ_s values between Hunt's 1-propanol data and our 1-butanol data in Table 1 may in part be a combination result of their kinetic model and assumptions and our reluctance to deconvolute into the electron pulse at this stage. Further work is planned to permit a full spectral and kinetic analysis of two specific long chain alcohols. Nevertheless, we may draw some qualitative conclusions about the nature of electron localisation in alcohols.

In the alcohols the electron finds preformed traps. These traps are hydrogen bonded clusters, polymers that exist in varying thermodynamic equilibria in all the alcohols. If this is the case then the number of electrons initially trapped will depend only on the availability of these trapping sites, not on various bulk liquid dielectric properties.

Now one envisages the time taken to reach a fully solvated, relaxed ground state as the sum of two components. (1) capture by the alcohol cluster, a radiationless transition to the unrelaxed but localised electronic state in which the electron is energetically stable, and (2) relaxation of the local solvent structure in the field of the excess electron, or "digging-in", to give a fully relaxed, ground electronic state. In a polar liquid both long range rotational and short range (rotational and radial) configurational changes may be involved. The first process is essentially an electronic transition, conceivably electron attachment via monomer or dipole rotation, which is so fast that it can be separated out from the second process, rotational relaxation of the solvent. The second time must be associated with the dynamics of the H-bonds in the solvent, the microviscosity, since the slowest dielectric relaxation time must be the rate-determining step, although of course in the

presence of the contiguous electron molecular rotations will be accelerated somewhat (6). Whether or not all initially captured electrons survive to become solvated electrons may to some extent depend on the time scale of the second process. However, since all initial G_e seem fairly high, and the same for different alcohols, it looks as though they do.

Thus, although we can see the absorption spectrum develop in some alcohols, viz decanol, the high G_e value argues against the trend (4) between G and τ_s hinted at in the published small alcohol psec data. If solvation is a two-step process, and there are preformed traps in alcohols, then the availability of the trapping sites or clusters will have more influence on the initial relative yields than will the dynamics of these clusters. The number of high mobility dry electrons undergoing geminate recombination will not be influenced by τ_s , where τ_s only governs the molecular reorientations after trapping has occurred.

Figure 1 Apparatus for Laser Saturation Studies of Solvated Electron
Inset: dye laser

50mV|div (vertical)
20ns|div (horizontal)

Figure 2(a) Incident laser pulse followed by saturating laser pulse after transmission along the optical delay line. Peak-to-peak separation is 32 nsecs.

Figure 2(b) (i) Control 694 nm laser pulse (ii) Low intensity laser pulse, transmitted through the e_s^- solution, and (iii) high intensity (saturating) pulse transmitted through the same solution. Note the absence of detectable photobleaching effects.

(i)

(ii)

(iii)

Figure 2: Oscilloscope Traces of Laser Pulses.

Figure 3. Appearance of e_s^- absorption in alcohols at 20°C:

1-Octanol, 1-Decanol. 47.5 ps per horizontal division; the reference and sample curves are normalized. Data for 514 nm.

1-octanol
v. ethanol

I_{abs}

1-decanol
v. ethanol

I_{abs}

Figure 4. Appearance of e_s^- absorption in alcohols at 20°C:

c-Héxanol. 47.5 ps per horizontal division; the reference and sample curves are normalized. Top set of curves apply to 514 nm, lower set to data taken at 740 nm.

c-hexanol
v. ethanol

I_{abs}

c-hexanol
v. ethanol

I_{abs}

Table 1

Electron Solvation Times, τ_s^* at 20°C

<u>Alcohol</u>	λ_{nm}	τ_s (ps)	τ_1 (ps) ^a	τ_2 (ps) ^b	E_{max} (eV)
methanol	600	~3 [†]	54		1.93
ethanol	600	10+2 [†]	200		1.70
1-propanol	600	13+2 [†]	430	22	1.67
1-butanol	514	159	668	27	1.82
1-pentanol	514	167	927	28	1.90
1-octanol	514	279	1780	39	1.90
1-decanol	514	810	2019	48	1.90

2-propanol	514	110			1.49
2-butanol	514	173			1.67
c-pentanol	514	250			1.50
c-hexanol	514	248			1.65

* time taken for the electron population to reach the fully solvated, ground electronic state.

† Hunt et al., 1973

^a τ_1 is the slowest relaxation time in alcohols corresponding to the breakup of the H-bonded clusters and subsequent rotation of the monomers to form another aggregate.

^b τ_2 is the time associated with monomer rotation only. All values are from Garg and Smyth, JCP 69, 1294 (1965).

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List of Publications

"Picosecond Studies of Electron Localization in Long Chain Alcohols", G.A. Kenney-Wallace and C.D. Jonah, in preparation.

(4) Personnel Activities

(a) Scientific Discipline Personnel

Throughout the contract period, October 21st 1973, to December 31st, 1974, the Principal Investigator, G.A. Kenney-Wallace, Assistant Professor of Chemistry, spent a minimum of 20% of her time on this project during the academic terms and three and one-half months full-time during the summer of 1974. She has been assisted most ably during this period by Mr. John Flint, a Yale undergraduate who spent approximately one day a week on the project during the spring semester, January to May 1974. He worked full-time for three months during the summer, and continued on the laser project for 2 days a week during the Fall semester, until November 31st 1974.

The experiments on the picosecond pulse radiolysis facility at the Argonne National Laboratory were conducted in collaboration with Dr. C.D. Jonah of the Chemistry Division. Two separate field trips were made, each totalling three days experimental time.

Professor Kenney-Wallace presented a paper at the 5th International Congress of Radiation Research in Seattle, July 1974.

(b) Biographical Details

Principal Investigator

The principal investigator, Professor Geraldine Kenney-Wallace, pursued undergraduate studies in Oxford and London and completed her graduate work (1966-1970) in chemical physics under the supervision of Professor David C. Walker at the University of British Columbia. The subsequent year was spent as a Postdoctoral Fellow at the University of British Columbia, and in June 1971 she joined the Radiation Laboratory, University of Notre Dame, to work as a Postdoctoral Research Associate with Dr. Robert R. Hentz, Associate Director. In 1972 she joined the Chemistry faculty at Yale University as an Instructor and was promoted to Assistant Professor in the spring of 1973. Her formal association with Yale ceased in December 1974 and she

is presently Assistant Professor of Chemistry at the University of Toronto.

Research Assistant

The research assistant on this project was Mr. John Flint, a Yale physics major with a strong background in chemical physics, electronics and data acquisition.

Other Support

In addition to this AEC contract Professor Kenney-Wallace is principal investigator on one other grant: ACS-PRF 3023-G2, a starter grant-in-aid of \$7,500 over a three-year period, 1973-1976. This grant is to aid research into the photophysical properties of tetra-thiofulvalene, a semiconductor organic molecule. Neither this research nor the funding in any way overlapped the AEC research presented here.