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Ultrafast Processes

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The development of flash photolysis by Norrish and Porter and by Porter (*1*) resulted in an extension of the time scale of experimental spectroscopy from the millisecond to the microsecond range. Many important new molecular species such as short-lived radicals and other intermediates became accessible to the experimental spectroscopist. The *Q*-switched laser has provided nanosecond pulses, yet its application to spectroscopic problems has been quite restricted because of the limited number of fundamental frequencies readily available, namely, 14,400 reciprocal centimeters for ruby and 9431 cm^{-1} for Nd^{3+}-glass. The infrared lasers, such as carbon dioxide and water vapor, produce far-infrared light with a frequency very much lower than that needed for electronic excitation of most molecules. However, lasers have made feasible the laboratory use of several important nonlinear phenomena.

The frequency limitations of the lasers can be partially overcome by the use of frequency doubling devices such as phase-matched potassium dihydrogen phosphate (KDP), ammonium dihydrogen phosphate, and lithium niobate crystals, whereas stimulated Raman lines partially fill the gap between the fundamental and harmonic frequencies. There are, of course, several thousand known laser lines emitted by gas lasers, the most prominent ones probably being argon at 20,486 cm^{-1} and nitrogen at 24,656 cm^{-1}. In addition, most of the visible region can be covered by dye lasers. In general, the output of the gas lasers is rather weak for use in nonlinear spectroscopic experiments. Crystals used for efficient doubling must have the electro-optical properties necessary for phase-matching the velocity of the fundamental and the second harmonic frequencies. The continuous shift of the laser frequency by parametric oscillators is in the development stage, and when perfected, this technique will probably be one of the most useful tools of experimental spectroscopy.

Although existing lasers have the disadvantage of not being tunable, other properties unique to lasers can be profitably used in spectroscopy. For example, picosecond-pulsed lasers permit one to study the radiationless relaxation of molecules, emission and absorption spectroscopy, energy transfer, and primary steps in photochemical reactions in a time domain previously unattainable (*2*).

It is generally known that a molecule excited to a high vibrational level of an upper electronic level usually relaxes nonradiatively to the lowest vibrational level of the excited electronic state ($v = 0$) and thereafter to the ground electronic state by emission, if emission is allowed (Fig. 1). Alternatively, a molecule may, in addition to undergoing vibrational relaxation within the excited electronic level, cross over to a manifold of different spin by intersystem crossing. Isomerization, and twisting or bending of the molecule, may accompany nonradiative processes and may occur in intervals of time that are several orders of magnitude smaller than nanoseconds (10^{-9} second). I shall describe new experiments that make feasible the study of some of these ultrafast radiative and nonradiative processes which occur subsequent to excitation by picosecond pulses from Nd^{3+}-glass and ruby lasers.

Laser Operation

The experiments described here were performed with Nd^{3+}-glass and ruby solid-state lasers. In the *Q*-switched mode radiation is emitted over a ~20-nanosecond time interval, with a power of ~200 megawatts. This *Q*-switching can be achieved by the use of bleachable dyes, such as cryptocyanine and phthalocyanines, a rotating prism, Pockels cells, or any technique that permits one to control laser action by modulating the *Q* of the laser cavity. The high power available from *Q*-switched lasers has been used to advantage in studies of nonlinear phenomena, two-photon processes, and harmonic generation. Scattering measurements, such as Raman and Brillouin scattering have greatly benefited from the high power available from *Q*-switched lasers.

The observation that *Q*-switching may also produce picosecond pulses is probably the result of an extension of the mode-locking techniques demonstrated first by Hargrove *et al.* with helium-neon lasers (*3*). In their first experiments, these investigators were able to lock the many modes of their laser oscillator to a fixed phase by means of an ultrasonic diffraction modulator. Since these first experiments, other lasers such as argon, ruby, Nd^{3+}, and many others have been mode-locked (*4*). Mode-locking results in a train of equally spaced pulses of ultrashort duration and extremely high peak powers that appears as a substructure within the *Q*-switched pulse envelope.

Measurement of Subnanosecond Pulses

The pulse duration from a mode-locked laser depends strongly upon the bandwidth of the laser. One is able to achieve pulses of ~ 10^{-10} second duration with a mode-locked helium-neon laser, whereas Nd^{3+}-glass is capable of producing pulses shorter than 10^{-12} second. Most currently available elec-

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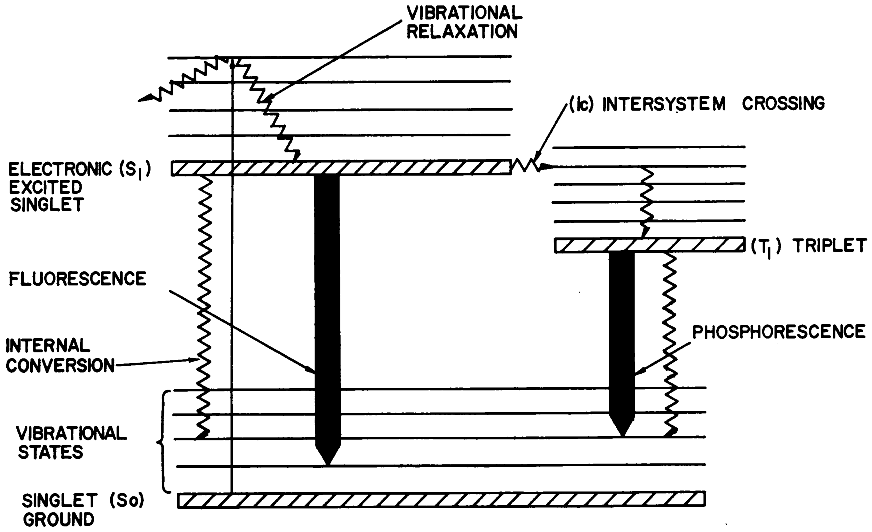

Fig. 1. Schematic diagram of the relaxation processes in large molecules, that is, intersystem crossing, internal conversion, fluorescence, and phosphorescence.

tronic equipment does not have the time response required for use in this time scale. In the following paragraphs I shall describe a new, nonelectronic method, based on two-photon fluorescence, developed in order to overcome this difficulty (*5*, *6*).

Two-photon absorption, followed by subsequent fluorescence, was predicted theoretically in 1931 (*7*), and confirmed experimentally in 1961 (*8*). The molecular or atomic energy levels involved in the two-photon fluorescence method must satisfy the following criteria: the energy level separation between the ground state and the first excited state, E, must be equal to or less than twice the frequency of the exciting light, 2ω, but greater than ω, that is, $\omega < E < 2\omega$. In essence, one may say that the two photons must be absorbed simultaneously in order to induce excitation. In view of the fact that the energy levels are separated by more than the frequency of the laser photon, one photon alone is not energetic enough to cause transitions. The simultaneous absorption of two photons, by means of a virtual transition, is required. The desired fluorescence with intensity proportional to the square of the incident light intensity can be achieved only when these conditions are satisfied.

In the first two cases reported (*5*, *6*), using this phenomenon for the measurement of the picosecond pulse, we used either two photons of the second harmonic of the Nd^{3+}-glass laser, 18,862 cm^{-1}, as the exciting frequency with a benzanthracene solution as the two-photon medium or the first and second harmonic with diphenyl cyclopentadiene (DPCP) as the two-photon solution. Obviously, a multitude of other solutions can easily be substituted that will satisfy the criteria for the two-photon fluorescence energy-level location and the properties outlined above. The experimental technique for utilizing this phenomenon in the direct measurement of the picosecond pulses is illustrated in Fig. 2A. A Nd^{3+}-glass laser is mode-locked and *Q*-switched by Eastman Kodak dye No. 9860. A train of pulses is emitted by the laser. The pulses are separated by an interval of ~ 4 nanoseconds which is twice the transit time, $2L/c$, of the laser cavity. Here L is the length of the laser cavity and c is the speed of light. The pulse length is known from the display of a photodiode output on a 519 Tektronix oscilloscope to be smaller than 10^{-10} second (Fig. 2B). The pulses traverse the benzanthracene solution (Fig. 2), are reflected by the dielectric mirror situated at the end of the sample cell, and return along the path of the incident pulse. The first pulse is reflected onto itself at the mirror surface, meets the oncoming second pulse L/c seconds later, then meets the third pulse, and so on. Two-photon absorption occurs whenever two pulses collide. If the intensity of the pulse is high, each pulse will also induce two-photon absorption with subsequent fluorescence along its path in the solution. However, because of the nonlinearity of two-photon absorption, the region of collision of the two pulses will exhibit an intensity three times brighter than that of the background (Fig. 3). When necessary, one can eliminate the background fluorescence by using both the fundamental and the second harmonic frequencies of the laser. In the first experiment of this type (*6*) we utilized the fundamental frequency of Nd^{3+}-glass at 9431 cm^{-1}

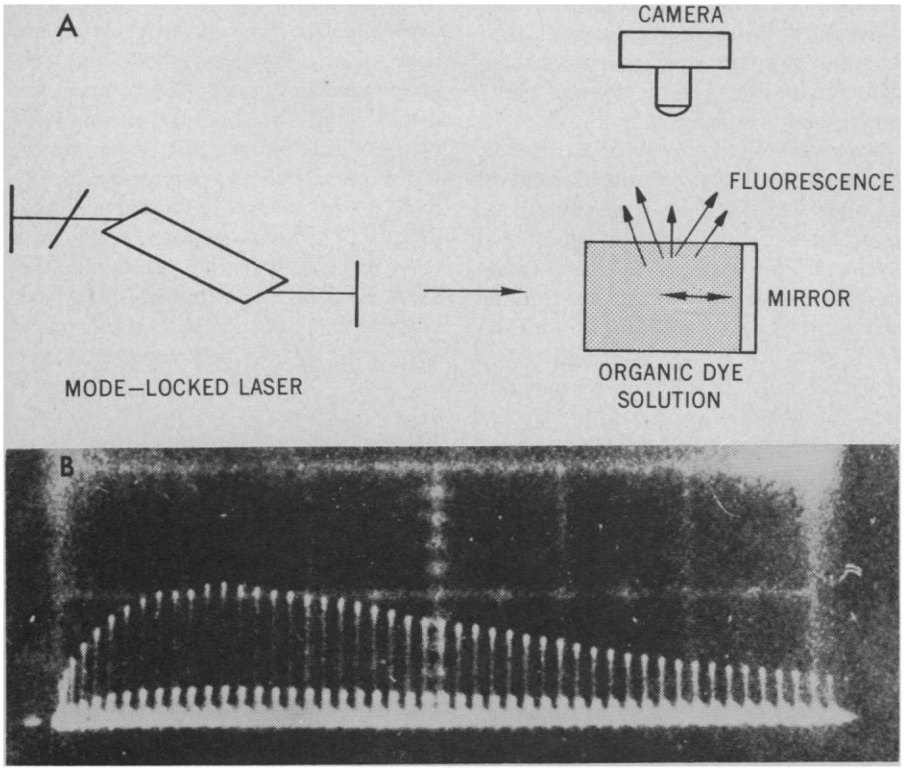

Fig. 2. (A) Experimental arrangement for the measurement of picosecond pulses by the two-photon fluorescence method. (B) Pulse train as seen on oscilloscope (50 microseconds).

(ω_1), and its second harmonic frequency at 18,862 cm^{-1} ($2\omega_1$). The DPCP solution was selected as the fluorescent medium; its excited electronic spectrum has no states either at the fundamental frequency, $\omega_1 = 9431$ cm^{-1}, or at the second harmonic frequency, $\omega_2 = 2\omega_1 = 18,862$ cm^{-1}. The first excited electronic level is an allowed singlet state located below 28,290 cm^{-1}, the sum of the photon energies ($\omega_1 + \omega_2$), but higher than either single photon frequency. The molecular absorption cross section and the fluorescence quantum efficiency are large, thus making it easy for one to photograph the two-photon fluorescence spot. Since the fundamental photon frequency, ω_1, is not energetic enough to induce two-photon excitations, no background fluorescence will be produced by this pulse as it traverses the sample cell. The frequency of the photons in the SHG pulse (second harmonic generated pulse) ($\omega_2 = 2\omega_1$) is sufficient to permit two-photon absorption but its intensity is purposely decreased to such an extent that it too fails to induce observable two-photon fluorescence by itself. However, when the two pulses collide both the intensity and the sum frequency ($\omega_1 + \omega_2 = 28,243$ cm^{-1}) are sufficient to induce two-photon absorption followed by emission at the point of collision. The length of the fluorescence spot observed is determined by the convolution of the two pulses, and, therefore, the convolution gives directly the duration of the ultrashort pulses.

An experimental arrangement that accomplishes this second experiment is shown in Fig. 4A. A train of equally spaced pulses with frequency ω_1 (9431 cm^{-1}) is emitted by the Nd^{3+}-glass laser. Interaction with the KDP crystal generates pulses of frequency ω_2 which emerge from the KDP crystal together with the pulses of frequency ω_1. Both pulses then enter a cell containing a dispersive medium such as bromobenzene. Because of the difference in group velocities (ω_1 travels faster than ω_2) the two pulses will emerge at different times. Hence, the pulse with frequency ω_1 passes through the cell containing the two-photon medium first and is reflected by the dielectric mirror situated at the end of the cell. No fluorescence is created by this pulse alone. After reflection by the mirror, the ω_1 pulse will meet the oncoming ω_2 pulse inside the sample cell. At the point of collision two-photon absorption will take place. The subsequent fluorescence will be emitted only at the area defined by the overlap of the two pulses. The pulse duration τ_p will then be determined by

$$\tau_p = \frac{nd}{\alpha c}$$

where n is the index of refraction, d is the length of the spot, and α is a function of the shape of the pulse. In a typical pulse $d = 0.7$ millimeter and $n = 1.5$; therefore, $\tau_p = 2 \times 10^{-12}$ second. As shown in Fig. 4, B and C, the background traces are eliminated and one may observe the pulse at any part of the cell by simply changing the delay between ω_1 and ω_2. Now I shall illustrate how variations of this technique may be used to observe electronic relaxation processes.

Nonradiative Transitions

The electronic energy of electronically excited molecules is dissipated either by emission or by nonradiative molecular processes. The nonradiative processes which occur from excited singlet states are intersystem crossing, usually by way of a radiationless transition from the excited singlet state S_1 to a lower lying triplet T_1 state, and internal conversion corresponding to strong coupling between the S_1 state and the ground state (*9*). In many organic molecules these radiationless transitions are the main paths of energy relaxation. When light emission is absent and relaxation rates are fast ($> 10^9$ second^{-1}), one can sometimes obtain an indirect estimate of the kinetics of these processes. Picosecond pulse techniques have made it possible to measure these processes directly (*10*). Thus far, these methods are illustrated by measurements on azulene, benzophenone, and a few other large organic systems (*11*).

Initial experiments were designed to measure the fluorescence spectrum of azulene subsequent to excitation to the S_2 state by the optical mixing of picosecond pulses from a Nd^{3+}-glass laser. The experimental arrangement is shown in Fig. 5. Filters and beam reflectors are placed at the appropriate positions in order to remove the SHG or fundamental frequencies as required for this and other experiments to be discussed below. The dispersing cell (bromobenzene) acted as a means for delaying the ω_2 pulses relative to ω_1 pulses. The delay was adjusted so that the ω_1 pulse entered the azulene solution (10^{-5} to $10^{-3}M$) ahead of ω_2 by ~ 40 picoseconds. Since under the conditions used here azulene does not fluoresce from its lowest excited singlet level, but rather from the second singlet, ω_1 travels through the solution without inducing (Fig. 6B) fluorescence by either one- or two-photon absorption ($\omega_1 = 9431$ cm^{-1}; $E_{(S_0 \rightarrow S_1)} \simeq 14,400$ cm^{-1}; $E_{(S_0 \rightarrow S_2)} \simeq 28,200$ cm^{-1}). The dielectric mirror at the end of the azulene cell reflects pulse ω_1, and this reflected pulse collides inside the cell with the oncoming ω_2 pulse. In the region of collision the

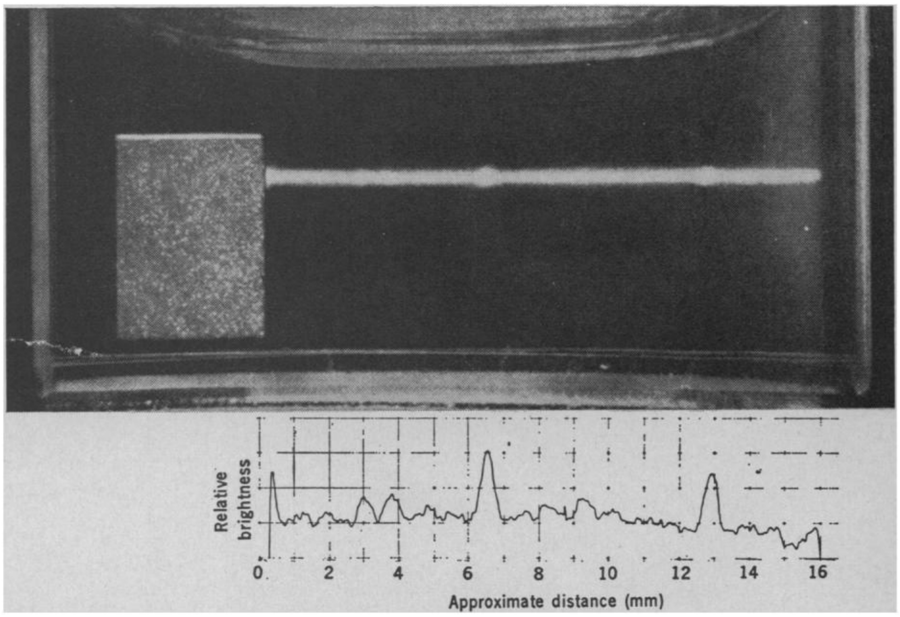

Fig. 3. A typical photograph of picosecond pulses; shown at the bottom is the photodensitometer trace ($\tau = 2 \times 10^{-12}$ second).

sum frequency of the two pulses is sufficient to excite the azulene molecule to the S_2 electronic state ($\omega_1 + \omega_2 =$ 28,293 cm^{-1}), thus inducing the fluorescence normally observed. Although pulse ω_2 could excite the second electronic level by a two-photon process, its intensity is purposely made low in order to avoid any observable fluorescence resulting from pulse ω_2 alone. A camera facing normal to the laser beam photographs the fluorescence of azulene. The frequency distribution of the fluorescence obtained by this method is essentially identical to that shown in published spectra, obtained by normal excitation methods.

One may use nearly the same apparatus to measure the lifetime of vibrational levels in the S_1 manifold. Let us consider the case where the azulene is excited first by the ω_2 pulses. This places the azulene in an excited vibrational level of the S_1 state ($\nu \approx 5$). The subsequent arrival of the ω_1 pulse can excite the azulene molecules from the S_1 state to the S_2 state by a sequential two-step excitation, provided that the molecules are still in the vibrationally excited state when the second pulse arrives. Therefore, the ω_1 pulse "interrogates" the population of the azulene in the vibrationally excited state as it propagates along the return path of the ω_2 pulse. The fluorescence produced as a function of the delay between the arrival of the two pulses provides a direct measure of the lifetime of the vibrational level. The photodensitometer traces (Fig. 6A) show the length of the laser pulse and the relaxation time of the vibrational level.

This procedure allows direct observation of rates of very fast processes. However, it does not permit one to elucidate the path of the radiationless transition, that is, whether the predominant process is vibrational relaxation in the same manifold or whether the predominant process involves other paths such as intersystem crossing. In order to identify this path, a variation of the above method was used that enables us to measure the intersystem crossing rate of azulene, benzophenone, or almost any other molecule.

Intersystem Crossing in Azulene

It is interesting that in azulene the two most common radiative processes, emission from the lowest singlet and triplet states, occur with very low efficiencies. The fluorescence which we have observed under strong optical pumping by laser light has a quantum efficiency ϕ, defined as that fraction of excited molecules which relax to the ground state by emission of a photon, of $\sim 10^{-6}$, and only the most intense bands are observed. This emission is increased by a factor of ~ 3 in deuterated azulene. The phosphorescence, which commences at $\sim$ 10,800 cm^{-1}, is also extremely weak and can be observed only at low temperatures ($\sim$ 77°K).

It seems obvious, therefore, that radiationless processes are predominately responsible for the depopulation of the lowest excited singlet state. One of the most probable possibilities for this type of process is energy transfer to a lower lying triplet state. The absorption of azulene in solution commences at $\sim$ 14,400 cm^{-1}, which is conveniently

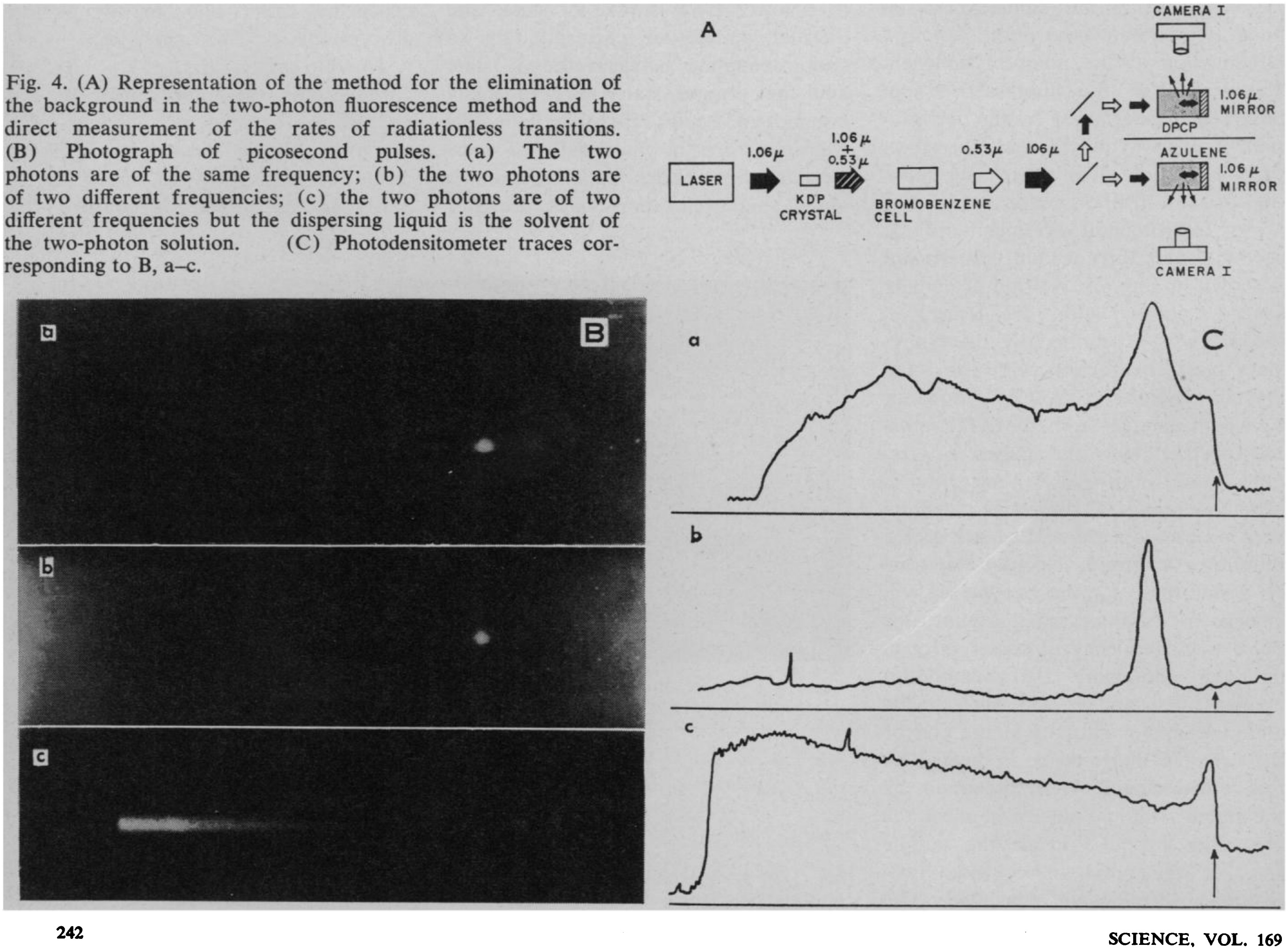

Fig. 4. (A) Representation of the method for the elimination of the background in the two-photon fluorescence method and the direct measurement of the rates of radiationless transitions. (B) Photograph of picosecond pulses. (a) The two photons are of the same frequency; (b) the two photons are of two different frequencies; (c) the two photons are of two different frequencies but the dispersing liquid is the solvent of the two-photon solution. (C) Photodensitometer traces corresponding to B, a–c.

resonant with the wavelength of the ruby laser.

A ruby laser, simultaneously *Q*-switched and mode-locked by means of a saturable dye, delivers a train of picosecond pulses ($\sim$ 4 picoseconds), each pulse separated from the next by $\sim 5 \times 10^{-9}$ second, to a cell containing the azulene solution in order to excite the azulene to the lowest vibration level of the first singlet level. Reflection by a mirror situated at the end of the cell again causes reflected and oncoming pulses to pass through one another. In regions where azulene remains in the S_1 state, molecules may be excited by a second pulse into the second singlet electronic level. The resulting fluorescence ($S_2 \rightarrow S_0$) spot is measured by the method described above. Since the level populated by the laser frequency in the transition from the S_0 state to the S_1 state is the lowest vibrational level of the S_1 state, the depopulation time of this level is a measure of either intersystem crossing or direct relaxation to the ground state. In order to establish further the path of the relaxation process, heavy atom solvents, such as dibromoethane, were substituted for the usual solvent, methanol (*10–12*). It is generally accepted that the heavy atom solvent affects the intersystem crossing rate by enhancing the spin-orbit coupling of the two states. Our experiments indicate that there is only a small effect due to the heavy atom solvent so that the $\sim 8 \times 10^{-12}$ second relaxation time from the $S_{1(v=5)}$ state most probably arises from the direct coupling with the ground state and the depopulation is predominantly to the ground state. The intersystem crossing is probably of less importance, as indicated by the small effect of the heavy atom solvent, and, as we shall see below, has an approximate lifetime of 6×10^{-11} second (*12*).

Since conventional experiments have not made it possible for one to establish whether azulene has indeed a triplet state between the ground state singlet and the first excited singlet, it is necessary to determine whether this triplet exists. Using the high power of a *Q*-switched laser, we have been able to do this by observing phosphorescence at 77°K. Although the quantum efficiency is as low as $\sim 10^{-6}$, the high power available gives sufficient triplet population to induce a phosphorescence corresponding to the transition from the T_1 state to the S_0 state, and to assign $E_{S_0 \rightarrow T_1}$ to $\sim 10{,}800$ cm^{-1}, which is in agreement with the theoretical calculations (*13*).

Having observed the lowest triplet state of azulene at $\sim 10{,}800$ cm^{-1} and weak phosphorescence, let us focus our attention on the process by which the triplet state is populated after excitation into the singlet manifold. This process, which is referred to as intersystem crossing, arises from the spin-orbit interaction and is usually a nonradiative ultrafast process. For many molecular systems the intersystem crossing rate is higher than the fluorescence rate. In the case of azulene the low quantum yields of spontaneous fluorescence and phosphorescence prevent calculation of the intersystem crossing rate by the classical method in which the quantum yields of the emission from the S_1 state to the S_0 state and from the T_1 state to the S_0 state are used.

The experimental approach that we followed is similar to that described for the vibrational relaxation except that we populated a low vibrational level of the first excited singlet state of azulene. The exciting pulse was a 4-picosecond (4×10^{-12} second) ruby laser beam with a frequency of 14,400 cm^{-1}. A second pulse interacts in the azulene solution with the first pulse and raises the excited azulene molecules to the second excited singlet state S_2. The fluorescence observed from this state is photographed, and the pulse convolution differences between the laser pulse length and the fluorescence spot length give a measure of the lifetime of the zero vibrational level of this state. If we take into account the effect that heavy atom solvents (*11*) have on the spin-orbit interaction, the intersystem crossing lifetime is calculated to be 60×10^{-12} second. In an alternate method we excited azulene by a 14,400 cm^{-1} picosecond pulse but in this case we interrogated the population buildup of

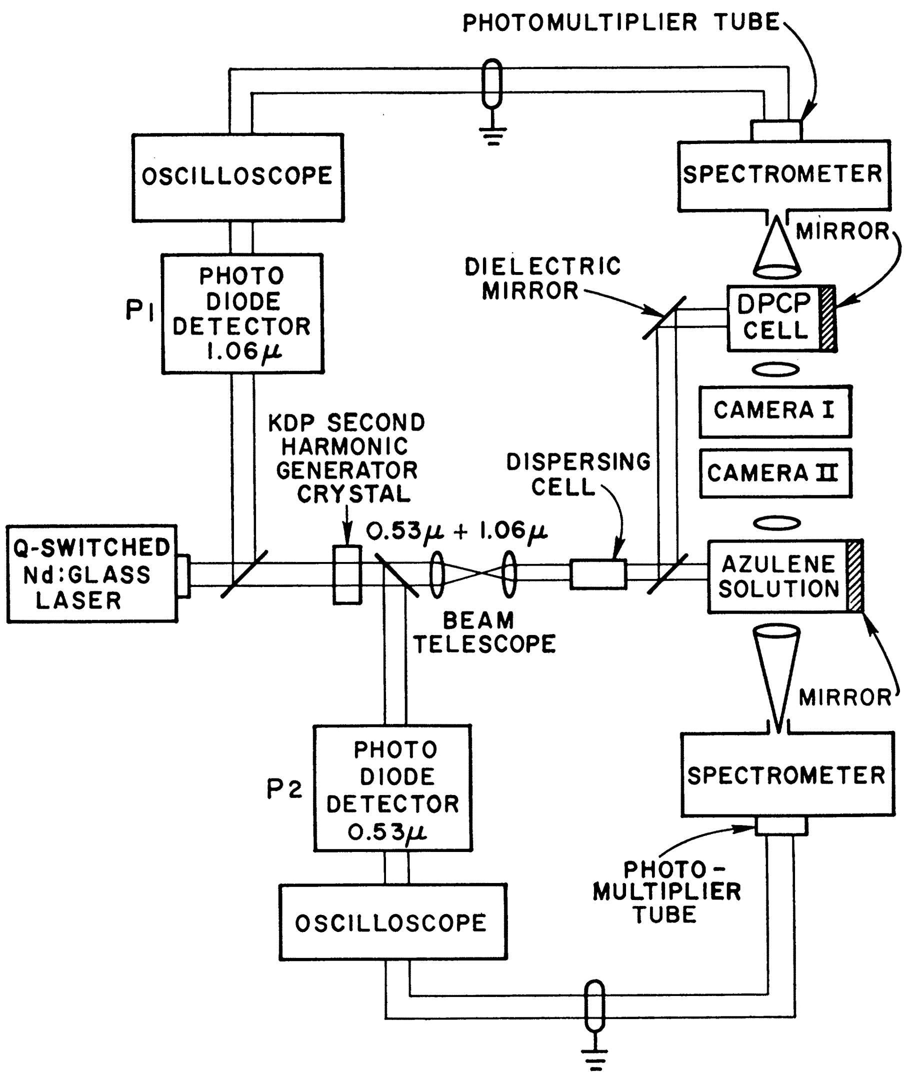

Fig. 5. Schematic representation of the apparatus used for the direct measurement of ultrafast processes. *P*, photodiode.

only the triplet state by a second picosecond pulse. In this case we obtained directly the rate of intersystem crossing since the population of the triplet state is achieved solely by that process.

Intersystem Crossing in Benzophenone

The depopulation of an excited singlet state is greatly influenced by the spin-orbit coupling between the singlet and a lower lying triplet state. The spin-orbit coupling between these two states can be of such magnitude that the transition to the triplet state is the predominant process that occurs, resulting in the absence of fluorescence. This is the case for benzophenone, where the absence of fluorescence and the unit quantum yield of triplet formation are indicative of a fast intersystem crossing rate.

We have measured the energy dissipation in benzophenone from the zero and higher vibrational levels of the first excited state by using short laser pulses (*14*). In addition, we have been able to observe a fluorescence between 25,600 cm^{-1} and 25,900 cm^{-1} which we interpret as emission from the S_1 ($n\pi^*$) state to the S_0 state of benzophenone (*15*). The observation of the weak fluorescence of benzophenone was achieved by optically pumping a solution of benzophenone with the second harmonic frequency of ruby at 28,800 cm^{-1}. The quantum efficiency for fluorescence is $\sim 10^{-6}$, and the observation of the weak fluorescence was possible as a result of the large power of the laser pulses. The intersystem crossing rate was measured by methods similar to those used for the measurement of the radiationless transitions of azulene. Measurements were made as follows.

A ruby laser was simultaneously *Q*-switched and mode-locked by 1,1-diethyl-2,2-dicarbocyanine iodide passive dye (*16*). The pulse duration was $\sim 4 \times 10^{-12}$ second and the total peak power was $\sim 5 \times 10^{-8}$ watts. The second harmonic frequency was generated in a phase-matched KDP crystal with an efficiency of ~ 10 percent. Several other pumping or interrogating frequencies can be derived from the stimulated Stokes-shifted Raman lines of hydrogen (4155 cm^{-1}), acetone (2921 cm^{-1}), bromobenzene (1000 cm^{-1}), and many others that cover the range between α-sulfur (216 cm^{-1}) and hydrogen (4155 cm^{-1}). The conversion efficiency to the Raman lines can be as high as 80 percent in certain molecules such as hydrogen and acetone. The experimental arrangement is similar to that shown in Fig. 5. The pumping pulse (ω_1) (26,800 cm^{-1}) excites the benzophenone to the S_1 ($\nu = 0$) state. The interrogating pulse (ω_2) (10,245 cm^{-1}), which is the stimulated Stokes hydrogen shift (4155 cm^{-1}) of the ruby fundamental frequency, enters at the end of the benzophenone cell traveling in the direction opposite to that of pulse ω_1 and collides with pulse ω_1 inside the cell. The frequency of the interrogating beam is sufficient for the transition from the S_1 ($\nu = 0$) state to the S_2 state but lower than frequencies for transitions from the S_0 state to the S_1 state or from the S_0 state to the T_1 state. It is obvious, therefore, that the interrogating pulse is absorbed only when there is population at the S_1 ($\nu = 0$) state. Furthermore, the extent of absorption of pulse ω_2 is a direct measure of the population of the S_1 ($\nu = 0$) state (Fig. 7A). A precision micrometer varies the distance that pulse ω_2 has to traverse before crossing pulse ω_1. Variation of the time (distance) delay of pulse ω_2 permits interrogation of the decay of the state excited by pulse ω_1 as a function of time and gives a direct measure of the lifetime of the state.

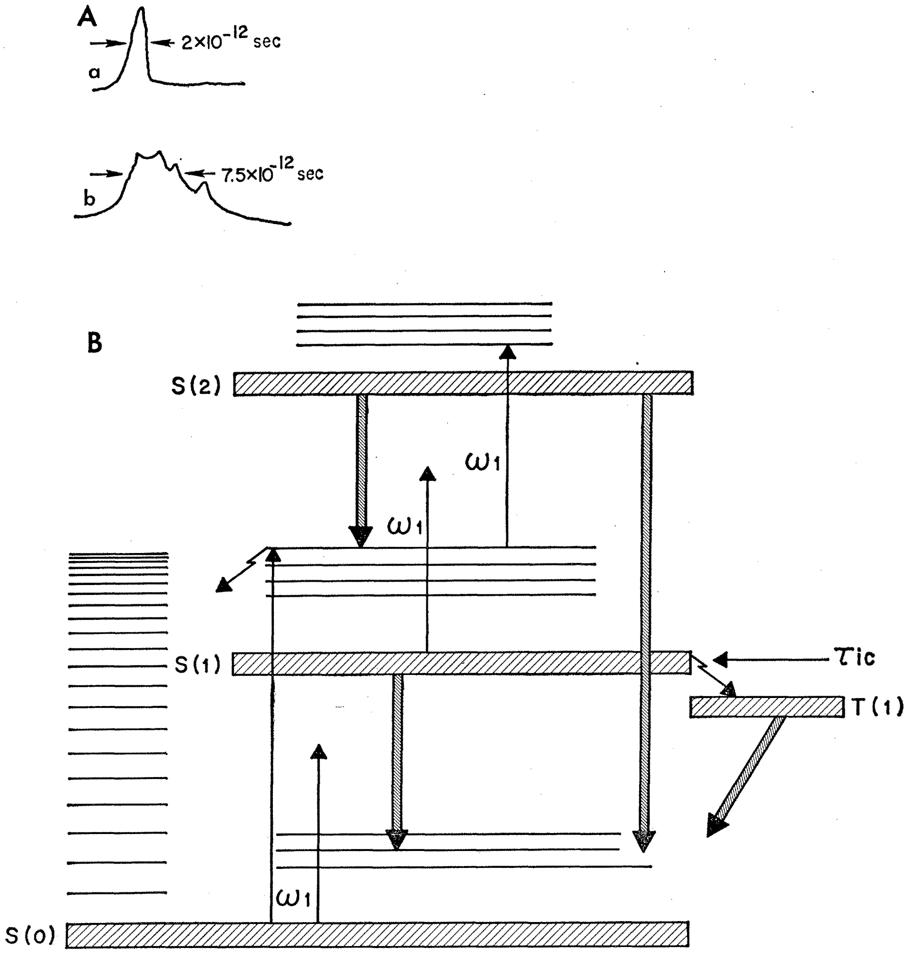

Fig. 6. (A) Photodensitometer traces of (a) pulse length and (b) relaxation of azulene. (B) Energy level diagram of azulene. τ_{ic}, intersystem crossing lifetime.

Because the quantum efficiency of triplet formation phosphorescence is nearly unity, the rate of energy dissipation from the S_1 ($\nu = 0$) ($n\pi^*$) state represents the intersystem crossing time and is $\sim 5 \times 10^{-12}$ second (limited by the duration of the pulse). By the same method, but with an exciting frequency (ω_1) of 28,800 cm^{-1} (SHG, ruby) and an interrogating ω_2 pulse of 10,245 cm^{-1}, the intersystem crossing rate was found to be slower by almost a factor of 3 ($\tau = 1.5 \times 10^{-11}$ second). This is possibly due to the stronger coupling at the lower vibrational level. This method with frequency variations has been applied to other molecular systems in the liquid and solid state and can be utilized with considerable success in a large number of molecular systems in the gaseous, crystalline, and liquid phases.

Repopulation of the Ground State

Another process of great importance is the nonradiative repopulation of the ground electronic state. Since many molecules have low quantum yields for emission, the nonradiative processes by which ground electronic states are repopulated are important in the deactivation of molecules. Repopulation of the ground state of *Q*-switch dyes has been studied and provides an example of how the use of picosecond pulses can give insight into the molecular spectroscopy of a particular system (*2*, *17*). We have also examined the repopulation of the ground state of azulene, which must occur at a very fast rate since neither fluorescence nor phosphorescence is normally observed with conventional excitation of the molecule to the first electronic state.

The picosecond output pulses of the mode-locked, passive-dye *Q*-switched laser were collimated to a beam 2 millimeters in diameter, which traversed a cell containing the solution or crystal under investigation. The path length of the cell was 0.5 millimeter, and the optical density in the cell was 1.0. The intense picosecond pulse excited the molecules to the first excited electronic level. A dielectric mirror, situated at a known distance behind the cell, reflects the light pulse back onto the cell after it passes through a set of attenuators (Fig. 7A). The time elapsed between the exciting pulse and the reflected (interrogating) pulse is varied by translating the mirror with a micrometer drive. A set of photodiodes and oscilloscopes are used to measure the light intensity of the pulses before and after each pass through the cell, and the laser pulse length is measured by the two-photon fluorescence method.

If the reflected picosecond pulse returns to the cell after an interval of time that is very short relative to the repopulation time of the ground state, only a very small amount of the interrogating light pulse is absorbed. If the pulse returns at a time when relaxation to the ground state is almost complete, absorption will occur. By varying the distance between the cell and the reflecting mirror we vary the time of the arrival of the interrogating pulse in the azulene cell. A plot of the relative transmitted intensity of the interrogating pulse as a function of time shows the lifetime of the relaxation process. In the case of azulene, the lifetime of the repopulation of the ground electronic state after excitation to the first singlet state is, on the average, ~ 8 picoseconds. This method obviously does not show which path the relaxation to the ground state takes, that is, whether the relaxation leads directly to the ground or whether it goes by way of intersystem crossing to the triplet state with subsequent decay to the ground state. We have seen above that the relaxation time from the ($v \sim 5$) vibrational level of the first excited state is 7.5×10^{-12} second. The relaxation time from the lowest vibrational level of azulene to the triplet state was measured to be $\sim 60 \times 10^{-12}$ second (*1*) (Fig. 8).

In view of the fluorescence and phosphorescence results, their low quantum efficiency, the strong coupling of the two singlet states, the effect of deuteration, and the fast ($\sim 8 \times 10^{-12}$ second) repopulation of the ground state electronic level, we tend to believe that the direct relaxation to the ground state as a result of level coupling between the excited singlet and ground states is the dominant process for the relaxation from the first excited singlet of azulene. Intersystem crossing can take place to a lesser degree, and the low quantum yield of phosphorescence indicates that it does.

Recently we have developed a simple technique for the observation of the saturation recovery time, that is, the excited state lifetime of an absorbing species. In this technique two picosecond pulses are used that may or may not be of the same frequency. During the passage of an intense bleaching pulse through a dye-containing sample cell, the cell is uniformly illuminated by a second interrogating pulse traveling at right angles to the first pulse.

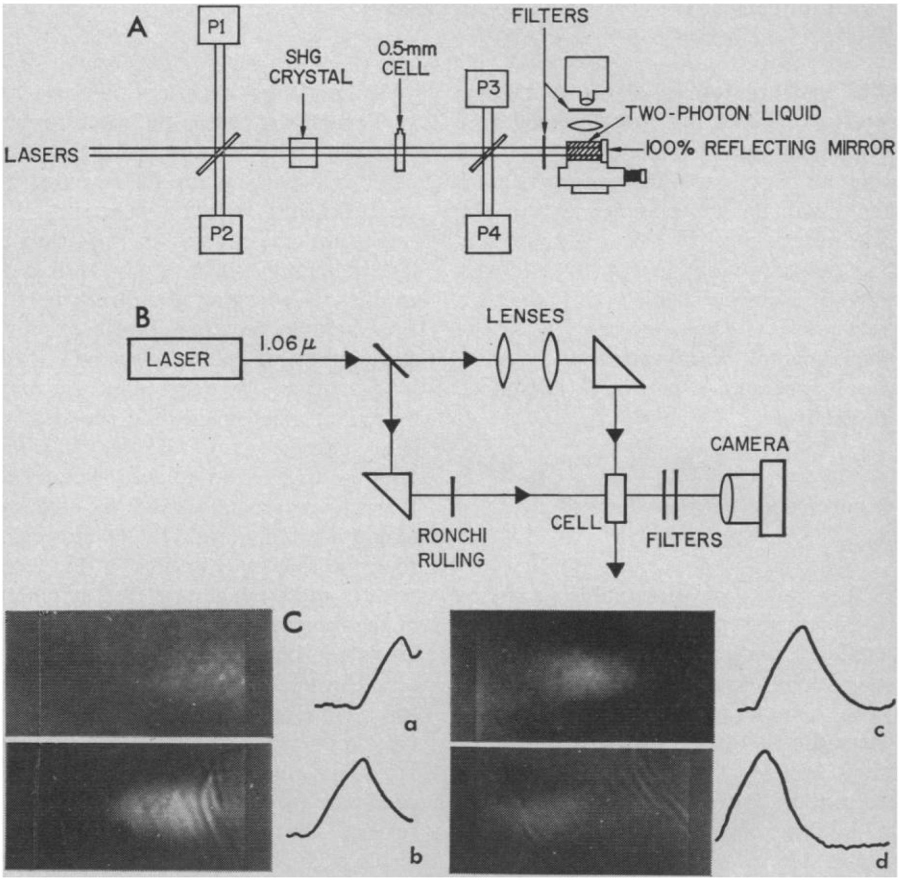

Fig. 7. (A) The method employed for the direct measurement of the lifetimes of the ground or excited states. *P*, photodiodes. (B) Alternate method for determining the rate of repopulation to the ground state. This method has the advantage of requiring only one pulse. (C) Pictures of the Kodak *Q*-switch dye No. 9860 (optical density = 5 per centimeter at 1.06 microns). The bleaching light pulse travels from right to left in these pictures. Various thicknesses of quartz [(a) 0, (b) 6.3 millimeters, (c) 12.5 millimeters, and (d) 18.8 millimeters] inserted into the interrogating beam delay the arrival time of the interrogating pulse relative to the bleaching pulse, thus moving the bright portions to the left of the cell. The observed transparency is a convolution of the two light pulses and the saturation recovery time of the dye. Assuming a simple model for the dye saturation, we can measure the saturation recovery time from the trailing edge of the bleaching light pulse. We find a value of 9 picoseconds for the Kodak *Q*-switch dye No. 9860.

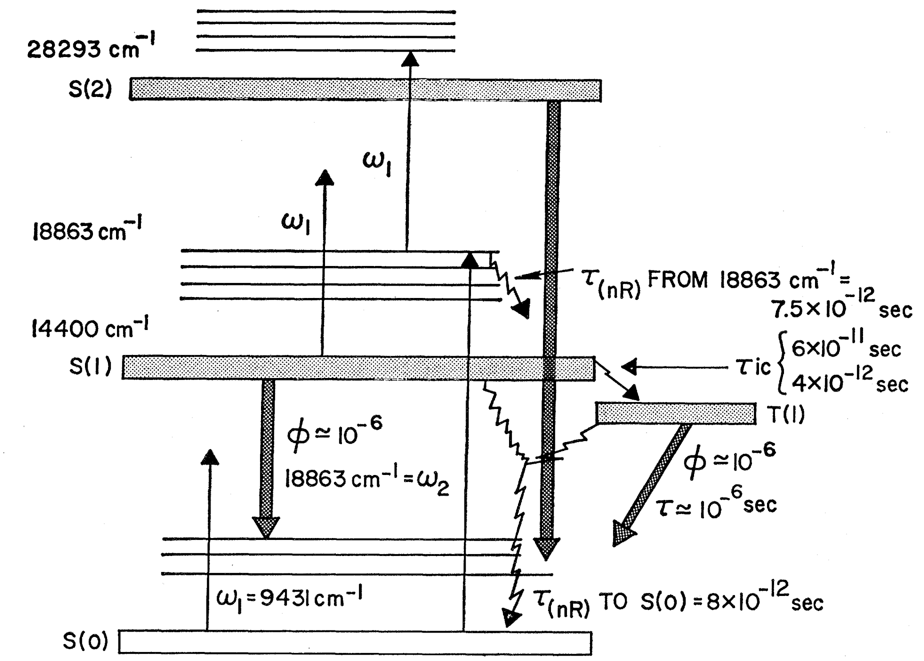

Fig. 8. Schematic diagram of the energy levels of azulene, excitation frequencies utilized in the experiments described, and experimental values obtained. $\tau_{(nR)}$, nonradiative lifetime; τ_{ic}, intersystem crossing lifetime.

The short duration of each of these pulses enables us to "freeze" the bleaching light pulse within the cell and to photograph the recovery process. From the transparency of the dye, measured along the path of the bleaching pulse, we obtain the time history (on a picosecond scale) of the dye relaxation with but one laser shot. The experimental arrangement and typical results are shown in Fig. 7, B and C, respectively.

Fluorescence between Excited States

The lack of observable emission from excited molecules can be attributed to any of several nonradiative transitions, such as strong coupling with another state, deformation of structure in the excited states, and energy transfer to surroundings such as solvent or buffer gas.

In the cases described above we were able to observe fluorescence primarily because of the high photon density and short duration of the laser pulse. The high laser power can, in many cases, compensate for low quantum yields of fluorescence (10^{-6} to 10^{-7}) and the possible short lifetime of emission ($\sim 10^{-9}$ second or less). This has been shown to be the case for azulene fluorescence from the first singlet, and for biphenylene and pyridazine, for both of which the quantum yields and the emission lifetimes are very small (*15*). For the same reasons that the laser is successful in these cases one can induce fluorescence between excited states, a process that is important in molecular spectroscopy but quite difficult to study with most of the available excitation sources (*18*). For example, reaction from high vibrational levels of excited electronic states is not generally considered the predominant mechanism of a chemical reaction because the rate of relaxation from an upper level to the lowest vibrational level is usually faster by orders of magnitude, in most large molecules, than the rate of relaxation of the $v = 0$ level to the ground state. The symmetry of the molecule in the upper vibrational levels can be different from that at the $v = 0$ level. Chemical reactions, therefore, from an upper vibrational level may very well have essentially different reactivity and may produce different products from the ones normally observed. The population of such upper levels by high-power lasers, such as the second harmonic frequency of ruby (28,800 cm^{-1}), the second harmonic of Nd^{3+}-glass (18,862 cm^{-1}), or the fourth harmonic (37,724 cm^{-1}) of the Nd^{3+}-glass laser could result in new chemical products.

Work now in progress indicates that the reaction products of certain aromatic molecules, excited by intense laser pulses to high vibrational levels, are not the same as those from chemical reactions occurring in the lowest vibrational level of the first excited state. The fraction of the products that are novel could be attributed to reactions taking place at the higher vibrational levels.

Molecular Distortion

A number of molecules that are planar in the ground states are bent or twisted in the excited states. The intensity distribution of the transitions is, therefore, altered in comparison to planar-planar intensities, as a result of the changes in the equilibrium position of the nuclei. If this change in equilibrium position is large, the shape of the potential energy curve in the excited state changes relative to that in the ground state, and the Franck-Condon principle will favor transition to the ground state at vibrational levels with high quantum-numbers. Under these conditions, the emission intensity will be shifted toward lower frequencies and for severe distortion it could result in a predominantly radiationless path for relaxation (*19*).

Biphenylene exhibits neither fluorescence nor phosphorescence (*20*) except under strong excitation such as that supplied by *Q*-switched laser sources. It is believed that the energy is dissipated from the excited electronic levels by way of a radiationless transition to the ground state because of the change in the geometric configuration of the molecule in the excited state. This distortion could result in the shift of the potential energy level of the excited state; thus the transitions favored by the Franck-Condon principle would be to high vibrational states of the ground electronic level, which probably take place nonradiatively and at fast rates.

The experimental arrangement shown in Fig. 7A is similar to that employed in the study of the repopulation of the ground state except that a polarizer or quarter-wave plates, or both, have been added. The biphenylene molecule is excited by the first pulse of a picosecond pulse train. The frequency of the pulses is selected so as to correspond to a transition in which the molecule is excited only if the long molecular axis is parallel to the electric field of the photon. Every successive oncoming pulse has the same frequency (28,800 cm^{-1}), length, and polarization characteristics. Thus molecules that are aligned with their long axis parallel to the plane of polarization are excited. At this stage, a second pulse is introduced for the purpose of determining the number of molecules remaining in this excited state and maintaining the same molecular configuration and orientation. It is assumed that after a change of molecular configuration the change of symmetry causes the amount of absorption to be relatively small. A ruby laser pulse is Raman-shifted by hydrogen to supply the second pulse. This interrogating pulse frequency is not absorbed by the ground state molecules because its frequency is too low to cause transitions between the ground level and the first excited electronic state ($\sim 26{,}000$ cm^{-1}); however, this frequency possesses sufficient energy to pump the molecule from the first excited electronic level to the second if the molecules remain planar.

When the exciting and interrogating pulses arrive at the same time, the interrogating pulse is absorbed strongly because of the relatively large number of molecules in the first excited state. As the degree of delay in the arrival of one of the pulses increases, the intensity of the transmitted interrogating beam increases. The increase in transmission can be interpreted as arising from the absence of molecules in the excited state decaying to the ground state or from the fact that the molecule in the excited state has altered its configuration by bending or twisting, so that the long axis has ceased to be a valid molecular axis. If the latter is the case, this experiment would indicate that the molecule changes its nuclear configuration in the excited state; that is, the change in transmitted intensity is a measure of the changes in dynamic configuration. Preliminary experiments show that the repopulation of the ground state takes $\sim 10^{-11}$ second, whereas the population of planar molecules in the excited state decreases twice as fast. One can, hopefully, experimentally probe the molecule during this proposed configurational distortion from the excited state to the "disturbed transition state." In the same way one can investigate the ground state intermolecular interactions by using a very similar technique.

In closing this account of some of our experiments in this very new field, I should like to mention potential extensions of this initial work on relaxation processes that I feel are provocative examples of cases in which one could successfully utilize the advantages of picosecond pulses. Although most of the experiments described are concerned with molecules in solution, it is obvious that the crystalline or gaseous states can be studied as well.

The Future

The production of two radicals from the same molecule, such as the azo (—N=N—) compounds, is very fast and the recombination rate may lie in the nanosecond range. The short pulse length and high peak power of the picosecond laser pulses are essential in order that an observable number of radicals be produced in an interval shorter than their recombination time. If one observes, by means of absorption techniques, the formation and decay of the radical population, one can obtain the recombination lifetime and some knowledge of the kinetics of the cage effect. Furthermore, by monitoring the products through time-resolved absorption or fluorescence one may possibly identify intermediate species and the kinetics of formation and dissociation.

Related processes such as isomerization rates, for example, *cis-trans* isomerization of stilbene, the rates of dimer formation in molecules such as anthracene, and the rate of energy transfer between donor and acceptor pairs, either as separate molecules or as molecules connected by a long chain as in biological molecules, are but a few of the basic processes that can be examined in many different chemical systems by the use of ultrashort laser pulses in some manner similar to the ones described in this article.

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