

Dynamics of solvation of an excess electron

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We have utilized the techniques of picosecond spectroscopy to study the localization of an excess electron in water. Quasifree electrons were generated by the photoionization of the ferrocyanide anion in aqueous solutions at 2650 Å. Time resolved absorption of the localized electron was monitored continuously from 1.06 μ to 5300 Å, while time and energy resolved absorption was monitored in the range 3100–9000 Å by a broad continuum of picosecond duration. Optical absorption of the initially localized electron in the infrared (1.06 μ) is observed within 2 psec after the generation of the quasifree electron. The optical absorption band evolves in time, shifting from lower to higher energies, and the "normal" absorption of the hydrated electron is developed in ~ 4 psec.

I. INTRODUCTION

We report the observation of an ultrafast relaxation process of an excess electron¹ from the quasifree state to the localized state²⁻⁶ in water, utilizing the techniques of picosecond spectroscopy.⁷ Localization of an excess electron in a dense fluid (i.e., polar or nonpolar liquid or dense gas) can originate from two distinct types of electron-medium interactions^{2,5,6}:

(a) Electron localization originating from short range repulsive interactions. In light and saturated nonpolar liquids,⁸⁻¹¹ (liquid He and liquid Ne) where the quasifree excess electron state is repulsive (relative to the vacuum level), the localized electron state will be energetically stable.

(b) Electron localization originating from attractive interactions.²⁻⁶ In polar liquids (such as water, ammonia, etc.) attractive short range and long range electron-solvent interactions result in a localized excess electron state which is energetically stable relative to the quasifree state.

Most of the extensive experimental and theoretical studies of excess electron states in polar and in nonpolar liquids monitor the physical properties of the energetically stable excess electron state.²⁻⁶ In any dense fluid the quasifree electron can be initially produced by an external or by an internal adiabatic process, where the liquid does not rearrange during the electron injection. Several types of adiabatic electron injection experiments into a conduction band of a liquid can be performed:

(a) Photoemission from a photocathode,⁸ or emission from a field-emission tip¹² into a nonpolar liquid. Such experiments may monitor the energy of the quasifree electron state in liquid rare gases.

(b) Intrinsic generation of quasifree electrons by pulse radiolysis in polar and in nonpolar liquids.¹³

(c) Optical photoionization^{14,15} of an impurity state (i.e., a foreign atom, molecule, ion, or the localized electron itself) in a nonpolar or in a polar liquid which involves excitation to the conduction band.

Adiabatic electron injection into a liquid where the localized excess electron state is energetically stable will be followed by the relaxation of the quasifree electron to the localized state. This relaxation process is accompanied by a formation of a cavity (i.e., electron bubble)^{9,10} in a nonpolar liquid and by both long range rotational and short range (rotational and radial) configurational changes in a polar liquid. The rate and the details of the dynamics of the localization of an excess electron in liquids are of considerable interest. The dynamics of electron localization in a liquid can be described in terms of two consecutive processes: (A) A radiationless electronic-nuclear relaxation process induced by nonadiabatic coupling between the quasifree and the ground localized state. The localized excess electron state will be initially formed in a nonequilibrium solvent configuration; (B) Further relaxation of the solvent around the localization center will subsequently occur, finally resulting in the equilibrium localized ground states. In a nonpolar solvent (such as liquid He and Ne) the "incipient bubble,"^{5,16} initially resulting in electron localization, will then expand further. In a polar solvent (i.e., liquid H₂O or NH₃) both the continuum polar modes⁵ and short range angular and radial fluctuation may initially provide a sufficiently deep potential well for electron localization. Subsequently, the first coordination layer around the electron localization center becomes fully oriented resulting in the equilibrated ground localized electron state. This description of the quasifree-localized electron relaxation process bears a close analogy to a wide class of radiationless processes

in molecules (internal conversion and intersystem crossing)¹⁷ and in solids (electron capture by holes and thermal ionization processes in semiconductors).¹⁸ It should be noted however that in most theoretical descriptions of radiationless processes of molecules embedded in a dense medium and of electronic relaxation processes in solids, rapid vibrational relaxations within each electronic manifold was taken for granted. It has been noted that this assumption has to be modified in the case of some ultrafast electronic relaxation processes.¹⁹ Now, provided that the excess electron localization process occurs on the time scale of solvent relaxation (which is analogous to vibrational relaxation in molecular and solid state radiationless processes), then the interstate electronic transition [Process (A)] and the solvent rearrangement [Process (B)] can be separated and both processes should be amenable to experimental observation.

From the experimental point of view, only indirect information is available concerning the dynamics of electron localization. In a nonpolar solvent such as liquid He an upper limit of $10^{+10} \text{ sec}^{-1}$ for the rate of electron localization was derived from positronium annihilation experiments,²⁰ while some further indirect information was inferred from electron injection studies.¹⁶ Most of the experimental data concerning polar liquids were obtained from pulse radiolysis studies. Baxendale and Wandman²⁰ have studied electron localization in alcohols at low temperatures, $\sim 180^\circ\text{K}$, by nanosecond pulse radiolysis. A broad infrared electron band was initially observed after $\sim 5 \text{ nsec}$ (the experimental time resolution) which subsequently shifts to the visible until the normal solvated electron band develops within $1 \mu\text{sec}$. An interesting experimental study of electron localization in liquid H_2O by pulse radiolysis was reported by Hunt *et al.*²¹ Utilizing ultrafast stroboscopic pulse radiolysis method with a time resolution of 20 psec , Hunt *et al.*²¹ conclude that the solvation rate of the electron in water is shorter than 10 psec . Kenny and Walker¹⁵ have studied the optical bleaching of solvated electrons in water by a Q-switched Ruby laser (pulse length 20 nsec) and by a courageous extrapolation of these data conclude that the quasi-free-bound electron relaxation rate is shorter than 6 psec . Finally, Beck and Thomas¹⁶ have studied the formation of solvated electron in ethanol and psec response. They find that in 1-propanol the formation of the solvated electron is over after 50 psec , in ethanol it is "formed rapidly with a possible delay of $2\text{--}5 \text{ psec}$."

The techniques of ultrafast picosecond spectroscopy⁷ utilizing mode locked lasers were applied by us for the study of the dynamics of electron localization in polar solvents. In view of the current interest in the properties of the hydrated electron we

have chosen to study initially the localization of an excess electron in water. However, we are also currently studying similar effects in alcohols and in solids. The quasifree electron was generated by photoionization of the ferrocyanide anion in aqueous solutions excited at 2650 \AA (i.e., the fourth harmonic of the Neodymium glass laser). The time resolved optical spectrum of the localized electron was monitored (a) at 1.06μ (the fundamental of the Neodymium laser),¹ (b) at 5300 \AA (second harmonic of Neodymium), and (c) in the range $3100\text{--}9000 \text{ \AA}$ utilizing a continuum picosecond pulse.²² Our results provide the first complete picture of the quasi-free-bound electron relaxation in water.

II. EXPERIMENTAL PROCEDURES

A. Mode Locked Lasers

A train of picosecond pulses was generated from a mode locked Nd^{+3} glass laser. A single pulse was extracted utilizing a spark gap charged to 20 kV , which is triggered by a pulse from the mode locked train and opens a pockels cell for $\sim 5 \text{ nsec}$. The single pulse was subsequently amplified by a 12 cm long rod amplifier. The single pulse had a width of $\sim 2 \text{ psec}$, measured by the three photon fluorescence method.²³ The fundamental wavelength of 1.06μ was converted to 5300 \AA by an angle phase matched KDP crystal and the second harmonic was doubled to 2650 \AA by a temperature matched ADP crystal.

B. Time Resolved Absorption of the Hydrated Electron

Photoionization of the ferrocyanide anion in aqueous solutions ($10^{-3}M \text{ K}_4\text{Fe}(\text{CN})_6$ in H_2O) was achieved by pumping at 2650 \AA and monitored at 1.06μ or at 5300 \AA . The experimental set up displayed in Fig. 1 portrays the optical path of the exciting 2650 \AA light and the time resolved absorption of the electron in H_2O at 1.06μ or at 5300 \AA . The echelon technique²⁴ was utilized to generate the interrogating pulses of identical duration and intensity, with selected constant time separation between echelon segments. The single 1.06μ , or 5300 \AA pulse, is passed through an echelon consisting of a stack of quartz plates 0.31 mm thick (Fig. 1). The pulse traveling through the echelon is split into a train of variably delayed pulses, the delay time of each pulse being determined by the length of the particular segment of the echelon through which the pulse travels. In the present experimental set up, the exciting 2650 \AA pulse and the third echelon segment of the interrogating 1.06μ or the 5300 \AA train arrived simultaneously in the 1 mm quartz cell containing the $\text{K}_4\text{Fe}(\text{CN})_6$ solution. This particular segment corresponds to $t=0$. Optical filters were used to reject all light of other wavelengths than the monitoring pulse, and the echelon was imaged on

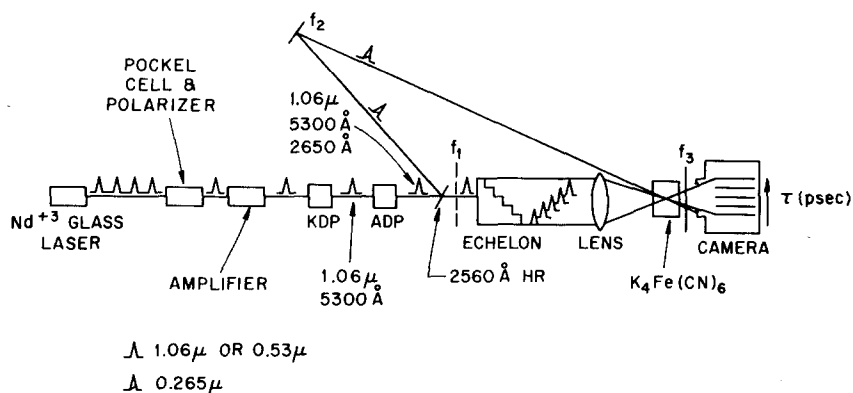


FIG. 1. Schematic representation of a method utilized for the measurement of time resolved absorption of electron in water at 1.06 and 0.53 μ .

the camera (see Fig. 1). The photographs of the echelon segments portray the time resolved absorption spectrum of the solvated electron at a given interrogating wavelength, the time resolution of this method being ~ 2 psec, which is the width of our pulse.

C. Time and Energy Resolved Absorption Spectrum

The time resolved absorption spectrum of the hydrated electron was monitored by a continuum which spans a frequency range of several thousand wavenumbers.²²⁻²⁵ The picosecond continuum²² is generated by collimating a single 1.06 μ pulse in a medium (i. e., CS₂, H₂O or quartz). Self-focussing effects result in filament formation in the liquid. The inherent nonuniformity of the beam intensity causes variations in the refractive index, so that different segments of the beam are characterized by different phase velocities, resulting in inhomogeneous beam contraction. The beam contraction is counteracted by diffraction effects, the final net effect is the propagation of "self-trapped" filaments in the liquid.²⁶ The physical self trapping mechanisms leading to filamentation are still a subject of some controversy.²⁷ The most important result from the experimental point of view is that filamentation is accompanied by a variety of cooperative effects such as stimulated Raman scattering. In liquids self-phase modulation results in a picosecond pulse characterized by a broad continuous spectral distribution.^{28,29} The spectrum observed by collimating a 5300 Å pulse in D₂O²² (see Fig. 2) spans the spectral region of 3100-8000 Å. The time width of the continuum pulse was determined using the experimental arrangement displayed in Fig. 3. A portion of the 5300 Å laser pulse is used to operate an optical Kerr cell shutter which consists of a CS₂ cell located between a pair of crossed polarizers.³⁰ The continuum pulse is transmitted through an echelon and then enters the optical shutter collinearly with the 5300 Å pulse. The thickness of each echelon segment corresponds to a time resolution of 2.8 psec, and the CS₂ Kerr liquid is characterized

by a rotational relaxation time of 1.8 psec. When the 5300 Å pulse was synchronized with one of the segments of the continuum, only this segment was exposed on the photographic plate (Fig. 4), indicating that the upper limit for the time width of the continuum is 3 psec. Subsequent experiments established that the time width of the continuum is equal to or may be less than the laser pulse duration. This is expected as the generation of the continuum pulse involves virtual processes. We have shown recently that the anti-Stokes shifted region of the continuum is actually delayed with regard to the Stokes shifted region. Special care, therefore,

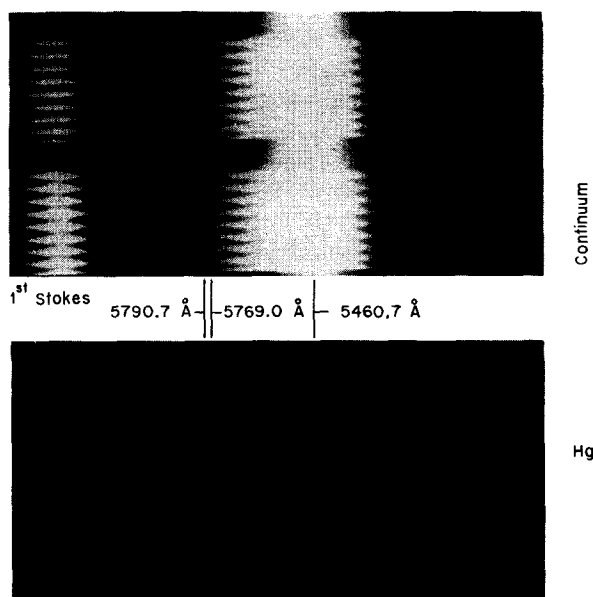


FIG. 2. A small region of the spectrum of picosecond continuum generated by the 0.53 μ second harmonic of a Nd³⁺ glass laser photographed through a $\frac{3}{4}$ Spex spectrometer after reflection by an echelon. The overexposed center region corresponds to a ~ 0.53 μ with portions of the low and high wavelengths of the continuum on either side.

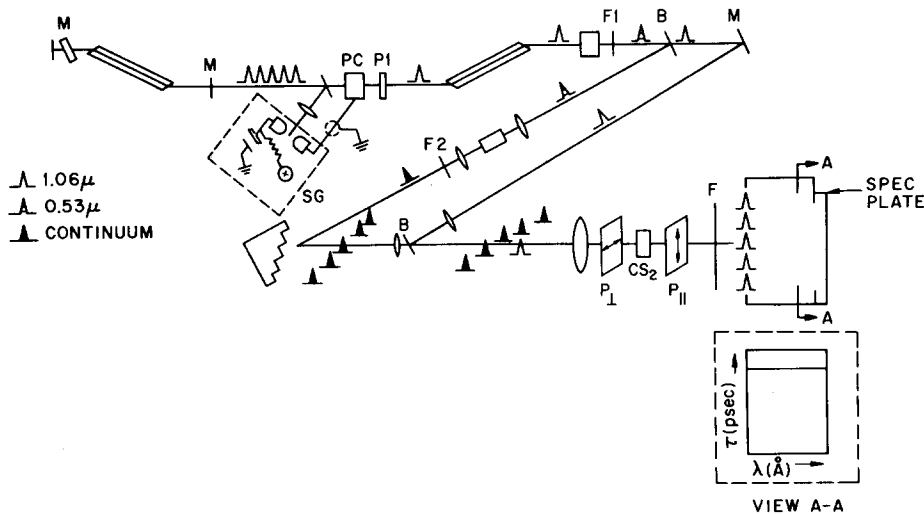


FIG. 3. Experimental arrangement for the measurement of the time width and wavelength of the continuum.

should be exercised in the time measurements in this region of the continuum.

The continuum generated by a single picosecond pulse (0.53μ) originating from a mode locked Nd^{+3} glass laser, amplified in a 12 in. rod, and doubled by KDP, traversed the optical path represented schematically in Fig. 5. The echelon divided the single continuum pulse into a set of pulses, each having the same time and frequency width but separated by 2.8 psec. This set is then focussed into a cell containing the ferrocyanide solution and subsequently imaged along the height of the slit. Consequently each echelon segment is imaged on a different portion along the slit height and subsequently

displayed along the y axis of the spectroscopic plate. Since the echelon generated pulses arrived at the slit at 2.8 psec time intervals, the y axis of the spectroscopic plate is in fact a time axis while the x coordinate displays the wavelength of the spectrum. Coincident in time and space with the arrival of the first echelon segment in the ferrocyanide solution, is the single (2650 \AA) picosecond pulse, derived from the quadrupole of the original 1.06μ pulse and which generates the electron and provides the $t=0$ time for the experiment.

With the insertion of the beam splitters filters and other components shown in Fig. 5 we were able to measure the time and energy absorption spec-

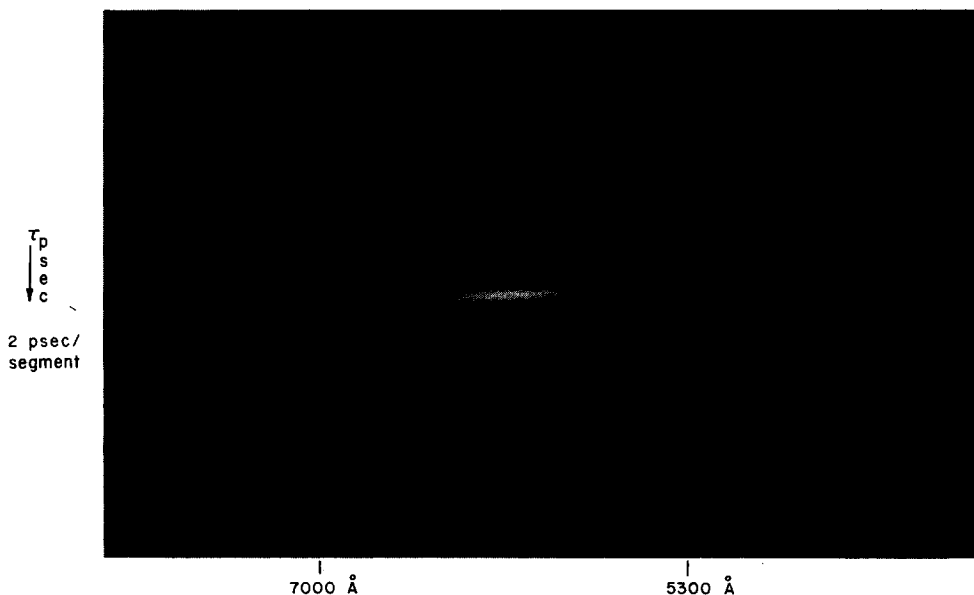


FIG. 4. The photographic recording obtained by the apparatus of Fig. 3. The single echelon segment from the continuum corresponds to ~ 2 psec.

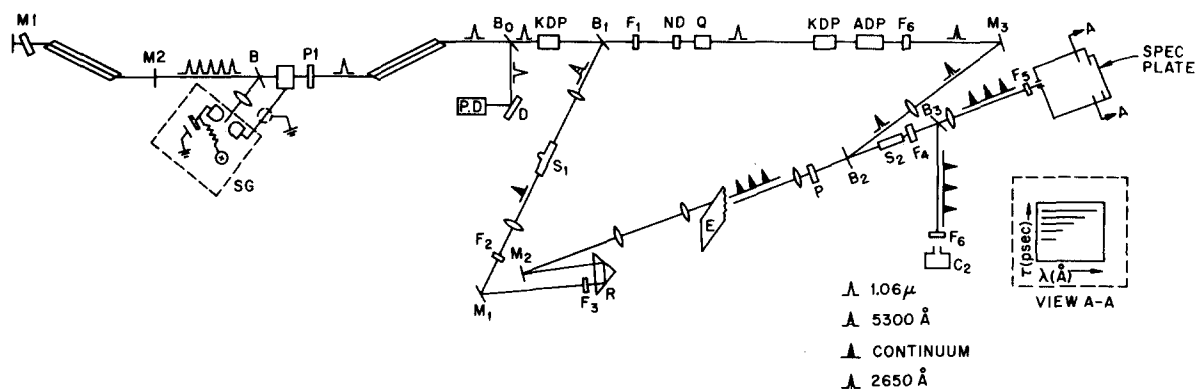


FIG. 5. Experimental arrangement for picosecond absorption spectroscopy using the picosecond continuum. In this case applied to the transient absorption of electrons in water, in the visible region of the spectrum.

trum of the electron in water, from potassium ferrocyanide and potassium iodide in water.

III. EXPERIMENTAL RESULTS

Our results can be summarized as follows:

(a) The infrared optical absorption of the excess electron in water at 1.06μ is observed ~ 2 psec after the generation of the quasifree electron (see Fig. 6).

(b) The optical absorption of the hydrated electron at 5300 \AA (see Fig. 7) occurs ~ 4 psec after the generation of the quasifree electron.

(c) The optical absorption band of the localized

hydrated electron evolves in time (see Fig. 8) shifting from lower to higher energies. The "normal" absorption spectrum of the hydrated electron (which is identical to the conventional spectrum of the hydrated electron observed in "long time" experiments)⁴ is developed after ~ 4 psec. When the intensity was low the obvious insertion of an image converter intensifier was made between the spectrometer and camera.

IV. DISCUSSION

We believe that the present data provide the first direct observation of the dynamics of electron lo-

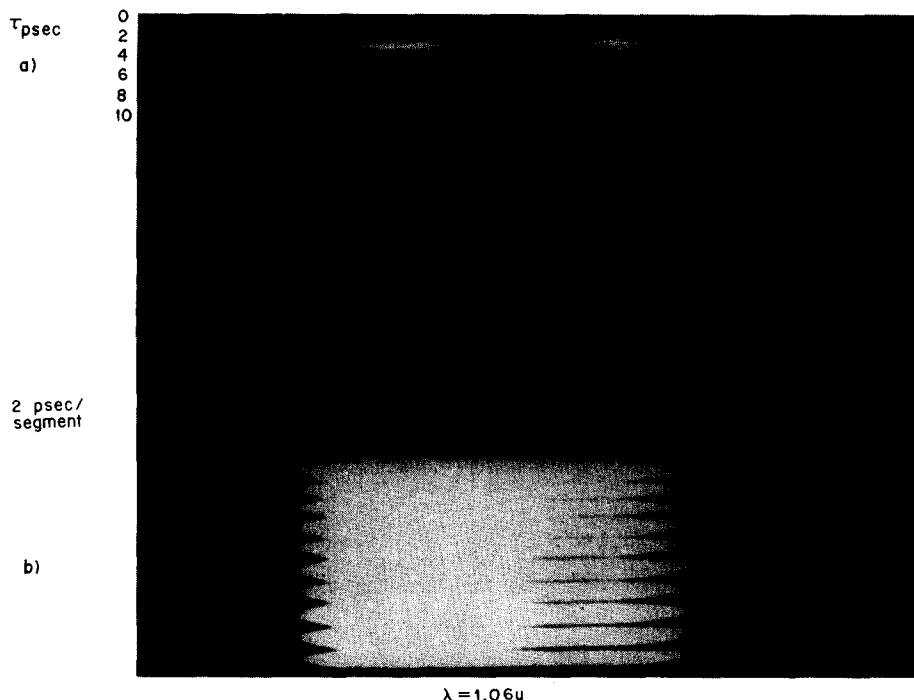


FIG. 6. (a) Actual photographic display of the time resolved absorption of an electron in H_2O at 1.06μ , obtained by use of the apparatus shown in Fig. 1. The electron was generated by excitation of $\text{K}_4\text{Fe}(\text{CN})_6$ in H_2O with 2650 \AA picosecond laser pulse. The single echelon shown for 1.06μ corresponds to ~ 2 psec and it is this segment which is coincident with the 2650 \AA exciting pulse. (b) Identical to (a) but without 0.265μ .

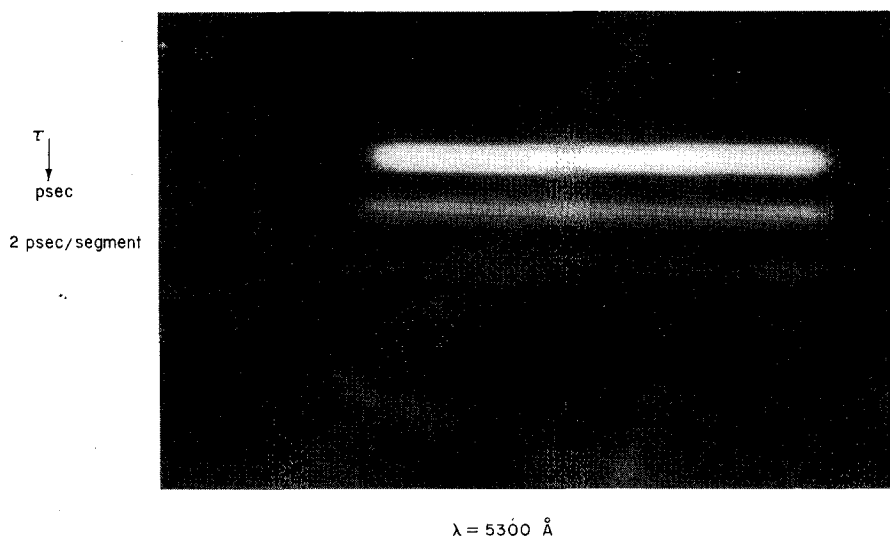


FIG. 7. Similar arrangement as Fig. 1 except that the interrogating pulse has a wavelength of 0.53μ . It is seen that two segments are transmitted after excitation of the $K_4Fe(CN)_6$ by the 2650μ pulse, corresponding to ~ 4 psec.

calization in water. We have stated that the quasifree electron is generated by direct photoionization of the ferrocyanide anion at 2650 \AA . In view of the uncertainty in the location of the conduction band of liquid water⁶ (relative to the vacuum level), we cannot rule out the possibility that excitation of the ferrocyanide anion in aqueous solution at 2650 \AA

(4.75 eV) results in a metastable excited (charge transfer to solvent) state of the ferrocyanide anion which subsequently yields the quasifree electron by thermal ionization or by autoionization.³¹ In this case the short relaxation time of ~ 2 psec monitors the overall rate of two consecutive processes, i. e., electron detachment from the excited negative an-

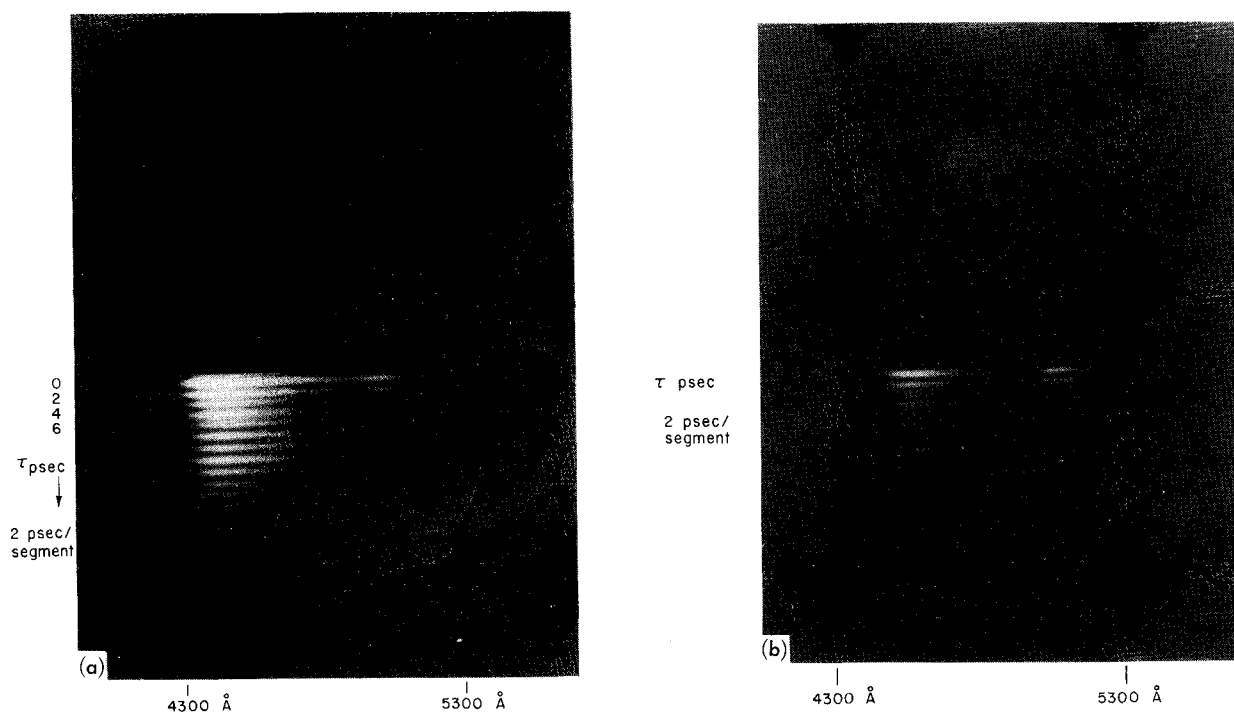


FIG. 8. (a) Photograph of the continuum passing through $K_4Fe(CN)_6$ using the apparatus of Fig. 5. With the exception that the 2650 \AA excitation pulse is blocked from reaching the cell. (b) The simultaneous time and energy resolved spectrum of electrons in H_2O between 4300 \AA using the apparatus of Fig. 5. The 2650 \AA excitation pulse is synchronous with the first echelon segment.

ion followed by the initial localization of the hydrated electron in ~ 2 psec.

The time scale for the evolution of the "normal" absorption spectrum of the hydrated electron (~ 4 psec) is consistent with the upper limits for this process estimated by Kenny and Walker¹⁵ (≤ 6 psec) and by Bronskill, Wolf, and Hunt²¹ (≤ 10 psec). The time evolution of the absorption band of the solvated electron from lower to higher energies on the time scale of 5 nsec–10 μ sec was observed by Baxendale and Wardman²⁰ in low temperature alcohols.

Our current theoretical understanding of the dynamics of localization of an excess electron in a polar solvent is rather incomplete. Concerning the initial localization process it is interesting to consider two extreme physical situations: (a) The quasifree electron creates its own potential well by interaction with collective long range polarization modes of the polar liquid. (b) Local radial and angular fluctuations provide an attractive potential well for the initial localization processes.

From the point of view of the general theory of nonradiative relaxation phenomena, it appears to us that these two processes cannot be separated. The nonradiative decay probability for the transition from the conduction band to the localized state is determined by an electronic matrix element of the nonadiabatic coupling between these two states and a Franck–Condon vibrational overlap factor.^{17,18} The latter is determined by the configurational changes between the initial and the final states, so that both short range structural modifications and long range polarization (i. e., optical) modes are involved. The contribution of the long polarization modes of the liquid, which were treated in a different context by Levich *et al.*³² to the initial electron localization process bears a close analogy to the polaron problem in crystals.³³ In view of the translational symmetry of a perfect solid, it seems inappropriate to consider the polaron as a localized particle, but rather as a particle interacting with a field.³⁴ Polaron localization can occur only provided that in the strong coupling situation the polaron bandwidth is considerably lower than the thermal energy.³⁵ This situation implies large configurational changes (relative to the unperturbed lattice). These appreciable configurational changes are provided in the polar liquid by short range structural fluctuations. We thus feel that both long range polar modes and short range solvent fluctuations contribute to the initial ultrafast localization process. It is important to note that the rate of the initial localization process is not directly related to the dielectric relaxation time of the solvent. This is revealed by our experimental result where the initial relaxation process (< 2 psec) is shorter than the dielectric relaxation time of water (7.4

psec at 30 °C).³⁶ Neither from the theoretical point of view is such a relation expected to hold.

The evolution of the solvated electron absorption band (on a time scale of ~ 4 psec) exhibits the solvent relaxation around the localized state initially formed. Thus the localized electron initially formed in a nonequilibrium solvent configuration "digs its own potential well" resulting mainly in short range solvent angular (and radial) displacements. This relaxation process, which is reminiscent of vibrational relaxation in large molecules, is expected to be roughly determined by the solvent dielectric relaxation time.

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