A Novel Combined Pulsed Laser Flash Photolysis–Optoacoustic Spectroscopy Technique for the Quantitative Study of Relaxation Processes of Excited Species Produced in Two-Laser, Two-Photon Experiments¹

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A novel combination of the established techniques of laser flash photolysis and optoacoustic calorimetry was used as a means for quantitative investigation of relaxation mechanisms in two-laser, two-photon excited species. Flash photolysis was used to determine the absorbance of the initially formed intermediate at the wavelength and exact time of the second laser pulse. The amplitudes of the optoacoustic signals due to heat emission from the excited intermediate following the second pulse were plotted as a function of the fraction of absorbed photons or of the laser energy. The slope of such a plot for the excited diphenylmethyl radical in cyclohexane was compared to that of a two-laser, two photon reference system (1-(chloromethyl)naphthalene in cyclohexane) where the excited intermediate (1-naphthylmethyl radical) releases all its absorbed energy rapidly by nonradiative means. From such measurements, the quantum yield of fluorescence of the excited diphenylmethyl radical in cyclohexane was calculated to be 0.31. Other possible applications of the technique are discussed.

Introduction

Pulsed lasers have found a variety of applications in the fields of photophysics and photochemistry; a host of established techniques have arisen that use lasers as an intense, coherent, monochromatic light source. One of the earliest developments was the application of lasers as excitation sources in flash photolysis experiments to probe the changes in absorption of samples on formation of a high concentration of transient intermediates. The short pulse duration allows for the study of very short-lived intermediate species. A somewhat later development was the use of lasers as excitation sources in the technique of laser-induced optoacoustic spectroscopy (LIOAS), which probes the photoacoustic phenomena resulting from localized heat deposition in the sample due to rapid nonradiative relaxation processes. This technique has become well established over the last decade, and its application to a variety of spectroscopic and analytical methods has been outlined in a number of comprehensive reviews.²⁻⁴

More recently, in the flash photolysis regime, two-color, twophoton techniques have been introduced, allowing the study of the photochemistry and photophysics of excited reaction intermediates.⁵⁻⁷ A related technique uses a combination of pulse radiolysis and flash photolysis for the same types of studies.^{8,9} Although two-photon processes can, under certain circumstances, be initiated by single-pulse excitation, quantitative evaluation of the mechanisms of deactivation of two-photon excited species is not easily undertaken. A more satisfactory route is by the utilization of sequential two-color, two-photon excitation through which a greater control of the experiment is achieved, allowing the selective study of the species obtained on excitation with the second photon. The first, or synthesis, laser is used merely to produce a high concentration of an intermediate state (e.g., triplet, free-radical, radical ion, biradical, carbene, etc.) that is then in turn excited (to upper states) by absorption of a photon from the

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second, or photolysis, laser. This technique has been fully outlined and applied to the study of a variety of systems both in this and other laboratories.^{10,11}

In spite of the fact that the above technique can be used to obtain a wide range of spectral and kinetic information, a direct quantitative study of the energetics or quantum yields of the processes occurring from the upper state is not trivial, although for at least one system (the benzophenone ketyl radical¹²) the full mechanistic scheme has been elucidated by a combination of flash photolysis with product analysis. The application of flash photolysis techniques to the study of reaction intermediates is further limited to those species that possess favorable absorptive properties that allow for optical detection. The complementary technique of LIOAS does not suffer this limitation and can be applied to give direct information regarding nonradiative deactivation of optically transparent transient intermediates in condensed media. From the related technique of laser-induced optoacoustic calorimetry (LIOAC), it is possible to obtain information on quantum yields of relaxation processes, ¹³⁻¹⁵ energy contents, ¹⁶ and in some cases lifetimes of excited states¹⁷ and heats of bond dissociation and formation.18-23

In much the same way as two-laser flash photolysis is applied to the kinetic and spectral study of short-lived reaction intermediates, two-laser LIOAC may be used to give information on energetics and quantum yields of processes that occur upon absorption of the second photon. The situation is exactly as in flash

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Figure 1. Experimental arrangement for combined flash photolysis-LIOAC measurements: S, shutter; ND, neutral density filter; SC/T, sample cuvette/transducer; RC/T, reference cuvette/transducer; FW, cutoff filter wheel; C, collimator; Mn, Monochromator, P, photomultiplier; BS, beam splitter; DIG 1, Tektronix R7912 digitizer; DIG 2, Tektronix 7D20 digitizer; A1 and A2, amplifiers; PC and PDP 11/23, computers.

photolysis where the synthesis laser is responsible for formation of the transient species that is then selectively excited by the photolysis laser. The photoacoustic phenomena arising from the absorption of the second photon are then analyzed to give information on the relaxation mechanisms of upper states.

We describe here the application of a novel combination of flash photolysis and LIOAC in a two-color, two-photon experiment that allows for the quantitative evaluation of relaxation processes from excited states of transient intermediates. The example we have chosen to illustrate the validity of the technique is the evaluation of the quantum yield of fluorescence of the excited diphenylmethyl radical. Further applications of the technique will be discussed.

Experimental Section

Although parts of the separate flash photolysis²⁴ and LIOAC²² apparatus have been described elsewhere, we feel that their combination in this novel technique warrants a detailed description of the experimental setup.

The experimental arrangement is shown schematically in Figure 1. The "synthesis" pulse used to produce the intermediate of interest was that from a Lumonics TE860-2 excimer laser (XeCl, 308 nm, 5-ns pulse duration, <10 mJ/pulse); a Molectron UV-24 nitrogen laser (337.1 nm, 8-ns pulse duration, <9 mJ/pulse) provided the "photolysis" pulse. The excimer laser emission was aligned perpendicular to the polychromatic analyzing beam (from a 150-W pulsed xenon arc lamp) of the flash photolysis system. The nitrogen laser is offset at a small angle from the analyzing beam as shown in Figure 1. All beams were concentrated within the sample cuvette, and care was taken such that the three beams were aligned to give maximum spatial overlap within the sample cuvette. Solutions for analysis were contained in a 10×10 mm flow-through quartz fluorescence cuvette (Helima Model 171 QS 10), flow being achieved by the use of a peristaltic pump. The use of a flow system is mandatory for the systems under study here as the formation of the intermediates involves degradation of the original sample. The flow rate was adjusted to ensure that the irradiated volume was completely renewed between laser shots. Transient absorption properties were studied by time resolution of the transmitted analyzing beam through the sample, resolved by a monochromator (2-nm bandwidth), and detected by an RCA 4840 photomultiplier (6 dynodes, 93- Ω termination). The resultant voltage signals were captured by a Tektronix R7912 digitizer

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(employing 7B92A time base and 7A16 amplifier plug-ins) that was in turn interfaced to a PDP11/23 computer where data analysis was carried out. The computer also provided control of the experimental parameters such as synchronization of lasers, lamp pulse, laser and analyzing beam shutters, monochromator wavelength drive, and cut-off and neutral density filter changers. The synchronization of the experiment will be outlined (vide infra). The delay between the pulses of the synthesis and photolysis lasers was controlled by a variable delay generator adjustable in 10-ns steps for a time range of 10 ns-1 ms. Kinetic traces displayed on the terminal as Δ OD vs time were obtained in hard copy form by dumping the screen display to a Tektronix 4631 hard copy unit.

The photoacoustic detection utilized a Panametrics A101 0.5-MHz transducer applied to the bottom surface of the sample cuvette. A thin layer of grease was interspersed between the cuvette and transducer surfaces to ensure efficient transmission of photoacoustic signals. The cuvette is held within a brass mount, and moderate pressure is applied to the top of the cuvette again to ensure a good contact between cuvette and transducer surfaces. Signals from the transducer were amplified with a Panametrics 5670 preamplifier modified to be powered by a home-made stabilized supply (NRC battery eliminator BIOE 6871). The amplified signals were fed to a Tektronix 7D20 programmable multichannel digitizer (equipped with 7603 oscilloscope) capable of internal signal averaging of the data. A beam splitter was placed before the sample cuvette to remove a fraction of the energy from the photolysis laser for energy monitoring purposes. The split fraction was focused in a cuvette/transducer/amplifier arrangement identical with that holding the sample for study. The solution contained in this reference cuvette was a continuously flowing solution of o-hydroxybenzophenone. This is an ideal reference system since it relaxes exclusively by nonradiative means within an extremely short time window.^{25,26} Thus, for each data point from LIOAC experiments on the sample under study, a normalization process is possible from the respective values of the LIOAC signals from the energy monitor cuvette (as signal amplitude is proportional to laser energy). The signals from both sample and reference solutions are simultaneously recorded in separate channels of the digitizer. The digitizer was interfaced to an MC8088-based personal computer for data analysis. Typically, in both photoacoustic and flash photolysis acquisition, 16 shots were averaged for each data point.

The most important aspect of the experimental setup is that the geometrical arrangement of both lasers and the sample cuvette is identical for flash photolysis or optoacoustic detection, thus allowing flash photolysis and LIOAC measurements to be directly correlated and making possible the accurate evaluation of the absorption of the intermediate at the exact time of the photolysis laser pulse. Identical beam geometry is critical due to the inhomogeniety of the distribution of intermediate species within the sample. Although the path length of the sample encountered by the photolysis laser is different from that experienced by the analyzing beam, the difference is the same for both sample and standard; thus, transient absorbance values may be utilized in a relative sense. Photoacoustic responses of the system under study were compared to those of a standard, the 1-naphthylmethyl radical (vide infra).

Tetraphenylacetone was prepared as described²⁷ and recrystallized twice from ethanol. 1-(Chloromethyl)naphthalene (Aldrich) was recrystallized twice from hexane/ether. Cyclohexane (Omisolv) was spectroscopic grade and was used as received.

Results

LIOAC is essentially a comparative technique in its application to quantitative analysis, requiring the use of a reference or standard sample whose photophysical and photochemical behavior is well

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Figure 2. Transient decay profile detected at 360 nm for 308 + 337 nm irradiation of 5×10^{-4} M 1-(chloromethyl)naphthalene in cyclohexane. The lack of bleaching following the 337-nm pulse verifies the photostability of the naphthylmethyl radical under these conditions.

established. Such a reference is one that ideally fulfills the following requirements:²⁸ (i) should be photochemically stable; (ii) should absorb in the same spectral region as the sample to be studied; (iii) should relax within the time frame of the response of the measurement apparatus; (iv) should lack emission (or have a reliably measured fluorescence quantum yield). A typical standard that fulfills the above is o-hydroxybenzophenone, which relaxes exclusively by nonradiative means with a very short excited-state lifetime (subnanosecond). However, for the two-color, two-photon LIOAC experiments, such a standard cannot be used (due to the particular geometry of the beams) and it proved necessary to find a reference system also involving a two-laser synthesis-photolysis experiment where the spatial distribution of the transient under study is mimicked, i.e., the reference is itself a species produced by the synthesis laser. For these studies, we chose the naphthylmethyl radical (I), the two-laser behavior of which has been characterized in our laboratory by flash photolysis.²⁹ The naphthylmethyl radical is formed in good yield on 308-nm photolysis of 1-(chloromethyl)naphthalene (II) as shown We assessed this system as a suitable reference for in eq 1.



LIOAC experiments as it has been demonstrated to (a) be photostable, i.e., no bleaching of its absorbance is observed on photolysis as shown in Figure 2; (b) have a considerable extinction coefficient at 337 nm for absorption of the photolysis photon; and (c) allow for selective photolysis of the naphthylmethyl radical at 337 nm, since the precursor 1-(chloromethyl)naphthalene has negligible absorption at 337 nm. In addition, although fluorescence emission from the excited naphthylmethyl radical is observable with sensitive detection, the quantum yield of this process has been estimated to be ~ 0.001 , so low that it contributes to the overall relaxation to a negligible extent in terms of the energetics.³⁰ Thus, the familiar energy balance equation is used

$$E_{\rm abs} = \alpha E_{\rm abs} + E_{\rm f} \Phi_{\rm f} + E_{\rm st} \Phi_{\rm st} \tag{2}$$

where E_{abs} is the absorbed energy, E_f and Φ_f are the energy and quantum yield of fluorescence of the excited state, and $E_{st}\Phi_{st}$ is the product of the energy content and quantum yield of formation of stable (on the time scale as the response) products. The parameter α is the fraction of the absorbed energy that is given up by nonradiative processes within the detection time window. For the 1-naphthylmethyl radical, the second and third term on the right-hand side of (2) have a zero value and thus $\alpha = 1$. To illustrate the application of the technique, we chose what appeared to us to be the most suitable system we could find in the literature, that being the diphenylmethyl radical (III),⁷⁻⁹ and undertook the evaluation of the quantum yield of fluorescence from its excited state. Diphenylmethyl radicals are formed in very high yield in the photolysis of tetraphenylacetone (TPAc, IV) by 308-nm light, as shown in eq 3.⁷ Absorption of a 308-nm photon



causes Norrish type I reaction (α -cleavage), giving one diphenylmethyl radical and a radical that rapidly (within the laser pulse) dissociates to give a second diphenylmethyl radical and a molecule of carbon monoxide. Tetraphenylacetone is an ideal precursor as it is transparent at the photolysis wavelength of 337 nm. The diphenylmethyl radical exhibits $\lambda_{max} = 334$ nm in its absorption spectrum and is thus ideally suited for excitation at 337 nm. Previous two-laser flash photolysis studies have characterized the absorption and fluorescence emission spectrum from the excited radical that was demonstrated to have a lifetime of 255 ns in cyclohexane.⁷ This long lifetime enforced the use of a slow response (0.5-MHz) transducer to ensure that all the heat emitted in its nonradiative relaxation was detected in the photoacoustic signal (previous calibration experiments showed the response of the transducer to be linear up to transient lifetimes of ~ 400 ns). The diphenylmethyl radical was shown to be photostable on 337-nm excitation as no bleaching of its absorption is observed, but an intense green emission is readily observable with the naked eye on 337-nm excitation of the radical. Thus, eq 2 reduces in this case to

$$E_{\rm abs} = \alpha E_{\rm abs} + E_{\rm f} \Phi_{\rm f} \tag{4}$$

which can be expanded to eq 5 where N_A is Avogadro's number,

$$N_{\rm A}h\nu_1 = \alpha N_{\rm A}h\nu_1 + N_{\rm A}h\nu_{\rm f}\Phi_{\rm f} \tag{5}$$

h is Planck's constant, ν_1 is the laser emission frequency, and ν_f is the weighted frequency of fluorescence from the excited diphenylmethyl radical. As we have in this case a competitive route to radiationless relaxation, the value of α is expected to be less than unity.

Evaluation of the Quantum Yield of Fluorescence from the Diphenylmethyl Radical. The method used for the quantification of the LIOAC data was as follows. Flash photolysis was carried out on both sample and standard systems in order to evaluate the absorbance of the respective intermediate species at the exact time of triggering and wavelength of the photolysis laser.

(i) On 308-nm excitation of the precursors, the transient absorption profile was recorded with detection at the wavelength of the photolysis laser, i.e., 337 nm, as in Figure 3A for 308-nm excitation of TPAc to give the absorption of the diphenylmethyl radical.

(ii) The exact timing of the triggering of the photolysis laser can be attained by a number of methods. For the diphenylmethyl radical, the excited radical has a sufficiently long lifetime and strong absorption that it can be detected easily at $\lambda_{max} = 360$ nm, as shown in Figure 3B. (The absorption of the excited radical is also seen following the 308-nm synthesis pulse, and its formation is due to two-photon absorption within the laser pulse). Alternatively, one can set the detection wavelength at 337 nm and use the scattered laser light signal as the marker of the timing of the second laser. Obviously, care must be taken in order to avoid overexposure of the photomultiplier tube.

(iii) As shown in Figure 3, it is then trivial to extrapolate the absorbance of the intermediate at the exact time of the 337-nm

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Figure 3. Transient decay profiles following excitation of 5×10^{-4} M tetraphenylacetone in cyclohexane by A, 308 nm alone, detected at 337 nm and B, 308 + 337 nm, detected at 360 nm.

photolysis laser. In all experiments, this absorbance was <0.06.

The shutters on both lasers and also on the analyzing beam open immediately before pulsing of the Xe arc lamp. The triggering of both lasers is controlled such that the output of the synthesis laser follows closely after the triggering of digitizer 1. The delay between synthesis and photolysis lasers is variable with digitizer 2, for LIOAC data accumulation, being triggered from the same pulse that triggers the photolysis laser. There occurs a delay before detection of the acoustic pulse due to the time taken for the acoustic wave to travel through the solution from the irradiated region to the bottom surface of the cuvette to which the transducer is coupled.

The delay between the laser pulses was adjusted in accordance with the optimum detection of the LIOAC signal. Signal analysis is complicated by the fact that the synthesis laser also generates an acoustic signal on which the signal arising from the photolysis laser is superimposed. The amplitude of the signal from the synthesis laser is greater as more energy is absorbed at 308 nm by TPAc than at 337 nm by the radical. We found it convenient (a) to allow a relatively long delay ($\sim 6 \ \mu s$) between lasers to reduce the extent of interference from the synthesis laser signal (this also allows for complete decay of the small amount of triplet 1-(chloromethyl)naphthalene formed on 308-nm photolysis²⁹) and (b) to adjust the delay such that the initial voltage deflection due to 337-nm laser excitation was superimposed over a region of positive oscillation in the 308-nm signal, i.e., in phase. Once attained, the synchronization of the system was unaltered throughout the experiment. Typical acoustic signals from irradiation by 308 + 337 nm, 308 nm only, and 337 nm only are shown in Figure 4A. The signals due to 337-nm irradiation of the precursor are over 1 order of magnitude smaller due to the very weak absorbance (<0.01) of the precursors at this wavelength. The signal forms for the single-laser irradiations were summed and then subtracted from the signal form obtained on two-laser excitation to give the signal form due exclusively to absorption by the ground-state radical, shown in Figure 4B. The signal amplitude (A_{int}) was then taken as the peak to peak voltage as shown.

In order to ensure that the acoustic signals following 308 + 337 nm are additive, we used o-hydroxybenzophenone, which absorbs at both these wavelengths in the ground state. Signal amplitudes were measured with first 308 nm and second 337 nm excitation alone. The amplitudes of both signals at the time of the maximum signal from the 337-nm laser were measured, added



A(int)

S

Intensity

ε

Intensity

2

10 10 20 time (microseconds) Figure 4. A. LIOAC signals obtained on irradiation of 5×10^{-4} M tetraphenylacetone by 308 + 337 nm; 308 nm alone; and 337 nm alone (a Y-axial shift has been introduced to allow clearer visualization of the individual traces). B. Difference LIOAC signal due to relaxation of excited diphenylmethyl radical obtained by subtraction of the signals [308+337] - ([308] + [337]) in A.

together, and compared to the signal amplitude at the same time following 308 + 337 nm excitation. The amplitude of the latter was found to be in agreement with the sum of the individual contributions, hence confirming the additive nature of the signals in our two-laser experiments.

To evaluate α values, the synthesis laser intensity was attenuated by the use of neutral density filters such that the concentration, and hence absorption, of the intermediate at the time of the photolysis laser was varied. For each filter, both the absorbance of the intermediate and the amplitudes of the LIOAC signals were measured. The use of an "energy monitor" optoacoustic detector (vide supra) allows normalization of the signals to the energy of the photolysis laser. The amplitude of the signal (A) is proportional to both the incident laser energy (E_0) and the absorption of the solution² (OD) through eq 6 where K is an apparative

$$A = K\beta v_{a}E_{0}(1 - 10^{-\text{OD}})/C_{p}$$
(6)

constant that includes geometrical parameters as well as the response characteristics of the detector, β , v_a , and C_p are the thermal expansion coefficient of the solvent, the acoustic velocity through the solvent, and the specific heat capacity of the solvent, respectively. A plot of normalized A_{int} vs $1 - 10^{-\Delta OD}$ or E_0 should give a straight line with a gradient that is directly proportional to α.

A plot of A_{int} vs $1 - 10^{-\Delta OD}$ for both diphenylmethyl and naphthylmethyl (standard) radicals is shown in Figure 5. The ratio of the slopes gives α for diphenylmethyl radical of 0.81 (as $\alpha = 1$ for the standard). In order that our values could be used as reference values in experiments regarding evaluation of quantum yields of emission from upper states by optical detection, we carried out the experiment on four independent occasions. The individual values obtained for α in these measurements were 0.81, 0.81, 0.77,



Figure 5. Dependence of the amplitude of the difference LIOAC signal (A_{int}) on absorbed photons $(1 - 10^{-\Delta OD})$ for (\Box) 1-naphthylmethyl radical and (\bullet) diphenylmethyl radical.



Figure 6. Dependence of the amplitude of the difference LIOAC signal (A_{int}) on the energy of the 337-nm excitation for the diphenylmethyl radical.

and 0.84. From these measurements, the reproducibility of the experiments was established. Substitution of the mean value of 0.81 in eq 5 along with the other parameters (the weighted frequency of fluorescence, ν_f , for the diphenylmethyl radical in cyclohexane is 5.36×10^{14} Hz,³¹ which corresponds to $\lambda = 560$ nm) allows the evaluation of the quantum yield of fluorescence from

the diphenylmethyl radical of 0.31 ± 0.10 (the error value is derived from statistical analysis of the data for each experiment). This value is in excellent agreement with that estimated by Meisel and co-workers (~0.3).^{8,9}

The linearity of A_{int} vs laser energy was also verified by utilizing the same energy from the 308-nm laser but in these experiments attenuating the 337-nm laser beam. The absorbance of the diphenylmethyl radical was monitored for each data point to allow normalization for small variations in the 308-nm laser energy, and the energy of the 337-nm laser was measured with the magnitude of the optoacoustic signal from the reference cuvette. A plot of A_{int} vs laser energy is shown in Figure 6 and exhibits good linearity.

Conclusions

We have demonstrated the use of a combined two-laser flash photolysis and LIOAC apparatus for the investigation of relaxation processes that occur from excited reaction intermediates. The example chosen to demonstrate the validity of the technique is by no means exceptional in its suitability to investigation by such a system. We envisage the use of this method as a calorimetric complement to two-laser flash photolysis inasmuch as the latter can be used to give information on mechanisms of relaxation in upper excited states. On elucidation of the mechanism, the application of our calorimetric technique may then allow quantification of the relaxation processes. For example, it would be possible to determine quantum yields of product formation given knowledge of the nature of the product and the energies of bond breakage and/or formation in the reaction of its upper excited precursor.

We are still in the process of developing this technique, especially with regard to data handling and instrumental improvements. It would obviously be a great advantage to use nonresonant detectors, such as poly(vinylidine fluoride) (PVF₂) film⁴ or heavily damped piezoelectric transducers, thus allowing the acoustic signal from the synthesis laser to damp out before the triggering of the photolysis laser. This would greatly simplify the measurement of the amplitude of the acoustic signal from irradiation of the intermediate species, which would be unencumbered with the superimposed resonances from absorption of photons from the synthesis laser. An obvious advantage is to be gained in extending the range of the laser wavelengths available for synthesis and photolysis pulses, which would greatly increase the scope for selective excitation of both precursor and intermediate. We now have available the Nd:YAG harmonics and plan the incorporation of this source within the existing apparatus. Ideally, a tunable dye laser would be used to access the entire visible region. It should be noted that for each combination of synthesis and photolysis wavelengths a suitable two-laser reference system, such as that described here, would be required.

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⁽³¹⁾ The fluorescence spectrum from emission from the excited diphenylmethyl radical was recorded with an optical multichannel analyzer (OMA) and corrected for detector response.