$$Co(CN)_5^{3-} \rightleftharpoons Co(CN)_4^{2-} + CN^- \quad (10)$$

$$Co(CN)_4^{2-} + (Hg \longrightarrow (NC)_4Co-(Hg \quad (11)$$

electrode surface — adsorption bond

controlled adsorption rates are usual except for class IV adsorbates which form more than a single isothiocyanate-to-mercury bond at the surface.[44]) This sluggishness in the adsorption rates may result from the small concentrations of the low-valent intermediates that are produced in the rapidly established equilibria which precede the formation of the metal–metal bond. The same slow rates are also observed during the homogeneous formation of the trinuclear complexes by the reactions between mercury(II) and the reactive rhodium(I) ahd cobalt(I) species shown in reactions 5 and 9.

Apart from their intrinsic interest as examples of heteronuclear metal–metal bonding on surfaces, these examples of class V adsorbates are intriguing because of their potential application as electrogenerated catalysts. For example, the cross sectional concentrations of $Rh(en)_2^+$ that can be generated at a mercury electrode by rapidly changing its potential to desorb the $Rh(en)_2^+$ that spontaneously coats the surface at selected initial potentials is very much larger than is obtainable by any other known means. The variety of cases in homogeneous solutions where $Rh(en)_2^+$ serves as an effective catalyst[45] adds to the attractiveness of this line of pursuit.

## Concluding Remarks

The division of the patterns of adsorptive behavior exhibited by simple molecules and ions on mercury electrodes into the five classes that have been discussed is, of course, arbitrary. A larger number of subdivisions might have contributed to greater precision in drawing distinctions among classes, but the five classes chosen seem to suggest themselves quite naturally. In any case, the intent of this article has not been taxonomical. Rather it has been to elaborate the diversity of the surface chemistry that controls the tendencies for molecules to accumulate at charged, metallic interfaces. Increasingly, electrochemical kineticists and energy harvesters are striving to exploit the spontaneous adsorptive tendencies of reactants to enhance reactivities and reaction efficiencies, and an important component in such efforts is an understanding of the ways that are available for attaching molecules to electrode surfaces.

*Many collaborators contributed signally to the research summarized here. All are identified in the references cited, but I wish to acknowledge particular indebtedness to Donald Barclay, Hong Sup Lim, Steven Frank, Janis Gulens, and Michael Weaver for their industrious experimentation and provocative interpretations of many of the topics treated in this Account. Various portions of this research have been generously supported by the National Science Foundation, the U.S. Army Research Office (Durham), and the Petroleum Research Fund, administered by the American Chemical Society.*

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# Picosecond Spectroscopy in Chemistry and Biology

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In recent years picosecond spectroscopy has been applied to the study of both chemical and biological systems. Some of the results obtained have been predicted by extrapolation from nanosecond studies, while others reveal phenomena never realized or expected before.

The application of mode-locked lasers is now almost a decade old. The technology which makes it possible to perform spectroscopic studies in the picosecond range is described in references 1–18. The

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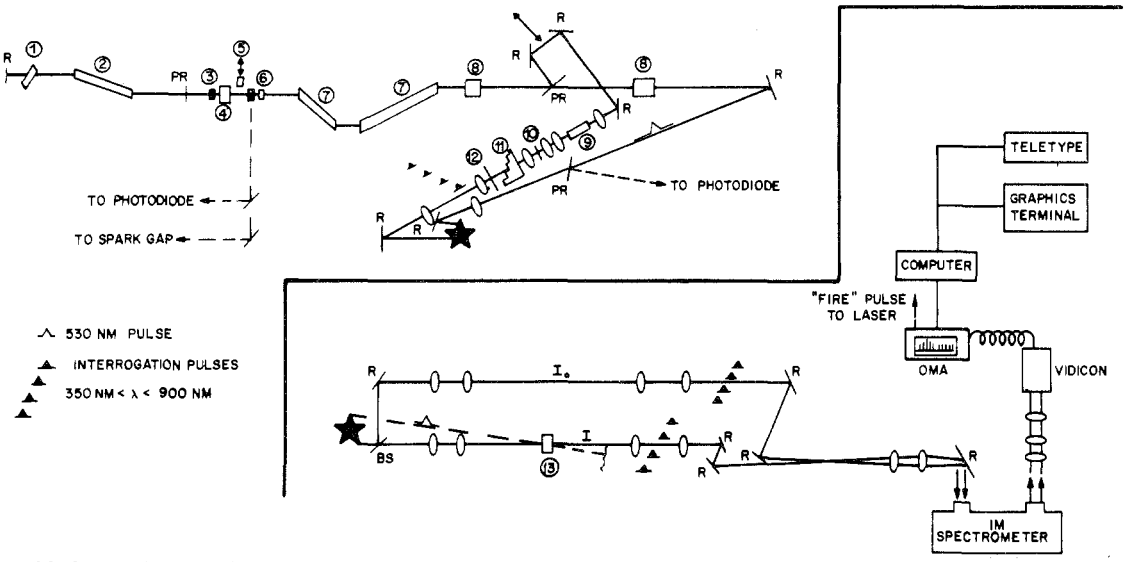


**Figure 1.** Double-beam picosecond spectrometer utilizing a silicon vidicon detector. Components: (1) mode-locking dye cell, (2) laser oscillator rod, (3) calcite polarizer, (4) Pockel's cell, (5) translatable 90° polarization rotator for 1060-nm radiation, (6) fixed-position 90° polarization rotator, (7) laser amplifier rod, (8) second harmonic (530 nm) generating crystal (KDP), (9) 20-cm octanol cell for generating the interrogation wavelengths, (10) ground-glass diffuser, (11) index matched glass echelon for producing picosecond optical delays between the stacked interrogation pulses, (12) vertical polarizer, (13) sample cell, (R) reflector, (PR) partial reflector, (BS) beam splitter, (OMA) optical multichannel analyzer.

experimental laser system utilized presently is composed of four essential components which satisfy the following constraints: (1) a well-defined pulse for excitation which is of picosecond duration with well-defined shape and spectral band width; (2) a picosecond clock which allows us to measure time in picosecond units; this is achieved by stepped delay; (3) a light continuum of picosecond duration and a wavelength range spanning several thousand wave numbers; (4) an electronic detection system such as a two-dimensional vidicon which can resolve simultaneously the time, wavelength, and intensity parameters with photon counting sensitivity and the reliability of a double-beam spectrometer.

A schematic diagram of the system incorporating all of these components appears as Figure 1. It is essentially a double-beam picosecond spectrometer with capability to detect and display transient optical density changes as small as ~0.03 and potentially much smaller. It is equipped with a two-dimensional vidicon detector and OMA which are coupled to a computer for pulse correlation and data processing and averaging. The data, in numerical or figure form, of the computed time–wavelength–intensity spectra are displayed on a screen with hard-copy access. Reference 17 contains a complete description of this system.

The types of experiments performed range from radiationless transitions[18] and cage recombination[19] to the dynamics of the solvating electron[20] and from chlorophyll[21] to fusion. With the actual number of picosecond experiments being very large, we do not even suggest that this is an encyclopedic inclusion of all picosecond experiments but rather a description of only a few illustrative experiments which we hope will demonstrate the versatility and wide scope of this field.

## Vibrational and Rotational Relaxation

The high power attainable with the neodymium glass laser permits facile excitation of vibrational modes via the Raman effect. A large number of workers have used this method to measure vibrational lifetimes and ascertain the mechanism of vibrational relaxation in the condensed phase. The usual technique is to excite molecules with the fundamental at 1060 nm and probe the relaxation with the second harmonic, by watching the decay of the antistokes signal.[22,23]

Recently Laubereau et al. have suggested that the vibrational relaxation of the 2900-$cm^{-1}$ C–H stretch in ethanol occurs via a splitting into two 1450-$cm^{-1}$ C–H bends.[22] In a deuterated ethanol–trichloroethane mixture the 2900-$cm^{-1}$ C–H stretch was found to decay via a near-resonant splitting between a 2200-$cm^{-1}$ C–D mode in the ethanol and a 700-$cm^{-1}$ C–Cl mode of the dichloroethane.[24]

Complementing this work is a recent study by Monson et al.[25] on liquid hydrocarbons. It was found that the rate of disappearance of the 2900-$cm^{-1}$ C–H stretch was proportional to the number of methyl groups in the molecule. For example, the lifetime of 1-heptene was twice that of heptane, while the lifetime of $CD_3CH_2CH_2CD_3$ was almost an order of magnitude higher than that of normal heptane. These results indicated the effect substituents may have in favoring one of several photochemical channels.

Chuang[26] and coworkers have explored rotational

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effects in the liquid phase by exciting Rhodamine 6G with the second harmonic of neodymium and observing the change in polarization ratio of the transmitted light with time. They found that hydrogen bonding has a negligible effect on the reorientation and that only solvent viscosity plays an important role. Very recently Shank and Ippen,[27] using their 0.3-psec pulse, measured accurately and directly the rotational relaxation of $CS_2$. They were able to show unequivocally that rotational relaxation is the predominant effect for the observed induced birefringence in $CS_2$.

### Radiationless Transitions

The greatest effort in picosecond spectroscopy has been devoted to studies of radiationless transitions. Starting with the now classical azulene study,[18] a large number of experiments have been performed. A good example is the formation and decay of dual fluorescence in *p*-dimethylaminobenzonitrile (DMAB) by Struve et al.[28] The DMAB is excited with 265-nm light into its $S_2$ state. The fluorescence is time resolved using an echelon and a $CS_2$ shutter. Several polar solvents of increasing viscosity at 25 and −78° were used to determine the relaxation dynamics. Vibronic relaxation of the $S_2$ state is found to be rather fast due to the interaction with the solvent molecules. Recent work[28] using solvents which do not strongly hydrogen bond indicated that the solvent reorientation is primarily responsible for the dynamics of the $S_2$–$S_0$ emission, although reorientation of $N(CH_3)_2$ has not been ruled out.

### Electron Dynamics in Liquids

Previous studies of the dynamics of electron localization in polar solvents yielded the rate for hydrating an initially quasifree electron.[20,29] It was shown that within 4 psec the electron digs its own potential well by continuous interaction with the developing polarization modes of a polar solvent. This nonradiative process was studied experimentally by photoionization of molecules such as $K_4Fe(CN)_6$ and KI in polar solvents as a result of excitation with a single 265-nm picosecond pulse. The simultaneous measurement of the spectral evolution in time of the solvating electron between 1000 nm and 500 nm indicated that energy of interaction continuously increased with time until the electron was completely solvated.

It was not possible in previous studies to determine unequivocably whether the solvated electron's interaction with the medium is homogeneous, or whether the absorption band consists of a dense set of discrete bands which overlap to form the well-known broad, blue, solvated electron band in the range of 450 to 1400 nm. Preliminary work on the solvated electron in sodium–ammonia solution by Huppert et al.[30] indicates that bleaching of this band must take place in about $10^{-13}$ sec, since approximately 10% of the band is bleached by a picosecond pulse. Experiments designed to determine whether or not the bleaching is homogeneous indicate that in the 1100- to 800-nm region the band is homogeneous.[30]

The picosecond kinetics of dianions in solution can be expected to provide a framework for studying electron–solvent interactions. The characteristic behavior of electrons is currently studied by the photoejection of electrons from dianions in solution. The effect of the solvent and associated cation in the generation and subsequent ultrafast kinetics of "electrons" in solution is exemplified by the photoejection of an electron from tetraphenylethylenesodium in THF.[31]

$$T^{2-},2Na^+ \rightarrow T^{\cdot -},2Na^+ + e^- \rightarrow T^{\cdot -},Na^+ + e^- + Na^+$$

The reaction is manifested by bleaching of the 480-nm absorption band of the dianion $T^{2-}$ and the appearance of a 660-nm band of the monoanion radical $T^{\cdot -}$. The latter can be the product of two processes, the photoejection and the capture of an electron by tetraphenylethylene.

$$T + e^- \rightarrow T^{\cdot -}$$

Addition of sodium tetraphenylboride, which greatly reduced the concentration of $T^{2-},Na^+$, does not affect the amount of bleaching of the $T^{2-}$ 480-nm band, indicating that photoejection takes place only from $T^{2-},2Na^+$. In dioxane solutions these transient effects were not found; therefore, one assumes that the electron must be much more tightly bound in this solvent system.

To observe the initial kinetics[32] of this reaction, a single frequency-doubled pulse (530 nm) from a mode-locked neodymium laser was split into two portions. One part served as the photolysis pulse, while the second part produced the continuum which was imaged on an echelon before entering the sample cell.

The kinetics of the photochemistry were followed by monitoring the time-resolved decrease of the dianion concentration in the 480–550-nm region. Also, the appearance of the $T^{\cdot -}$ intermediate was sought in the 660-nm region of its absorption unsuccessfully.

In dioxane the 480-nm $T^{2-},2Na^+$ band was bleached for a period of time corresponding to the laser pulse (~10 psec) and totally recovered after the duration of the excitation pulse. This is in contrast to a tetrahydrofuran (THF) solution in which two rates are observed. About one-half of the $T^{2-}$ 480-nm band intensity bleaches and recovers within the period of the pulse, while in the other half, the bleaching continues for several microseconds. Similar bleaching dynamics were monitored throughout the band at 490, 510, and 540 nm. These observations suggest two different relaxation processes for the photoejected electron, whose existence and identification have been determined by Szwarc and colleagues.[33] In the case of dioxane, it is tightly bound or perhaps in this case does not even photoeject since the bleaching of $T^{2-}$ could only be observed during excitation of the dianion. On the other hand, increasing the dielectric

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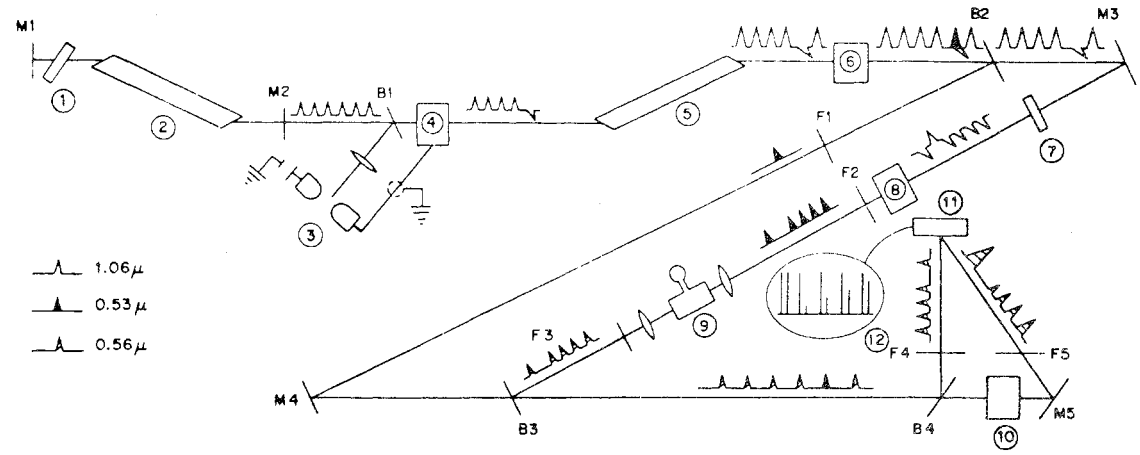


**Figure 2.** Diagram of the apparatus used to observe the decay of prelumirhodopsin. Components: (1) cell containing saturable absorbing dye, (2) $Nd^{3+}$ glass-laser rod, (3) spark gap, (4) Pockel's cell, (5) $Nd^{3+}$ glass-amplifier rod, (6) KDP SHG crystal, (7) 1.06-$\mu$m 90° polarization rotator, (8) KDP SHG crystal, (9) 15-cm cell containing benzene, (10) sample cell, (11) fast photodiode, (12) fast oscilloscope.

constant of the solvent permits some of the electrons to tunnel away from the monoanion.

The characteristic absorption of the monoanion has not been observed in this system, most likely because of orientational effects. The equilibrated $T\cdot^-$ ion has a configuration very much like the neutral tetraphenylethylene molecule, while the $T^{2-}$,$2Na^+$ dianion has the two $Ph_2$ chromophores in mutually perpendicular planes. The 480 nm band of the latter is identical with compounds such as $CH_3CPh_2$. During the period of our observation (~60 psec), the monoanion would not have reached its equilibrium conformation; therefore, absorption in the 660-nm region is not possible. Alternatively, the monoanion could be produced in an excited state which might not absorb within the spectral region of our experimental studies.[34] Several studies with tetracene dianions conducted by Hoytink et al. show the effect of upper states absorptions.[35-37]

## Ultrafast Intermediates in Vision

Even more dramatic results were obtained while applying the methods of picosecond spectroscopy to biological systems. To the best of our knowledge, the first application of this technique to biology was the measurement of the rate of formation and decay of prelumirhodopsin at room temperature by Busch et al.[38] The aim of this project was to detect, identify, and measure the primary events of vision. Specifically, the identification and rate of the first step in the isomerization of rhodopsin at biological or room temperatures. These studies were impossible to perform by classical spectroscopy due to the shorter than nanosecond rate of formation of the first intermediate, thought to be prelumirhodopsin. Previous studies at 77 K established that a band appearing at ~560 nm, which was not observed at room temperatures due to its fast rate of formation and decay, should be attributed to an intermediate, prelumirhodopsin. This is now believed to be the first step in the photoisomerization of the polyene chromophore rhodopsin (retinal and protein).

The experiment was performed with a single 1060-nm picosecond pulse which is amplified, and frequency doubled to 530 nm. Part of the green light pulse was focused into a cell containing benzene generating the stimulated Stokes Raman at 561-nm interrogating light.

In the first set of experiments, an echelon with a 20-psec intersegment time was utilized. Absorption of 561-nm light was found to occur at the segment coincident with the excitation pulse and remain for a period of time longer than the 400-psec (cumulative time width of all segments of the echelon and movement of the translation stage). When instead 2-psec echelon was used, the rise time of prelumirhodopsin absorption was found to be limited by the width of the excitation pulse. Since the rise time of the prelumirhodopsin is governed by the excitation pulse, only an upper limit of 6 psec can be placed on its rate of formation.

The size of the echelons constructed so far has limited their use to times of only several hundred picoseconds although, in conjunction with a movable mirror or an appropriately spaced string of mirrors, one can increase the time to several nanoseconds. In this case a somewhat different apparatus configuration was utilized to observe the long (nsec) decay time of the prelumirhodopsin intermediate (Figure 2).

The pulse train was passed through a Pockels' cell where one of the earliest pulses was rotated in polarization by $\pi/2$. The entire train was amplified and then entered a KDP crystal oriented such that only the rotated pulse could be frequency doubled. A dichroic beam splitter was used to extract this pulse. The remainder of the train was now rotated $\pi/2$ in an optically active quartz rotator and passed through a second KDP crystal, followed by the usual Raman cell of benzene. The 561-nm pulse train (Raman shifted) and the 530-nm single pulse were recombined and focused into a cell containing the bovine rhodopsin. Beam splitters before and after the sample cell were set to send $I_0$ and $I$ into a fast photodiode where output was fed into a Tektronix 519. The decay of prelumirhodopsin could now be monitored every 7 nsec (pulse separation) by observing

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changes in the ratio of $I/I_0$. When analyzed in terms of exponential decay[39] (Figure 3) the data revealed decay rates at 17.5, 22.5, and 24.3° of $2.7 \times 10^7$, $3.7 \times 10^7$, and $4.1 \times 10^7$ $sec^{-1}$.

Oesterhelt and Stoeckenius[40] proposed that the purple membrane patches of the bacteria *Halobacterium halobium* consisted of retinal bound to an opsin-like protein. Due to its close similarity with rhodopsin it is referred to as bacteriorhodopsin; however, unlike bovine rhodopsin, optically clear aqueous solutions can be obtained with the chromophore remaining bound to the membrane.

Utilizing the double-beam spectrometer (Figure 1) Kaufmann et al.[41] observed the formation of the first light-induced intermediate in bacteriorhodopsin by measuring a difference spectrum between 500 and 660 nm (Figure 4). The intermediate was found to have a rise time limited by the 6-psec width of the excitation pulse. In addition to the dynamics of the formation of this intermediate, a previously unknown transient state was observed. The spectral location of this state at the isosbestic point at 580 nm and the calculated lifetime of ~16 psec make it a candidate for the first intermediate which could play an important role in the photoinduced cycle of the purple membrane.

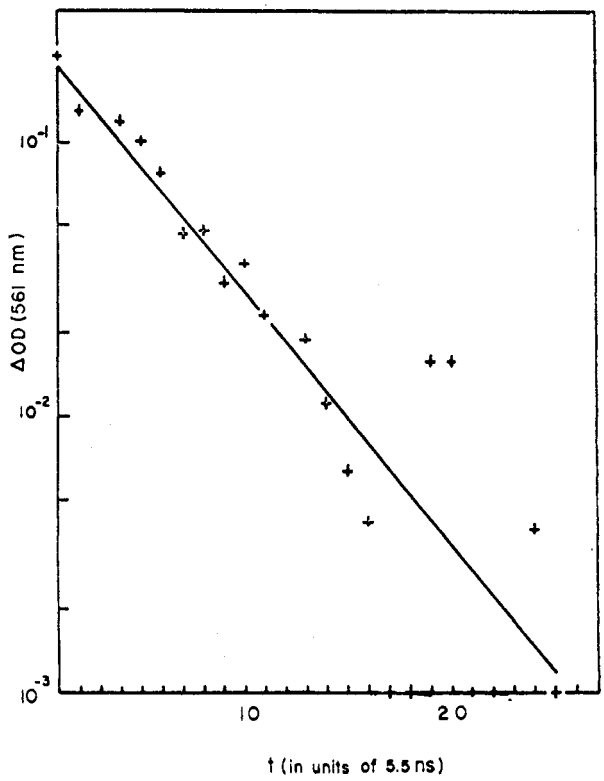


**Figure 3.** Log [prelumirhodopsin] vs. $t$. From the slope, lifetime ≈ 30 nsec.

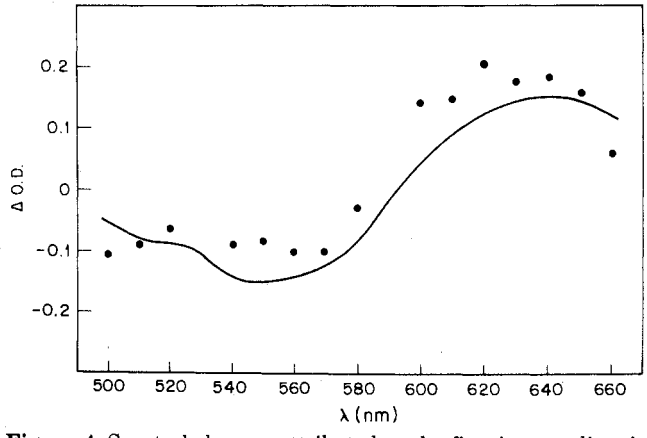


**Figure 4.** Spectral changes attributed to the first intermediate in the light-adapted photochemical cycle of bacteriorhodopsin, 13 psec after excitation; the solid curve represents microsecond spectra at 1°.

## Primary Events in Photosynthesis

During the past 2 years, an extensive program has been devoted to the study of the primary events of photosynthesis initially in reaction centers by Netzel et al.[21] and subsequently in chromatophores.[42]

The primary events leading to photooxidation of reaction centers containing bacteriochlorophyll were studied by excitation of the bacteriopheophytin band at 530 nm and interrogating the 865-nm band. The excitation was achieved by a single 1060-nm picosecond pulse which was amplified and subsequently frequency doubled to 530 nm while the picosecond kinetics were studied by following the time-resolved bleaching of the 865-nm bacteriochlorophyll band. The energy decay characteristics of this band were measured directly by the picosecond continuum. The disappearance of the 865-nm band, which is thought to have at least some association with photooxidation, was found to take place within 7-psec excitation. This establishes a limit for the very rapid energy transfer between bacteriopheophytin and bacteriochlorophyll.

As a result of the high sensitivity of the double-beam system it became possible to detect and characterize the absorption of a new band located in the visible region.[43] It is broad smooth band covering the entire 500- to 660-nm region with the exception of observed bleaching at 540 and 600 nm as shown in Figure 5a.

To elucidate the function of this new absorption band time, identical experiments were performed, first with the primary acceptor at its normal oxidized state when photochemistry can proceed and then with the primary acceptor reduced, thus preventing subsequent photochemistry. It was found that in the first case the positive optical density changes associated with the absorption band decayed with the same rate as the bleaching at 540 nm; however, an increase in the bleaching at 600 nm was observed. In the latter case, although the sample was at a −200-mV potential compared to +200 mV in the first case, the positive optical density changes as well as the bleaching persisted. These results are plotted in Figure 5b. Analysis of the data indicates that we have observed the state which precedes the electron transfer from the chromophore to the primary acceptor. The rate of

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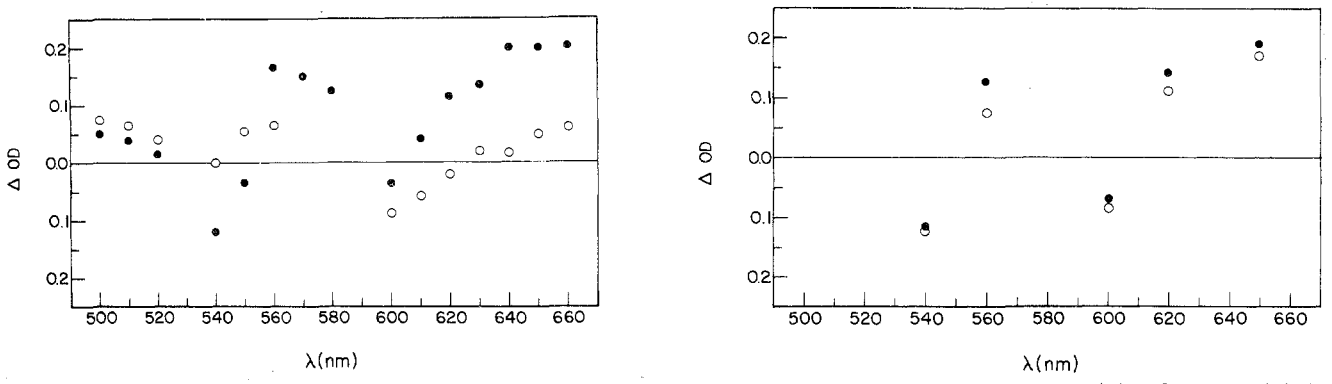


**Figure 5.** Laser-induced spectrum of *Rps. spheroides* R26 reaction centers. Optical density changes after 13 psec (●) and 250 psec (○). (a, left) Reactions at ~+200 mV; (b, right) reaction centers reduced at <−200 mV.

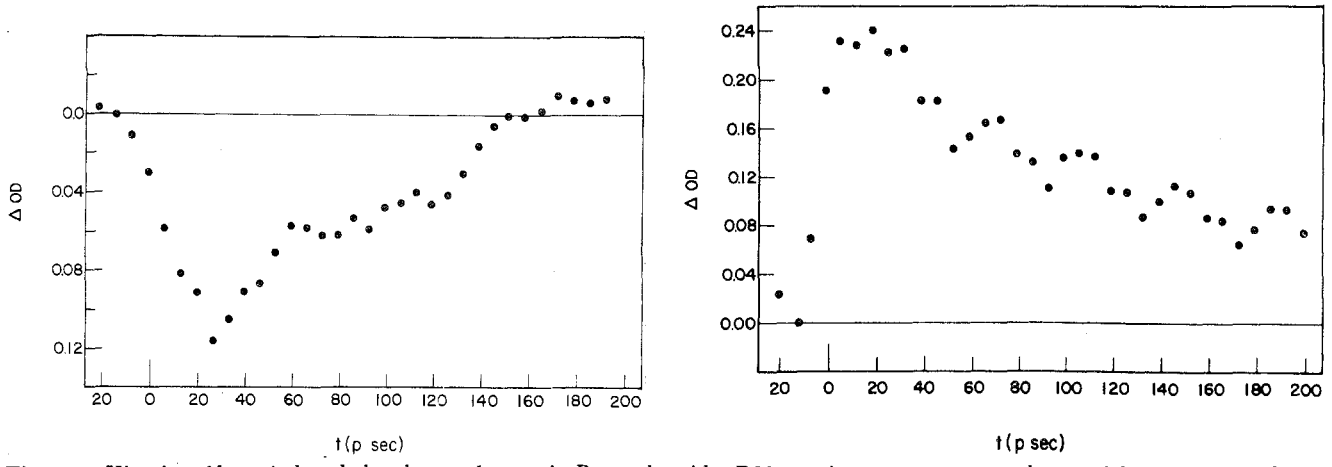


**Figure 6.** Kinetics of laser-induced absorbance changes in *Rps. spheroides* R26 reaction centers at normal potential, ~200 mV. (a, left) λ 540 nm; (b, right) λ 640 nm.

decay of this band in both the positive ΔOD region and the bleaching at 540 nm was measured with the system of Figure 1. A plot of the data (Figure 6) reveals a risetime for this photochemical event of ~150 psec.

In addition to the 540-nm experiments, similar studies were performed at the 760-nm band of bacteriopheophytin and the 600- and 865-nm band assigned to bacteriochlorophyll. The essentially identical rate of bleaching of all these bands strongly suggests that both types of chromophores are part of this excited state.[43]

Applications of picosecond spectroscopy to small molecules in the gas phase include our recent studies of predissociation of ICl. A single well defined picosecond pulse is tuned to excite preselected vibronic levels of ICl. Then a second pulse of different wavelength interrogates the population of this excited level by either absorption, of the probe pulses to an upper electronic state $S_1 \rightarrow S_n$, and/or by Raman scattering. It has been possible to measure the lifetimes of several vibronic levels and thus map out with some certainty, the crossing of the potential surface of the excited state and the dissociative continuum. Preliminary results indicate that the rate of the population decay of the $v = 3$, $B_0^+$ level of ICl is ~3 × $10^{10}$ $sec^{-1}$. Details of this experiment will be presented elsewhere.[44]

These studies of rhodopsin, and chemical systems will, we hope, be a stimulant for many other picosecond investigations in chemical and biological systems.

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