Ann. Rev. Phys. Chem. 1977. 28: 207–32

PICOSECOND SPECTROSCOPY

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INTRODUCTION

In the last decade lasers have been developed that can generate light pulses of the order of 10^{-12} sec duration and are capable of peak powers in excess of 10^{13} W, thus enabling the investigation of the interactions of light with matter in a time and power domain not previously possible. Picosecond lasers provide a new and powerful tool for the study of physical and chemical phenomena at the most fundamental level. In chemistry today one of the key issues is the evolution of a system from some initial distribution of energy and geometric structures through various intermediate structures and energy states to some "final" state. The identification and lifetimes of the energy states, geometric structures, and chemical species through which the system rapidly passes is necessary to understand the mechanisms of chemical and physical changes. The competition between various pathways for energy dissipation and structural change determines whether light is emitted or the manifold nonradiative physical and chemical processes dominate the system.

What are some of these key energy-degrading pathways, and how can the unique features of picosecond spectroscopy illuminate some of these basic questions in chemistry? As an example, if we consider a molecule in an excited electronic state, it can dissipate its energy by emitting light, by internal conversion to lower-energy electronic and vibrational states, by flipping a spin and going from a singlet to a triplet state and decaying down the triplet manifold, by intermolecular energy transfer to some other molecule, or by chemical reactions such as unimolecular decomposition or reaction with a neighboring molecule. These processes often occur in the subnanosecond time region. Internal conversion and vibrational relaxation, singlet to triplet intersystem crossing, electron and proton transfer, excited-state structural changes, and collision-induced predissociation often occur in this ultrafast time domain. Picosecond lasers can perturb the system (e.g. by excitation to a given energy state or alignment of molecules by the intense laser electric field). Subsequently, the return to the initial equilibrium state or the development of new structures or chemical species can be measured with picosecond resolution. The monitoring steps are usually spectroscopic and utilize picosecond probe pulses or an ultrafast streak camera to follow absorption, emission, Raman scattering, and changes in the polarization of the probe light as the system evolves.

INTERMOLECULAR ENERGY TRANSFER

The efficiency of intermolecular energy transfer depends on the nature of the inter molecular coupling, the molecular separations and relative orientations, the exten of energy overlap, and the lifetime of the excited donor molecule (1–6). For exampl a dipole-dipole coupling mechanism can lead to transfer over distances of the orde of 100 Å as opposed to an exchange coupling that is short-range and can extend t distances of the order of 10 Å. The donor and acceptor states involved in the transfe process can be excited- and ground-electronic states of various multiplicities con taining variable amounts of vibrational excitations. This "diffusion" of energy fro some initial distribution of excited and unexcited molecules through a variety o alternative distributions plays a vital role in a variety of physical, chemical, an biological processes (7–11), such as the quenching of the donor fluorescence an the appearing of new emission bands, the initiation of chemical reactions by transfe to a reactive molecule or site, and has been used as an aid in mapping distance between chromophores in biological molecules.

Prior to the development of picosecond lasers, studies of the dynamics of energ transfer were restricted to times of the order of 10^{-8} sec or longer and were generall limited to light-emitting molecules. Thus, the nature of the laws governing the transfe could not be examined in the subnanosecond time scale.

Singlet-Singlet Transfer

One approach to the study of singlet-singlet energy transfer uses the linear polariza tion of the picosecond exciting light to induce an orientational anisotropy in th distribution of ground and excited molecules (9, 10). Molecules whose transitio moments have a large component along the polarization direction of the light ar preferentially excited. Thus, the formerly isotropic system becomes anisotropic, i.e more excited molecules are oriented parallel to the field direction, and hence mor unexcited molecules are oriented with their transition moments perpendicular t the field direction. In a rigid environment the induced anisotropy can only rela by unimolecular decay of the excited molecules and by energy transfer. In a syste where the donor and acceptor molecules are of the same species, the randomizatio results from energy transfer between molecules of different orientations. On th other hand, in a mixed system, the anisotropy in donor orientations can also relax by transfer between donor and acceptor molecules regardless of their mutual orientation. The decay of the anisotropy can be monitored by measuring the polarization-dependent change in either the ground- or excited-state donor absorption with time. The ground-state donor absorption is greater for probe light polarized perpendicular to rather than parallel to the polarization of the exciting light because of the relative depletion of ground-state molecules in the "parallel configuration." By probing at successively later times after excitation, the decay of the dichroism due to the continued effects of energy transfer and the unimolecular excited-state decay can be determined. Measurement of the latter quantity in the absence of transfer is then combined with the measured decay of the dichroism to obtain the energy-transfer dynamics.

To determine the nature of the transfer it is advantageous to study a two-component system, i.e. distinct donor and acceptor molecules, versus a one-component system for which the acceptor molecules are the ground-state donor molecules. For the two-component system the acceptor molecules are randomly distributed both in orientation and distance with respect to the anisotropically distributed excited donor; hence the donor decay function can readily be calculated. In the one-component system, although the distribution in distances is random, the distribution in orientations is perturbed by the excitation pulse (11–15). Furthermore, in the two-component system only one transfer step from the donor to acceptor need be considered, assuming that vibrational relaxation in the excited acceptor molecule is rapid compared with excitation transfer. In the one-component system several steps may be necessary before randomization has occurred and would therefore have to be included in any theoretical treatment.

Picosecond experiments with rhodamine 6G as the donor and malachite green as the acceptor showed that the dipole-dipole interaction was a good description of energy transfer up to the earliest time measured, i.e. 20 psec. The critical transfer distance, R_0, was found to be about 53 Å, which is in good agreement with the value calculated from the spectra (48 Å). In experiments of this type one must consider the possibility of stimulated emission caused by the probe pulse and amplified spontaneous-emission processes. For the rhodamine 6G molecule excited-state vibrational relaxation is known to be complete at the time of the earliest measurement (20 psec) (16–18). The power densities used in the excitation pulse must be adjusted to avoid the complications of amplified spontaneous emission. In addition, if the full pulse train is used, rather than a single pulse, the possibility of buildup effects must be considered.

Triplet-Triplet Transfer

Since triplet-triplet energy transfer occurs via an exchange interaction, it is a short-range process and generally occurs between neighboring molecules, perhaps as far as 10–15 Å apart. Most studies in solution are therefore limited by the diffusion of the donor and acceptor molecules to some neighboring or near-neighboring molecular configurations. If the concentration of acceptor molecules is sufficiently high, then the rate of transfer is too rapid to study by conventional flash photolysis methods. Furthermore, earlier studies covered a time domain that was long compared to vibrational relaxation times. Thus the initial and final states of the donor-acceptor pair monitored were thermally equilibrated. Information on the vibronic energy in the excited donor prior to transfer and the distribution of vibronic energy in the ground-state donor and excited acceptor after transfer is thus unobtainable. Since the energy transfer process is dependent on the energy distribution of the interacting states and also on the rate of vibrational relaxation, both intramolecularly as well as intermolecularly, this short-time information is of key importance.

With the application of picosecond laser methods we are now gaining some insight into the role of vibrational energy distribution in triplet excitation transfer processes (19). Some of the donor-acceptor pairs that have been studied include benzophenone as the donor and *cis*-piperylene, *trans*-piperylene, and 1-methylnapthalene as the acceptors. In these investigations the solvent was composed of the acceptor molecules and hence translational molecular diffusion was not the rate-determining step. For some systems rotational motion may be important in satisfying orientational requirements of the donor-acceptor pair for energy transfer (20, 21). The method used for determining the triplet-triplet dynamics was to excite the donor to an excited singlet state with a picosecond pulse and monitor the donor triplet population with a picosecond probe pulse at a wavelength corresponding to a donor triplet-triplet absorption. In this way we obtain both the buildup of the donor triplet due to intersystem crossing from the donor singlet and the decay of the donor triplet due to energy transfer to the acceptor molecule.

A small but definite difference is found in the rate of energy transfer from benzophenone to *cis*- vs *trans*-piperylene with the *cis* form the faster one. The difference in the observed transfer is attributed to the different vibrational overlap functions (Franck-Condon factors) for the two forms. In this interpretation the final vibrational energy distribution would not be the same for the two pairs. In addition the rapid rate of energy transfer observed (10 psec) is in the time domain of vibration relaxation, and thus the transfer might occur from a thermally nonequilibrated triplet benzophenone. This latter point is used in part to explain the slower rate of energy transfer from benzophenone to 1-methylnapthalene (20 psec). However, it is also clear that the differences in the electronic contributions to the transfer can be different for the piperylenes and 1-methylnapthalene, and thus could contribute to the observed differences in transfer rates.

In another type of experiment the dynamics of triplet energy transfer in crystals have been investigated. The fluorescence risetime and decay in a tetracene crystal excited by a picosecond pulse (at 530 nm) has been used to estimate the incoherent hopping rate of triplet excitons (22). Tetracene is a rather interesting system in that one channel for the decay of the singlet exciton involves fission into two triplet excitons. The rate of this process is dependent, in part, on the velocity at which the newly formed triplet excitons separate and thus avoid a geminate recombination process leading to the initial singlet exciton. This triplet energy hopping or transfer from neighbor to neighbor is estimated to be at a rate greater than 10^{13} sec^{-1}. By postulating an average lifetime for the triplet exciton of 100 μsec and an average jump distance of 7 Å, a diffusion length of the order of microns is obtained.

ORIENTATIONAL RELAXATION OF MOLECULES IN LIQUIDS

Although a number of methods have been used to study orientational relaxation processes, the exciting feature of the recent applications of picosecond laser techniques is that rotational motions are measured directly in the time domain. In one method that uses the optical Kerr effect the birefringence induced by an intense picosecond pulse is monitored with an attenuated picosecond pulse as a function of time. This method is most appropriate for studies of pure liquids and highly concentrated mixtures. A second approach monitors the decay of the dichroism induced by picosecond laser excitation of solute molecules present at low concentrations in the solution being investigated. In a related method the decay of the anisotropy induced by picosecond excitation is followed by measurement of the time dependence of the fluorescence polarization. The dichroism and fluorescence polarization decay as the solute molecules rotate and thus transform the orientational distribution from an anisotropic to an isotropic one. The fourth method involves the creation of a transient grating by the intersection of two coherent light pulses in the liquid. Time-resolved measurements can be obtained by monitoring the decay of the induced diffraction pattern with a probe light pulse.

Optical Kerr Effect

The optical Kerr effect results from an intensity-dependent change in the refractive index induced by an intense light pulse propagating through a material. The optical Kerr effect was first observed in a number of liquids using a Q-switched nanosecond ruby laser (23, 24); this followed a theoretical prediction and treatment of the phenomenon (25–29). The use of picosecond lasers to induce a significant nonlinear refractive index in liquids has made it possible to measure the rotational motion of molecules in liquids (30), investigate the short-term nature of optical self-trapping in liquids (31), and study a variety of ultrafast processes with a laser-generated ultrafast light gate (30).

Due to the polarization of the optical field, the change in the refractive index parallel to the beam polarization (assuming a linearly polarized beam) can be different from the change in the perpendicular directions. Therefore an isotropic medium, such as a liquid, can be made anisotropic, and thus birefringent. In a liquid composed of anisotropic molecules, such as carbon disulfide (CS_2), we can view a major contribution to the refractive index difference as resulting from the partial alignment of the CS_2 molecules along the optical field direction. The light pulse induces a dipole in the CS_2 molecules. The induced dipole interacts with the light field and leads to a torque on the dipole that tends to orient the long axis of the CS_2 molecule along the polarization direction of the light field. This induced anisotropy in the orientation of the molecules produces a phase difference as the probe light propagates through the liquid, between the components polarized parallel vs perpendicular to the initial intense picosecond light pulse. Thus by measuring the decay of the birefringence with the probe pulse as a function of time subsequent to the intense alignment pulse, the orientational relaxation can be determined. In addition to rotational motions there can also be an electronic contribution to the nonlinear refractive index that will have a relaxation time far shorter than the picosecond light pulse (30, 32–36). The birefringence due to the electronic part of the nonlinear refractive index will thus only last as long as the initial pulse duration, i.e. it will "instantaneously" follow the excitation pulse in time.

In studies (30, 37, 38) of nitrobenzene the measured decay time of 32 psec, although somewhat lower than the orientational relaxation times obtained from depolarized Rayleigh scattering, 36 psec (39), 39 psec (40), and 50 psec (41), does indicate that the primary contribution to the decay of the optically induced birefringence is orientational in nature. It has been suggested that the lower values found for the time constant of the birefringent decay as compared with the orientational relaxation values obtained from light scattering in a variety of liquids (nitrobenzene, *m*-nitrotoluene, and various liquid mixtures) arise from the coupling of the orientational motions with shear modes (38). This explanation, although interesting, has not yet been clearly established and requires further study. It has, however, been demonstrated that the rotational motion of nitrobenzene cannot be described by very small angular jumps characteristic of Debye-type rotational diffusion nor by very large jumps. This result has been established by comparing the optically induced birefringence or light-scattering results with dielectric relaxation measurements (37).

Picosecond measurements of liquid CS_2 using a high-repetition-rate rhodamine 6G dye laser yielded a value for the relaxation of the optical Kerr effect of 2.1 psec (42). This is in good agreement with light-scattering results of 1.96 psec (43) and indicates that for CS_2 the decay of the induced birefringence is due to orientational relaxation. Studies of a variety of other liquids including bromobenzene, toluene, iodomethane, and mixtures of CS_2 and CCl_4 indicated fair agreement between the orientational relaxation and the macroscopic viscosity as given by the Debye relation, i.e. the relaxation time scales linearly with the viscosity (37). In mixtures of CS_2 and CCl_4 the scaling appears to be linear, although not for the full concentration range studied. Great care should be exercised in studying mixtures since the contributions of both components to the induced birefringence must be included. Correspondingly, if one seeks to obtain relaxation times from light scattering, the background scattering due to the solvent must also be considered.

Picosecond laser methods have recently been used to induce relaxation processes in liquid crystals (44). This work follows earlier work on liquid crystals that used Q-switched lasers (45). Direct measurement of the orientational relaxation has yielded information about the phase transition and temperature dependence of the viscosity coefficient for the liquid crystal *p*-methoxybenzilidene *p*-*m*-butylaniline (44).

Induced Dichroism Method

Unlike the induced birefringence method previously described, the induced dichroism method (46) is suitable for studies of solute molecules at low concentrations and can be carried out in any solvent into which the solute can be introduced. The optical Kerr method requires high concentrations, at least several percent of the species of interest, whereas the induced dichroism method is limited to low concentrations of the solute molecules. In the latter method the rotational motions of the individual solute molecules are obtained, whereas in the induced birefringence method the concentration of solute molecules is so high that solute-solute interactions as well as the solute-solvent interactions must be considered. As a further point, the dichroism method is applicable to molecules that have absorptions at frequencies corresponding to the frequency of the picosecond light pulse. The birefringence method can be applied to any liquid that has an optical Kerr constant sufficiently large to yield an induced birefringence. These two methods can be viewed as complementary in the systems amenable to study.

The principal idea of the dichroism method (46) is to induce an anisotropy in he orientational distribution of the excited- and ground-state populations with an ntense picosecond pulse in the same way as in the singlet-singlet energy-transfer experiments. The return of the system to an isotropic state is monitored with an attenuated picosecond pulse as a function of time. The difference in absorption of probe light polarized parallel and perpendicular to the polarization of the excitaion pulse will decay in time as a function of excited-state lifetime, solute concentraion, and solution viscosity. For example, in a fluid environment the anisotropic orientational distribution can transform to an isotropic one via the rotational motion of the molecules. At low concentrations in a highly viscous medium the rotations are frozen out, and the anisotropy decays as the excited molecules return to the ground state. At high concentrations the anisotropic distribution can also decay n time by intermolecular energy transfer between molecules of differing orientations n the way discussed in the energy-transfer section. Clearly, for the study of rotational motions, low concentrations are necessary to avoid the complicating effects of energy ransfer.

This method has been used to study the orientational relaxation of rhodamine 6G (46, 47). In particular the effects of solute-solvent hydrogen bonding interactions on the rotational motions of rhodamine 6G in a variety of solvents have been nvestigated (47). A linear relation between the relaxation times and the solution viscosities was obtained for the series chloroform, formamide, and the alcohols from methanol through octanol. The observed linear scaling, in agreement with the Debye-Stokes-Einstein hydrodynamic model, is surprising since the volumes of the hydrogen-bonded complexes should vary considerably through the series from methanol to octanol. Furthermore one might expect that since the strengths of hydrogen-bonding interactions of rhodamine 6G with chloroform and methanol are different, the relaxation times would not be equal even though the viscosities are the same. Similar arguments can be applied to the results obtained in the liquids formamide and 1-pentanol. To explain the apparent insensitivity of the orientational relaxation times to the volumes of the hydrogen-bonded complexes and the strengths of hydrogen-bonding interactions, it was proposed that the rotational motion of the complex cannot be described as that of a rigid particle. By invoking flexibility n the hydrogen bond as well as a dynamic process of bond formation and dissolution, t was proposed that the rotational motion of the solute could be roughly the same whether it is hydrogen-bonded or not. Thus the hydrodynamic volume was unchanging through the series of liquids studied, and linear scaling of τ_{OR} with η becomes plausible. Furthermore, if the time varying torques experienced by the solute molecule are primarily determined by the solvent-solvent interactions (which also determine the solution viscosity), then the linear scaling of τ_{OR} vs η found in the rhodamine 6G–solvent systems is not surprising. The observed deviation from inearity of τ_{OR} vs η in the liquids 1-decanol and 1-undecanol is probably due to the breakdown of the continuum hydrodynamic model since the solvent molecules are larger than the solute molecule. The sharp deviation observed in the ethyleneglycol solvent is thought to be due to the extensive solvent-solvent aggregation via hydrogen bonding. If the solute does not experience the full frictional effects of thi aggregation, τ_{OR} will be faster than the measured viscosity would lead one to expect which was found to be the case in this system.

Fluorescence Depolarization Method

In the method discussed above, the orientational relaxation is followed by the deca of the induced dichroism, i.e. the polarization dependence of the absorption. If th ground-state absorption is monitored, the decay of the induced anisotropy can b dependent not only on the ground-state molecular rotation but upon that of th excited molecule as well. The time constants for the ground and excited-stat rotations can be different. On the other hand, measurement of the excited-stat absorption is dependent only on the rotational motions of the excited-state molecul

Another way to follow the orientational relaxation of excited-state molecules i to measure the time dependence of the fluorescence depolarization. In this case the decay of the anisotropy in the excited-state population is being measured, i.e the rotational motion of the molecule in its excited state is obtained. If the excited-state molecules, before emitting light, rotate and thereby change the orientation o their emission dipoles (note that it is the orientation of the emission dipoles that i being monitored), the polarization of the fluorescence is decreased. The time dependence of this loss of fluorescence polarization is a direct measure of the orientational relaxation time of the excited-state molecule. The advantage of the fluorescenc depolarization method over the induced dichroism method is that it is easier t monitor fluorescence than absorption. The limiting features of the fluorescenc method are that a reasonably good emitter is required and only excited-state rotational motions can be measured.

By using a picosecond-excitation pulse in combination with a streak camera fo detection of the fluorescence, the orientational relaxation times of the dyes ros bengal in a series of alcohols and eosin in water have been obtained (48a). Th time-dependent fluorescence depolarization indicated that the rotational motion could be described as those of spherical molecules. The hydrodynamic volume were found to be more than twice the estimated volume of the free molecule. Th volume differences and the apparent spherical hydrodynamic shapes are attribute to solvent attachment. In addition, the reorientation times were found to scale onl approximately with solvent viscosity.

Transient Grating Method

By using the rather novel approach of a transient grating technique the rotationa relaxation times and fluorescence lifetimes of rhodamine 6G in several alcohol have been obtained (48b). Frequency-doubled mode-locked Nd:Yag laser pulses o about 60 psec duration and 530 nm wavelength were used to excite the rhodamin 6G molecules. Attenuated pulses at the same wavelength were used to probe th decay of the induced grating by the time-dependent changes in the probe ligh diffraction pattern. The grating, which results from strong absorption at the antinode of the colliding excitation beams, decays as the molecules rotate, i.e. the orientational anisotropy decays; the grating also decays as the excited molecules return to the ground state. The rotational-motion times were found to be in agreement, within experimental error, with the values obtained from the induced dichroism method (47).

PHOTODISSOCIATION AND THE CAGE EFFECT

The chemistry following the dissociation of a molecule in the liquid state is dependent on the relative probabilities of the original fragments recombining (which results in no net chemical change), or escaping each other and subsequently reacting with other fragments or molecules in the medium. In a liquid the original fragments are surrounded by solvent molecules that interfere with their escape. The enhanced probability of recombination of the original fragments, referred to as the cage effect (49), is dependent on the kinetic energy of the fragments and on the nature of the fragment-solvent interactions. To determine the nature of cage-effect reactions it is necessary to obtain information on the early time motions of the fragments since this is the key to the partitioning between geminate (original fragment) and nongeminate processes. Studies of these reactions (50) provide information not only on the chemistry of the reactions but also on the properties of the liquid state with which they are intimately connected.

Prior to picosecond studies (51) of the photodissociation of iodine molecules in solution, the following questions had been unanswered: Did the recombination in the cage take 10^{-12} sec, 10^{-11} sec, or 10^{-10} sec? Or, could the cage be thought of as a static structure? The validity of various theories of the kinetics of recombination in the subnanosecond time domain (50, 52, 53) also remained unconfirmed. The I_2 studies (51) involved excitation of molecular iodine to the $^3\pi_{0^+u}$ state, where the excited molecule undergoes a collisionally induced predissociation and produces a pair of ground-state, $^2P_{3/2}$, iodine atoms. The dissociation of the iodine molecules and the subsequent recombination of the atoms were studied by monitoring the time-dependent population of molecular iodine with an attenuated picosecond laser pulse. It was determined that the lifetime of the "cage," i.e. geminate recombination, was 70 psec in hexadecane and 140 psec in CCl_4. From the time scale of these geminate recombinations, it seems unlikely that a description of the cage effect in terms of a static solvent cage would be physically reasonable. With regard to a theoretical model, it was found that a random flight picture was inadequate in describing the experimentally determined cage kinetics. However, a diffusion-theoretical model (54) that introduced some correlation in the motion of the atoms by treating the atoms as hard spheres (i.e. there is a volume excluded to motion) described the recombination dynamics very nicely. In addition, these experiments provided the first direct observations of the dynamics of a collision-induced predissociation in the liquid state. A rate constant of about 10^{11} sec^{-1} for predissociation from the $^3\pi_{0^+u}$ was obtained. This is about 10^5 larger than the spontaneous predissociation process observed in gas phase I_2 at low pressures.

ELECTRON PHOTOEJECTION AND SOLVATION

Pulse radiolysis, conventional flash photolysis, and picosecond lasers have been used to investigate the dynamics of electron localization in a variety of solvents (55–85). With these methods, information has been obtained on the structure and energies of the solvated electron, ionic aggregates in liquids, and the structure and relaxation properties of the liquid itself.

In picosecond flash-photolysis studies of ionic aggregates (77), such as the sodium salt of tetraphenylethylene dianions (T^{2-}, $2Na^{+}$), marked differences were observed in the relaxation processes in the solvents tetrahydrofuran and dioxane. The bleaching of the (T^{2-}, $2Na^{+}$) absorption with a picosecond excitation pulse was found to last 10 psec in dioxane and several nanoseconds in tetrahydrofuran. In the latter, solvent electron ejection occurs. However, the absorption due to the $T^{\cdot -}$ radical that is expected to be generated by the ionization was not observed. Further experiments are necessary to clarify these interesting results.

EXCITED STATE CHARGE-TRANSFER COMPLEXES

In addition to intermolecular energy transfer there is another important class of excited-state interactions that quenches molecular fluorescence. It involves the transfer of charge rather than energy. Charge-transfer interactions not only quench fluorescence, but give rise to a new emission in low dielectric solvents characteristic of the exciplex $(A^{-} - D^{+})^{*}$, produce ion radicals in high dielectric solvents, provide new pathways for energy degradation, and change the chemistry of the system (86–98).

Just as cage-effect reactions can be used to probe translational motions of atoms and molecules in liquids, the study of electron-transfer reactions can also provide insights into the nature of translational motions in liquids. In the cage-effect experiments, the fragments (e.g. the iodine atoms) generated by the dissociation are not initially uniformly distributed in the solution. In the early time domain the fragments are near each other, and the cage-effect experiments thus yield information on the relative motions of neighboring particles, i.e. within roughly 10 Å of each other. For the excited-state electron-transfer reactions, the excited-state acceptor molecules A^* (produced by picosecond-pulse excitation) and the ground-state donor molecules D are initially uniformly distributed in the liquid. These reactions can therefore be used to examine the theoretical treatment of what are commonly referred to as diffusion-controlled reactions. Although the reactants are initially distributed randomly in the liquid, the reaction in the early time domain preferentially depletes the distribution of donor and acceptor molecules that happen to be near each other. The spatial distribution of A^* with respect to D is no longer random, i.e. uniform, and the nonequilibrium spatial distribution is thus changing with time. This leads to a rate "constant" that is also changing with time. The reaction cannot be described therefore as a bimolecular reaction with a time-independent rate constant dependent on the diffusion coefficients of D and A^*. The kinetics of formation of $(A^- - D^+)^*$ do not follow a simple exponential form but contain transient terms.

Picosecond-laser studies (93) of a hexane solution consisting of anthracene, serving as the acceptor (i.e. excited to S_1 with a picosecond pulse), and ground-state N,N-diethylaniline as the donor showed that a diffusion model that included all transient terms was in excellent agreement with the experimental results. Speculation that all transient terms were not necessary to describe the dynamics for times >10 psec was found to be incorrect; the full transient description was necessary to conform with the experimental findings. However, at very high concentrations of the donor, 3 M or neat N,N-diethylaniline, no transient behavior was observed. The formation of the exciplex followed an exponential time dependence characteristic of a bimolecular process with a time-independent rate constant of 10^{11} sec^{-1}. At these high donor concentrations the excited anthracene molecules have donor molecules as immediate neighbors and translational motions are not rate-determining.

In addition to the distance requirements for excited-state electron transfer there can also be orientational restrictions on the transfer process. To examine the role of geometry on the dynamics of the electron-transfer process (98), the acceptor anthracene was linked to the donor dimethylaniline, DMA, via three methylene groups, $A\text{-}(CH_2)_3\text{-}D$, which was initially done by the Weller group (99), Chandross & Thomas (88), and Mataga and co-workers (89). As in the free system, the A moiety was excited with a 347.2 nm pulse, and the electron-transfer step was monitored with a 694.3 nm pulse. The behavior in polar solvents such as acetonitrile and methanol was found to be considerably different than that observed in nonpolar solvents such as hexane. In nonpolar solvents the initial charge-transfer step is rapid and then either levels off or increases very slowly after about 40 psec. However, electron transfer does not occur for all of the $A^*\text{-}(CH_2)_3\text{-DMA}$ molecules in the system. This is thought to be due to a distribution of ground-state geometries. It was proposed that molecules that are in the "appropriate" configuration can undergo exciplex formation, whereas molecules that are in the "wrong" configurations (e.g. extended form) cannot achieve the appropriate geometry within the lifetime of the A* moiety (5.5 nsec) to effect electron transfer.

On the other hand, the observation that electron transfer occurs for almost all $A^*\text{-}(CH_2)_3\text{-DMA}$ molecules in polar media can be due to favorable molecular configurations for electron transfer in these media. Packing effects due to molecular shapes and sizes as well as strong solvent-solvent interactions could favor the more compact configuration of $A\text{-}(CH_2)_3\text{-}D$ in the polar solvents, thereby minimizing disruption of the solvent structure. Another possibility is the relative shifting of the $A^*\text{-}(CH_2)_3\text{-DMA}$ and $\cdot A^-(CH_2)_3\text{-DMA}^+$ energy surfaces, leading to an enhanced electron-transfer probability for an "extended" configuration in polar media. In polar media that there is also a fairly rapid decay (probably back-electron transfer), though it is slower than the initial transfer step. This back transfer is not observed in the nonpolar media, at least for times up to 1 nsec. For the polar media the fairly rapid decay process 760 ± 80 psec can involve formation of the acceptor triplet in the back-transfer step, i.e. $A\cdot^-\text{-}(CH_2)_3\text{-}D\cdot^+$ to $^3A^*\text{-}(CH_2)_3\text{-}D$. The center-to-center separation in an extended form is about 4–5 Å. From the studies (91, 93) of the free donor and acceptor systems at donor concentrations of 3 M or higher, it is known that the electron transfer is completed in about 20–25 psec. At the distances separating the linked donor and acceptor, one would thus expect the transfer to be completed in this same time period (20–25 psec) rather than the longer times observed in both the polar and nonpolar solvents. It is concluded that the differences are due to the less than favorable geometries achievable in the linked molecule.

INTERNAL CONVERSION AND INTERSYSTEM CROSSING

Internal conversion refers to the nonradiative processes by which a molecule in an excited state converts to a lower energy state of the same multiplicity. Intersystem crossing involves the nonradiative transition between states of differing multiplicity. Picosecond-pulse techniques afford special opportunities for studying internal conversion and intersystem crossing since many organic molecules possess lifetimes of the order of nanoseconds or less because of these ultrafast processes. The interactions responsible for internal conversion and intersystem crossing in molecules are not well understood.

Two picosecond techniques have mainly been used to measure rapid-energy relaxation in large molecules: an absorption technique and a fluorescence emission method. In the former, the sample is prepared with an exciting pulse and the transmission of the sample is probed with a weak interrogation pulse at varying delay times. If a molecule emits sufficient fluorescence, rapid relaxation can also be investigated by observing the emission with either a picosecond-resolution optical gate or a streak camera.

An interesting measurement of rapid internal conversion was carried out (100) on the crystal-violet dye molecule $[(CH_3)_2NC_6H_4]_3C^+$. The structure of this molecule is known to be D_3-propeller-shaped with the phenyl rings rotated 32° from the central plane. The molecule, although exhibiting intense visible absorption bands, is almost completely nonfluorescent with a quantum yield below 10^{-4}. The crystal-violet molecules were excited with an intense 530 nm pulse that promoted the molecules from S_0 to S_1. A very weak interrogating pulse was used to probe the return of the molecules to the ground state. Because the recovery was very rapid and complete within 100 psec, it was concluded that the rapid internal conversion process was being measured. By choosing a series of solvents that covered a viscosity range from 0.01 to 120 P, it was shown that the ground-state recovery time varies as $\eta^{1/3}$, where η is the viscosity of the solvent.

Solvent effects other than viscosity are judged to be relatively unimportant. A model developed (101) for a series of triphenylmethane dyes predicts a viscosity dependence for the quantum yield of $Q = C\eta^{2/3}$. In this model, absorption of light produces a Franck-Condon vertically excited state with the phenyl rings still at a ground-state equilibrium angle, θ_0. The rings then rotate toward a new equilibrium angle, θ, and the nonradiative deactivation of the excited state depends upon $(\theta - \theta_0)^2$. It was further assumed that the radiative rate is independent of θ. A new model is necessary to explain the new data since the present model predicts the same $\eta^{2/3}$ dependence for the lifetime as well as for the quantum yield, whereas the measured dependence for the lifetime is $\eta^{1/3}$.

Further measurements on another triphenylmethane dye, malachite green, have been made using the superior resolution available from a mode-locked CW dye laser (102). With 0.5 psec excitation pulses it was found that the recovery time is only 2.1 psec for malachite green in methanol and that the decay is exponential. By studying the recovery time in a number of solvents it was determined that there was always a long-term recovery, whereas in the higher viscosity solvents, there was also an initial, more rapid, partial recovery. Since the fast initial recovery is in agreement with the S_1 lifetime calculated from the quantum efficiency, it was suggested that on a short time scale, molecules in S_1 rapidly convert to a highly energetic level of S_0, giving rise to a partial recovery of the absorption. Subsequently, this hot distribution in the ground state relaxes, giving rise to the slower rate observed for complete recovery of the absorption. The longer lifetimes were found to depend on the viscosity of the solvent approximately as $\eta^{1/2}$, but the $1/e$ point of the total-recovery curves varies closely as $\eta^{1/3}$ in agreement with the previously described work (100).

Studies (103, 104) of benzophenone and nitronaphthalene have shown that the intersystem-crossing rates for these molecules are solvent dependent. In other investigations on benzophenone, it was found that intersystem crossing was dependent on the wavelength of excitation (105–108). These phenomena may be quite complex, if vibrational relaxation is occurring on a time scale comparable to that of intersystem crossing. The solvent-dependent risetimes indicate that conventional singlet-triplet mixing appears to be an insufficient explanation, because this mechanism is quite sensitive to the spacing between the singlet and triplet states. It has been suggested (104) that the variations in buildup time may be due to the effectiveness of different solvents in relaxing the excited benzophenone molecules vibrationally to or from singlet levels that are strongly coupled to the triplet manifold.

Studies of the internal conversion between excited electronic states of the molecule 4-(1-naphthylmethyl)-benzophenone in a benzene solution have been undertaken (109a). In these experiments the benzophenone molecule and the methylnapthalene molecule are connected by a sigma-type chemical bond so that energy may be transferred from one part of the connected molecule to the other. The benzophenone portion of the molecule is excited to the S_1 state by a pulse at 353 nm, and the triplet formation is probed by the absorption at 530 nm. An initial absorption with a lifetime of 10 psec is accompanied by the development of a much weaker absorption with a decay time greater than the longest delay time used in the experiment. The short-time and long-time components were interpreted as originating from triplet-triplet absorptions from the benzophenone and 1-methylnaphthalene parts of the molecule, respectively. The initial rapid decay of the absorption of the double molecule can be contrasted against a very slow decay of about 1 nsec observed for an equimolar solution of benzophenone and naphthalene in benzene with each solute at 0.2 M to simulate the double molecule experiments at 0.2 M. Thus the contribution to quenching by nearest neighbors is small. The results appear to support a model in which the wave functions of the low-energy states of the double molecule are approximately products of naphthalene- and benzophenone-like single-excitation functions, with the coupling provided by the small interactions between the chromophores.

A mode-locked CW dye laser was used to generate UV (307.5 nm) pulses for excitation of coronene to S_3; 615 nm pulses were also generated to monitor absorption from S_1. With the unusually high time resolution achieved with this system (0.2 psec), the internal conversion from S_3 to S_1 was found to be 2 psec (109b).

A more general extension of the probe technique has been used by several groups to measure internal conversion and intersystem crossing. A pulse at a given "wavelength" excites the sample, but the probe pulse consists of a picosecond continuum that spans the entire visible region and sometimes extends beyond it. These very broad continua, generated by nonlinear optical techniques, were first used (35, 110–112) to monitor inverse Raman spectra, and their use for picosecond flash photolysis experiments was suggested. These continua make it possible to study systematically the picosecond transient behavior of molecules, which are weak emitters.

Experiments using these flash photolysis techniques have helped to resolve discrepancies in the literature on the lifetime of DODCI (3,3′-diethyloxadicarbocyanine iodide) dye (113). In further studies (114) the effect of the solvent on the decay kinetics of bis-(4-dimethylaminodithiobenzil)-Ni(II), or BDN for short, was investigated. BDN is a nickel complex that absorbs in the infrared and is difficult to study by emission spectroscopy because it has a low quantum yield, and the emission probably extends well into the infrared. BDN was excited with a single intense pulse at 1060 nm, and excited-state absorption was then monitored with a picosecond continuum. The excited-state absorption lifetime was measured to be 220 psec for BDN in iodoethane; 3.6 nsec for BDN in 1,2-dichloroethane; 2.6 nsec for BDN in 1,2-dibromoethane; and 9 nsec for BDN in benzene. An external heavy-atom effect apparently leads to the more rapid recovery in the halogenated solvents. Analysis indicates that the excited-state absorption represents the lifetime of a state, or states, in which the $3b_{2g}$ orbital is occupied.

Porphyrin molecules have also been studied by excitation with a 530 nm pulse and the evolution of the absorption spectra probed with picosecond resolution by means of a continuum (115). For octaethylporphinatotin(IV) dichloride [(OEP)SnCl$_2$] the absorption spectrum of the excited singlet state, the decay of the S_1 state, and the growth of the T_1 triplet state have been observed. The S_1 state decays in about 500 psec, and the spectrum represented by T_1 appears in about the same time. By analysis it was found that the quantum yield for triplet formation is 0.8 ± 0.008 for (OEP)SnCl$_2$, and from the known fluorescence quantum yield of about 0.01 the quantum yield for internal conversion from the S_1 to the S_0 state was deduced to be about 0.19. The difference between the absorption spectrum of the first excited singlet state and that of the first excited triplet state in a porphyrin molecule has also been obtained by using these methods. For many of these experiments picosecond flash photolysis is used to locate a number of new absorption bands, and standard techniques are then used to observe changes of optical density at a particularly interesting wavelength.

In other experiments using the picosecond continua, two cyanine dyes, cryptocyanine (1,1′-diethyl-4,4′-carbocyanine iodide) and DTTC (3,3′-diethyl-2,2′-thiatricarbocyanine iodide), were excited with 694.3 nm pulses, and the evolution of transient absorption bands was examined (116). A new absorption band, which decayed in 90 ± 30 psec, was detected in DTTC at 525 nm. Since the ground state was also observed to recover in about this time, the newly observed band was attributed to a transition between excited singlet states. Measurements of the recovery time for the ground state of cryptocyanine were found to be consistent with the results of earlier workers (117).

Picosecond flash photolysis methods have also been used to measure the $S_n \leftarrow S_1$ and $T_n \leftarrow T_1$ absorption spectra of anthracene in solution (118). The anthracene is excited with pulses at 347.2 nm, and a continuum covering the entire region from 390 to 920 nm is used to probe the transient spectra. At short delay times of 250 to 300 psec, a strong absorption band at 600 nm that corresponds to the $S_n \leftarrow S_1$ transition is observed, while at much longer delay times, 4 to 5 nsec, a strong transition is found at 420 nm that is assigned to $T_n \leftarrow T_1$.

Lifetimes of the excited states of a number of transition-metal compounds have been established (119) by use of probe techniques and picosecond flash photolysis. Lifetimes in the subnanosecond range were established for some nonluminescent compounds of iron and ruthenium. For a number of transition-metal complexes the interstate nonradiative processes such as intersystem crossing were found to be extremely fast. A recent improvement for measuring time-resolved absorption spectra in the picosecond range has been developed (120). The system consists of a ruby picosecond laser (694.3 nm) for excitation and a 6 μsec Xe probe flash pulse whose transmission is time-resolved with a streak camera that has a 65 psec resolution capability. With this system, the excited singlet absorption of a number of dyes was obtained. Since there are streak cameras that have better than 5 psec resolution capabilities, the combination of picosecond excitation, Xe probe pulses, and an ultrafast streak camera will make this method increasingly attractive.

Emission Measurements of Internal Conversion and Intersystem Crossing

One of the first applications of the mode-locked laser was its use in measuring the nanosecond fluorescence decay times of dye molecules in solvents. In an early technique the sample was excited with either the fundamental or the second harmonic of pulses generated by a mode-locked ruby laser, and the fluorescence was detected with a planar diode detector used in conjunction with a traveling-wave oscilloscope (121, 122). In these experiments both the ultrashort pumping pulses for minimizing deconvolution problems and the high-intensity picosecond-pulse source were used. Prior to these measurements more conventional schemes used either nanosecond flashlamp pumping or more cumbersome fluorometry techniques. These experiments were still limited, however, to a resolution of about 0.5 nsec.

The first studies in which fluorescence phenomena were detected with "true" picosecond resolution used the optical gate to study the emission from two dyes, DDI (1,1′-diethyl-2,2′-dicarbocyanine iodide) and cryptocyanine, dissolved in methanol (117). The samples were excited with pulses at 530 nm, and the emission was sampled at variable delay times by means of an ultrafast shutter operated by intense pulses at 1060 nm. The fluorescence from DDI in methanol decayed in 14 ± 3 psec, while that of cryptocyanine decayed in 22 ± 4 psec. This ultrafast recovery time in cryptocyanine has since been verified (116, 123, 124). The ultrashort fluorescence decay time demonstrates the rapid internal conversion of the first excited singlet state to the ground state.

Using an optical gate technique, measurements have been obtained for the fluorescence decay time of erythrosin in solution (125–127). For erythrosin in water the measured decay times were found to be 90 psec (125), 110 ± 20 psec (127), and 57 ± 6 psec (126). Since the quantum yield is 0.02 for erythrosin in water, the higher values should probably be preferred. The fluorescence risetime is "instantaneous" as shown in two of the studies (126, 127), although other work (125) mistakenly identified their prompt risetime as a slow one because of the long delay between the peak of the fluorescence curve and the calibrated zero time. These apparent delays originate because of the continuous accumulation of excited-state singlets produced by the wings of the pulse. The fluorescence lifetimes of a number of fluorescein derivatives have also been measured (127). The lifetimes of fluorescein (Fl), eosin ($FlBr_4$), and erythrosin (FlI_4), were measured to be 3.6, 0.9, and 0.11 nsec, respectively. The data is in excellent agreement with quantum-yield predictions, and the decrease in lifetime observed upon addition of heavy halogen atoms has been taken to be consistent with heavy-atom-enhanced intersystem crossing and published triplet quantum yields.

A precautionary note should be added for measurement of fluorescence lifetimes. At high excitation intensities, nonlinear processes such as stimulated emission may occur. Stimulated emission effects were pointed out in two early studies (128, 129a). These effects lead to a nonexponential decay of the fluorescence and a shortening of the lifetime. Other common effects are 1. the formation of transient species when an entire train of pulses is used to excite fluorescence and 2. concentration quenching. A fairly common effect is that leftover triplet states modify the lifetime for singlets produced by later pulses in the train. Such problems have led to a wide range of estimates for the lifetime of DODCI, for example. The correct fluorescence lifetime of about 1.2 nsec has now been firmly established by a number of investigators (42, 113, 129b–132).

The photochemical decomposition of *s*-tetrazene in benzene has been studied by both excited-state absorption and fluorescence techniques (133). The excited-singlet lifetime was found to be about 450 psec, and a new excited-state transition peaking at 473 nm was observed. In fluorescence experiments (134) on the polymethane dye DTTC in methanol the lifetime from a highly excited singlet state (blue-emitting) was found to be roughly 35 psec.

In a number of experiments a streak camera has been used in conjunction with picosecond excitation to examine fluorescence emission with picosecond resolution. Emission from a number of dyes under mode-locking conditions (135, 136), such as fluorescence from DODCI (132), emission from dye vapors, from photosynthetic samples, and scintillator materials (137–139), has been obtained in this way. In the dye-vapor experiments (137), dimethyl POPOP [1,4-bis-2-(4-methyl-5-phenyloxazolyl) benzene] and perylene molecules were excited in the gaseous phase with picosecond pulses at 353 nm, and then, by using a streak-camera detection technique, the risetime of the fluorescence was found to be ⩽20 psec for dimethyl POPOP and $\leqslant 30$ psec for perylene. Since the vapors were at 300°C, the collision rate between dye molecules could have been no more than 10^8 sec^{-1}. A dye molecule in the liquid phase would collide with the neighboring solvent molecules at a rate of about 10^{12} sec^{-1}. Since fluorescence is commonly observed from the ground vibrational state of the first excited singlet state, the rapid risetime in the vapor was interpreted as direct evidence supporting rapid internal relaxation of the molecules, even in the absence of collisions. The ability of large dye molecules to relax internally, independent of their surroundings, is a manifestation of the fact that such molecules have a large number of vibrational and rotational modes; the probability of mutual interactions among the modes, thus, is very high. These interactions reduce the lifetime of any particular level, because the energy provided by the excitation can be rapidly redistributed over the large ensemble of densely packed levels.

It has been shown that the decay of benzophenone in the vapor phase is nonexponential and in the microsecond range (140, 141). The nonexponential decays have been verified and interpreted in terms of coupling with triplet states (142). These more recent workers indicate that oscillations observed in the tail of the decay previously observed (141) are probably experimental artifacts and not quantum beats.

In another interesting application of picosecond fluorescence techniques, emission originating from upper singlet states has been observed by means of a two-photon absorption technique (143). Ordinarily, these emissions can only be observed in rare cases since the fluorescence is emitted from higher singlet states with a very low quantum efficiency. Two-photon excitation allows the excitation of levels that are spectroscopically forbidden by one-photon excitation. Two-photon excitation also permits a more uniform spatial distribution of excited molecules in a sample that is strongly one-photon-absorbing, e.g. a solid, concentrated solution, or a very intense transition. Furthermore, states that are one-photon-allowed but hidden by stronger overlapping transitions can be amenable to detection by two-photon absorption. In addition, direct-scattering processes that would tend to obscure any weak emission are avoided with two-photon absorption techniques. By irradiating samples with a combination of the wavelengths 1060, 530, and 354 nm, generated from the fundamental or harmonics of the Nd:glass laser, spectra were obtained for the excited states of such dyes as rhodamine 6G perchlorate in 2-propanol, rhodamine B in 2-propanol, and acridine red in 2-propanol. From the intensity of typical spectra, an upper limit of 10^{-4} can be placed on the fluorescence quantum efficiency from the upper states, and the lifetime of these states is estimated to be less than 5 psec.

In addition to the experimental progress due to picosecond lasers, there have been important theoretical advances in recent years in the description of radiationless transitions and optical coupling in complex molecules (144–151).

VIBRATIONAL RELAXATION IN EXCITED ELECTRONIC STATES

With regard to the rapid relaxation of large dye molecules, a number of innovative techniques have been introduced for measuring vibrational relaxation times (16, 17, 153a). In the first technique, molecules are excited from the ground state S_0 to the first excited singlet state S_1 by photons of frequency ω_1, and the molecules then decay to the ground vibrational state of S_1. This decay can be followed by measuring the gain produced by a probe pulse of frequency ω_2, which is usually chosen to correspond with the red end of the fluorescence band. In the second technique, ground-state vibrational relaxation can be monitored by exciting the molecules to S_1, permitting a suitable delay for the molecules to relax to the ground vibrational state of S_1, stimulating these molecules to relax to an upper vibrational state of S_0 by an intense beam at frequency ω_2, and then probing the vibrational relaxation by the return of absorption at ω_1, caused by return of the population to the ground state. Because the pulsewidths were of the order 5 to 6 psec, and the vibrational relaxations were very fast, deconvolution of the pulse-shape function was a difficult matter, but it was concluded that the vibrational relaxation times in the rhodamines were approximately several picoseconds, with an uncertainty also of several picoseconds.

In the other studies (153a) of excited-state vibrational relaxation in rhodamine 6G and rhodamine B in a variety of solvents, the vibrational population lifetimes were found to be 0.5–1 psec, independent of the solvent or its viscosity. Two methods were used that gave consistent results. In one method the nonlinear transmission of an intense picosecond pulse as a function of its intensity was used to calculate the vibrational relaxation time. In the other, the transient population of the initially excited vibrational levels of S_1 was measured with a weak probe pulse. Using subpicosecond pulse excitation (18), it has been possible to apply a previously used technique (16) with greater precision to the study of vibronic relaxation. Rhodamine 6G and rhodamine B molecules were excited in a number of solvents up to a higher electronic state with a subpicosecond pulse (0.9 psec) at 307.7 nm, and the gain of the emission was then probed with a subpicosecond pulse (9.9 psec) at 615 nm. Gain measurements show that the fluorescence emission begins promptly. After deconvolution, the risetime is less than 0.2 psec, which is the resolution of the apparatus. The result is at first somewhat surprising because, in order for the excitation to reach the first excited singlet state, the molecules must relax through an ensemble of levels with a total energy gap of $\sim 14{,}000\ \mathrm{cm}^{-1}$. Although for these complex molecular systems other possible explanations present themselves, e.g. the stimulated emission cross section of the higher vibronic levels of the first excited singlet state is the same as that from vibrationally relaxed S_1, the following interpretation (18) seems to be indicated: deactivation of the excited state of rhodamine 6G is exceedingly fast.

The rapid deexcitation of an excited electronic state has also been obtained by determining the risetime of the spontaneous fluorescence intensity for a number of dyes (152). Dyes such as rhodamine B, rhodamine 6G, and erythrosin B in such solvents as water, ethanol, and methanol were excited with 530 nm, 10 psec pulses and the emission was detected with an optical shutter. The observed risetime corresponded to a delay of less than 1 psec, consistent with later work (18).

Previously, it was claimed that the time- and frequency-resolved vibrational relaxation in an excited state of rhodamine 6G had been determined (153b). It was observed, upon pumping rhodamine 6G with intense 530 nm pulses of several picoseconds' duration, that intense stimulated emission occurred many picoseconds after the zero time of the apparatus, and it was therefore concluded that the vibrational relaxation time was about 6 psec. It is now clear that the onset of stimulated emission in this experiment is governed more by parameters such as the integral of the excitation pulse-shape function, which is closely related to the number of molecules in the excited state, and by the stimulated emission cross section, and is only indirectly related to any vibrational relaxation time.

Recent experiments carried out in several laboratories (154–156) on azulene in its lowest excited singlet state indicate that the relaxation is $\leqslant 1$ psec. The physical processes contributing to the ultrafast decay time are not clear. The measured relaxation time can be a superposition of vibrational relaxation in S_1, internal conversion to S_0, and intersystem crossing to the triplet manifold.

INTRAMOLECULAR PROTON TRANSFER

One of the elementary processes by which molecules in excited electronic states can relax is by an intermolecular or intramolecular transfer of a proton (157–167). The excited-state proton transfer can generate an anion, e.g. the naphtholate ion (159, 162, 163), or lead to an enol-to-keto isomerization, e.g. salicylic ester (162), or produce the tautomer via a double-proton transfer in the 7-azaindole dimer (164, 165). With these processes, new emissions, new routes for energy degradation, and chemical changes become available to the system.

A picosecond ruby laser was used to measure the proton-transfer kinetics of 2,4-bis-(dimethylamino)-6-(2-hydroxy-5-methylphenyl)-*s*-triazine in cyclohexane at 298°K (167). The lifetime of the excited singlet (enol form of the molecule) was found to be 6.3×10^{-11} sec, and the rate constant for proton transfer was found to be 1.1×10^{10} sec^{-1}. This proton-transfer rate constant, measured at 298°K, is about a factor of 100 greater than that found for the double-proton transfer in the 7-azaindole dimer measured at 77°K (164, 165). The difference may be due to a quantum mechanical tunneling in the latter case vs going over a potential barrier in the former case.

CONFORMATIONAL CHANGES IN EXCITED ELECTRONIC STATES

The coupling between the electronic systems of identical molecules, one of which is in an excited electronic state whereas the other is in the ground state, can lead to the formation of a transient species, the excimer, whose spectral properties differ markedly from those of the isolated chromophores. Examples of systems composed of two identical parts that are, however, not free, are double molecules such as the biaryls, i.e. biphenyl, binaphthyl, bianthryl, etc. They consist of two planar aromatic molecules connected by a carbon-carbon bond. Unlike the usual excimers that are formed from free molecules, the relative orientations of the two moieties in a double molecule are severely constrained by the bond joining them.

Spectroscopic and X-ray studies (168–173) of one of the members of this series, 1,1′-binaphthyl, have indicated that in the ground state the orientation of the naphthalene moieties is close to 90° and thus weakly interacting, whereas in the excited singlet state in solution at room temperature the moieties are strongly interacting and this indicates a more coplanar configuration. Picosecond dye-laser pulses were used in the recent investigation (174) of the kinetics of the excited-state structural change that results from the internal rotation about the carbon-carbon connecting bond. In addition to the excited-state twisting motion that changes the relative orientation of the naphthalene moieties, the rotational motion was also obtained for the 1,1′-binaphthyl molecule in its equilibrium excited-state configuration. The approach used was to excite 1,1′-binaphthyl with a picosecond light pulse at 307.5 nm and monitor the motion towards coplanarity by the appearance of a strong excited-state absorption at 615 nm, characteristic of the equilibrium "coplanar" excited-state configuration. The experiments were carried out at room temperature in the solvents: benzene, *t*-butyl benzene, and *n*-heptanol. The kinetics of the conformational changes were found to be polarization-dependent, consisting of a very rapid part of about 2.5 psec in all of the solvents used and a slower part varying from 11–12 psec in benzene and *t*-butyl benzene to 22 psec in *n*-heptanol. The polarization-dependent kinetics were discussed in terms of the shift in energy levels during the motion from the perpendicular to coplanar configurations. As different states come into resonance at the probe wavelength of 615 nm, the polarization of the absorption changes. Although the excited-state structural change, i.e. the internal rotation, does not follow a simple (linear) viscosity dependence, the overall rotation of the molecule in its equilibrium excited-state geometry does scale linearly with viscosity, which suggests a Debye hydrodynamic rotational motion.

VIBRATIONAL RELAXATION IN THE GROUND ELECTRONIC STATE

Vibrational relaxation processes in the condensed phase are extremely rapid, 10^{-10} sec–10^{-12} sec, with liquid nitrogen being one of the notable exceptions. Before the application of picosecond lasers, information on the dynamics of condensed-phase vibrational relaxation was obtained from the measurement of infrared and Raman linewidths. One difficulty with this approach is that the experimentally observed line shape is often determined by a number of different physical processes. These include population (energy) relaxation, dephasing, and isotope effects. If the line is homogeneously broadened, the dephasing time can be obtained from the spectral width. The population lifetime can be obtained from the measured linewidth if the dominant relaxation process is the population decay. In this case the dephasing time and the population lifetime are equal. However, if dephasing processes, e.g. dephasing collisions, are important, the population lifetime (energy relaxation) is hidden by the rapid dephasing processes and cannot be extracted from the linewidth measurements. In such a case, measurements in the time domain are necessary to find the population decay time. If the line is inhomogeneously broadened, neither the dephasing time nor the population decay time is directly related to the observed linewidth. The linewidth is determined by the distribution of closely spaced resonance frequencies, e.g. a Doppler-broadened line in a gas or the overlapping components due to isotope line splittings, and is not determined by the relaxation processes. In this case, time-resolved measurements can yield the various dephasing and population decay times.

A further limitation of the spectral linewidth measurements is that the decay of a vibrational mode into other vibrational modes of the molecule, e.g. stretching into bending, cannot be determined. In a similar way intermolecular vibrational energy transfer is not obtained from linewidth measurements. However, with direct time-resolved measurements, the dephasing times, population decay times, and channels for population decay can be found.

The basic idea of the time measurements is to generate a large excess population in a specified vibrational mode with an intense picosecond light pulse and then probe the relaxation processes with a weak picosecond light pulse (175–178). In the first, and most commonly used, method (179), the large vibrational population is achieved by a stimulated Raman process followed by an anti-Stokes Raman-scattering process with a time-delayed picosecond probe pulse (175–178). If the probe scattering is carried out under phase-matching conditions (coherent Raman scattering), the dephasing time is obtained. If the system is monitored by the spontaneous (incoherent) anti-Stokes Raman scattering of the probe pulse, the population decay is obtained.

Although this method has proved to be a powerful one, it, too, has its shortcomings. Some of the limitations are the selectivity of the stimulated Raman scattering in exciting only a given vibrational mode of the molecule and thus not permitting study of other vibrational modes, the requirement of very high concentrations, the weakness of the anti-Stokes spontaneous scattering, and the difficulty in studying low-frequency vibrations (<1000 cm^{-1}) due to their large Boltzmann populations at room temperature.

To avoid the limitations of the stimulated Raman-scattering approach, a technique has been developed that utilizes tunable infrared picosecond pulses for vibrational excitation (180,181). It has several advantages: it selectively excites different vibrational modes of a molecule, the excitation is a one-photon process rather than the nonlinear stimulated Raman process, and it can be used to study dilute systems. Since the selection rules for infrared absorption are different from those for Raman scattering, the techniques can be viewed as complementary ones. The probe method is the same for both techniques, namely, measurement of the spontaneous anti-Stokes Raman scattering as a function of delay time with an attenuated visible-wavelength picosecond pulse. In studies (180) of ethanol (4×10^{-2} M) and methyl iodide (5×10^{-2} M) in carbon tetrachloride, it was found that intramolecular relaxation of the excited methyl vibrations (2940 cm^{-1} in ethanol and 2950 cm^{-1} and 3050 cm^{-1} in methyl iodide) to neighboring energy states was very rapid (1–2 psec). The decay to lower energy states was found to be much more rapid in methyl iodide than in ethanol.

In an earlier section, I detailed one method for measuring the population decay of ground-state vibrational modes that used a sequence of three picosecond pulses (16, 17). Another technique has recently been developed that combines infrared and visible pulses with fluorescence measurements (181). The infrared pulse, generated by a parametric process at the frequency of interest, is used to excite a vibration of the molecule. A time-delayed visible pulse that cannot excite the molecule to its lowest excited electronic state, S_1, from the $v = 0$ level but can reach S_1 from the vibrationally excited level ($v = 1$) is used to probe the population relaxation. Measurement of the fluorescence from S_1 as a function of the time delay between the visible and infrared pulses gives the vibrational population for that time. By this method (181), the vibrational energy relaxation of the 2970 cm^{-1} asymmetric CH_3-stretching mode of coumarin 6 in CCl_4 at 295°K was found to be 1.3 psec. The appealing features of this approach include the ability to excite different vibrational modes of the molecule by adjusting the frequency of the infrared pulse, the high sensitivity, and the applicability to dilute systems. However, the method requires molecules that have a reasonable quantum yield of fluorescence. Another factor to be considered is the difficulty in separating two relaxation channels: 1. a channel to neighboring energy states that have different transition probabilities to S_1 (and thus would alter the fluorescence intensity), and 2. a channel to lower-energy vibrational states. In all of these time-domain measurements of ground-state vibrational relaxation, a large excess (relative to thermal) vibrational population must be generated. This is very difficult to achieve at room temperature for the lower frequency vibrations (<1000 cm^{-1}) because of the large Boltzmann populations. For the moment at least, line-width measurements are necessary for the lower frequency vibrations.

CONCLUDING REMARKS

It is hoped that this review of picosecond spectroscopy has helped the reader perceive not only the diversity of experiments and impact of this young field but also, most importantly, its unusual promise. The applications of picosecond lasers to problems in chemistry, physics, and biology are expanding rapidly. Unfortunately, due to space limitations, I have not discussed the use of these lasers in biology. The enormous gaps in our understanding of the liquid state, molecular motions, physical decay processes, and chemical reactions provide important opportunities for this new field.

ACKNOWLEDGMENTS

I wish to acknowledge support for this work by the National Science Foundation and the US Army Research Office.

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