

PICOSECOND OBSERVATIONS OF MOLECULAR PROCESSES USING LASER TECHNIQUES

P. M. Rentzepis and M. R. Topp
Bell Telephone Laboratories, Incorporated
Murray Hill, New Jersey, 07974

Abstract

This paper was presented as an invited lecture at the International Solid State and Liquid Scintillation Conference on July 7, 1970.

Introduction

The pulsed laser, in the few years since its realization, has increasingly become a tool for the photochemist rather than remaining a physical phenomenon. Many papers have been published to date on the applications of the Q-switched laser in the study of nanosecond chemical processes.

More recently, the mode-locked laser was developed,⁽¹⁾ and has found some applications in the field of picosecond processes.⁽²⁻⁷⁾ It is the purpose of this article to describe some of the most recent advances in our laboratory in this direction.

Mode-Locked Lasers

By special Q-switching techniques, usually by the use of a saturable absorber, it is possible to modulate the essentially homogeneous 10^{-7} sec pulsed laser output into a burst of subnanosecond pulses with a uniform time separation.⁽¹⁾ This separation is equal to the reciprocal of the cavity oscillation frequency, typically 5-10 nsec. The duration of the pulses is, for ruby lasers, ~ 5 psec, and for Nd^{3+} -glass, ~ 2 psec, although there is recent evidence to suggest that these pulses, too, are envelopes of even shorter-duration pulses.⁽³⁾ The power in these pulses may

easily be as high as 10 GW or 10^{16} photons per pulse. The radiation is still nearly monochromatic, though less so than for the Q-switched pulse, the bandwidths being for Nd^{3+} -glass $\sim 100\text{ cm}^{-1}$, and for ruby $\sim 10\text{ cm}^{-1}$.

The energy in these pulses, as will be seen, is sufficient to perform useful photochemical experiments on subnanosecond processes. The high powers available using these pulses have allowed the generation with remarkable efficiencies of certain non-linear processes such as second harmonic frequencies (up to 50%) and stimulated Raman radiation (80% max).⁽⁴⁾ Fortunately, stimulated Brillouin radiation is almost absent,⁽⁵⁾ allowing these high powers to be passed through delicate, non-absorbing optical components.

Organic scintillators have been particularly useful for a number of purposes in conjunction with spectroscopic investigations using picosecond laser pulses, owing to their high absorption coefficients both linear and non-linear, high fluorescence efficiencies, short fluorescence lifetimes and stability even at high temperatures (i.e. in the molten state).

Multiphoton Absorption

The high intensity of mode-locked laser pulses has made possible the observation of the fluorescence following two-(2,3) (TFP) and three-photon^(4,8) (3PF) absorption processes, using solutions of, for example BBOT (2,5 - bis-[5-t-butylbenzoxazolyl (2')]-thiophene) in ethylene dichloride. The recorded fluorescence enables one to measure the duration of ultrafast pulses. Because of the higher contrast ratio between the fluorescent spots and the background (10:1 max for 3PF as opposed to 3:1 max for TFP)⁽⁹⁾ the three-photon fluorescence method has been adopted in our laboratory as a standard method for picosecond pulse measurement. (Fig. 1)

However, an additional benefit may be derived in that it is now possible to measure by the three-photon method the true shape of the pulses. It should be noted that the convolution method of pulse measurement usually used (two-photon fluorescence) yields a symmetrically-shaped fluorescent spot, irrespective of the true shape.⁽¹⁰⁾ Consider the standing-wave pattern produced by placing a mirror in a fluorescent solution irradiated by a mode-locked laser. The fluorescent intensity at a point in the solution (X)

ORGANIC SCINTILLATORS

where the pulses overlap is derived from an autocorrelation function:⁽¹¹⁾

$$G^{(n)}(\tau_1, \tau_2, \dots, \tau_{n-1}) = \frac{\langle I(t)I(t+\tau_1) \cdots I(t+\tau_{n-1}) \rangle}{\langle I^n(t) \rangle}$$

where n is the order of the non-linear absorption process preceding fluorescence, and τ is the delay time between pulses overlapping at (X) .

For example, the fluorescence intensity for the two-photon process is given by:⁽⁵⁾

$$F(\tau) = 1 + 2 G^{(2)}(\tau)$$

where τ here is the optical time to and from the mirror from the point (X) .

Now, while $G^{(2)}(\tau)$ is symmetric to inversion, $G^{(3)}(\tau_1, \tau_2)$ is not,⁽¹¹⁾ and from it may be derived both the phase and duration of the pulse, and hence its true shape. In order to obtain the required information, namely, the two delay times τ_1 and τ_2 it is necessary to overlap not two, but three pulses. The apparatus, shown in Fig. 2, shows how this can be done. A more recent design allows the overlap of three pulses, two by normal reflection, and the third by crossing the original path perpendicularly, care being taken to retain parallel polarization throughout in order to optimize the three-photon absorption. The results and detailed analysis of this work may be found elsewhere.^(12,13)

Optical Third Harmonic Generation

A considerable amount of work has been reported for the conversion of the fundamental frequency of a laser to the third harmonic.⁽¹⁴⁻¹⁷⁾ The largest effort has been applied in crystals, gases and solutions but essentially none to our knowledge in pure organic liquids. The observation of high two-⁽¹⁸⁾ and three-photon absorption cross-sections⁽⁴⁾ in our laboratory, and large fluorescence quantum yields, in organic scintillators such as BBOT and dimethyl POPOP, indicate also high third harmonic coefficients for these materials.

Experimental

The apparatus used for generation of the third harmonic in liquefied organic compounds is shown schematically in Fig. 3.

A train of pulses from a mode-locked neodymium laser was partially focussed by a 1 meter lens through a 1 mm cell of the organic liquid. The high temperature was maintained by enclosing the cell in a thermostated, heated copper block. The degree of mode-locking was monitored from the three-photon fluorescence spots generated by a standing wave⁽⁴⁾ in a solution of BBOT in ethylene dichloride. The beam transmitted through the cell was filtered of the fundamental radiation, and passed to the diagnostic apparatus. The spectrum was measured by a Jarrell-Ash 3/4 meter spectrograph and RCA 1P28 photomultipliers with suitable filters (P_1, P_2) were used to measure the relative pulse intensities. The radiation from the cell consists of a narrow-band ($\Delta\nu \sim 100 \text{ cm}^{-1}$) at 353.4 nm, which corresponds exactly to the third harmonic of the Nd^{3+} laser frequency.

Confirmation of the nature of the harmonic beam was made by measurements of the cubic intensity dependence on fundamental intensity, the third-power shape of the beam cross-section, the parallel polarization,^(17,19) and the absence of a threshold.

It is apparent that the efficiency of third harmonic generation for the various compounds discussed here depends strongly on the value of the first-order absorption cross-section, the positions of the relative absorption maxima being secondary in importance. However, the build-up of the third harmonic wave is restricted both by reabsorption and by loss of coherence between the fundamental and the third harmonic beams due to index mismatching. Experiments are at present in progress to determine the correlation between the refractive index and the conversion efficiency for the third harmonic.

For other liquids such as butyl-PBD, the absorption is low, and the refractive index mismatch between the fundamental (1.06 μ) and third harmonic (353 nm) is the critical limiting factor for THG conversion, (Conversion $\leq 10^{-5}$). Techniques of index matching via anomalous dispersion,^(20,21) for example by introduction of narrowband absorbers between the w and $3w$ regions would improve the conversion efficiency into third harmonic by several orders of magnitude.

ORGANIC SCINTILLATORS

Generation of third harmonic by this method would lead to subpicosecond pulses, as opposed to the method of frequency mixing between the fundamental and the second harmonic. The use of reproducibly subpicosecond pulses at 353 nm (Nd³⁺-glass - THG) could be used advantageously instead of the inherently longer (>3 psec) and less stable second harmonic pulses from the ruby laser (347 nm).

Use of a Mode-locked Dye Laser for Pulse-Amplification Measurements

An organic scintillator, when dissolved in, for example, methyl cyclohexane can act as a four-level laser medium, (18,22) and may be excited either by one- or two-photon absorption, as seen in Fig. 4. Thus, with a finite population in the excited states S₁(v=0) a population inversion is achieved with respect to the upper vibrational levels of the ground state (S₀(v>0)). At low irradiation intensities, dimethyl POPOP (1,4-bis-2-(4-methyl, 5-phenyloxazolyl) benzene) (DMP) fluoresces strongly between 400-450 nm, and if it is pumped optically into S₁ by the second harmonic of the ruby laser (2w = 28800 cm⁻¹), stimulated emission at 420 nm, the peak of the 0-1 fluorescence band is observed. (23,24) This dye laser may be mode-locked, (25) and the train of pulses amplified in a second cell containing the same dye (DMP). If the second cell is pumped via two-photon absorption, it is possible to calculate, from the observed amplification, the two-photon molecular absorption cross-section (σ_{II}), according to:

$$\sigma_{II} = \frac{\ln G}{\sigma_F L t I_0^2 n_0} \quad (1)$$

where G = gain in amplifier cell

σ_F = fluorescent emission cross-section

L = length of cell

t = laser pulse duration

I₀ = laser pulse intensity

n₀ = density of solute dye molecules in amplifier cell.

The above equation is a simple extension of Beer's Law.

Experimental

A train of mode-locked ruby laser pulses was passed through a red filter (F₁) into a resonant cavity terminated

by two dielectric mirrors (M) (100% reflecting at 420 nm, 90% transmitting at 695 nm). The optical length of the 420 nm (w_d), and 694.3 nm (w_r) cavities was the same. The maximum power in the pulse train was about 7 GW (7×10^9 W) and the pulses were separated by exactly 5 nsec. (Fig. 5)

The dye solution used in both cells C_1 and C_2 was dimethyl POPOP (DMP) in methyl cyclohexane. The train of mode-locked ruby laser pulses (w_r) had a dual function in exciting the dye cell as follows. The frequency w_r was used to excite dye cell C_1 by two-photon absorption. The second harmonic of the red pulses ($2w_r$ generated by the KDP crystal) was used to generate the stimulated emission from the dye cell C_2 , which became mode-locked owing to the identity of the two laser cavity optical lengths.⁽²⁵⁾ The time-spacing of the two sets of mode-locked pulses (w_r and w_d) being identical (Fig. 6), a dye laser pulse was reflected from M_1 simultaneously with, or slightly behind, the arrival of the succeeding w_r pulse at M_1 . The pulses travelled together through C_1 where w_r excited the dye by two-photon absorption, and w_d stimulated it to emit resulting in amplification of w_d . The fluorescence lifetime of the dye (1.5 nsec) was sufficiently short that no excitation remained after the 5 nsec pulse separation and each amplification process could be considered to be a separate experiment.⁽¹⁸⁾

The gain within the cell C_1 was monitored for each pulse by the same photodiode by observing the pulse before and after passing through the dye cell, corresponding to a separation of 1.5 nsec.

The response time of the photodiode-oscilloscope system was adequate to resolve the 1.5 nsec separation of the pulses. The inclusion of a reference trace of laser fundamental intensity gave an oscilloscope trace having three distinct trains. Hence, a series of data points could be obtained, which made possible the calculation of σ_{II} from equation (1). The linearity of the plot indicated that gain saturation was not reached at this pumping level. The value of σ_{II} , obtained from the slope of the plot was found to be 4.0×10^{-48} cm⁴ sec photon⁻¹.⁽¹⁸⁾

This method for the determination of the two-photon absorption cross-sections (σ_{II}) has certain advantages over other techniques in use at the present. Two-photon absorption is usually monitored by the fluorescence of the absorbing species, which provides an order-of-magnitude estimate for the quantity σ_{II} . The technique discussed here measures

ORGANIC SCINTILLATORS

directly the population of excited states, and moreover, since a train of mode-locked pulses is used, one laser shot provides sufficient data for a determination of σ_{II} . The accuracy is within a factor of two, and is largely dependent upon the accuracy of the measurement of the laser pulse intensity. This method also enables one to measure σ_{II} easily for other fluorescent species, or for the same species in different solvents by changing the solution in the amplifier cell.

Cascade

The above results have shown that it is possible to create, via two-photon absorption a sufficiently populated first excited singlet state in dimethyl POPOP to undergo stimulated emission. It is of interest to consider the reverse process of downward stimulated two-photon emission from a highly populated upper singlet state. This effect has been discussed theoretically by Letokhov⁽²⁶⁾ and by Sorokin and Braslau,⁽²⁷⁾ and more recently by Hope and Vassell.⁽²⁸⁾ The two-photon cascade process would be capable of producing pulses of extremely high intensities and ultrashort duration. Unlike the two-photon absorption process, which is not cumulative, the emission process is cumulative, i.e. as the light level increases throughout the excited medium the efficiency of the stimulated emission process increases. Under such conditions, the photon intensity would increase very rapidly as the light pulse propagated through the laser medium.

The analogy with the model of Sorokin and Braslau⁽²⁷⁾ may be carried further in a consideration of the expected output from a medium undergoing two-photon stimulated emission (TPSE). Their model allows for optical pumping of a potential TPSE system by a normal-mode laser which would self-Q-switch and yield a nanosecond-duration pulse above the threshold for TPSE. By analogy, the pumping of such a system by mode-locked (picosecond) pulses, may yield shorter pulses of lower energy than the pumping pulses, and of much higher intensities. Since the picosecond pulses produced by conventional solid-state lasers have bandwidth-limited durations:

$$\tau \approx 1/\Delta\nu$$

it can be seen that only a small further pulse-shortening

(to 3×10^{-13} sec) may be obtained with these systems. However, the large bandwidths available from mode-locked dye lasers ($>100 \text{ cm}^{-1}$) indicate that pulses of duration $\sim 10^{-14}$ sec may be available in suitable cases.

Calculations have shown (Eq. 12, Ref. 27) that the incident photon density required for the cascade process to occur in a typical system would be of the order of 10^{30} photons $\text{cm}^{-2} \text{ sec}^{-1}$ for a σ_{IIF} value of $10^{-50} \text{ cm}^4 \text{ sec photon}^{-1}$ (σ_{IIF} = emission analog of the two-photon absorption cross-section σ_{II} , and $\sigma_{\text{IIF}} \sim \sigma_{\text{II}}$).

For dimethyl POPOP, with a σ_{IIF} value of $4 \times 10^{-48} \text{ cm}^4 \text{ sec photon}^{-1}$, the process may be expected to reach threshold with the laser intensities currently available.

Apart from the "degenerate" two-photon cascade process, there is also a less efficient non-degenerate process, as discussed by Garwin⁽²⁹⁾ and Hope and Vassell.⁽²⁸⁾ It is pumped in the same way, but stimulated by photons whose sum frequency is equal to the inherent lasing frequency of the medium. This process would provide a wide variety of frequencies with picosecond pulse duration simply by tuning the emitting dye.

Organic Scintillators

It can be seen that the organic scintillators which have been discussed so far can be used quite advantageously in several spectroscopic and non-linear experiments and their applications. Some of these are summarized below:

- (a) Third harmonic generation in the liquid,⁽³⁰⁾
- (b) The single crystals of these molecules should be suitable for frequency mixing and phase-matched harmonic generation with high efficiencies.
- (c) Their application as a background fluorescence source in laser absorption spectroscopy.⁽²³⁾
- (d) In the two-(2,3) and three-photon fluorescence^(5,12,13) methods of measuring the duration and shape of pulses.
- (e) The stimulated emission, with an onset time of ~ 8 psec⁽³¹⁾ can be used also as an absorption background source for picosecond absorption spectroscopy.
- (f) The wavelength of stimulated emission may be shifted either by temperature or concentration, therefore short-range laser tunability is possible.

ORGANIC SCINTILLATORS

Saturation of Absorption

It has recently been observed⁽³²⁾ that certain molecules exhibit anomalously low absorptions when irradiated with picosecond pulses, as compared to nanosecond or c.w. excitation. This effect cannot be accounted for in terms of self-induced transparency⁽³³⁾ due to the absence of extensive bleaching, and most obviously from the experimental observation that the pulse does not exhibit the sharpening encountered in the above phenomenon.

The first evidence for this process came from the observation of apparently decreased fluorescence quantum yields following picosecond irradiation.⁽³²⁾ On closer inspection this was found to be due to decreased absorption.

This behavior can, in some cases, be explained in terms of the line-width-pulse-duration relationship as discussed in a recent paper.⁽³²⁾ Here, decrease in absorption will occur if both of two conditions are satisfied:

$$\begin{aligned} (1) \quad & \gamma \tau_p \ll 1 \\ (2) \quad & P^2 \epsilon^2 \tau_p^2 / \pi^2 \ll 1 \end{aligned}$$

where τ_p = pulse duration in cm^{-1} .

γ = line width of absorption in cm^{-1} .

P = polarization

ϵ = field amplitude

This treatment is similar to the description of Brillouin and Sommerfeld.⁽³⁴⁾ The difference lies in that this latter discussion is classical and deals with bound wave-train propagation through a non-absorbing medium.

The physical consequence of condition (1) being satisfied is that the irradiation bandwidth is much larger than the absorption bandwidth of the irradiated species. For gaseous atomic systems under picosecond pulse irradiation, this is the case, but for large organic molecules in solution, condition (1) is definitely not satisfied. Typical values of the quantities τ_p and γ being 10 cm^{-1} and 1000 cm^{-1} respectively. In such cases, saturation of portions of the absorption band followed by relaxation in a time approximating to the pulse duration, could occur. In other words, the absorption band must be considered to be heterogeneously broadened.

Let us consider an organic molecular system whose energy-level diagram and absorption spectrum are shown

together in Fig. 7. The bandwidth of a typical mode-locked ruby laser emission is about $\sim 10 \text{ cm}^{-1}$, whereas the absorption band of the organic molecule in solution may be inhomogeneously broadened to 1000 cm^{-1} . This absorption band may be considered to consist of contributions from many discrete but unresolved molecular environments having different energies within the bandwidth, and which interchange with one another in a time longer than the pulse duration. It is quite possible, using laser irradiation, effectively to saturate the narrow bandwidth of $\sim 10 \text{ cm}^{-1}$, which would correspond to the removal of the instantaneously resonant ground state species from solution. According to the Born-Oppenheimer approximation the same group appears in the excited state. After this process has occurred, the absorption within the laser bandwidth will be observed to have decreased. Two possibilities remain open:

- (a) Further laser irradiation may result in the well-known self-induced transparency⁽³³⁾ via stimulated emission of the absorbed energy.
- (b) The process of interchange of environmental states will continue, resulting in the relaxation of the displaced equilibrium of environment in both the ground and excited states. In turn this results in a temporary Boltzmann distribution of the excitation energy among neighboring environmental states which would ultimately decay to the lowest level of S_1 let us say via rotational and vibrational relaxation.

The result of this relaxation would be that the "hole burned" in the absorption band would "fill in" as the relaxation occurred, the greatest contribution coming, from states closest in energy i.e. those with the greatest overlap. The effect would be a broadening of the hole, resulting in a transient decrease in sideband absorption according to the variation in population difference between the ground and excited states across the band.

Further experiments in progress, designed to elucidate the mechanism involved and measure the rate of this "environmental equilibration", include measurements of sideband absorption changes in addition to studies of the more straightforward vibrational relaxation. The techniques^(6,35) for these measurements have already been discussed elsewhere.

The type of apparatus used for time-resolved picosecond absorption spectroscopy is shown in Fig. 8.⁽⁶⁾ After excitation of the solution the residual pulse travels to and from

ORGANIC SCINTILLATORS

the mirror shown such that the weak reflection delayed by the time required for light to travel the round-trip distance meets the next pulse in the train exactly in the cell. Translation of the mirror on the micrometer slide can alter the return time for the interrogating pulse and thus, one may measure, using photodiodes (2) and (4), the durations of any absorption changes in the cell.

Variation of the interrogating frequency by laser harmonics, stimulated fluorescence, or stimulated Raman frequencies adds to the versatility of the process. From the nature of the absorption characteristics of a solution upon irradiation by picosecond laser pulses, it should be possible to determine the nature of broadening, i.e. whether it is homogeneous or heterogeneous. For example, as discussed above, it is possible if sufficient laser energy is supplied to excite all the resonant molecules, such that an apparent saturation of absorption will occur even though only 1% of the total molecules may have been excited. This occurs only in the case of inhomogeneous broadening of the absorption band, and only then, when the pulse duration is appreciably shorter than the relaxation time within the band.

Solvated Electrons

One extremely interesting aspect of the study of picosecond solvent-relaxation processes, apart from the organic scintillators mentioned above is that of the solvated electron.

A convenient way of generating electrons photochemically in solution is by the irradiation of the blue solutions of alkali metals in inert organic solvents, in particular, ethylenediamine or ammonia.

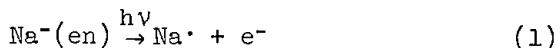
Solutions of alkali metals in amines have recently been studied with respect to their absorption spectra,⁽³⁶⁾ solubilities and conductivities,⁽³⁷⁾ e.s.r. behavior⁽³⁸⁾ and flash photolysis.⁽³⁹⁾ However, it was not until very recently that the nature of the blue color in these solutions was understood. While in dilute metal ammonia solution the blue color is due to the solvated electron at higher concentrations solvated electron-cation ion pairs are formed. The visible absorption band of metal-ammine solutions originates from an electron trapped by a metal atom leading to the formation of negative ions, i.e. M^- .⁽⁴⁰⁾

The absorption spectrum of sodium dissolved anaerobically in ethylenediamine consists of a broad, structureless band extending from 400 nm to 800 nm (10% width) with a maximum at 660 nm. In addition there is an underlying broad absorption, from 500 nm to 2000 nm (10%) peaking at 1280 nm, whose maximum intensity is about 1% of that of the 660 nm peak. This latter absorption is due to the free solvated electron; e^- (en). From their relative absorptions (100:1) and extinction coefficients (1.4:1) it can be seen that the metal anion is in approximately 70-fold excess over the solvated electron.

In addition, e.s.r. experiments show a dominant resonance due to the solvated electron together with a weaker resonance showing metal hyperfine-splitting. This is thought to be due to a small amount of the species: $Na^+ \dots e^-$.⁽⁴¹⁾ It is unlikely that the free atom is present in solution as such. Hence, it can be seen that the solution of sodium in ethylenediamine is essentially a simple ionic solution of metal cations and anions, with a small amount of free solvated electron, and the ion-pair species mentioned above.

Upon irradiation into the visible absorption band, the blue color disappears, and the absorption characteristic of the free solvated electron increases proportionately. These absorption changes have recently been studied independently by nanosecond laser flash photolysis,⁽²³⁾ both in our laboratory⁽⁴²⁾ and by Huppert and Bar-Eli.⁽⁴³⁾ The technique used in our laboratory was essentially the same as used by Porter and Topp,⁽²³⁾ using a pulsed ruby laser (20 nsec pulse, 6943 Å) for irradiation and surplus light from the laser flash lamp (500 μsec) as a background continuum source.

The irradiation process is expressed by the following:



followed by:

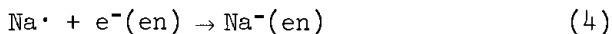
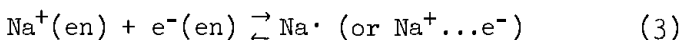


Equation (1) denotes the release of a free electron, and (2) the resolution to form a solvated electron. K_2 is too fast to be resolved by nanosecond techniques. An optical density difference spectrum taken immediately after the laser pulse, and shown in Fig. 9 is compared with a

ORGANIC SCINTILLATORS

difference spectrum synthesized assuming that equations (1) and (2) are the only important processes taking place on this time scale.

The good fit shows that these assumptions are correct. If the time-scale is extended into the microsecond range it can be seen that there is a second-order disappearance of the solvated-electron absorption according to:



and the rate of reaction is found to be close to diffusion-controlled. The chemistry of this is well understood from our work, and agrees with theoretical predictions. The equations used to describe the processes are analogous to those proposed by Glarum and Marshall⁽⁴⁴⁾ for the solvation of potassium in dimethoxyethane, by Arnold and Patterson⁽⁴⁵⁾ for metal-ammonia solutions, and by Golden, et al.⁽⁴⁶⁾

However, the processes of interest to the picosecond photochemist have not yet been studied.

Experimental Note

It can be seen from the above discussion, that this system may be conveniently studied also using the neodymium glass laser. This is important, owing to the shorter pulse duration, and greater stability of output compared to that of the ruby laser. The second harmonic (530 nm) may be used to excite the system, and the fundamental to interrogate the growth of the transient electron absorption at (1.06 μ). In addition, there exist convenient stimulated Raman frequencies with which to study the side-band absorption changes. (Fig. 8)

There are several interesting questions which arise immediately:

- (a) What is the structure of the visible absorption band?
- (b) What is the structure of the electron absorption band?
- (c) How fast does the free electron relax to its ground solvated state?

Homogeneous or Heterogeneous Broadening

Huppert and Bar-Eli⁽⁴³⁾ state that they observe the visible band to be homogeneously broadened; "...provided that there are no rapid fluctuations compared with 50 nsec..". It is extremely unlikely that the environmental relaxation for $\text{Na}^-(en)$ would be of this order of magnitude as it has a relatively low viscosity (1.54 cP),⁽³⁷⁾ a more reasonable figure being 3 orders of magnitude less.

Bronskill, Wolff and Hunt⁽⁴⁷⁾ estimated that the solvation time of the electron in water was less than 20 psec.

Since the whole absorption band is bleached by the irradiating nanosecond laser pulse, it can be stated that there is no bound excited state having a lifetime of this order. The possibilities therefore are as follows, (see Fig. 10):

- (1) That no bound excited state exists at all, i.e. that the irradiation ejects an electron from the sodium trap straight into the free-electron band. In this case, the broadening of the absorption band is probably homogeneous. (Fig. 10a).
- (2) That a short-lived excited bound state does exist, from which the electron subsequently "boils out" thermally into the free electron band. From Fig. 10b this would be the case if the energy separation of BF is $<kT$ (i.e. 200 cm^{-1}).
- (3) Since the thermal process would be expected to be slow, it is possible that the mechanism recently suggested by Jortner,⁽⁴⁸⁾ involving a considerable mixing of this bound state with the free electron continuum would account for its reduced lifetime. This latter process is equivalent to a tunneling between the states involved.

Conditions (2) or (3) could be indicative of either homogeneous or inhomogeneous broadening.

On the basis of present evidence, it is likely that there is no distinct bound excited state of the $\text{Na}^-(en)$ species, as no high-frequency absorption bands exist in the region $33000\text{-}25000 \text{ cm}^{-1}$.⁽³⁹⁾ This becomes clear when it is considered that the tunneling process must lead to a degenerate level (B) which is, at most $10,000 \text{ cm}^{-1}$ below the free-electron continuum band (F). (Fig. 10b).

Hence, picosecond pulse measurements on the appearance lifetime of the solvated electron would be measuring the relaxation of the excited electron from the continuum and

ORGANIC SCINTILLATORS

creation of the cage, rather than the lifetime of some intermediate level in the $\text{Na}^-(en)$ manifold.

Polarization

Use has been made of the linear polarization of the laser pulse in studying rotational motion in solution.^(35,49) In very much the same way as it is possible to create a hole in an absorption spectrum left by the type of absorption saturation discussed above, it is possible to excite preferentially the molecules having a particular polarization component, creating a deficiency of absorption of light of a particular polarization.

Using this technique, the use of which has already been described elsewhere,^(7,35) it is possible to study:

- (a) the polarizations of absorptions between excited levels,
- (b) the rotational period of molecules in solution,
- (c) as in the case of biphenylene,^(7,35) the mechanism of degradation of the electronic excitation energy of the first excited singlet state via a geometrical deformation of the molecule,
- (d) the effects of polarization on the relaxation of an inhomogeneous solvent cage.

For the above problem the apparatus used in Ref. 6 (Fig. 8) or a modification of it, would be suitable.

However, there are certain emission processes which are also of great importance:

- (a) The time dependence of the stimulated Raman output upon laser radiation⁽³¹⁾
- (b) The time dependence of stimulated fluorescence⁽³¹⁾
- (c) The study of fluorescence processes which, due to a variety of reasons, have subnanosecond lifetimes.

Picosecond Light Gate

An ultrafast shutter can be made using the electro-optically induced birefringence in a highly polarizable liquid such as CS_2 . The accurate plane-polarization of the mode-locked laser pulse, combined with its high electric field ($\sim 10^6 \text{ V cm}^{-1}$) and short duration provide an ideal transient birefringence having a relaxation time of 1.8 psec.⁽⁵⁰⁾ Hence, if this liquid cell is placed between two polarizers, oriented with their axes at 45° to the

irradiation pulse polarization, a shutter is formed. This effect has been utilized for making shutters in the nanosecond⁽⁵¹⁾ and picosecond range.⁽⁵²⁾

This shutter may conveniently be used to time-resolve picosecond luminescent events, a recent application in our laboratory being time-resolved studies of stimulated emission from laser-pumped organic dyes.⁽³¹⁾

The apparatus used in reference 31 is shown in Fig. 11. The output from a mode-locked Nd³⁺-glass laser is frequency-doubled. The harmonics are split, the second harmonic being used to excite the sample and cause traveling-wave stimulated emission, while the fundamental pulses trigger the picosecond light-shutter in a crossed-beam arrangement.⁽⁵³⁾ It is obvious that this method⁽⁵³⁾ can be easily adapted to time-resolve picosecond absorption processes.

This article was intended to be a summary of some of our own recent studies. No attempt has been made to present a comprehensive review.

Acknowledgments

We would like to thank Dr. D. C. Douglass for his valuable discussions.

References

1. (a) A. J. DeMaria, R. Gagosz, H. A. Heynau, A. W. Penney and G. Wisner, *J. Appl. Phys.* 38, 2693 (1967).
(b) A. J. DeMaria, D. A. Stetser, and W. H. Glenn, *Science* 156, 1557 (1967).
2. J. A. Giordmaine, P. M. Rentzepis, S. L. Shapiro, and K. W. Wecht, *Appl. Phys. Lett.* 11, 216 (1967).
3. P. M. Rentzepis and M. A. Duguay, *Appl. Phys. Lett.* 11, 218 (1967).
4. P. M. Rentzepis, C. J. Mitschele, and A. C. Saxman *Appl. Phys. Lett.* 17, 122 (1970).
5. S. L. Shapiro, J. A. Giordmaine, and K. W. Wecht, *Phys. Rev. Lett.* 19, 1093 (1967).
6. P. M. Rentzepis, *Chem. Phys. Lett.* 3, 717 (1969).
7. P. M. Rentzepis, *Science* 169, 239 (1970) and references cited therein.
8. P. M. Rentzepis and M. R. Topp, unpublished work.
9. K. H. Drexhage, *Appl. Phys. Lett.* 14, 318 (1969).
10. H. P. Weber and R. Dändliker, *Phys. Lett.* 28A, 77 (1968).

ORGANIC SCINTILLATORS

11. E. I. Blount and J. R. Klauder, *J. Appl. Phys.* 40, 2874 (1969).
12. M. R. Topp, P. M. Rentzepis, and R. P. Jones, to be published.
13. P. M. Rentzepis and D. C. Douglass, to be published.
14. P. D. Maker, R. W. Terhune, and C. M. Savage, *Proc. 3rd Q. E. Conference, Paris 1963* (Ed. P. Crivet and N. Bloembergen).
15. N. Bloembergen, *Non-linear Optics* (Benjamin, N. Y. 1965).
16. Y-H Pao and P. M. Rentzepis, *J. Chem. Phys.* 43, 1281 (1965).
17. J. F. Ward and G. H. C. New, *Phys. Rev.* A185, 57 (1969).
18. M. R. Topp and P. M. Rentzepis (in print) *Phys. Rev.* (1970).
19. P. P. Bey, J. F. Giuliani, and H. Rabin, *Phys. Lett.* 26A, 128 (1968).
20. P. P. Bey, J. F. Giuliani, and H. Rabin, *Phys. Rev. Lett.* 19, 819 (1967); *I.E.E.E.J.Q.E.* 4, 932 (1968).
21. (a) P. M. Rentzepis, J. A. Giordmaine, and K. W. Wecht, *Phys. Rev. Lett.* 16, 792 (1966); (b) J. A. Giordmaine and P. M. Rentzepis, *J. Chim. Phys.* (1) 215 (1967).
22. See for example, A. E. Siegman, *An Introduction to Lasers and Masers*, (McGraw-Hill, 1968).
23. G. Porter and M. R. Topp, *Nature (London)* 220, 1228 (1968); *Proc. Roy. Soc.* A315, 163 (1970).
24. M. R. Topp, Ph.D. thesis, University of London, England (1969).
25. W. H. Glenn, M. J. Brienza and A. J. DeMaria, *Appl. Phys. Lett.* 12, 55 (1968).
26. V. S. Letokhov, *J.E.T.P. Lett.* 7, 284 (1968).
27. P. P. Sorokin and N. Braslau, *I.B.M.J. Res. & Devel.* 8, 179 (1964).
28. L. L. Hope and M. O. Vassell, *Phys. Lett.* 31A, 256 (1970).
29. R. L. Garwin, *I.B.M.J. Res. & Devel.* 8, 338 (1964).
30. M. R. Topp, P. M. Rentzepis, and R. P. Jones, to be published.
31. M. M. Malley and P. M. Rentzepis, to be published.
32. P. M. Rentzepis, I. Tobias, and N. Balazs, *Chem. Phys. Lett.* 4, 205 (1969).
33. S. L. McCall and E. L. Hahn, *Bull. Am. Phys. Soc.* 10, 1189 (1965); see also *Phys. Rev. Lett.* 18, 908 (1967) and *Phys. Rev.* 183, 457 (1969).

34. L. Brillouin, Wave Propagation and Group Velocity, Academic Press, (New York and London, 1960).
35. P. M. Rentzepis and M. R. Topp, *Trans. N. Y. Acad. Sci.* (in print).
36. R. R. Dewald and J. L. Dye, *J. Phys. Chem.* 68, 121 (1964).
37. R. R. Dewald and J. L. Dye, *J. Phys. Chem.* 68, 128 (1964).
38. R. R. Dewald and J. L. Dye, *J. Phys. Chem.* 68, 135 (1964).
39. S. Windwer and B. R. Sundheim, *J. Phys. Chem.* 66, 1254 (1962).
40. I. Hurley, T. Tuttle and S. Golden, *J. Chem. Phys.* 48, 2818 (1968).
41. J. L. Dye, *Accts. Chem. Res.* 1, 306 (1968).
42. M. R. Topp, S. H. Glarum and P. M. Rentzepis, unpublished work.
43. D. Huppert and K. H. Bar-Eli, *J. Phys. Chem.*, to be published.
44. S. H. Glarum and J. H. Marshall, *J. Chem. Phys.* 52, 5555 (1970).
45. E. Arnold and A. Patterson, *J. Chem. Phys.* 41, 3089 (1964).
46. S. Golden, C. Guttman, and T. R. Tuttle, *J. Am. Chem. Soc.* 87, 135 (1965); *J. Chem. Phys.* 44, 3791 (1966).
47. M. J. Bronskill, R. J. Wolff, and J. W. Hunt, *J. Phys. Chem.* 73, 1175 (1969).
48. J. Jortner, private communication.
49. K. B. Eisenthal and K. H. Drexhage, *J. Chem. Phys.* 51, 5720 (1969).
50. S. L. Shapiro and J. D. Broida, *Phys. Rev.* 154, 129 (1967).
51. G. Mayer and F. Gires, *Compt. Rend. Acad. Sci. Paris*, 258, 2039 (1964).
52. M. A. Duguay and J. W. Hansen, *Optics Communications* 1, 284 (1969).
53. M. M. Malley and P. M. Rentzepis, *Chem. Phys. Lett.* 3, 534 (1969).

ORGANIC SCINTILLATORS

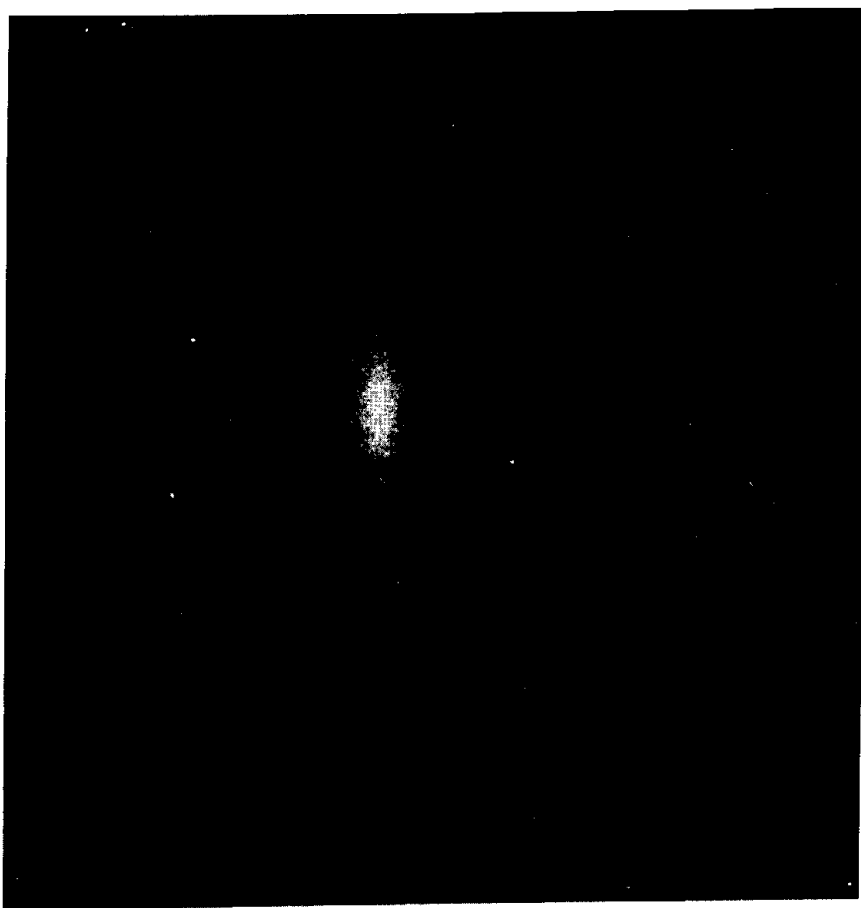


Fig. 1 Measurement of picosecond pulses by three-photon fluorescence.

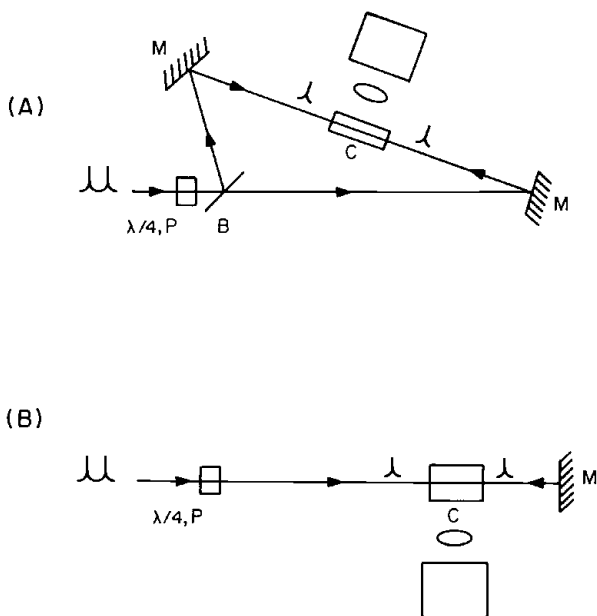


Fig. 2 Various designs of apparatus for the measurement of picosecond pulses by three-photon fluorescence:
 (a) single pulse - two pulse overlap - duration only.
 (b) multiple pulses - two pulse overlap - duration only.

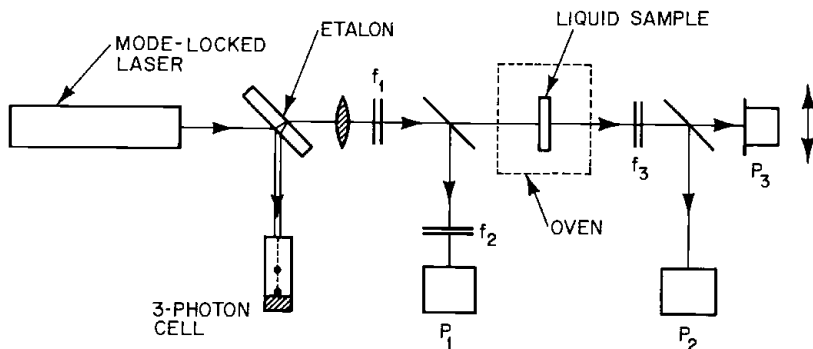


Fig. 3 Schematic diagram of the apparatus used to generate the neodymium laser third harmonic using molten organic scintillators.

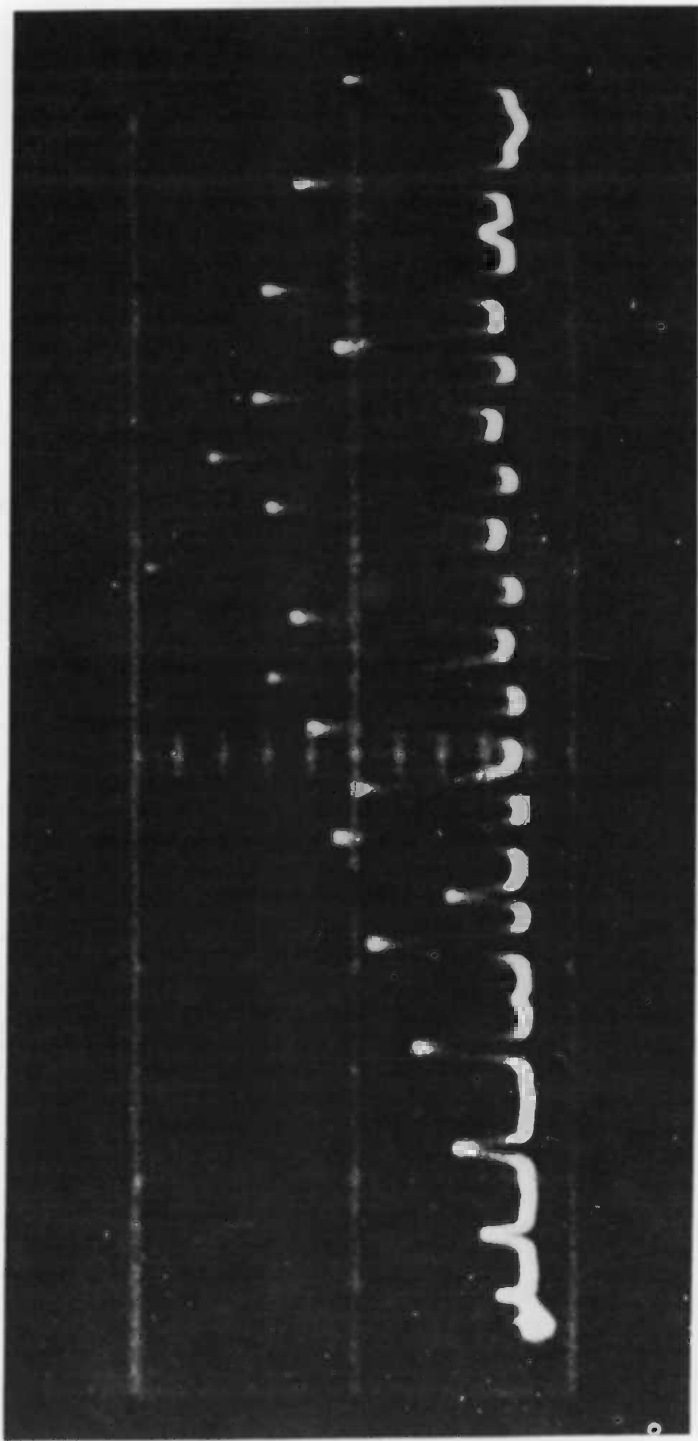


Fig. 6 Interleaved trains of a mode-locked dye laser and the pumping ruby laser fundamental radiation. They are separated optically for clarity.

ORGANIC SCINTILLATORS

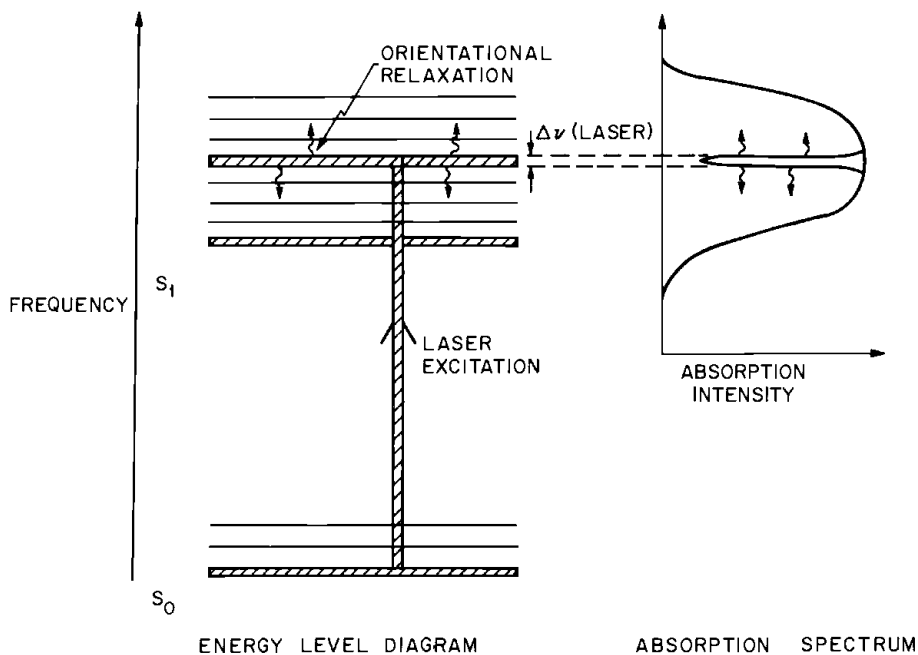


Fig. 7 Energy-level diagram and absorption spectrum demonstrating the possibility of "hole-burning" in the absorption band by selective excitation of a small portion in a short time.

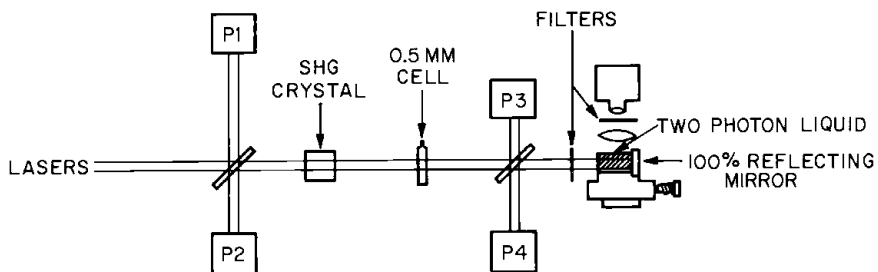


Fig. 8 Apparatus used for time-resolved picosecond absorption spectroscopy.

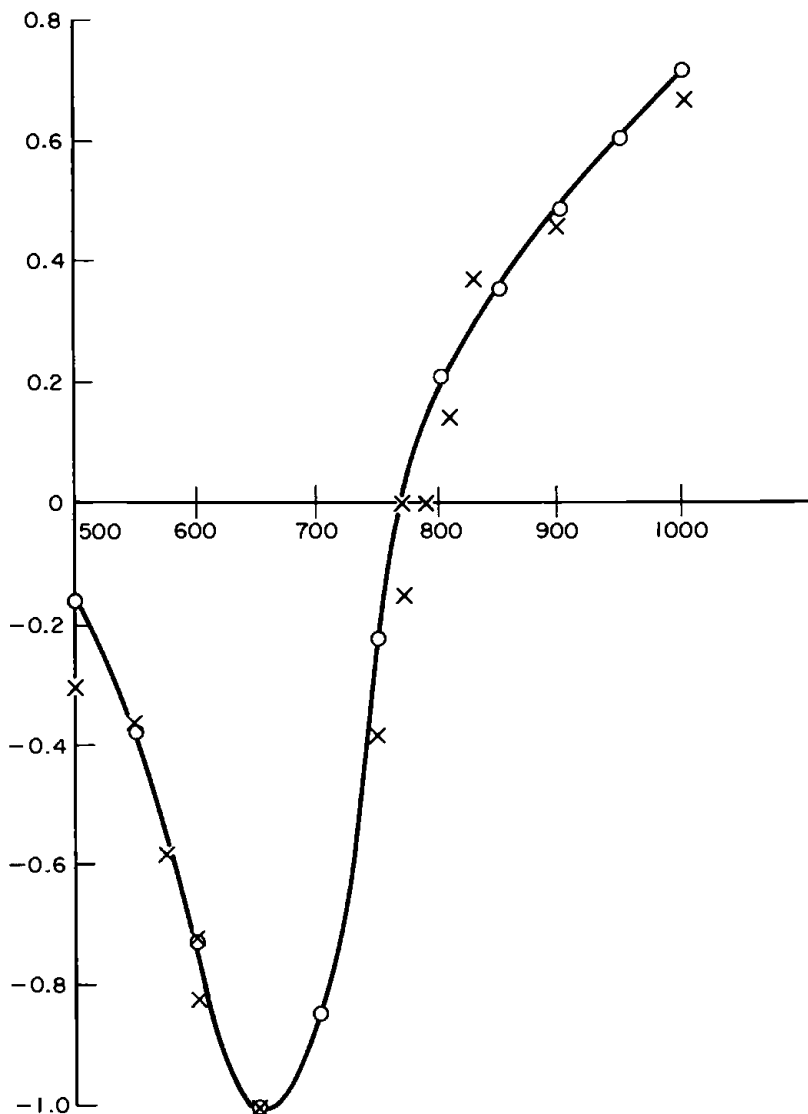


Fig. 9 Optical density difference spectrum taken immediately (<100 nsec) after the irradiation of $\text{Na}^+(\text{en})$ by a ruby laser pulse.

X - observed difference spectrum,

O - calculated difference spectrum, assuming equations (1) and (2) to be representative of the reaction mechanism.

ORGANIC SCINTILLATORS

ENERGY LEVELS OF $\text{Na}^{\ominus}(\text{en})$ AND $e^{\ominus}(\text{en})$

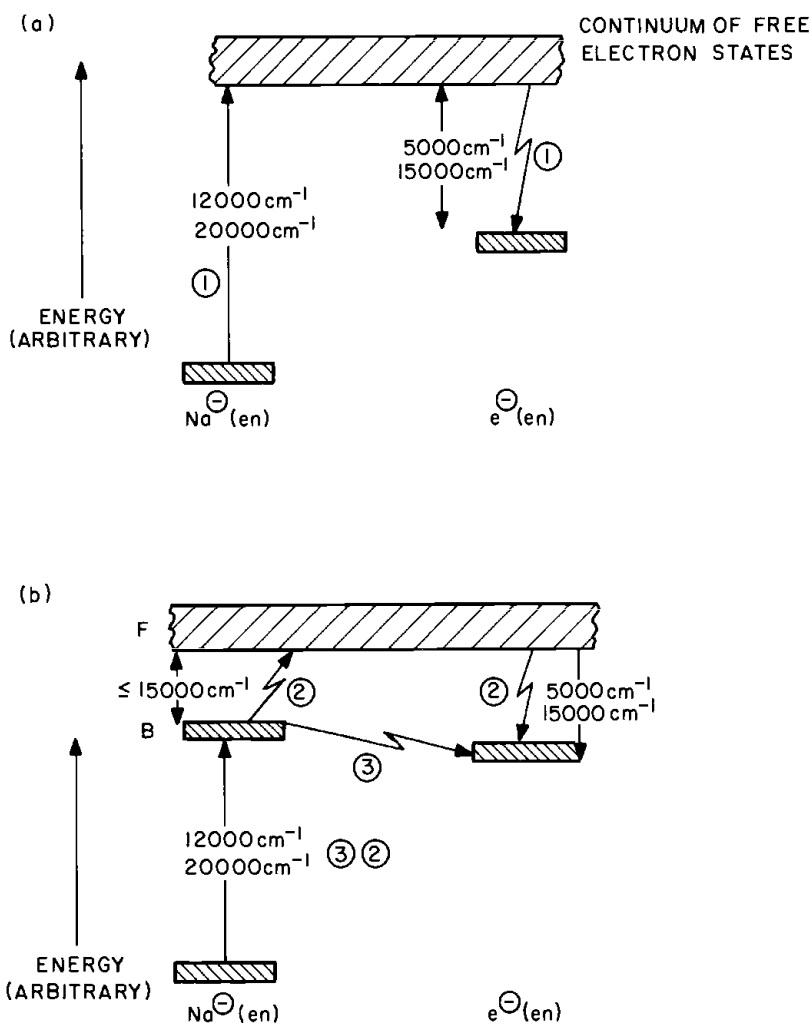


Fig. 10 Energy-level diagrams for the solvated electron in a solution in ethylenediamine. These illustrate the possibilities of the two types of broadening of the $\text{Na}^{\ominus}(\text{en})$ absorption band.

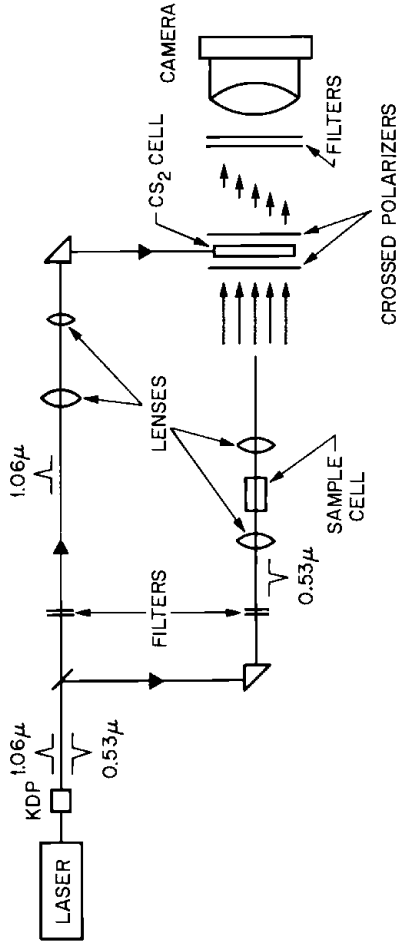


Fig. 11 Apparatus used for time-resolved picosecond emission spectroscopy using a crossed-beam picosecond light-gate.