

Transient magnetization following photoexcitation

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Contents

I. Introduction	107
II. Individual systems: Photoejected electrons in liquid solutions	111
III. Triplet states in single crystal hosts	112
IV. Summary	120
V. Acknowledgment	120
VI. References	120

I. Introduction

Studies of paramagnetic intermediates evoked by photoexcitation have evolved from the early experiments in which steady state concentrations produced by continuous photoexcitation were monitored with conventional electron paramagnetic resonance spectrometers to ones with ever shorter time resolution for observations of transient responses following pulsed excitation. In this article we summarize our recent observations of a variety of processes evoked by pulsed laser excitation. Although our analyses of the data are by no means complete we describe the experiments because of our hope that they may stimulate further work. Our aim in this article is to indicate the usefulness of the methods and their experimental simplicity. Detailed analyses, should we succeed in making them, will be published elsewhere.

All the experiments to be described in this report were carried out in substantially the same way:¹ The material under investigation is illuminated by pulses of light produced by either a pulsed nitrogen laser or by a tuneable dye laser pumped by the nitrogen laser. The pulse duration (full width at half maximum) is between 3 and 6 nanoseconds. The sample is contained in the cavity of an X-band electron paramagnetic resonance spectrometer and is continuously bathed in the microwave radiation. No field modulation is used. The time evolution of the intensity of the microwaves reaching the detector is monitored following each light pulse. For phenomena with characteristic times of 1 microsecond or longer the preamplifier of a Varian E-3 spectrometer is adequate. For shorter times the diode is connected directly to a wide band amplifier (PAR 115, rise time 5 nanoseconds). The signal is captured in an appropriate recorder (in our case Biomation 8100, a transient digitizer with 2048 channels and shortest dwell time per channel 10 nanoseconds). If the material under investigation has already been examined under continuous irradiation steady state (C.W.)

conditions, the search for transients is carried out at static fields near those where C.W. responses are found. But in some cases we have found it more convenient to locate the resonances by observing the transient response as the field is swept, and in others have uncovered resonances not seen in C.W. Most of the results to be reported here were obtained with no signal averaging, single optical pulses, some of them containing only 15 microjoules of energy, having evoked satisfactory transients.

In the circumstances attending the kind of transient experiments here described (and in a different time domain their optical analogs) the frequently stated dictum that the intensities of the responses are proportional to the population differences between the eigenstates in question must be modified. The statement is certainly not true for the connection between instantaneous response and instantaneous population difference. Consider a situation in which the apparatus is tuned to detect the absorptive component of the response and the population differences are evoked by a light pulse. The material is irradiated with a constant intensity monochromatic microwave field at a frequency resonant to a particular pair of eigenstates. Prior to the light pulse neither eigenlevel is occupied. At $t = 0$, during a time short compared with the characteristic times of the system, one of the eigenlevels acquires a finite population owing to action of the light pulse. What is the rate of absorption of energy from the microwave field at that instant? It is zero and grows with time and reaches a maximum when the populations of the two levels are equal.² The time required for reaching the maximum absorption rate is the familiar time associated with a $\pi/2$ pulse. (Those who have experience with pulsed magnetic resonance will probably find these statements so well known that they may be bored, repelled, or irritated to read them.) The basis of our statement may be presented in several ways (all really the same). Consider the macroscopic relations for energy transfer between a material system and an oscillating field, $\vec{B}(t)$. P , the rate of transfer of energy from the radiation field to the material system with magnetization \vec{M} is given by $P = -\vec{M} \cdot d\vec{B}/dt$. In the conventional resonance apparatus the oscillating field is transverse to the static field. If the photoexcitation produces population in one of the eigenlevels in the static field, there is no magnetization at $t = 0$ parallel to $d\vec{B}/dt$. In a spin 1/2 system the initial magnetization is finite but parallel or antiparallel to the static field. In a spin 1 system the initial magnetization is usually zero. In either case the initial rate of energy absorption is zero. A more general description runs as follows:

Suppose we are dealing with a two-level system, or in case of a multilevel system one in which only one pair of levels is close to resonance with the radiation field. The expectation value of the energy is $N(\rho_{UU} - \rho_{LL})\hbar\omega_0/2$ where ρ_{UU} is the occupation probability of the upper state, ρ_{LL} of the lower state, $\hbar\omega_0$ the energy difference and N the number of molecules. The rate of absorption of energy is $N(\hbar\omega_0/2)\partial(\rho_{UU} - \rho_{LL})/\partial t$.

The Schrödinger equation requires that $\partial(\rho_{UU} - \rho_{LL})/\partial t = -i\gamma B_1(e^{i\omega t}\rho_{UL} - e^{-i\omega t}\rho_{LU})$, where $\rho_{UL} = \overline{C_U C_L^*}$; C_U and C_L are the amplitudes of the upper and lower states and the bar denotes an ensemble average. The array of products of

coefficients $\rho_{ij} = \overline{C_i C_j^*}$ is the density matrix of the system. The off-diagonal elements of the density matrix represent *coherences* between the state in question. We have not yet encountered a case in which photoexcitation of a polyatomic molecule in condensed phase prepares a system with coherence among its eigenstates: at $t = 0$ $\rho_{UL} = \rho_{LU} = 0$, and consequently the rate of energy absorption is zero. As time passes the radiation field produces the coherence required for the energy transfer, *i.e.*, a change in the occupation probabilities of the states in question. The coherence is developed again according to the Schrödinger equation

$$\frac{\partial \rho_{UL}}{\partial t} = i\{\rho_{UL}\omega_0 + (\rho_{UU} - \rho_{LL})\omega_1 e^{i\omega t}\}$$

$\hbar\omega_0$ is the difference in energy between the states in question, $\omega_1 = \gamma B_1$ and ω is the frequency of the radiation field. γ is the coupling constant to the radiation field. Since the density matrix is Hermitian the rate of energy absorption is given by the imaginary part of ρ_{UL} .

Similarly if the dispersive response, proportional to the real part of ρ_{UL} , were monitored, it too would be zero at instant of birth of the spins. The equations reveal that any effect which is associated with transitions between a pair of levels vanishes at the instant of creation of population in the levels unless the creation process itself produces coherence between the levels. In the optical spectroscopy of atoms instances of such effects have been found,³ *i.e.*, a coherent optical pulse excites a system directly into a coherent superposition of close-lying states which produce oscillatory responses at the beat frequencies between the levels (quantum beats). A succinct description of the sort of processes we shall discuss may be given *via* the density matrix. Consider a two-level magnetic system, with a third level as source or sink. Prior to excitation the system is entirely in the source level. Label the levels $|\uparrow\rangle$, $|\downarrow\rangle$, and $|S\rangle$. The excitation into the magnetic levels occurs at $t = 0$; assume the excitation is completely selective and produces population in only one of the magnetic levels, say $|\downarrow\rangle$. The system is constantly irradiated by an exactly resonant monochromatic microwave field of amplitude ω_1 . The time evolution of the density matrix is given by:

$$\rho = \begin{pmatrix} |\uparrow\rangle & 0 & 0 & 0 \\ |\downarrow\rangle & 0 & 0 & 0 \\ |S\rangle & 0 & 0 & 1 \end{pmatrix} \quad t < 0 \quad (1)$$

$$\rho = \begin{matrix} & \begin{matrix} |\uparrow\rangle & |\downarrow\rangle & |S\rangle \end{matrix} \\ \begin{matrix} |\uparrow\rangle \\ |\downarrow\rangle \\ |S\rangle \end{matrix} & \begin{pmatrix} e^{-kt} \sin^2 \frac{\omega_1 t}{2} & \frac{i}{2} e^{i(\omega_0 - kt)} \sin \omega_1 t & 0 \\ -\frac{i}{2} e^{-i(\omega_0 + kt)} \sin \omega_1 t & e^{-kt} \cos^2 \frac{\omega_1 t}{2} & 0 \\ 0 & 0 & 1 - e^{-kt} \end{pmatrix} \end{matrix} \quad t \geq 0 \quad (2)$$

$\hbar\omega_0$ is the energy difference between $|\uparrow\rangle$ and $|\downarrow\rangle$, k is the rate constant for return to $|S\rangle$. (The only relaxation process included in this treatment is the return to $|S\rangle$.) The rate of energy absorption per molecule which is given by $i\omega_1(\rho_{\uparrow\downarrow} - \rho_{\downarrow\uparrow})$ is then $e^{-kt}\omega_1 \sin \omega_0 t \sin \omega_1 t$. In most cases of interest the resonant frequency ω_0 is much larger than the nutation frequency ω_1 . In electron paramagnetic resonance work the resolving time of the detecting instrument is much longer than $2\pi/\omega_0$, the Larmor period, and the response is the integral over many Larmor periods. Such response removes the high frequency component and leaves only the more slowly varying response with frequency proportional to B_1 .

In case the radiation field is not oscillating at the resonant frequency the response is somewhat more complicated. For a two-level system with resonant frequency ω_0 irradiated at frequency ω with a field of amplitude ω_1 experiencing no relaxation and is at time $t = 0$ in the $|\downarrow\rangle$ state

$$\rho = \begin{array}{c} |\uparrow\rangle \\ |\downarrow\rangle \end{array} \begin{array}{cc} \begin{array}{c} |\uparrow\rangle \\ |\downarrow\rangle \end{array} & \begin{array}{c} |\downarrow\rangle \\ |\uparrow\rangle \end{array} \\ \left(\begin{array}{cc} \frac{\omega_1^2}{\Omega^2} \sin^2 \frac{\Omega t}{2} & -\frac{\omega_1}{\Omega^2} \left(\Delta \sin^2 \frac{\Omega t}{2} - i\Omega \sin \frac{\Omega t}{2} \cos \frac{\Omega t}{2} \right) \\ -\frac{\omega_1}{\Omega^2} \left(\Delta \sin^2 \frac{\Omega t}{2} + i\Omega \sin \frac{\Omega t}{2} \cos \frac{\Omega t}{2} \right) & \frac{1}{\Omega^2} \left(\Omega^2 \cos^2 \frac{\Omega t}{2} + \Delta^2 \sin^2 \frac{\Omega t}{2} \right) \end{array} \right) \end{array} \quad (3)$$

$$\Delta = \omega - \omega_0$$

$$\Omega = \sqrt{\Delta^2 + \omega_1^2}$$

Although most of the systems which we describe are three-level ones, the essential features of the above two-level description apply if only one of the triplet transitions is close to resonance. The system can then be treated in the familiar way as a fictitious two-level one. Nevertheless there are important physical distinctions as we mentioned earlier. A triplet system born at high field in its central level or with equal populations in its upper and lower levels has zero magnetization at birth while a doublet spin system born in either of its eigenstates has nonzero magnetization parallel to the field. These effects are not important when transverse magnetization is detected, but they would be significant in detection of the longitudinal component of magnetization.

The relations presented in the preceding paragraphs exhibit the principal features of the phenomena with which we deal but do not include certain complications, to be discussed as we present our experimental results. We summarize these features: The transient phenomena are characterized by several characteristic times: $2\pi/\gamma B_1$, the Rabi period or the time required for the radiation field to return a system (in the absence of relaxation processes) to its state at time $t = 0$;

relaxation times: T_1 , T_2^* , spectral diffusion times, and chemical reaction times. T_1 stands for a longitudinal relaxation time and T_2^* for an appropriate phase memory time. All these times enter into the transient response. Generally relaxation phenomena, being associated with random processes, produce exponential time evolution. Interaction with the coherent radiation field produces oscillatory responses. If the Rabi period is the shortest of the characteristic times oscillatory responses are expected.

II. Individual systems: Photoejected electrons in liquid solutions

We describe first observations of the transient behavior of electrons ejected from the anions of rubidium and cesium.^{4,5} This system serves as a good one for demonstrating whether there are serious instrumental distortions of the transient patterns. Solutions of the anions in tetrahydrofuran exhibit, under C.W. conditions, very narrow Lorentzian light induced resonances with magnetogyric ratio close to the free electron value. The chemical lifetime is several milliseconds, much longer than $T_1 = T_2$ and than $2\pi/B_1$, at the amplitude of B_1 (~ 0.2 oersted)

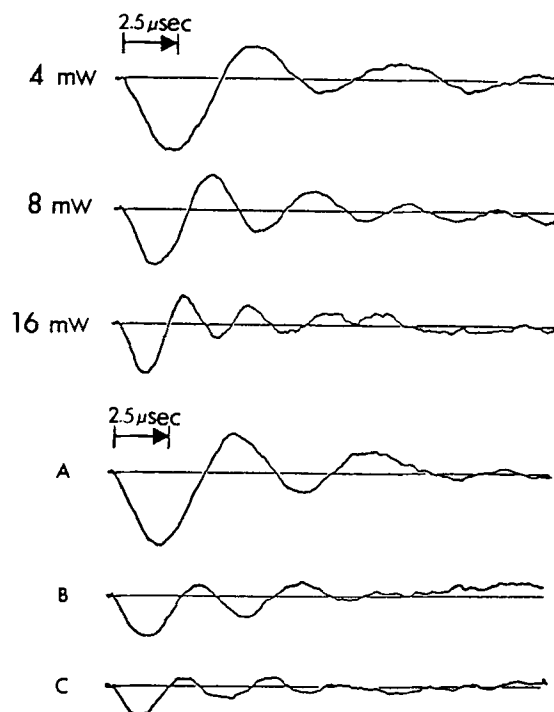


Figure 1. Transient nutations of photoelectrons from Rb^- at 230°K . Upper three curves, on resonance at different microwave powers. Lower 3, constant B_1 , A on resonance, B off resonance 0.05 oersted, C off resonance 0.07 oersted. Concentration of Rb^- approximately 10^{-3} M. Single transients excited by $\sim 5 \times 10^{-13}$ photons at 680 nm.

attainable in our apparatus. For the transient work the system is excited by 15 microjoules pulses at 690 nm, each about 3 nanoseconds in duration, from a tunable dye laser. The dye is Nile Blue A perchlorate. The responses follow very closely the relation $s(t) \propto e^{-t/T_2} \sin \omega_1 t$ where $s(t)$ is the signal at time t (Figure 1). It should be noted that there are no difficulties associated with saturation through use of too large a microwave field. The relaxation time T_2 is 6 microseconds. At $B_1 = 0.1$ oersted, the relaxation parameter $(\gamma B_1)^2 T_1 T_2$ is about 50. The C.W. signal is severely saturated but the transient amplitude is present at full strength. The only precaution in use of high microwave power is the avoidance of responses too fast for the detection system.

We make one final remark concerning the photoejected electrons. The nature of the nutation pattern demonstrates that the electrons appear within 10^{-7} seconds after the flash of light.

III. Triplet states in single crystal hosts

The uncertainty alluded to earlier concerning a " T_2 " appropriate for the transient experiments appears in the study of solids. The C.W. resonances are usually of the order of several oersteds in breadth. If the C.W. breadth represented a truly homogeneous one, little could be expected from the transient experiments, owing to the correspondingly short relaxation time of less than 10^{-7} seconds. Nevertheless when oscillating fields with amplitudes only one or two tenths of an oersted are applied to five or ten oersted broad lines, trains of oscillations persisting for 30 microseconds or longer are frequently evoked by the light pulse. Such a result indicates that the phase memory time for each spin packet is not only much longer than the inverse total line breadth, but is also longer than the inverse breadth of the section of the line which is excited by the finite amplitude of the microwave field. This situation is different from the one described earlier for the photoelectrons in liquid solvents. In the latter case we may be confident that had we studied the free induction decay following a $\pi/2$ pulse (by switching off the microwave field at the time of the first maximum in the response) that an exponential free induction decay with time constant equal to the one for the nutations would have ensued. The solid on the other hand would give a free induction decay, probably nonexponential, which would decay with a time constant of the order $1/\gamma B_1$. The continuous microwave irradiation which can be thought of as continuously refocusing the packets produces the long-lived oscillatory response.

As the first example of behavior of photoexcited triplet states we describe our observations of pentacene in dilute solid solution in either *p*-terphenyl or naphthalene. Excitation was done with either the radiation of 337 nm from the nitrogen laser, or at various wavelengths between 400 and 540 nm provided by either a pulsed neon laser or tunable dye laser. The responses are independent, except for their intensities, of the wavelength of the exciting light.

In Figure 2 are shown a series of responses at various power levels from protonated pentacene molecules in the *p*-terphenyl host aligned so that the static

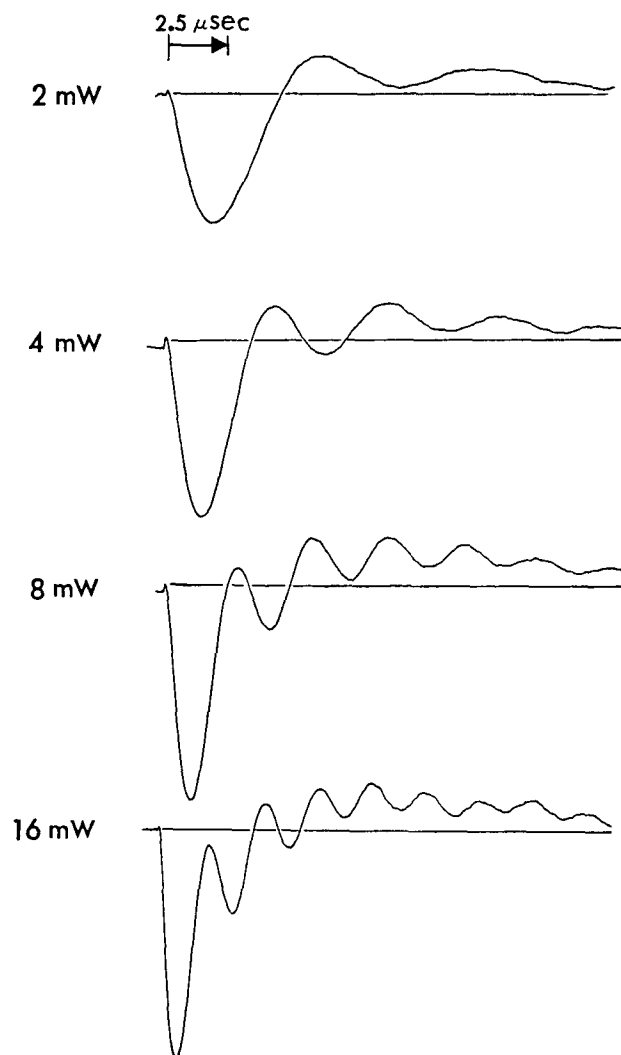


Figure 2. Transient response at 275°K from pentacene in *p*-terphenyl. B_0 is perpendicular to the molecular plane. Low field emissive responses at indicated microwave powers. Single transients excited by $\sim 10^{15}$ photons at 337 nm.

magnetic field is normal to the molecular plane. The response of the low field resonance is displayed; the temperature is 275°K. (Between 4°K and 275°K the responses are singularly independent of temperature.) The phase of the response indicates that it is initially emissive. The period of the oscillations is inversely proportional to the square root of microwave power. In Figure 3 are shown the responses for pentacene- h_{14} and pentacene- d_{14} for molecules oriented in each of the canonical orientations (X is the long in plane axis, Y the short in plane axis, and Z the out of plane axis). All experiments are at 300°K except for the y

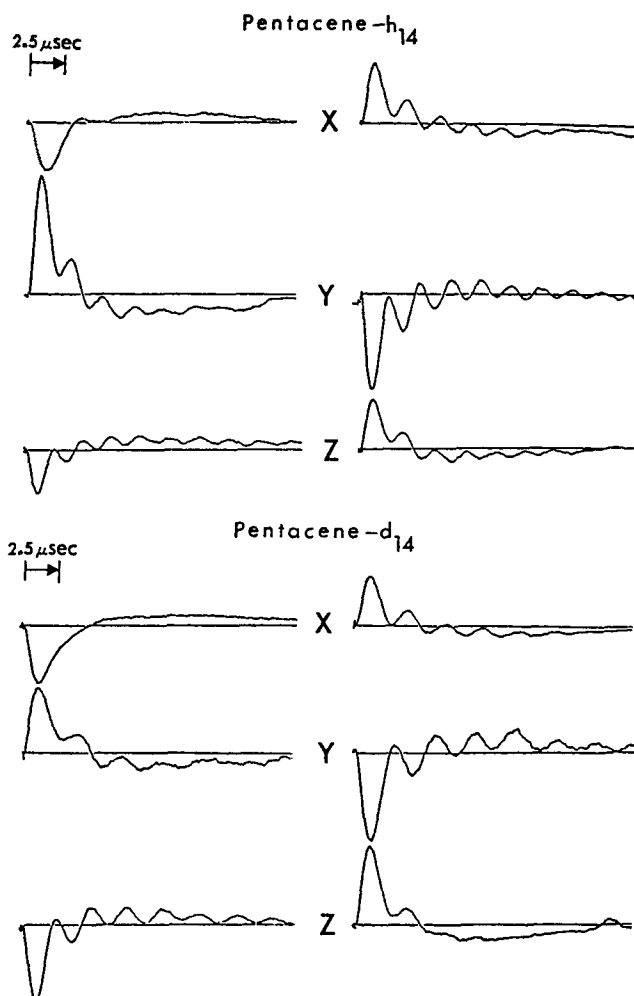


Figure 3. Transient responses at 16 milliwatts microwave power from pentacene- h_{14} and pentacene- d_{14} with B_0 parallel to each of the molecular axes. All are at 300°K except for pentacene- h_{14} with B_0 parallel to Y where $T = 210^\circ\text{K}$. Relative intensities at the different orientations are arbitrary. Single transients, each excited by $\sim 10^{15}$ photons at 337 nm.

axis ones for the protonated pentacene which are at 210°K. In Figure 4 is shown an effect of misalignment. The shape of the pattern is almost independent of the position in the C.W. line which is being excited; the shape of the C.W. spectrum may be pretty well mapped out by plotting the amplitude of the first peak against field.

It will be noted that the shapes of the patterns are qualitatively different from those of the photoejected electrons in liquid phase. We have been able to achieve a moderately good fit to all of them by superposition of a set of patterns within the breadth covered by the B_1 field, with allowance for spectral diffusion among

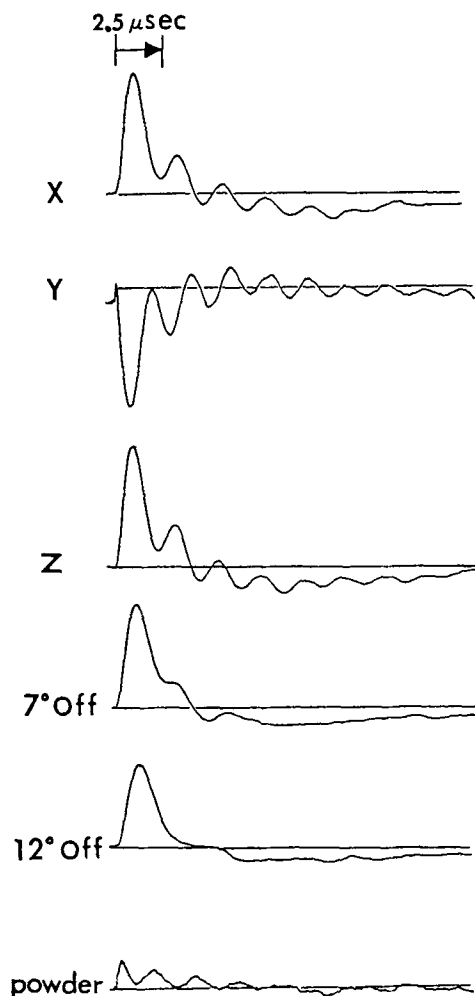


Figure 4. Responses at 16 milliwatts, 215°K, from pentacene-h₁₄ in *p*-terphenyl. The fourth and fifth traces display effects of small misalignments. The field has been rotated in the *ZX* plane by the specified amount. Single transients; $\sim 10^{15}$ photons at 337 nm.

them. We are not at all confident that this procedure gives anything more than an empirical fit. Despite the uncertainties in interpretation of the patterns certain features are apparent. It is possible to extract the relative populating rates of the zero field levels from the amplitudes of the first peaks. The rise times are generally short compared with relaxation times so that the early intensities represent early populations. Note however that in each case the initial intensity is zero as is required for any model. We are puzzled by the differences between high and low field responses at a given orientation and by the effects of small displacements from the canonical orientations. A proper theoretical account will certainly have

to include the departures from adiabaticity accompanying the photoexcitation.⁶ Before the light is turned on the system is in thermal equilibrium. Abrupt excitation into the triplet state leaves the nuclei neither at thermal equilibrium nor in their eigenstates owing to the nonadiabatic switching on of the hyperfine interaction. The temporal evolution of nuclear spin states should be taken into account in a more realistic way than adjustment of a spectral diffusion rate.

A second set of experiments deals with the photoexcited triplet states found in a host doped with a low concentration of phenazine. At temperatures between 4°K and 200°K the C.W. spectra are characteristic of phenazine triplets. Transient responses are shown in Figure 5. Again there are the characteristic but

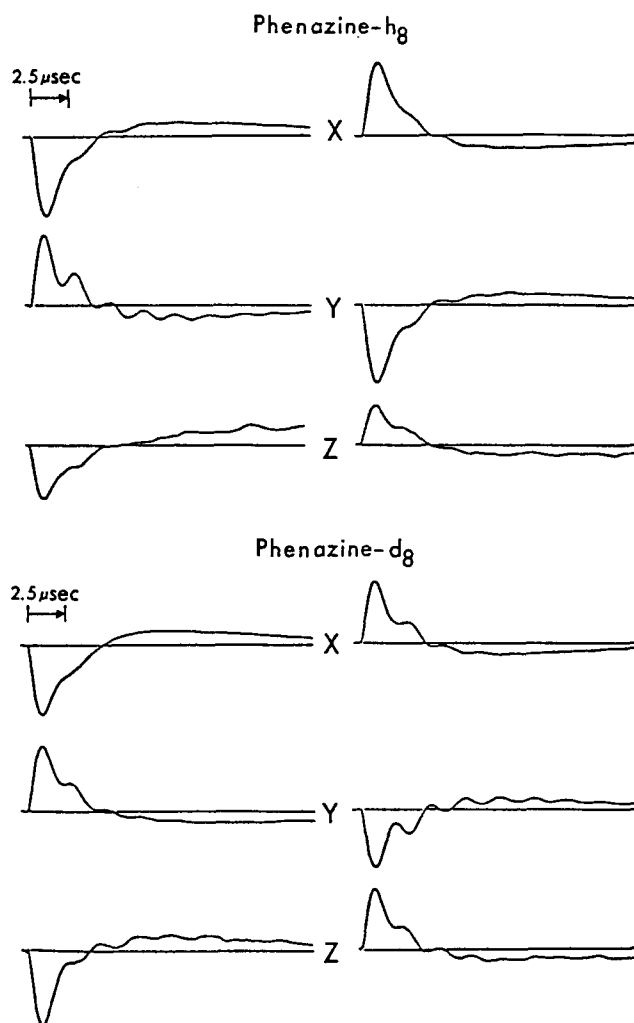


Figure 5. Phenazine- h_8 and phenazine- d_8 in fluorene at 77°K, 16 milliwatts. Responses with B_0 parallel to each of the molecular axes. Single transients; $\sim 10^{15}$ photons at 337 nm.

unexplained differences between low and high field resonance. Relative populating rates may be extracted from the observations.

At higher temperatures a second set of resonances ascribed to a triplet complex between phenazine and fluorene appears.⁷ In C.W. the intensity of the spectrum of the complex relative to that of phenazine increases with increasing temperature, but the C.W. intensities of both decrease at temperatures above 350°K. The transient spectra, on the other hand, are observable up to the melting point (390°K) of fluorene. The peak intensity of the transient of the complex increases

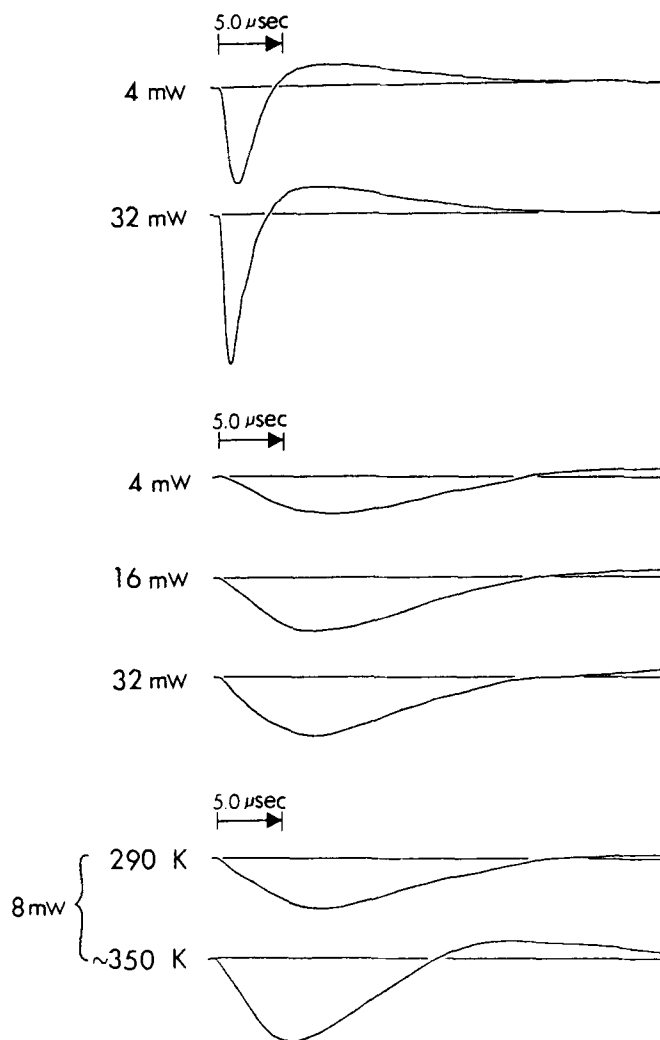


Figure 6. Responses from phenazine at 300°K, B_0 parallel to X upper two traces; the heteroexcimer next three. Lower two, the heteroexcimer at constant microwave power at 290°K and 350°K. Each excited by $\sim 10^{15}$ photon laser pulses at 337 nm. Single transients for phenazine. Average of 100 pulses for heteroexcimer.

monotonically with temperature, but its decay time decreases. On the basis of experiments at long resolving times (10^{-4} seconds) we had concluded that the complex was formed from a phenazine triplet precursor. The transient patterns of phenazine and complex are qualitatively different, those of phenazine showing the expected shortening of rise time with increasing B_1 , those of the complex being almost independent of B_1 (Figure 6). Neither pattern exhibits oscillations. We have not yet completed a quantitative analysis of the observations, but hope to glean from them kinetic information concerning formation of the complex.

Finally we describe observations of excitation of a guest molecule *via* an exciton band of the host. It has long been known that photoexcitation of phenazine doped with anthracene in the phenazine absorption region leads to population of the anthracene triplet levels and that a mechanism by which the phenazine triplet exciton band is selectively populated and transfers excitation with conser-

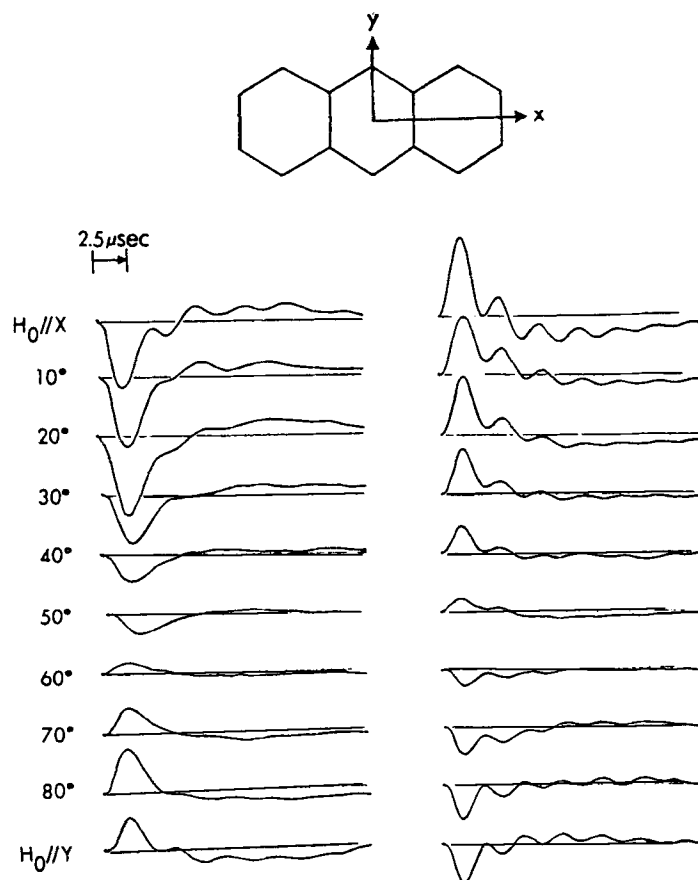


Figure 7. Anthracene h_{10} in phenazine at 77°K . Excitation at 450 nm. 8 milliwatts power. Designated angles are between B_0 and X . B_0 lies in the XY plane. Single transients; $\sim 10^{14}$ photons at 450 nm.

vation of polarization to the anthracene accounts for the observations.⁸ We have investigated the system for transients. Our first attempt with excitation at 337 nm yielded no signals despite the fact that our experience with other substances had demonstrated that the light source was more than adequate for exciting observable transients. The difficulty is traced to the very high absorbance of the host; the exciting light is absorbed in a layer about 5×10^{-6} cm deep. In this layer there are too few anthracene molecules to yield an observable signal and the absence of the signal demonstrates that the excitation does not migrate promptly an appreciable distance in the crystal. Our next experiments were done with a tunable dye laser. As the wavelength of the exciting light is decreased from ~ 500 nm, the anthracene triplet transients appear, with maximum intensity at ~ 450 nm. The dependence of initial populations on composition of the eigenstates is demonstrated in Figure 7 which gives a series of responses as the static field is rotated in the molecular plane. Further work on dependence of the phenomena on the spatial distribution of the excitation should yield information concerning exciton dynamics.

Another set of measurements (initially achieved by accidental misalignment of the crystals) is shown in Figure 8. The nutation has a beat structure. We had first thought that at last we had found a system in which the photoexcitation produces a coherent superposition with quantum beats, but further investigation revealed the less glamorous reason. The orientation at which the beats are observed is one in which two nonequivalent molecules have identical eigenfrequencies. The composition of the states is such that the coupling parameters to the radiation field, the γ 's are different and consequently the nutation frequencies are different. This effect may be distinguished from a quantum beat because the beat frequency is found to be proportional to B_1 : it would be independent of B_1 for a true quantum beat. Detailed calculation of the effective γ 's is in complete agreement with the observations.

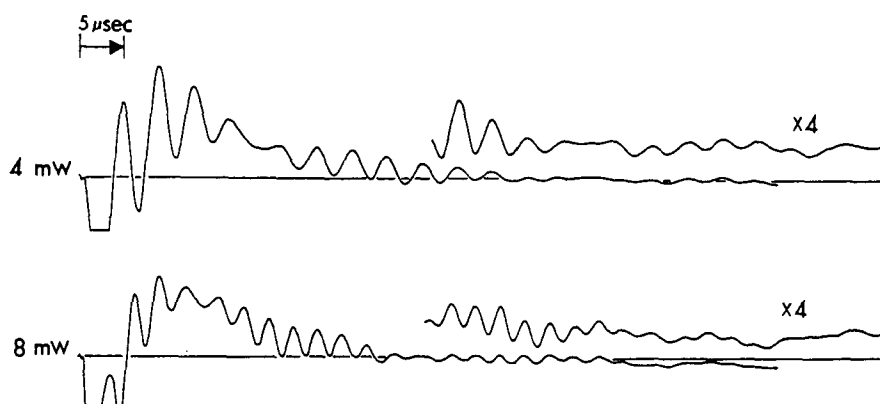


Figure 8. Anthracene $h_{1,0}$ in phenazine. 65°K . B_0 at an orientation in which resonances of two nonequivalent molecules overlap. Average of 20 transients, $\sim 10^{14}$ photons at 450 nm per pulse.

IV. Summary

We have demonstrated that with wide-band detection short-lived paramagnetic intermediates produced by laser excitation are easily observed. The time dependence of the transient responses requires analysis which includes an adequate quantum theoretical treatment of the evolution of the system at short times after excitation. The conventional elementary perturbation treatments of interaction with the radiation field are inadequate. Further refinements of experimental and interpretive methods are required, but much kinetic information is obtainable at the present state of development.

V. Acknowledgment

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VI. References

- (1) S. S. Kim and S. I. Weissman, *J. Mag. Res.*, **24**, 167 (1976).
- (2) H. C. Torrey, *Phys. Rev.*, **76**, 1059 (1949).
- (3) S. Haroche, M. Gross, and M. P. Silverman, *Phys. Rev. Lett.*, **33**, 1063 (1974).
- (4) S. H. Glarum and J. H. Marshall, *J. Chem. Phys.*, **52**, 555 (1970).
- (5) S. S. Kim and S. I. Weissman, *Chem. Phys. Lett.*, **58**, 326 (1978).
- (6) L. G. Rowan, E. L. Hahn, and W. B. Mims, *Phys. Rev.*, **137A**, 61 (1965).
- (7) R. Furrer, J. Gromer, M. Schwoerer, and H. C. Wolf, *Chem. Phys.*, **9**, 445 (1975).
- (8) R. Clarke, *Chem. Phys. Lett.*, **6**, 413 (1970).