Time-Resolved Photothermal and Photoacoustic Methods Applied to Photoinduced Processes in Solution

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1. Introduction

Interaction of radiation with a medium produces several effects, depending on the nature of the medium, on its absorption, and on thermoelastic properties. The use of lasers with their high photon density and high monochromaticity has made possible the study of various processes arising from the interaction of radiation with matter. In the liquid phase, on which we concentrate our review, vaporization might occur when using high photon densities. In the absence of this process (i.e., for relatively low photon densities), radiation pressure, electrostriction, Brillouin scattering, and thermoelastic expansion are the processes triggered by a laser pulse. For solutions with a finite absorption coefficient and a relatively large cubic expansion coefficient ($\beta = 1/V \cdot \partial V/\partial T$, see section entitled "Molecular Volume Changes"; see the list of "Symbols, Acronyms, and Definitions"), the last is by far the most important process.

After excitation of the absorbing molecules, radiationless deactivation of the metastable species formed causes local heating in the medium, giving rise to thermal waves (thermoelastic expansion). Although all methods sensing directly or indirectly the thermal waves may be generically referred to as photothermal, the term photothermal or optothermal has been restricted to sensor devices which directly detect the temperature rise. The sound waves generated by thermal expansion may be detected using acoustic detectors and in this case the methods are referred to as photoacoustic or optoacoustic methods.

The measurement of the heat produced in a medium following absorption of a pulse of electromagnetic radiation can provide kinetic (quantum yield of formation and decay lifetime) and thermodynamic (energy content) information on the excited or otherwise metastable states produced directly or indirectly (e.g., by energy transfer) in the system.

In the last decade photothermal and photoacoustic methods have gained popularity among photochemists as tools complementary to other well-established spectroscopic methods (e.g., absorption of various types of radiation by and emission from transients), providing energetic and kinetic information about species (excited singlets, triplets, isomers, radicals, biradicals, etc.) resulting from the absorption of light. These techniques are truly complementary to those other methods since, when technically feasible, other types of detection after pulse excitation, e.g., optical with UV-vis and IR radiation, Raman scattering, photo CIDNP, and ESR, deliver spectroscopic and kinetic information about transients with lifetimes in a wide dynamic range. Particularly, in many systems for which optical detection is not possible, either due to strong overlapping of spectra between transients and ground-state species or due to turbidity or opacity of the medium, photothermal techniques can be advantageously applied. Additionally, in order to get thermodynamic information on the transients, complex procedures are required when using noncalorimetric detection procedures (see Kliger, 1989 for references).[1]

Before the use of laser sources, the transient species were produced by flash lamps or amplitude-modulated light sources and—for the purpose of photothermal and photoacoustic spectroscopy—the volume expansions created in the sample by the heat released were detected using gas-coupled microphones. This approach, which permits a time resolution in the millisecond to microsecond range, was initiated by Hey and Gollnick in 1968[2]

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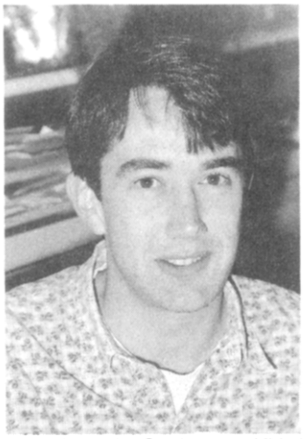

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and has proven successful in the long microsecond range.[3-5]

Pulsed lasers opened the way to measurements below the microsecond time range, and various techniques are used in conjunction with this excitation to monitor either the thermal wave or the acoustic wave generated thereafter. In the former case the temperature rise can be monitored directly (optical calorimetry,[6] laser calorimetry) or through the change in refractive index, n, induced in the medium or in the gas phase above the sample (e.g., thermal lensing, probe beam deflection or refraction, and thermal grating). Some of these methods, in particular transient thermal grating, have subnanosecond (sub-ns) capability[1,7-9] making possible the study of early transient species in photochemical reactions.

This review concentrates mainly on the analysis of laser-induced photothermal (including acoustic detection) methods since they offer the best possibilities for the study of transient species with lifetimes in the range of major interest for photochemists, i.e., in the picosecond to microsecond range. Only studies related to well-defined molecular steps are treated leaving out the discussion on complex systems, in particular on intact biological units in cases for which no unequivocal identification of the molecular step studied has been possible. The theories of the photothermal effect are not treated in detail. Only the basic equations and assumptions needed for the evaluation of properties of transient species are given, and reference is made to the original work in which the theories have been developed. Referencing covers papers which have appeared up to March 1992.

Given the fact that other laser-induced time-resolved techniques, like e.g., excitation followed by absorption, emission, or conductivity detection, are in widespread use among photochemists, detection of the thermal or acoustic effects is a relatively straightforward extension of the already available facilities in many laboratories. This is particularly so for time-resolved thermal lensing (TRTL), the related probe beam deflection (PBD) technique, and laser-induced optoacoustic spectroscopy (LIOAS, which is the term we mainly use in this review). This latter technique is also called photoacoustic calorimetry, PAC, or laser-induced optoacoustic calorimetry, LIOAC (see the list "Symbols, Acronyms, and Abbreviations").

For the detection of the sound waves produced after pulsed excitation, piezoelectric detectors with high sensitivity are most frequently used in condensed phase studies, due to the easy handling of detectors and signals.[10-13] Photothermal methods, in particular thermal lensing, have also been successfully applied in chemical kinetics, more frequently in the gas phase,[14] and also in liquid phase photochemistry with unique advantages.[15-17] The measurement of the temperature rise by means of a calorimeter[6] has found less acceptance, due to the more cumbersome construction, difficulty of handling, and very low time resolution (ca. 25 s).

A description of the methods most used by photochemists for the study of reaction rates in the range 10^3–10^9 s^{-1}, including discussion of advantages and disadvantages of the various techniques, was already presented (see also the references quoted there).[11] Descriptions of the equipment are supplied in this review only when required for the better understanding of the results discussed.

The choice of method depends on the particular application. For example, while the photoacoustic methods require calorimetric references in order to calibrate the system, TRTL, being a self-calibrated technique, does not need such a reference.[11,18] However, for the latter method the sample should be of high optical quality and show no absorbance by ground states and by transients at the wavelength of the monitoring laser beam. These requirements, which are also needed for transient grating experiments,[1,8,9] cannot always be fulfilled.

Since the transport of thermal or acoustic waves is involved in every case, the magnitude of the photothermal effect with any of the photothermal methods depends on the thermoelastic properties of the system, as well as on the amount of energy absorbed. In photochemical work with dilute solutions, it is important to validate the assumption that the thermoelastic properties are those of the solvent, while the optical properties are those of the solute. This can be advantageously exploited in order to determine thermoelastic properties in particular cases, e.g., in detergents, like sodium dodecyl sulfate (SDS) and hexadecyltrimethylammonium chloride (CTAC).[19]

Photothermal methods are extremely sensitive, permitting the monitoring of absorptivities as low as 10^{-7}–10^{-8} cm^{-1},[20,21] and absorbance changes of ca. 10^{-4} units.[22] Thus, they have been used as analytical tools to follow fast kinetics involving substances at low concentrations or with low absorption coefficients.[22,23] This sensitivity is, however, sometimes hampered by the absorption by the solvent which results in a background signal. In particular, water is an unfavorable solvent for this reason, having large absorptivity in the visible and near-UV ($>10^{-1}$ cm^{-1}) arising from vibrational overtones.[24]

The dependence of the magnitude of the signals on the thermoelastic properties of the medium imposes constraints on the measurements. Thus, the signals in water are much smaller than in other solvents, since in this solvent the value of β/C_p (see eqs 2 and 3) is the smallest among all solvents (e.g., a factor 30 smaller than in acetonitrile), mainly determined by the low value of β.[11] This poses a technical difficulty for studies with biological material.

In addition to the thermal component originating from radiationless processes of the excited molecules, the acoustic wave generated after a light pulse may have a component born out of the intrinsic volume changes taking place during the reaction under study. This concept was put forward in 1972 by Callis et al.[25] and applied to the determination of volume changes occurring during photoinduced biological reactions. The authors proposed that measurements of the light-pulse-induced effect as a function of variation in one of the thermoelastic parameters (e.g., β) should yield the individual contributions of the thermal and the intrinsic volume change to the total wave.[25] This proposal has been developed in detail by various research groups as discussed in a special section ("Molecular Volume Changes"). In particular, the large variation of β with temperature in water was successfully used for the study of volume changes in biological samples[25] (see the corresponding section for references).

2. Energy Balance

Photothermal techniques are calorimetric in essence. Thus, after the absorption of energy in the form of radiation (E_a), simple energy balance considerations lead to the general eq 1 which establishes the relationship between the various forms of dissipation of energy by the excited species.

$$E_a = \Phi_f \cdot E_f + \alpha \cdot E_a + \Phi_{st} \cdot E_{st} \qquad (1)$$

In this equation, E_a is the absorbed molar energy. On the right hand of the equation, the first term is the energy dissipated in the form of fluorescence expressed as the product of fluorescence quantum yield, Φ_f, times the molar energy of the fluorescing state, E_f, the second term is the fraction α of energy deposited in the medium as heat released as a result of rapid, i.e., within the heat-integration time of the experiment, vibrational relaxation including relaxation to the fluorescing state. This heat release is referred to as prompt heat (see section entitled "Time Resolution"). The third term is the energy stored by species living longer than the heat-integration time and expressed as the product of quantum yield of formation, Φ_{st}, times the molar energy content E_{st}. These species may be stable products or entities living longer than the time resolution of the experiment (see section entitled "Time Resolution"). When other processes take place (e.g., phosphorescence), terms should be included which take into account the energy involved in such process(es).

3. Time Resolution

In this section we address questions concerning the time resolution of photothermal methods detecting the effect after the absorption of a single laser pulse. For related techniques involving more than one pulse, see section 3.3.

The separation of the prompt and the stored heat (second and third terms, respectively, on the right hand side in eq 1) depends on the relation (i) of the time response of the electronic equipment used for signal handling, (ii) of the time width of the pulse, and (iii) of the geometrical arrangement of the experiment (which determines τ_a, vide infra), to the time constant of the process monitored.

The overall change following delivery of the heat pulse to a medium is fully described by the changes in density, ρ, and in pressure, p, as a function of time, t, and distance from the source, r. As a consequence, the equations for the transport of the time-resolved heat pulse in the particular medium should be solved for p and ρ.

In order to analyze these equations governing the evolution of the properties of a liquid medium after receiving a laser pulse, two cases should be considered corresponding to the high and low optical absorbance limits.

3.1. High Absorbance

For the case of excitation of high-absorbance liquids, e.g., otherwise transparent liquids excited with IR lasers or highly concentrated dye solutions, a focused laser induces the formation of a semispherical heat source. Equations describing the propagation of this type of pulse were treated by Hu[26] for the case of a laser pulse width, τ_l, longer than the acoustic transit time, τ_a, of the acoustic wave across the heat source radius, r_0 (r_0 is determined in this case by both the laser beam focal radius and the absorbance of the sample), i.e., small source diameter and long laser pulses: $\tau_l \gg \tau_a = r_0/v_a$ (v_a is the speed of sound in the liquid).

Sigrist and Kneubühl demonstrated that for $\tau_l \ll \tau_a$, which is the more common case with nano- or subnanosecond and non-tightly focused lasers (in order to avoid multiphoton effects and/or solvent breakdown), the amplitude and form of the pressure wave at a distance r from the source and at time t depends on τ_a.[27]

Hutchins made a critical and complete analysis of the factors determining the magnitude and the form of the pressure waves generated in condensed phases under the various conditions.[28,29] This author pointed out that a bipolar acoustic pulse (a maximum corresponding to an expansion and a subsequent minimum corresponding to the rarefaction) is expected theoretically and found experimentally for all geometries of the thermoelastic experiment which do not involve a thin layer with a constraining surface. In particular, for the case of high-absorbance media, Hutchins proposed that for intermediate cases, i.e., $\tau_l \approx \tau_a$, an effective time duration, $\tau_{ef} = (\tau_l^2 + \tau_a^2)^{1/2}$, should be introduced, as in the case of cylindrical heat sources arising in low-absorbance samples. In optically dense solutions, when metastable species are generated with a time constant for radiationless deactivation, τ_{nr}, comparable to τ_a, the effective time duration should become $\tau_{ef} = (\tau_l^2 + \tau_a^2 + \tau_{nr}^2)^{1/2}$.

Melton et al.[30] used diffuse-beam excitation in a front-face cell design. A plane wave was thus generated both in optically dense and in low-absorbance samples. For short laser pulses, the time resolution reached was in the order of few nanoseconds. This cell design is discussed in more detail in the section entitled "Time Behavior of Pressure Changes".

A theoretical description of PAS signal parameters (phase and amplitude) in highly absorbing samples was presented recently.[31] Such phenomena as phase shift as a function of modulation frequency and amplitude variations arising from the existence of long-lived (ms) metastable species were simulated and investigated experimentally (see section entitled "Triplet Lifetimes").

3.2. Low Absorbance

Photochemists working on liquid-phase problems are mostly interested in dilute solutions, in order to avoid concentration effects which in most cases strongly influence the decay kinetics of the metastable species. Therefore, in this review we treat the dilute solution case in greater detail. A design for optoacoustic experiments has evolved in which the detector is externally pressed to a cuvette wall in a plane parallel to the propagation direction of the exciting laser beam.[11,32-34] This design is based on the long experience with fluorescence measurements of dilute solutions, and it employs readily available fluorescence cuvettes which are easy to handle and clean. Since the acoustic wave propagates perpendicularly to the laser beam direction, this arrangement is designated as a right-angle configuration. For this arrangement and low absorbances, the heat source has a cylindrical geometry with dimensions equal to the laser beam diameter and the cuvette length, and it expands radially. This problem is similar for the case of TRTL and PBD techniques in which a coaxial laser beam monitors the variations in n (see section entitled "Time Behavior of Density Changes"). The equations necessary to handle this problem are those developed by Landau and Lifschitz to treat the general problem of sound generation by a cylindrical line source.[33,35]

Taking into account that the changes in p and in ρ are much smaller than the initial values of these parameters and that the heat conductivity can be neglected (vide infra), inhomogeneous differential equations eqs 2 and 3 describing $p(r,t)$ and $\rho(r,t)$ result:

$$(\nabla^2\rho - v_a^{-2}\cdot\partial^2\rho/\partial t^2) = -\beta/C_p\cdot\nabla^2 Q \qquad (2)$$

$$(\nabla^2 p - v_a^{-2}\cdot\partial^2 p/\partial t^2) = -\beta/C_p\cdot\partial^2 Q/\partial t^2 \qquad (3)$$

In these equations ∇^2 is the Laplace function, $\beta = 1/V\cdot\partial V/\partial T$ is the cubic volume expansion coefficient (V = volume, T = temperature), C_p is the heat capacity at constant pressure, and $Q = Q(r,t)$ is the heat evolved in the system integrated up to time t at a distance r from the source.

Equation 2 serves as a basis for the treatment of signals in methods like TRTL and PBD since it describes the behavior of $\rho(r,t)$, while eq 3 expresses the form of the pressure wave generated by the heat pulse, providing a description of the laser-induced optoacoustic signals in e.g., LIOAS, LIOAC, and PAC.

Equations 2 and 3 neglect any damping of the acoustic wave by the viscosity of the solvent; generally, these effects are small. In cases where there are chemical equilibria of high concentration species which exhibit large molar volume changes, the assumptions in eqs 2 and 3 might not be valid.

3.2.1. Time Behavior of Density Changes

The main relationship to be used in TRTL and in PBD can be derived from eq 2 in an oversimplified manner, which is nevertheless useful for the analysis needed in photochemistry. Integration of eq 2 is not necessary provided that the following two conditions are met: (i) heat diffusion can be neglected and (ii) the density change takes place under isobaric conditions.[36] Since the time constant for thermal diffusion, $t_c = R^2/4k$ is ca. 10^{-1} s for R of ca. 50 μm and k of typically 10^{-7} m^2 s^{-1},[11] (with R the halfwidth of the laser at $1/e$ of the maximum laser amplitude, and k the thermal diffusivity of the medium), condition i is met for heat pulses shorter than 10^{-1} s (the length of the heat pulse depends either on the laser pulse length or on the time constant of the radiationless processes, whichever is longer; vide infra). Condition ii means that in general $p'v_a^{-2} \ll \rho'$ (p' and ρ' refer to the values of pressure and density immediately after the pulse), which is a reasonable assumption in condensed phase. This also results in a time limit for the prompt heat (vide infra). With conditions i and ii and for short laser pulses ($\tau_l \ll \tau_a$; the laser pulse can be considered a delta function in the time coordinate) it can be demonstrated that all heat produced in a time shorter than the acoustic transit time, $\tau_a = R/v_a$, contributes to the amplitude of the signal, i.e., it is included in the prompt signal.

Radiationless processes with decay time $\tau_{st} > \tau_a$ release heat slowly, resulting in a slow thermal-lensing

Table I. Properties of Solvents at Room Temperature[11,a]

solvent	k (W m^{-1} K^{-1})	dn/dT (−10^{-4} K^{-1})	β (10^{-4} K^{-1})	c_p (J g^{-1} K^{-1})	v_a (10^3 m s^{-1})	ρ (10^3 kg m^{-3})
water	0.58	0.9	1.8–2.0	4.19	1.48	1.00
water, D_2O	0.58	1.0	0.9	4.22	1.39	1.01
cyclohexane	0.12	5.3	12.0	1.86	1.28	0.78
benzene	0.16	5.6–6.4	10.6	1.74	1.25	0.87
toluene	0.15	5.7	10.8	1.70	1.17	0.86
methanol	0.20	3.9	11.9	2.50	1.00	0.80
ethanol	0.18	3.7	10.6	2.45	1.01	0.79
ethylene glycol	0.26	(3.0)	6.2	2.42	1.60	1.11
glycerol	0.28	(3.0)	5.0	2.39	1.90	1.26
acetone	0.16	5.4	14.3	2.20	1.05	0.80
dichloromethane	0.14	5.4	13.7	1.26	1.09	1.34
chloroform	0.12	5.9	12.8	0.95	0.99	1.49
carbontetrachloride	0.11	5.8	12.2	0.85	0.94	1.59
acetonitrile	0.17	4.6	13.7	2.14	1.30	0.78

[a] The values in the table are averages from the literature. They should serve only the purpose of relative comparison of the various parameters in the different media. The values in parentheses are not from literature, they are deduced from similar liquids. Thermal conductivity, k; temperature gradient of refractive index, dn/dT; cubic expansion coefficient, β; specific heat capacity, c_p; sound velocity, v_a; and density, ρ.

signal. Under this condition, eq 4 results for the density after the pulse, ρ'.

$$\rho'(r,t) = -\beta/C_p{\cdot}Q(r,t) \tag{4}$$

For pulsed irradiation of samples producing energy-storing species with τ_{st} on the order of or larger than τ_a, the amount of energy delivered per unit time and unit volume, $q(r,t)$, to the medium as heat is expressed by eq 5 as a sum of a fast (or prompt) term, ϕ_1, and a slow, time-dependent term, $\phi_2(t)$.

$$q(r,t) = E_l{\cdot}(1 - 10^{-A}){\cdot}g(r){\cdot}[\phi_1 + \phi_2(t)] \tag{5}$$

E_l is the laser-pulse energy, A is the absorbance of the medium, and $g(r)$ is the spatial distribution of the pump laser intensity.

It should be noted that a very small amount of the energy is carried away by the acoustic wave, as shown by Bialkowski.[37] This correction is, however, negligible in most cases.

The time-dependent thermal lens signal, $U(t)$, determined as the relative value of the diode signal, V, after the laser pulse (eq 6), is proportional to ρ' through

$$U(t) = [V(t) - V(t = 0)]/V(t = 0) \tag{6}$$

the derivative of the refractive index of the medium with respect to density, dn/dρ, length of the heated region, l, and $q(r,t)$ as described by eq 7.

$$U(t) = \underline{C}{\cdot}l{\cdot}\mathrm{d}n/\mathrm{d}\rho{\cdot}\beta/C_p{\cdot}E_l{\cdot}(1 - 10^{-A}){\cdot}g(r){\cdot}[\phi_1 + \phi_2(t)] \tag{7}$$

Relevant properties of commonly used solvents are listed in Table I.

$\underline{C}$ is an instrumental factor. Since for the purpose of determining parameters of the energy-storing species only relative measurements are necessary, there is no need to know the values of $\underline{C}$ and $g(r)$. It is essential, however, to keep the experimental parameters constant within a series of measurements. In particular, the spatial distribution of the laser beam profile should be kept constant which implies that fluence changes should be carried out by the insertion of neutral density filters in the beam path, preventing any changes in the beam profile, e.g., by changes in the voltage of the power supply.

The separation of r and t dependent terms in expressions 5–7 is possible only for first-order kinetics. For second-order or mixed-order kinetics, these terms cannot be separated so that the shape of the photoinduced optical element (lens, grating, or deflection) changes with time. For the particular case of second-order atom recombination kinetics analyzed by thermal grating, Zhu and Harris presented a solution of the problem using a Fourier analysis of the time-dependent spatial heat distribution[38] (see also section entitled "Reactive Intermediates"). So far, the problem has not yet been fully treated for PBD or thermal lens.

The variation of n can be monitored by a second continuous-wave (cw) probe laser, preferably at a wavelength absorbed neither by the ground state nor by any transient produced upon excitation.[36,38,39] When the probe laser is coaxial to (or at a slight angle to) and overlapping with the pump laser, the technique is called TRTL.

In PBD,[40] a technique related to TRTL, the refractive index gradient is sensed at the edge of the excitation region, and the probe beam (aligned parallel to the pump beam) suffers a change in propagation direction (instead of defocusing, vide infra). While the temporal response and sensitivities of TRTL and PBD are similar, the advantage of the latter is that it is less dependent on the proper Gaussian spatial distribution of the pulsed beam.[41]

Bailey et al.[42] carried out a complete analysis of the creation and decay of the thermal lens in particular for the gas phase and applied the treatment specifically to energy-transfer processes.

The theory of photothermal effects in fluids was reanalyzed recently by Gupta.[43] In particular, the case of a flowing fluid was treated in detail.

Using an approach based on the diffraction theory of Sheldon et al.,[44] Carter and Harris successfully predicted absolute values of the thermal lens response.[45] In order to achieve accuracy, the aberrant nature of the photoinduced lens was taken into account.

Dovichi[21a] made a critical evaluation of all thermooptical methods as applied to analytical chemistry (including thermal lensing), which contains theoretical considerations as well as instrumental descriptions, and Kitamori and Sawada reviewed the recent developments in the analytical applications of this and other photothermal methods.[21b]

In general, the key component in the TRTL equipment is a pinhole or a sharp edge (the latter is also the key component in PBD), located before the photodiode, which limits the cross section of the monitoring beam detected. In TRTL the irradiance incident on the diode decreases proportionally to the defocusing of the monitoring beam (this is the general case since in most solvents dn/dT < 0).[11]

As an alternative to the pinhole, and in order to use all the spatial information in the probe beam, Jansen and Harris[46] used a parabolic transmission mask in the far field. The second spatial moment of the probe beam intensity distribution was then optically computed. With this arrangement the authors improved the signal-to-noise ratio 20 times over a pinhole measurement.

Extrapolation to $t = 0$ of the slow-decay signal in TRTL[16] affords ΔU, the part of heat delivered to the medium with a time constant longer than τ_a, while the total heat, U_{tot}, is derived from the maximum level reached by the signal. The ratio between the two values, using eq 7 and simple energy balance considerations (eq 1), is given in eq 8, which in order to be valid requires a linear correlation of ΔU with U_{tot}, with zero intercept.

$$\Delta U/U_{tot} = \Phi_{st}\cdot\Delta E_{st}/N_A h\cdot(\nu_e - \Phi_f\cdot\nu_f) \qquad (8)$$

where ν_e is the frequency of excitation and N_A is Avogadro's number. This equation shows that, for the short time range, TRTL (and PBD in a similar manner) is a self-calibrated technique, provided that no heat is permanently stored in reaction products. Knowing the fluorescence properties (Φ_f and ν_f) of the sample, the molar amount of heat stored by a species living longer than τ_a, $\Phi_{st}\cdot\Delta E_{st}$, is determined in one experiment, without the use of a calorimetric reference. No knowledge of the instrumental or solvent-dependent parameters is required. The analysis of the slow part of the TRTL (or PBD) signal yields the decay lifetime of the energy-storing species or energy transfer time constants. For the determination of lifetimes of relatively long-lived energy-storing species (>100 μs) a correction (performed using a calorimetric reference) is needed which takes thermal recovery into account, since this effect influences the signal at longer times.[16] From the thermal recovery of the signal, thermoelastic parameters of the medium can be derived.[47]

As pointed out by Poston and Harris,[41] the upper time limit reached by TRTL or PBD is much longer than that with acoustic detection, due to the fact that the density changes in the heated region are sensitive to the accumulation of heat release for a time much longer than the time scale of sound moving across the laser beam, which determines the time resolution of the acoustic methods (vide infra).

The disadvantage of the methods detecting refractive index changes (e.g., TRTL, PBD, and thermal grating) is the requirement of a monitoring beam well off resonance from transitions of ground and excited species (as already mentioned), which may represent a strong impairment in some cases.

In this section we treated the variations of the refractive index induced in a solution by a heat pulse, under the assumption that the concentration of the chemical entities do not vary during excitation. Franko and Tran developed a theory which takes into account contributions of concentration changes during the formation of the thermal lens.[48] With this theory the thermal lens technique can be applied to the study of fast bimolecular reactions, taking advantage of the high sensitivity of the photothermal methods.[49,50] The potential applications of the theory were discussed in a further paper by Franko and Tran.[23] Essentially, after the starting of a reaction by any means, like photochemistry, stopped flow, or temperature jump techniques, the concentration of the reactants or products is probed with a cw laser by steady-state thermal lensing. The method was tested with the well-understood photochemical nucleophilic substitution of 1,2-dimethoxy-4-nitrobenzene (DN) by hydroxide. High accuracy and precision was reached in the determination of the rate constant for the reaction as (0.025 ± 0.003) s^{-1} for 3.0×10^{-7} M DN. The concentration levels measurable by the technique are ca. 100 times lower than by absorption, making this technique very useful for kinetic studies of low concentrations and weakly absorbing species. Fast bimolecular rates can thus be measured with microsecond time resolution.[23] Similar results were reported using laser-induced optoacoustics to monitor reactants in fast reactions.[22]

3.2.2. Time Behavior of Pressure Changes

Lai and Young,[51] Heritier,[52] and Patel and Tam[33] presented quantitative approaches to the solution of eq 3 for the pressure measured by the acoustic detector, derived from the original concepts by Landau and Lifschitz.[35] In all these cases the derivations were made for a right-angle cell design. Tam[10] and Hutchins[28,29] summarized and compared the conclusions of the various treatments. In every treatment heat diffusion was neglected, and a Gaussian function in time and space was assumed for the laser pulse profile. This is not just convenient mathematically, but it also is a relatively good approximation to the shape of Q-switched and mode-locked laser pulses.[28] Lai and Young[51] also studied non-Gaussian beam profiles. Since they only worked with microsecond pulses, Patel and Tam[33] considered the case of long laser pulses, i.e., $\tau_1 > \tau_a$ (thin beams), while Lai and Young[51] and Heritier[52] analyzed the case of short laser pulses (wide beams).

Lai and Young[51] made an elegant derivation of the time behavior of the optoacoustic signal, and Sullivan and Tam demonstrated that the forms obtained by the various authors for the pressure wave as a function of time and distance from the detector (always for the right-angle cell design) are very similar.[53]

According to Lai and Young, $p(r,t)$ is proportional to $d\phi_0(\xi)/dt$, i.e., to the time derivative of the velocity potential $\phi_0(\xi)$. $d\phi_0(\xi)/dt$ determines the spatial form of the pressure pulse. In the absence of slow radiationless processes, $\phi_0(\xi)$ is a shape function determined by the laser pulse shape, where $\xi = (t - r/\upsilon_a)/\tau_{ef}$ is a modified time.[51]

Equation 9 results by solving eq 3 for $p(r,t)$,

$$p(r,t) = \beta\cdot E_a/8\pi^{1/2}\cdot C_p\cdot(\upsilon_a/r)^{1/2}\cdot\tau_{ef}^{-3/2}\, d\phi_0(\xi)/dt \qquad (9)$$

with r being the distance of the detector from the source, which should be shorter than the length of the cylindrical heat source (the length of the cuvette) for the problem to be considered two dimensional.

Equation 9 was derived for the case of rapid and total radiationless deactivation of the excited species. In this case the pressure is determined by the absorbed energy E_a which for very dilute solutions is proportional to the laser energy E_1 and the absorbance A; in a more precise manner, $E_a = E_1\cdot(1 - 10^{-A})$, and $\tau_{ef} = (\tau_1^2 + \tau_a^2)^{1/2}$ with $\tau_a = R/\upsilon_a$. Again two cases should be distinguished: thin beams (long laser pulses) for which τ_1 dominates, and wide beams (shorter pulses) in which case τ_a dominates.

An important feature of expression 9 is that it predicts a bipolar signal. For the case of thin beams (long pulses, $\tau_1 > \tau_a$), a signal with a maximum located at $t = (r/\upsilon_a$

$- \tau_1$) and a subsequent rarefaction minimum at $t = (r/\upsilon_a + \tau_1)$ is derived from the numerical analysis of eq 9.[54]

Using a piezoelectric β-polyvinylidene difluoride (PVF_2) film and nanosecond pulses (wide beams case) it was shown that for a solution of a calorimetric reference, such as $CuCl_2$, the magnitude of the amplitude, the time of arrival of the wave to the detector, and the shape of the curve depend on the acoustic transit time.[34,55] This was demonstrated by analyzing the signals as a function of the laser beam diameter, i.e., of the acoustic transit time, τ_a. For the case of wide beams a bipolar signal is again expected, with the maximum for the expansion larger than that for the rarefaction peak and at times different to those for the thin-beam case. This was calculated by Lai and Young[51] and verified experimentally by Sullivan and Tam using a He–Ne laser for the detection of the acoustic pulses.[53] Since the time at which the maximum appears depends on υ_a, measurements of this parameter are straightforward in, e.g., microheterogeneous media.

For the magnitude of the pressure pulse, eq 10 is obtained:

$$|P(r,t)| \propto \beta \cdot E_a / 8\pi^{1/2} \cdot C_p \cdot (\upsilon_a / r)^{1/2} \cdot \tau_{ef}^{-3/2} \qquad (10)$$

For reasons of convenience, and in view of the various definitions found in the literature, we prefer to reserve the term acoustic transient time to $\tau_a = R/\upsilon_a$ (Lai and Young)[51] and effective acoustic transit time to $\tau_a' = 2R/\upsilon_a$, which corresponds better to the time resolution in LIOAS.[11,34]

In the presence of a radiationless process with lifetime τ_{nr}, in the range of τ_a' or longer, eq 9 has to be modified introducing (i) the decay time of the radiationless processes and (ii) the form of the pressure pulse, which now is a function of the heat evolution, $q(r,t)$ (eq 5).

For $\tau_{nr} > \tau_a$, Kuo et al.[56] calculated and Heihoff[34] showed experimentally, that the magnitude of the maximum, the form, and the arrival time of the signal depend on τ_{nr}. This is clearly demonstrated by using either PVF_2 films which are nonresonant and therefore follow in real time the behavior of the heat evolution in the sample,[34] or by using a beam deflection technique to detect the acoustic wave. On the basis of this fact, τ_{ef} in eq 9 results in $\tau_{ef} = (\tau_1^2 + \tau_a^2 + \tau_{nr}^2)^{1/2}$.

The signal of resonant PZT detectors is dominated by their own resonance, which complicates the real-time detection of the heat evolution, although these detectors have a larger sensitivity. The form of the pulse thus reflects the resonance of the crystal and is essentially insensitive to the broadening effect brought about by the slow heat release originating from the decay of the longer-lived species.[11,12] However, the magnitude of the maximum with PZT is a measure of the prompt heat.

By making use of the various parameters of the signal which vary when energy-storing species with τ_{st} (eq 1) $> \tau_a'$ are produced in the sample, two procedures have been developed to apply LIOAS to the determination of properties of transients.

According to one of the procedures, the amplitude of the first maximum, H, is used as a measure of the prompt heat delivered to the medium. This procedure is based on the fact that H is related through an instrumental constant to $p(r,t)$ from eq 9[33] and that H decreases when energy-storing species are produced in the system.[11,34,52,55,57] A factor α for the heat delivered promptly was introduced[58,59] in eq 11, derived from eq 9, in which

$$H = K \cdot \alpha \cdot \mathrm{n} \cdot E_a \qquad (11)$$

K contains the thermoelastic parameters from eq 9 as well as instrumental constants, and n is the number of einsteins contained in the laser pulse of molar energy E_1. The fraction of heat dissipated promptly originates from all processes with deactivation lifetime shorter than τ_a', such as vibrational deactivation in the excited singlet manifold, internal conversion of the excited state to the ground state, charge transfer, intersystem crossing, and other chemical transformations.

Terazima and Azumi derived the LIOAS signal intensity as a function of the slow-decay rate constant for the radiationless process. The authors calculated limits for the value of $1/\tau_{nr}$ in comparison to the value of τ_a for various ratios of slow and fast heat releasing processes.[60]

Barra et al. proposed that in order to ensure good separation between fast heat-evolving and slow heat-storing processes, the lifetimes of the former should have an upper limit of ca. $\tau_D/5$ (τ_D is the detection time $= \tau_a'$ in most cases), whereas the energy-storing species should have a minimum lifetime of ca. $5\tau_D$.[61] However, these limits depend on the fast and slow heat contributions to the total heat release.[60] Furthermore, the contribution of the latter to the prompt heat can be calculated provided that the decay kinetics of the energy storing species is known.[11]

In order to eliminate K from eq 11, a calorimetric reference is needed (see section entitled "Calorimetric References") with an α value of 1 (or a value known from independent measurements). The α value for a sample and a particular τ_a' is calculated as the ratio of the fluence-normalized optoacoustic signal for the sample to that for the reference, H_n^S/H_n^R.

Whenever possible, it is advisable to measure both reference and sample solutions at various concentrations (absorbances) in order to avoid technical problems related to the matching of absorbances. For studies in the liquid phase, the slopes of the linear plots of the photothermal (e.g., optoacoustic or thermal-lensing) signal vs laser fluence are, in turn, plotted against the fraction of absorbed fluence ($1-10^{-A}$) for solutions of various A of sample and reference. The ratio of the slopes of the latter plots affords α for the sample under study.[11,62] It is essential that the linearity of the fluence-dependent plots as well as the zero value of the intercept in these plots is verified, since nonlinear effects are readily produced with focused lasers. In fact, photothermal techniques, e.g., TRTL, LIOAS, and thermal grating have been successfully applied to the determination of multiphoton cross sections in several cases.[63] We do not treat this aspect in detail in this review. Linearity of the plots alone, however, is no guarantee that multiphotonic (coherent or consecutive) effects are absent.[64] In fact, using TRTL, PBD, or right-angle LIOAS, there is a trade off between time resolution (limited by τ_a') attainable by reducing the laser beam diameter and the laser power density ($2P/\pi R^2$) which drives the nonlinear behavior. Thus, depending on the system, the use of tightly focused beams in order to reduce τ_a' might be unwise, while skimming the beam might be impractical due to the reduced sensitivity.

Making use of α, the energy balance eq 1, and the possible energy loss by luminescence, the product $\Phi_{st}\cdot E_{st}$ is readily calculated. Provided that one of the two factors is known, the other is derived without assumptions as to the optical properties of the energy-storing species produced.[62] This has been applied for the determination of Φ_{st} or E_{st}, depending on the system. The results are reviewed in the various sections.

Since for species with τ_{nr} in the range of τ_a, the fraction α depends on the relationship between τ_a' and τ_{nr}, variation of τ_a' (through changes in the laser beam diameter) offers the possibility of determining τ_{nr}.

Reorganization of eq 1 affords eq 12 for the fraction of energy stored by a transient.

$$1 - \alpha = \Phi_f \cdot E_f / E_a + \Phi_{st} \cdot E_{st} / E_a \qquad (12)$$

In many cases of photochemical interest the decay of the energy-storing species follows unimolecular kinetics. Thus, integration of the exponential decay function between τ_a' and infinity, which affords the heat dissipated slowly, leads to $E_{st} = \Delta E^0_{st} \exp(-\tau_a'/\tau_{nr})$, in which ΔE^0_{st} is the molar energy content of the energy-storing species. Therefore, the slope of the linear semilogarithmic plot of $1 - \alpha$ vs τ_a' yields τ_{nr} and the extrapolation of the plots to short τ_a' values affords the product $\Phi_{st} \cdot E^0_{st}$.[11,55] From eq 12 and the expression for the time-resolved emission of heat by the transients, it is clear that for $\tau_a' \gg \tau_{nr}$, no heat is stored in any transient. In this case $1 - \alpha$ affords a value of $\Phi_f \cdot E_f / E_a$ for the energy loss by fluorescence, while for $\tau_a' \ll \tau_{nr}$ $E_{st} = \Delta E^0_{st}$ (or $= E_p$, energy content of the product) results from eq 12.

The alternative procedure to handle the optoacoustic data is based on the convolution of a signal obtained with a calorimetric reference (see the corresponding section) and a simulated slow-heat dissipation function in order to fit the data curve. This procedure has been applied by several research groups, mostly using resonant PZT detectors[12,65,66] as well as piezoelectric films.[34,55] Essentially, this method involves the analysis of the differences in amplitude and in temporal position of the maximum of the optoacoustic signal between a solution in which a slow energy-storing species is produced and a calorimetric reference solution (see section entitled "Calorimetric References"). The function simulating the slow-heat dissipation reflects the molecular model applied to the particular system under study, thus containing, e.g., τ_{nr}, E_{st}, and possible energy transfer rate constants.

Rudzki-Small et al. developed the Method of Moments as applied to laser-induced optoacoustic data in order to deconvolute and analyze fast radiationless decays. The quality of the method was analyzed in detail by introducing two types of nonrandom error in the data. Successful deconvolution of noisy synthetic data with up to three decay components was demonstrated. Various procedures for the recovery of the heat decay rate constants by deconvolution of the optoacoustic signals for sample and reference were compared.[67]

The question of the experimental arrangement best suited for the measurement of laser-induced pressure changes merits special consideration in this review. As already mentioned, a front-face cell design developed by Melton and co-workers reaches a time resolution independent of the cell thickness due to the generation of an in-phase expansion of the sample solution.[30] The sensitivity of this arrangement is larger (a factor 100 was measured for a particular system) than that of the right-angle cell. This allows measurements at much lower fluences. The latest version of the front-face cell also permits the measurement of very dilute samples thus overcoming problems encountered with the earlier design. With the latest design, a transient lifetime of 7.5 ns was measured, a value difficult to measure with the right-angle cell.[68] A complete treatment of the factors determining the performance of the front-face cuvette was offered by Arnaut et al.[68]

The background signal with the front-face design is, however, much larger than that with the right-angle configuration. Up to 95% background signal was estimated by the authors for optically thin samples when using aluminum mirrors (as in the original version of the design).[30] This value was substantially reduced by using dielectric mirrors and careful filtering of spurious radiation from the laser.[68] A further potential disadvantage of the front-face cell is its relative complexity. Additionally, the dynamic time range is smaller with the front-face cell. The fact that multiple reflections necessarily occur in the front-face design, necessitates the use of iterative reconvolution of the experimental signal from a calorimetric reference with the simulated rates of heat release from the system under study to obtain the signal measured. This procedure is undoubtedly more complex than the simpler analysis of the signal amplitude, possible with the right-angle cuvette.[11]

For the right-angle arrangement and solutions of low absorbance, it has been claimed that electrostriction may produce a significant contribution to the optoacoustic signal.[52] However, the analysis made by Burt[69] of the optoacoustic signal generation indicates that this phenomenon appears at extremely low absorbance values, i.e., it is negligible in most cases.

Laser-induced optoacoustics was used to monitor the concentration of the reactants during several reactions in order to unravel the kinetics of relatively fast bimolecular reactions. The high sensitivity of the method allows working at low concentrations, permitting the lengthening of the time range available for the studies.[22]

3.3. Subnanosecond Time Resolution

In order to achieve a time resolution better than a few nanoseconds, the typical limit for all photothermal methods and single-pulse excitation, two different approaches have been developed. In both cases two pump beams are employed.

Pump-probe methods using a pulsed laser delayed with respect to a picosecond pump laser, with acoustic detection of the heat evolved by the short-lived transients, deliver information on the absorption spectra of the transients. This method is promising for the future, although not much work has been carried out in this area after the initial publications.[70-72] The time resolution in these cases is determined by the instrument function which in turn depends on the pump laser width and on the delay between the pulses.

Another photothermal technique reaching picosecond time resolution is laser-induced dynamic thermal grating. An excellent review has been recently written by Miller[9] (see also Genberg et al.[73]). The method is based on a combination of a transient grating technique[8] which involves the creation of an interference pattern by the interaction of two crossed, time-coincident short pulses (in most cases one laser pulse split into two beams) absorbed by the medium and detection of the changes in refractive index induced in the sample by the radiationless processes of the excited states. The time resolution is determined by the sound speed crossing through the grating fringe spacing in the medium. It can reach ca. 10 ps, provided that the excitation pulse width is shorter than this time, i.e., ca. 3 orders of magnitude better than that of LIOAS, TRTL, and PBD. However, the optical requirements are highly demanding and the alignment needed is relatively complex.

The latter two subnanosecond methods give, like all photothermal methods, information on energetics, kinetics, and molecular dynamics of the systems under study. Therefore, with a combination of the various photothermal methods, information can be obtained on these parameters for photoinduced reactions producing metastable species in a wide dynamic time range (from a few picoseconds to seconds).

4. Molecular Volume Changes

The two terms constituting the volume changes in a photoinduced chemical reaction, i.e., the volume difference between reactants and products and the contraction or expansion of the solution through cooling or heating, can be separated by means of photothermal measurements as a function of one of the thermoelastic parameters of the medium. Thus, in addition to the enthalpy change, the volume change associated with the given reaction can be evaluated. Callis et al.[25] for the first time explicitly drew attention to this concept. In the following paragraphs a simple derivation of the equations for the treatment of the data is made, similar to that originally derived by these authors.

As expressed in eqs 9 and 11, the optoacoustic signal, H, and the volume expansion coefficient, β, are directly proportional. β has the value of ca. (10–14) $\times 10^{-4}$ K^{-1} for most typical organic solvents and 2×10^{-4} K^{-1} for water at room temperature,[11] showing a pronounced temperature dependence for the latter solvent between 4 and 20 °C.[74]

The thermally produced volume change, ΔV_{th}, can be simply expressed by eq 13 in terms of the temperature change in the heated volume.

$$\Delta V_{\mathrm{th}} = \beta \cdot V \cdot \Delta T = \alpha \cdot n \cdot E_{\mathrm{a}} \cdot \beta / (C_p \cdot \rho) \tag{13}$$

The direct volume change, ΔV_{r}, originating from a molecular process other than heating or cooling, should frequently be added to ΔV_{th}. Contrary to ΔV_{th}, ΔV_{r} is independent of temperature, at least in a first approximation. Thus, the equations describing the behavior of the optoacoustic signal for a sample (S) displaying such a volume change should be expanded in order to take ΔV_{r} into account resulting in eq 14:

$$H^{\mathrm{S}} = k''[\Delta V_{\mathrm{th}} + \Delta V_{\mathrm{r}}] \tag{14}$$

Factor k'' contains geometrical and instrumental parameters.

From eqs 9 (or 10) and 11, eq 15 is readily derived.

$$H^{\mathrm{S}} = k''[\alpha \cdot E_{\mathrm{a}} \cdot \beta / (C_p \cdot \rho) + \Delta V_{\mathrm{r}}] \tag{15}$$

$\rho \propto 1/v_{\mathrm{a}}^{1/2}$ has been used in eq 15.

For this treatment, the value of $\alpha \cdot E_{\mathrm{a}}$ should be independent of temperature over the typically small temperature range used for these studies.

Since at room temperature ΔV_{r} is frequently small as compared to the thermally determined term, it can be neglected when not performing temperature-dependent measurements. However, this should be carefully evaluated in each case (vide infra).

On the other hand, the variation of β with temperature or with solvent can be (and has been) advantageously exploited in order to measure ΔV_{r}. Unfortunately, β shows an extremely small variation with temperature for all solvents, but water. Thus, temperature studies carried out with the purpose of determining ΔV_{r} are not expected to be successful in nonaqueous media.

A key assumption is that for the calorimetric reference ΔV_{r} equals 0. Therefore, for the reference (R)

$$H^{\mathrm{R}} = k'' \Delta V_{\mathrm{th}} \tag{16}$$

A ratio between eqs 15 and 16 leads to eq 17:

$$H_{\mathrm{n}}^{\mathrm{S}} / H_{\mathrm{n}}^{\mathrm{R}} = \alpha + (\Delta V_{\mathrm{r}} / E_{\mathrm{a}}^{\mathrm{S}}) \cdot C_p \cdot \rho / \beta \tag{17}$$

in which $H_{\mathrm{n}}^{\mathrm{S}}$ and $H_{\mathrm{n}}^{\mathrm{R}}$ stand for the fluence-normalized optoacoustic signal of the sample and reference, respectively.

This concept has been applied to complex biological systems, like *Chromatium* chromatophores,[25] bacteriorhodopsin,[75,76] and reaction centers of *Rhodopseudomonas sphaeroides*,[77] using relatively long (microsecond) light pulses and in all cases in aqueous media.

The value of ΔV_{r} in each case was calculated from measurements of the acoustic signal at various temperatures. All these systems are quite complex, forming very rapidly (in picoseconds after the first photons) intermediates which in turn absorb light and establish photochromic equilibria with the starting ground-state species. Thus, the values of ΔV_{r} derived, in spite of the use of very low pulse energies, almost certainly contain contributions from the volume changes originating from photoreactions of the transients.

For the case of bacteriorhodopsin (BR) a negative value of ΔV_{r} was obtained in our laboratory,[78] indicating that a molecular contraction takes place after excitation of the molecule. For a heat integration time of 650 ns (see section entitled "Time Resolution") and using 500-fs pulses, the value obtained for the volume change, $\Delta V_{\mathrm{molec}} = 0.82 \times 10^{-24}$ cm^3 per molecule of K produced, is remarkably small and is most probably associated with both the reorganization of charges in the protein around the isomerized chromophore and the chromophore isomerization. Using femtosecond excitation pulses, information could be derived on the energetics and quantum yield for the photoreaction BR → K, whereas with nanosecond pulses which establish a photochromic equilibrium between BR and K, information was obtained about the quantum yield for the back-photoreaction K → BR.[79] With the longer pulses and due to sensitivity reasons, it was not possible to reach energies low enough to avoid excitation of the first intermediates.[79]

Marr and Peters[80] studied by temperature-dependent optoacoustic measurements, the conversion of rhodopsin to the first intermediates using 500-ps pulses and determined a volume expansion for the transition rhodopsin–lumirhodopsin, as well as for the transition isorhodopsin–lumirhodopsin. The possible formation of a photochromic equilibrium built within the laser pulse duration was not considered, although the batho form is already present in less than 6 ps after the pulse. In our own study of bacteriorhodopsin, the photochromic equilibrium with the first intermediates is rapidly reached, even using very low fluence nanosecond pulses.[81]

In order to avoid the fluence problem in systems in which transient species are produced with similar spectra to that of the initial state, either optoacoustic measurements with femtosecond pulses should be performed or extremely low fluences (less than one photon per molecule) should be used, and the results should be checked for fluence linearity.[81] The latter condition might not have been fulfilled in every study in the past. Another problem requiring extreme care is the choice of calorimetric reference. The calorimetric reference should be carefully checked for any temperature dependence of the fluorescence, especially in the case of complex dye molecules.

Westrick et al. obtained a value of ΔV_r, called conformational volume change, ΔV_{con}, for the photodissociation of CO from sperm whale myoglobin,[82] using 500-ps pulses, a heat-integration time of ca. 1 μs,[83] temperature-dependent measurements, and deconvolution techniques. By using these techniques a time resolution of 100 ns was reached. The biexponential heat source was interpreted as arising from two consecutive processes, the first leading from carboxymyoglobin, MbCO, to the geminate pair Mb:CO, followed by the dissociation to deoxymyoglobin plus CO. From these results ΔV_{con} associated with the first process was found to be a contraction of ca. 10 cm^3/mol (equivalent to 0.17×10^{-28} m^3/molecule) and that associated with the CO detachment was an overall expansion of ca. 6 cm^3/mol (relative to carboxymyoglobin). The thermodynamics of the system were also studied in the same work, leading to the surprising result that the formation of the geminate pair in 0.1 M tris buffer (pH 8.0) was exothermic by ca. 9 kJ/mol.[82,84] In a further study, the enthalpy change for the formation of the geminate pair in 0.1 M phosphate buffer (pH 8.0) was quoted as endothermic by ca. 3 kJ/mol.[85,86] According to the authors, the latter value takes into consideration the temperature response of the detector, not properly accounted for in the former report.[87]

Using a different interpretation of the laser-induced heat release, Leung et al.[88] assigned an endothermicity of 56 ± 2 kJ/mol to the formation of the geminate pair in horse heart carboxymyoglobin and reported an unspecified volume change for the reaction.

In order to establish the role of the arginine-45 salt bridge in the CO dissociation from carboxymyoglobin, temperature-dependent optoacoustic measurements were performed on site-directed mutants of sperm whale carboxymyoglobin. Replacing arginine-45 by either asparagine or glycine resulted in a contraction of ca. 4 cm^3/mol (instead of 10 cm^3/mol for the wild type, vide supra), as well as an increase in the endothermicity of ca. 32 kJ/mol for the formation of an intermediate geminate pair, while the total enthalpy and volume changes for the dissociation remained the same for the mutants as for the wild type. The authors concluded that upon photoinduced detachment of CO from the iron, the arginine-45 propionate salt bridge undergoes a rupture which, after diffusion of the CO out of the protein matrix, is reformed.[87] Similar measurements were performed by the same group with horse carboxymyoglobin, in a further study on the influence of the various amino acids in the CO channel within the protein. The values determined for the enthalpy of, and the ΔV_r value associated with, the geminate pair formation were ca. 36 kJ/mol and −1.2 cm^3/mol, respectively, for horse carboxymyoglobin, compared with an endothermicity of ca. 3 kJ/mol and a ΔV_r of −9 cm^3/mol for whale myoglobin. Taking into account both the similarity between the values for horse carboxymyoglobin and those for the arginine-45 mutants (vide supra), and the amino acid sequence of the horse protein, the authors rationalized the results with a model for the various salt bridges involved in the channel formation for the photochemical CO extrusion.[85]

Notwithstanding their complexity, protein conformational changes in hemoglobin and myoglobin in the picosecond range were studied using thermal grating. In both proteins, the changes observed within 30 ps after CO dissociation were attributed to a collective displacement of atoms driven by the CO splitting.[89]

All these biological systems are extremely complex, and simpler systems should be analyzed in order to assess the meaning and limitations of these undoubtedly interesting types of measurements.

Simpler systems have been studied using the principle described above of variation of β with temperature in water. Strauss and Walder[90] used PBD in order to measure the spatial relaxation around $[Mn(H_2O)_6]^{2+}$. The volume change per excited ion was found to amount to a contraction of 7×10^{-30} m^3 which corresponds, as calculated by the authors on the basis of symmetry considerations of the ground and excited states involved, to a contraction by 0.14×10^{-10} m (0.14 Å) of the Mn–O equilibrium distance after excitation.[90] In contrast to other aqueous ion complexes, e.g., $Cu(H_2O)_6^{2+}$ and $Co(H_2O)_6^{2+}$ which show no volume changes and are used as references for the photocalorimetric measurements, $Mn(H_2O)_6^{2+}$ undergoes intersystem crossing and the slow decay of the transient (4.6 μs) makes possible the detection of a volume change in this case.

Herman and Goodman derived from laser-induced optoacoustic studies (PAC) the nonthermal contribution to the volume change in photoinduced reactions leading to stable products.[19,66,91] When studying the photoreactions of 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH), diphenylcyclopropenone (DPC), and *trans*-stilbene (TS), the separation of the thermal part from the nonthermal conformational contribution to the total volume change was accomplished by changing either the composition of a binary solvent mixture, or the temperature.[19] With the former method β, ρ, and C_p are varied, whereas with the latter only β is responsible for the changes.

The values of ΔV_r (expansions in the three cases) were as follows: 48.5 ± 5.3 cm^3/mol for the N_2 photoelimination of DBH in 0.06 M SDS in water, 60.1 ± 4.5 cm^3/mol for the CO elimination of DPC in the same solvent, and 5.6 ± 4.3 cm^3/mol for the photoisomerization of TS in 0.014 M CTAC in water. These three values were determined by the temperature-dependence method. For the first two reactions, the values were identical to those determined by the method consisting of changing the solvent composition. According to the authors, this gave an internal check of the validity of the methods. In every case, the heat integration time was much longer than the lifetimes of the transient species formed in the various systems upon photolysis, which implies that the value of ΔV_r corresponded to the production of the final stable product.[19]

For the case of TS, the value obtained was in agreement with previous estimates, while for the cases of DBH and DPC comparisons were made with retro Diels-Alder reactions, for which reaction volumes between 30 and 60 cm^3/mol had been reported. The authors confirmed that the method of temperature variation is able to resolve with higher sensitivity the contribution of the volume changes due to molecular movements, to the total volume change detected. It was also confirmed that the use of micelles greatly facilitates the study of photochemical reactions of water insoluble compounds. Of course, a possible specific influence of the micelles on the photochemical reaction under study must be taken into account. The additional important conclusion of this study was that in some cases, depending on the value of β and C_p, and on the nature of the reaction (e.g., extrusion of small molecules vs isomerization) the contribution of ΔV_r might be very large (cf. eq 15). Thus, the failure to account for it might yield erroneous thermochemical data.[19] This was the case of a previous study of DPC photodissociation,[92] for which, as pointed out in a later study, the reaction enthalpy was erroneously derived, since the contribution of the reaction volume to the total volume change had not been taken into account.[93]

Hung and Grabowski also used the variation in the thermal expansivity, $\chi = [\beta/(\rho \cdot C_p)] \cdot \mathrm{MW}$ (MW = molecular weight) in order to evaluate ΔV_r values for the photodecarbonylation of diphenylcyclopropenone. Eight alkanes differing in their χ values from 2.2 to 4.7 cm^3/kcal were used and an expansion of 23 ± 4 cm^3/mol was extracted,[93] much smaller than the value of ca. 60 cm^3/mol reported for the same reaction in acetonitrile/water mixtures and in 0.06 M SDS in water (vide supra).[19] Since from different types of measurements it could be concluded that a cleavage of an average C–C bond results in a volume expansion of ca. 10 cm^3/mol,[94] the ΔV_r = 23 ± 4 cm^3/mol value was attributed to the breaking of two covalent bonds, accompanied by a minor rearrangement of the solvent upon relaxation of electrostriction, which should strongly depend on the polarity of the solvent.[93] Hung and Grabowski remarked that ΔV_r values obtained from optoacoustic measurements are extremely sensitive to the values used for the thermoelastic parameters.[93] The value determined with due consideration to the volume change due to the reaction was ΔH_{rxn} = (−28 ± 5) kJ/mol,[93] ca. 30% smaller than the previous value.[92]

Volume changes of photoreactions of coordination compounds were analyzed by Herman and Goodman.[66,91] A contraction of between 1 and ca. 5 cm^3/mol was measured for the excitation of $^*M(L)_3^{n+}$ (M = Ru(II) or Cr(III), and several ligands, especially L = bpy). The value of ΔV_r for the back thermal reaction was determined as well, being in all cases identical to that for the forward reaction. The authors calculated an isotropic radial volume change of ca. 10^{-2} Å for the formation of the excited state and postulated that it is related to a small reduction in the Ru–bpy bond length upon excitation. This small value contrasts with the 10 times larger change calculated by Strauss and Walder for the variation of the Mn–O bond length (anisotropic) upon excitation of the hexaaquo Mn complex (vide supra).[90] An even smaller radial decrease was calculated by the same method for the $^4A_2 \rightarrow {}^2E$ transition of $Cr(bpy)_3^{3+}$ and an alternative explanation was offered for the origin of the volume change, viz. to a photoaquation of the complex in the excited state.[66]

Values of ΔV_r were also derived for the formation and complexation of $Pt_2(P_2O_5H_2)_4{}^{4-}$ by studying the temperature-dependent optoacoustic signal in water. While a negligible value of ΔV_r was observed upon excitation of $Pt_2(P_2O_5H_2)_4{}^{4-}$ to its excited state (several explanations were offered to account for this observation), a large contraction was obtained for the excitation of $Pt_2(P_2O_5H_2)_4{}^{4-}$ in the presence of Tl^+, presumably due to the formation of $Pt_2(P_2O_5H_2)_4Tl^{3-}$ exciplexes.[91]

Picosecond optical calorimetry was used for the study of enthalpy and volume changes taking place during the cis–trans isomerization of tetraphenylethylene. In this case, the values of ΔV_r were derived from measurements in various alkanes differing in their thermal expansivity value, χ. A volume contraction of 29 ± 7 cm^3/mol was determined for the formation of the twisted excited p* state.[95]

5. Calorimetric References

Especially when using acoustic detection (LIOAS, LIOAC, PAC) and for the determination of the value of α (eqs 1 and 11), a calibration of the experimental setup is required, by which the quantitative relationship between the heat released and the signal is determined. This is normally performed by using calorimetric references. A calorimetric reference is ideally a substance with an absorption spectrum overlapping that of the sample, which does not fluoresce (or does so with a known yield), delivers all the absorbed energy to the medium as heat within the observation time (α = 1, eq 11), and is measured under identical conditions as those employed for the sample, including geometrical parameters. This essentially means eliminating the factor K in eq 11. As already stated, the possibility of multiple-photon excitation should be carefully eliminated by performing the experiment for the calorimetric reference over a wide laser-fluence range (again in this case the fluence should be varied by introducing neutral density filters in the laser-beam path, thus avoiding the perturbation of the beam profile). As time resolution improves, some of the calorimetric references will become obsolete. The time constant for the heat release of the reference must be shorter than the heat-integration time of the experiment.

A calorimetric reference may be external or internal. An external reference is typically a dye with a relatively large absorbance in the region of interest (in order to avoid a large perturbation of the thermoelastic properties of the solvent), for which the prompt heat is measured in an experiment separate from, but in the same medium and under the same conditions as, the sample.

Depending on the medium and on the wavelength range, several substances have served as calorimetric references. For excitation at 308 nm of ethanol solutions, anthracene, fluorenone, xanthone, and bis(*o*-methylstyryl)benzene were employed,[96] with the photophysical parameters previously reported for these compounds.[97,71] While xanthone complies with the requirement of promptly delivering all the absorbed energy as heat, the other compounds do not necessarily do so. However, since the photophysical parameters were known, the prompt heat was readily calculated using eq 12. When using this approach, it is important to calculate the prompt heat for the reference under the conditions of the experiment. For highly fluorescent samples that neither form long-lived transients nor perform photochemistry (e.g., rhodamine 6G), the procedure is straightforward.

The heat-conversion efficiencies were determined for pyridazine, dicumarol, 8-quinolinol, and naphthalene in acetonitrile, using TRTL with 308-nm laser excitation and measuring the total energy delivered. The value for total-heat release efficiency was unity for the first three and 0.8 for the last compound.[98] However, these are total-heat efficiencies and not just prompt-heat efficiencies, since the total thermal lens signal was measured. For pyridazine it was confirmed that the two quantities were similar, due to the rapid deactivation of the excited state. The performance of this compound was similar in methanol, ethanol, and benzene. For the other compounds the condition of prompt-heat release within the acoustic transit time was not reported.[98]

For near-UV or blue excitation, benzophenone + KI ([KI] > 3 mM rapidly quenches the triplet state) in acetonitrile/water was used as calorimetric reference.[55] Care must be exercised with this system, however, in view of the multiphoton effects already shown at relatively low fluences (vide infra). In organic media α-hydroxybenzophenone (λ_{exc} = 300–370 nm) with rapid excited-state deactivation through intramolecular excited-state proton transfer[57,99] and ferrocene (λ_{exc} = 300–550 nm)[65] have been used as references. α-Aminobenzophenone (2AB), α-hydroxybenzophenone (2OB), dihexyloxatrimethinecyanine iodide (OXA6), dioctadecylmonomethineoxacyanine perchlorate (OXAM18), iron(III)–acetylacetonate (Feacac), ferrocene, *p*-(*N*,*N*-dimethylamino)nitroaniline (PNDNA), and benzophenone (B) quenched by KI were reinvestigated as possible references for optoacoustic studies using ultraviolet radiation.[100] For 2AB, PNDNA, Feacac (λ_{exc} = 355 and 320 nm), and OXAM18 (λ_{exc} = 355 nm) a similar value of $\alpha = 1$ was obtained in ethanol, acetonitrile, tetrahydrofuran, ethyl acetate, and diethyl ether, using 2OB as reference. Ferrocene was excited at 355 nm and OXA6 at 320 nm. With the exception of a solution of B plus KI in ethanol, linearity of the fluence-dependent optoacoustic signals was obtained for all compounds with laser-pulse fluences < 20 μJ and τ_a' = 250 ns. For the B plus KI solutions deviations of linearity were observed already at pulse fluences below this value. Above the quoted value all substances showed deviations from linearity in the fluence-dependent curves due to either biphotonic processes or ground-state depletion.[100]

For longer wavelengths, carotenes (λ_{exc} = 400–800 nm, depending on the chain length),[62] cobalt(II)–tetraphenylporphin (530–560 nm; with a short-lived triplet state),[62] and I_2 (in the visible region in order to avoid photolysis)[62,101] have proven to be good calorimetric references in nonpolar solvents. Within a similar region, azulene (435–715 nm) and crystal violet (λ < 640 nm) were shown to be good references in acetonitrile.[98]

From all the substances listed in organic solvents, ferrocene and α-hydroxybenzophenone have found the widest acceptance as calorimetric references in their respective absorption regions.

With 355-nm excitation, $K_2Cr_2O_7$ was used in ethanol/water mixtures containing detergent[102] while *meso*-tetra(4-*N*-sulfonatophenyl)porphin sulfate (*meso*-TPPS) served as a calorimetric reference in buffer solutions at 355 nm, with known data on its photophysical properties (Φ_f and singlet energy as well as triplet yield and energy).[103] In addition to Na_2CrO_4, $FeCl_3$ was used as a calorimetric reference in aqueous medium for λ_{exc} = 365 nm.[96] Also in aqueous media, $Na_2Cr_2O_7$, Na_2CrO_4, and $Fe(bpy)_3Cl_2$ were employed for the range 405–505 nm,[66] while in the visible, copper(II) and cobalt(II) salts (chloride, sulfate, perchlorate, etc.) served as references.[104,105]

Salts of colored anions not displaying fluorescence or photochemistry, like e.g., M_2CrO_4 (M = Na or K), or $MMnO_4$ have been also used as references for the visible in polar media, in particular in aqueous solutions. Bromocresol purple with Φ_f ca. 10^{-3} was used in buffer solutions for excitation in the visible.[77,80]

Malachite green cation in aqueous solution serves as calibration standard with $\alpha = 1$ as shown by Indig et al.[106] for the pH range 1.8–13 (λ_{exc} = 624 nm). These authors also showed that similar species formed from other triphenylmethane dyes (like bromocresol purple and bromocresol green) serve as calorimetric standards with 100% prompt heat release in various pH domains. When attached to proteins, malachite green does not undergo 100% prompt heat release, but 2.6% of the absorbed energy is stored in longer-lived species. Malachite green triplets were postulated as possible energy storing species.[106]

Substances used as external calorimetric references are listed in Table II, classified according to the medium (organic first and aqueous later) and within this classification in increasing order of wavelength.

When the reaction under study can be inhibited in some way, the system so treated serves as an internal calorimetric reference, since upon inhibition, all absorbed energy is delivered as heat. The use of internal references in photocalorimetric measurements was introduced in 1972 by Callis et al. while working with photosynthetic units[25] and further used extensively by several groups, e.g., Malkin and Cahen and Carpentier et al.[107] In these chromoprotein complexes, electron transfer can be inhibited, for example, by applying a strong white background light (closing the reaction

Table II. Substances Used as Calorimetric References[a]

wavelength[b]	medium[c]	compound[d]	ref(s)
308	ethanol	anthracene	96
308	ethanol	fluorenone	96
308	ethanol	xanthone	96
308	ethanol	bis(*o*-methylstyryl)-benzene	96
308	CH_3CN, benzene, alcohols	pyridazine	98
308	CH_3CN	dicumarol	98
308	CH_3CN	8-quinolinol	98
308	CH_3CN	naphthalene	98
300–370	organic	α-OHBP[e]	57,100
300–550	organic	ferrocene	65,100
320,355	organic	α-aminoBP[e]	100
320	organic	OXA6	100
355	organic	OXAM18	100
320,355	organic	Feacac	100
320,355	organic	PNDNA	100
400–800	nonpolar organic	carotenes	62
530–560	nonpolar organic	CoTPP	62
450–550[f]	nonpolar organic	I_2	62,101
435–715	CH_3CN	azulene	98,110
520–600[f]	CH_3CN	crystal violet	98
355	CH_3CN/H_2O	BP[e] + KI	55,100
355	H_2O/ethanol	$K_2Cr_2O_7$	102
355	buffer	*meso*-TPPS	103
365	aqueous	Na_2CrO_4	66,96
365	aqueous	$FeCl_3$	96
405–505	aqueous	$Na_2Cr_2O_7$	66
405–505	aqueous	$Fe(bpy)_3Cl_2$	66
$\lambda > 450$	aqueous	Cu(II) and Co(II) salts	104,105
480–560[f]	aqueous	$MMnO_4$ (M = Na, K)	
500	aqueous	bromocresol purple	77,80
620	buffer (pH 1.8–13)	malachite green	106

[a] Not every compound listed promptly releases all the absorbed light energy as heat. For details on the use of the references see section entitled "Calorimetric References" and literature quoted. [b] As reported by authors; the wavelength range of application may be much wider. [c] As reported by authors; the range of solvents may be much larger. [d] For the complete names of the compounds see text (Calorimetric References). [e] BP stands for benzophenone. [f] Range defined by the absorption band.

centers). Deoxymyoglobin has been used as a quasi-internal reference for the time-resolved calorimetric study of the photodetachment of CO in carboxymyoglobin.[82,108]

In some cases, properties of triplet states have been determined by performing photothermal measurements in oxygen-free media, then in the presence of oxygen. Since oxygen quenches the triplet state an internal calorimetric reference is formed.[82] By this procedure, singlet molecular oxygen, $O_2(^1\Delta_g)$, is produced which owing to its relatively long lifetime in most solvents acts as an efficient energy-storing species.[109] In fact, photothermal methods have been applied to the accurate determination of yields of formation and lifetimes of $O_2(^1\Delta_g)$ [see section entitled "Singlet Molecular Oxygen, $O_2(^1\Delta_g)$"]. Therefore, the use of O_2-quenched solutions as calorimetric references is limited to cases in which the heat-integration time is longer than the lifetime of $O_2(^1\Delta_g)$.

When performing temperature-dependent photothermal studies in order to derive values of molecular volume changes (see previous section), the possible temperature dependence of the photophysical parameters of the calorimetric reference should be checked.

As already pointed out, when applying TRTL for the determination of short lifetimes (nanoseconds to microseconds) and/or yields of production of energy-storing species, there is no need to use a calorimetric reference.[16] However, when using the same method for the determination of lifetimes on the order of the thermal-diffusion time in the medium, a calorimetric reference is required in order to determine the latter time and correct for it.

Calorimetric references having ultrafast radiationless deactivation should be used for thermal grating. Andrews and Hochstrasser used azulene for this purpose, when studying the quantum yield of radiationless deactivation of iron(III) tetraphenyl chloride in $CHCl_3$ by thermal grating with 5-ps time resolution.[110]

6. Excited Singlet States

6.1. Fluorescence Quantum Yields and Spectra

When no chemistry takes place (third term in the right hand side of eq 1 is zero), conventional calorimetry can be utilized, employing a thermistor to detect the heat produced through relaxation from excited states,[111] thus deriving precise values of the product $\Phi_f \cdot E_f$. The measurements are rather tedious and the sensitivity is low.

On the other hand, the last term on the right hand side of eq 1 is dropped when time-resolved techniques are applied to systems which do not undergo a photochemical reaction upon irradiation, i.e., when $\Phi_{st} \cdot E_{st} = 0$, or when the lifetime of the energy-storing species, τ_{st} is much shorter than the time resolution. Consequently, the product $\Phi_f \cdot E_f$ is obtained from the evaluation of α by measuring the ratio of the heat evolved by the sample to that evolved by a calorimetric reference (see section entitled "Calorimetric References"). Since the value of E_f is in the general case readily derived from the weighted average fluorescence frequency, precise values of Φ_f are obtained by this procedure.

The inherent experimental limitations in the determination of absolute Φ_f values by other more conventional methods have been thoroughly discussed in a review by Demas and Crosby.[112] These include refractive index differences between sample and reference fluorophore solutions, reabsorption and reemission phenomena, and polarization considerations. Photoacoustic and photothermal techniques avoid the kinds of errors common to the detection of emitted light. However, as indicated by Magde et al. for the case of thermal lensing,[113] photothermal methods are not the methods of choice for the determination of $\Phi_f < 0.25$. Below this value the error may exceed 20%, due to the differential nature of the method.

Photothermal experiments have been applied to determine values of Φ_f that are either difficult or impossible to measure accurately by optical methods. In addition, since the yield obtained is absolute it can be used as a reference value. In particular, for fluorophores emitting in the far-red end of the spectrum, these are the only experiments delivering reliable yields since in this region the calibration of emission spectra with standards is difficult.[62] The earliest methods used were steady-state thermal lensing (also called thermal blooming)[39,54,113-115] and optoacoustics.[116,117]

The technique of steady-state thermal lensing is based on the deflection of a cw beam due to the variation of n resulting from the temperature rise in the volume irradiated by a cw beam (the same beam as used for monitoring the variation in n or another one). With this excitation method, frequently combined with low-frequency ($f < 100$ Hz) amplitude modulation and lock-in detection (as a way to improve the S/N ratio), Φ_f is obtained even if relatively long-lived transients are formed, provided that $\tau_{st} \ll 1/2\pi f$ and the transients return to more stable products releasing their higher energy content as heat.

The more sophisticated time-resolved methods developed later give essentially the same information with respect to Φ_f. The Φ_f values for standard dye molecules such as rhodamine 6G, rhodamine B, and fluorescein, measured by LIOAS, were in excellent agreement with those measured by conventional optical methods. This was very encouraging and it established photothermal techniques as reliable for such measurements.[116,117]

Some recent reports have cautioned users of the thermal lens method for Φ_f determination to beware of errors associated with solute dependences of the signal, even after corrections for absorbed energy, luminescence, and photochemical reactions.[118,119] In order to explain their results, Terazima and co-workers advanced a hypothesis based on a vibrational mode dependence of the vibrational to translational energy transfer for benzene vs carbon tetrachloride,[118] although a recent study examining solvent effects on the photoacoustic signal production revealed a predictable behavior for both of these solvents, on the basis of the linear relationship between the signal and a term containing the thermoelastic properties of the solvents.[68]

Chartier found deviations from expected signals for compounds exhibiting high intersystem crossing yields and raised questions about principle differences between equilibrium and nonequilibrium thermal lens measurements.[119] A recent study examined the effect of excited-state proton transfer on the apparent value of Φ_f for fluorescein, as measured by thermal lensing. The intensity of the fast-heat release varied with acid concentration in pH regions where the ground- and excited-state proton transfer was expected to take place during the production of the fast heat. The fluorescence properties should therefore not be those of the initially excited species, but rather those of the deprotonated species. This phenomenon does not seem to operate in highly acidic or basic conditions.[120]

As discussed in the section entitled "Calorimetric References", the optoacoustic equipment must be calibrated in order to determine the value of α in eq 1. A convenient and commonly used alternative to internal or external calorimetric references for molecules that deactivate only either by fluorescence or by internal conversion takes advantage of the general validity of Kasha's rule of internal conversion from upper excited states. Since the probability of internal conversion from these states is unity for the great majority of molecules, the variation of excitation energy can be used to determine K (see eq 11) and, subsequently, Φ_f. However, the validity of Kasha's rule should be checked for each new system. In case the rule is validated, the absorbed energy must be corrected so that an equal number of photons is absorbed by the sample at each wavelength. This procedure was applied using amplitude-modulated photoacoustic spectroscopy (PAS).[121]

Cahen and co-workers presented an important extension of this type of PAS data analysis by calculating the heat-dissipation spectrum, i.e., the heat dissipated as a function of λ_{exc}. In spectral regions where Φ_f/λ_f is constant, this relationship is linear, and extrapolation of this plot to zero dissipation gives a more accurate determination of Φ_f than a measurement at a single wavelength.[122] An energy balance equation was used, $\rho/a = f(1 - (\Phi_f/\langle\lambda_f\rangle)\lambda)$, correlating the PAS signal, ρ, with Φ_f. a is the fraction of light absorbed in that part of the sample which participates in the generation of the photoacoustic signal, f is an instrumental factor, and $\langle\lambda_f\rangle$ is the mean fluorescence wavelength.[122] This method is only applicable to systems in which the triplet and photochemical yield are zero or are known across the spectral range under study.

The determination of a in the above mentioned equation is critical and is dependent on the proper evaluation of the thermal-diffusion length of the sample, which in PAS is related to the thermal diffusivity, the thermal conductivity, the density, and the heat capacity of the sample, as well as the pulsing frequency. If the thermal-diffusion length is known to be less than the optical pathlength, the measurements remain valid. Photoacoustic saturation occurs when high fluorescence quencher concentrations are used, diminishing the optical pathlength and leading to low signals and, accordingly, to Φ_f values which are too high. This error is cancelled when the value of Φ_f is determined from extrapolation of the heat-dissipation spectrum. Effects of this kind and suggestions as to their minimization were discussed.[123] The use of higher modulation frequencies for samples with photoacoustic properties near the saturation condition can reduce the optical pathlength sufficiently to provide satisfactory results, although the signal intensity suffers through such a procedure.[123] Görtz and Perkampus observed a reduction in PAS signal intensity as the thickness of PVA sample films containing organic dyes was reduced below 15 μm, also due to a shortened optical pathlength with respect to the thermal pathlength.[124]

The technique described above, which measures the heat emission as a function of the photon energy, was used by the group of McGlynn to measure Φ_f for the S_2 emission of azulene in the gas phase, making use of the nonemissivity of the S_1 state. The laser-induced optoacoustic measurements yielded a Φ_f value between 0.00 and 0.06, in good agreement with other techniques. This study is important from a practical viewpoint, a boxcar integrator having been used together with a rather modest electronic apparatus to obtain a very high quality photoacoustic fluorescence excitation spectrum. It was also demonstrated that the photoacoustic spectrometer is considerably more sensitive (a factor of 10^6 is estimated by the authors) than conventional spectrophotometers and exhibits improved resolution (approximately 10-fold).[125]

Rothberg et al. also obtained a heat-dissipation spectrum using pulsed-laser excitation and derived previously unknown Φ_f values of several dye molecules in solution as well as previously unmeasurable yields of dyes absorbed on sapphire.[126]

By using deconvolution methods applied to the optoacoustic waves, values of Φ_f were derived for anthracene, azulene, 2,5-diphenyloxazole, and pyrene, as well as for several fluorescent markers for proteins.[127] Good results were obtained for the first three com-

Table III. Fluorescence Quantum Yields from Photothermal Techniques[a]

compound	medium	Φ_f	ref
rhodamine 6G	water	0.96 ± 0.02	117
rhodamine 6G	PVA film	0.85	124
rhodamine 6G	PMMA[b]	0.93 ± 0.04	129
rhodamine B	PVA film	0.80 ± 0.02	124
rhodamine B	ethanol	0.66	116
rhodamine 640	methanol	0.98 ± 0.01	126
fluorescein	0.01 N NaOH	0.93 ± 0.03	122
fluorescein	PVA film	0.83	124
acridine orange	PVA film	0.55	124
eosin	PVA film	0.75 ± 0.02	124
oxazine 720	methanol	0.70 ± 0.03	126
fluorol 555	methanol	0.68 ± 0.04	129
fluorol 555	PMMA[b]	0.88 ± 0.03	129
crystal violet	water	0.02 ± 0.10	121
crystal violet	glycerol	0.0087 ± 0.0006	113
cresyl violet	glycerol	0.53 ± 0.03	113
cresyl violet	nitrobenzene	0.54 ± 0.03	113
cresyl violet	methanol	0.54 ± 0.04	113
azulene	ethanol	0.04 ± 0.01	127a
PPO[c]	ethanol	0.89 ± 0.03	127a
anthracene	ethanol	0.22 ± 0.06	127a
prodan[d]	cyclohexane	0.26	127b
prodan[d]	chloroform	0.67	127b
prodan[d]	acetonitrile	0.70	127b
prodan[d]	ethanol	0.70	127b
prodan[d]	methanol	0.57	127b
acrylodan[e]	ethanol	0.01	127b
dansyl glycine	buffer[f]	0.12	127b

[a] Errors as reported by authors. [b] Poly(methyl methacrylate). [c] PPO, 2,5-diphenyloxazole. [d] Prodan, 6-propionyl-2-(dimethylamino)naphthalene. [e] Acrylodan, 6-acryloyl-2-(dimethylamino)naphthalene. [f] 20 mM MOPS, 150 mM KCl, pH 7.0.

pounds which exhibited simple fluorescence-decay kinetics. For pyrene, exhibiting complex kinetics including a relatively long decay, the analysis did not yield satisfactory results.[127]

The fluorescence efficiencies of two newly synthesized rhodamine derivatives, in which the amino groups were fixed in five- and six-membered rings, were measured by thermal blooming. The six-membered-ring compound showed improved performance over rhodamine 6G in continuous dye laser application. Several other trichromophoric derivatives containing 2,5-diphenyloxazole substituents were similarly investigated.[128]

Luminescent properties of Fluorol 555, a dye with potential as a solar energy collector, were investigated in methanol and in poly(methyl methacrylate) (PMMA) polymer matrix. In the matrix, Φ_f was found to increase to 0.88 ± 0.03 as compared to methanol (0.68 ± 0.04). Rhodamine 6G showed a Φ_f in PMMA matrix (0.93 ± 0.04) which agrees well with values in solution.[129]

Table III gives Φ_f values determined with both steady-state and time-resolved photoacoustic and photothermal methods.

Photothermal techniques also permit the determination of the fluorescence excitation spectra since the signal intensity varies with excitation wavelength as an inverse function of the relative contribution of fluorescence, producing an action spectrum of heat evolution. These experiments often give a unique opportunity to obtain such spectra in the presence of species with competing absorption. The work of Cahen et al. using PAS also demonstrates the utility of the heat-dissipation spectrum method of data analysis for the detection of fluorescence from species with similar emission characteristics (an example of the dimerization of cresyl violet in glycerol was given).[122] Bonch-Bruevich et al. used the heat-dissipation spectrum obtained with pulsed excitation to derive the fluorescence-excitation spectrum of two-photon emission from polymethine dyes and from anthracene.[130]

The effect of aggregation on the spectroscopic properties of zinc phthalocyanine derivatives was studied using several spectroscopic techniques including steady-state thermal lensing. With this technique it was shown that a reduced total Φ_f resulted upon increasing water content in DMF solutions. The addition of water is known to lead to the formation of nonfluorescent aggregates; therefore, the reduction in overall fluorescence was ascribed to the lack of emission from the aggregates. It was independently shown in this study that the spectroscopic properties of the monomer are invariant with respect to solvent composition and the presence of aggregates.[131]

Both the Φ_f values and thermal-lensing signals of various anthracene derivatives were found to be higher when in micelles, by a factor of ten in some cases. These effects were assumed to arise from different mechanisms. The Φ_f enhancement was postulated to arise from a combination of increased local viscosity inside the micelles and protection of the fluorophores from quenchers, while the TRTL signal enhancement was attributed to the isolation of the emitter in a hydrophobic environment where a more sensitive response of the refractive index to changes in the local temperature is expected.[132]

In contrast to this proposal, Redmond suggested that the local environment of the chromophore has little influence on the LIOAS signal intensity, and that the acoustic properties of the bulk phase dominate the acoustic wave propagation. From studies of rose bengal-sensitized production of $O_2(^1\Delta_g)$ in reverse micelles, the author concluded that there is potential for the use of calorimetric references in the nonaqueous phase of the reverse micelle solution and simultaneous determination of heat release from the sample in the aqueous interior, provided that the interior of the reverse micelle is large enough for its aqueous phase to approximate bulk water. Otherwise, the photophysics may be considerably affected.[102]

Several groups have studied the behavior of solid-state materials with the use of photoacoustic and/or photothermal detection. Although most of this work lies outside the scope of this review, some of the results are of general interest. Strauss and co-workers studied lasing materials such as Cr^{3+} species and measured Φ_f values of these substances as well as the excited-state cross sections by PAS in efforts to quantitate lasing emission performances.[133,134] The luminescence of F_2^+ and $(F_2^+)_H$ color centers in NaCl:OH^- crystals was studied using LIOAS. Both types of centers have very similar luminescence. The conclusion was that the oxygen impurities which are associated with the latter centers and greatly increase their stability do not significantly quench their fluorescence.[135]

6.2. Singlet Lifetimes

Picosecond pulses were used in conjunction with photoacoustic detection to probe the singlet lifetimes and cross sections of rhodamine dyes,[72] the singlet lifetimes of the stilbenes, and the stimulated emission cross sections of benzophenone and coumarin 485.[71] By varying the time delay between two picosecond pulses, the measurement of a fast relaxation process is principally limited by the uncertainty in the delay between pulses and by the pulse width. Heritier and Siegman[72] found the excited-state cross section of rhodamine 6G not to be in agreement with that found by Starobogatov[136] or Penzkofer and Wiedmann.[137] It was speculated that the experiments were not comparable and that beam misalignment may be the source of error.[72] While the claim that picosecond photoacoustic techniques will outperform optical detection at low concentrations and pump powers may be true, the number of papers published along these lines in recent years is too few in order to make general assessments.

One such study using picosecond optical calorimetry was recently reported by Zimmt's group who treated the solvent dependence of the relaxed singlet-state energy for tetraphenylethylene. The singlet energy of 280 ± 5 kJ/mol in alkane solvents was reported and the volume of the singlet-excited state was ca. 30 cm^3/mol smaller than the ground state, indicating an increase in alkane–tetraphenylethylene interactions in the twisted excited state. Although the reported differences in the singlet energy in alkanes vs other solvents are within the error limits, the magnitude of the dipole moment (6 D) resulting from the analysis of this data with a dielectric continuum model, suggested that the twisted excited singlet state of tetraphenylethylene is a zwitterion.[95]

7. Triplet States

In the case that intersystem crossing (ISC) is significant, the triplet state can be probed by photothermal techniques, unless the phosphorescence quantum yield is high, in which case heat release is minimal. Since LIOAS (LIOAC, PAC) and TRTL (as well as PBD) experiments are sensitive to processes having lifetimes as short as ca. 15 ns, they can be used to measure kinetic and calorimetric properties of many triplet states directly (see section entitled "Time Resolution").

All photothermal techniques are subject to constraints, requiring specific knowledge of the photochemistry of the system. As already pointed out, the measured quantity is the product $E_{st}\cdot\Phi_{st}$ ($E_T\cdot\Phi_{isc}$ for the case of formation of a triplet state), summed over all such heat-releasing processes, as discussed in the section entitled "Energy Balance" (eq 1). In the examples described below, Φ_{isc} values were calculated from the triplet energies (E_T) measured in most cases from 0–0 phosphorescence bands. Conversely, values of E_T were evaluated from measured or estimated Φ_{isc} data. Triplet lifetimes, τ_T, may be simultaneously obtained from these techniques, and experiments designed to determine this parameter as a primary goal will be treated as a separate subject.

For the simple case of the formation of a triplet state from the singlet with unit efficiency, the heat released during ISC to the lowest triplet generally occurs within a few nanoseconds. Thus, it is measured as a prompt response to the excitation pulse. Using LIOAS (LIOAC and PAC) the energy stored by the triplet is readily calculated from the input energy and a comparison with the heat given off by an appropriate reference solution (eq 12). Should the triplet enter onto reaction pathways other than nonradiative relaxation (product formation, phosphorescence, triplet–triplet annihilation), the quantum yields of the various processes must be known, along with the energy and lifetime of the subsequently formed species. Various assumptions can be used, as mentioned in the next sections. As earlier discussed, if the laser is resonant with electronic absorption bands of species directly or indirectly produced by the laser pulse, fluence-dependent experiments should be performed, and extrapolation to zero fluence should be made. This kind of measurement is standard procedure for the method based on amplitude measurement in LIOAS, as well as in TRTL.

7.1. Intersystem Crossing Yields

As was pointed out by Carmichael and Hug,[138] the measurement of Φ_{isc} is hampered by experimental constraints associated with the determinations of transient molar absorption coefficients.[139] With the advent of photothermal techniques, a new independent method for the determination of Φ_{isc} became available. The E_T value is generally determined from phosphorescence measurements at room or low temperature. Callis et al. recommended the use of an average of the energies of the 0–0 bands of the $S_0 \rightarrow T_1$ absorption and the $T_1 \rightarrow S_0$ emission, since the desired value is the energy of the triplet above the ground state, not the average energy of phosphorescent photons.[3] The method of heavy-atom perturbation of the $S_0 \rightarrow T_1$ absorption can also be used to determine the value of E_T, although this spectroscopic E_T value can vary substantially from the relaxed value in cases where the molecule undergoes a large geometrical distortion in the excited state.[140]

The use of photothermal methods, in particular with acoustic detection, to study the properties of excited triplet states was first described in 1968 using PAS.[2] The relaxation of eosin through the triplet state was studied using the E_T value from phosphorescence, thereby determining an Φ_{isc} value of ca. 1 and $\tau_T = 100$ ms.[2] The values of Φ_{isc} for anthracene and acridine orange were similarly determined by Callis et al.[3]

Φ_{isc} of several standard organic compounds (anthracene, acridine, phthalazine, and quinoxaline) were measured with LIOAS comparing the signals produced by deaerated and air-saturated solutions. Although this method induces the formation of $O_2(^1\Delta_g)$ with a long lifetime (see corresponding section), the calculation used cancelled this contribution. Consequently, there is no effect of various efficiencies and mechanisms of oxygen quenching in this study.[141]

Approximately similar values of Φ_{isc} (ca. 0.47) for phthalazine in ethanol and benzene were measured with TRTL with a time resolution of 200 ns, but the τ_T values were 2.7 μs in benzene and 11 μs in ethanol. The authors suggested that the $n \rightarrow \pi^*$ triplet which is stabilized in nonpolar solvents is generally nonphosphorescent for orthodiazaaromatics, an effect which is presumably due to mixing of $n\pi^*$ and $\pi\pi^*$ states in such solvents.[17] This conclusion was supported by EPR measurements which indicate a heavily mixed triplet character for phthalazine.[142] The Φ_{isc} value agreed well with a determination made using a sensitized isomerization method (0.43)[143] but was lower than a value measured using

LIOAS (0.69).[141] The authors declined to comment on possible reasons for the discrepancy.

Φ_{isc} was determined by TRTL for *N*-methyl-*p*-nitroaniline in a solid matrix of poly(methyl methacrylate),[144] as well as for pyridazine in hydrocarbon solvent at 60 K (0.66).[145] A slow component in the signal at low temperature was observed which was not present at room temperature. However, the concentration of pyridazine was not reported and the question of self-quenching and possible subsequent intermediate formation leading to the low-temperature signal was not addressed.

The advantage of non-optical detection for use with poorly emitting molecules was utilized in a Φ_{isc} determination for pyridine by a two photon TRTL technique.[146] For pyridine at room temperature $\tau_T = 1.0 \pm 0.3$ μs was determined, similar to the phosphorescence lifetime in the gas phase at room temperature.[147] The high value of $\Phi_{isc} = 0.9$ at room temperature in solution as compared to the gas-phase value (0.3–0.5)[148] was attributed to collisional enhancement of the intersystem crossing process.

The triplet–triplet absorption spectrum of anthracene was determined with TRTL,[149] in good agreement with the spectrum obtained by optical absorption spectroscopy.[150] Terazima and co-workers have also recently begun using transient thermal grating techniques for the determination of Φ_{isc} of several aromatic molecules with short τ_T. The authors point out the difficulties in determining long-lived (microsecond) triplets with this technique.[151]

LIOAS was applied to the determination of the Φ_{isc} of chromium compounds by Endicott and his group.[152] Upper excited-state processes with lifetimes of 15–100 ns were postulated to occur for some of these compounds, on the basis of two observations: (1) the Φ_{isc} value was >1, in other words, more energy was released by the compound studied than by the reference, which is indicative of absorption by some intermediate species, and (2) a slight time shift of the maximum of the signal for $Cr(4,7\text{-}Ph_2phen)_3$ vs $Cr(phen)_3$. The overall complexity of the state diagram, as revealed by 30-ps pulse absorption experiments,[153] indicates that LIOAS with 15-ns pulses is not the method of choice for such investigations. This line of investigation was extended to a variety of ammine ligands which affect the photophysical processes of the central metal.[154] The conclusions about the upper excited-state processes would be much better supported by a study in which the absorption spectra of the excited states were determined. It is also not clear which values for the energy content of the excited state were used to calculate the values of Φ_{isc}.

The Φ_{isc} value for porphycenes was determined by LIOAS using a value of E_T derived from the room temperature near-IR phosphorescence of these low-triplet energy compounds which are potential candidates for application in tumor treatment. The Φ_{isc} values were subsequently used to calculate the triplet-minus ground-state absorption coefficients for porphycene and its tetra-*n*-propyl derivative, overcoming the problems usually found for the determination of these properties from optical data.[62]

Scaiano and co-workers used LIOAC to measure Φ_{isc} of α-terthienyl (a botanical phototoxin) as being between 0.9 and 1.0, allowing for generous error limits. These results were combined with the $O_2(^1\Delta_g)$ production yields, Φ_Δ, determined by oxygen phosphorescence in order to derive the efficiency of $O_2(^1\Delta_g)$ formation relative to the total collision deactivation of the triplet by $O_2(^3\Sigma_g^-)$ which is 0.6–0.8 in both polar and nonpolar solvents.[155]

A recent report from Scaiano's group described the application of a triplet quencher in order to separate the triplet contribution from contributions due to radical or radical ion formation, even if the yields and energetics of such processes are not known.[61] The validity of such an internal calibration technique depends on the assumption that the triplet quencher (0.05 M 2,5-dimethyl-2,4-hexadiene in this case) reacts negligibly with the additional species present. Should the triplet be the precursor of such species, this assumption would no longer be enough to ensure meaningful results.

7.2. Triplet Lifetimes

Although transient optical spectroscopy is generally better suited to the determination of τ_T values, there are numerous examples in which the species of interest absorbs weakly, its electronic absorption band is masked by other species present in the sample, or the medium is too strongly absorbing or scattering. In this case, photothermal techniques can be of use. The issue of time resolution in these techniques was treated in an earlier section.

Strauss and co-workers used high-frequency modulation (up to 10 kHz) to obtain τ_T of erythrosin in glycerol using PAS.[156] The dependence of the slow-heat release on the modulation frequency and the phase of the photoacoustic signal was used to calculate τ_T, which was found to decrease with increasing dye concentration. The low-concentration lifetime was measured to be ca. 380 μs. The derived rate constant was consistent with an energy-transfer process involving either Förster-type energy transfer or diffusional self-quenching, although the observed exponential phosphorescence decay supports the latter assignment.[156]

A similar approach specifically designed for highly absorbing systems with long (millisecond) metastable species was applied to the triplet lifetimes of acridine orange in various media in the absence and in the presence of oxygen.[31] This paper includes an involved theoretical treatment of the PAS signal parameters (phase and amplitude).

Poly(vinylidene fluoride) (PVF_2) acoustic detectors were applied to the determination of τ_T of benzophenone after laser-pulse excitation of the solutions using the right-angle configuration detection, and a method of variation of τ_a' as a function of laser-beam radius (*R* as discussed in the section on the temporal behavior of pressure changes). A time resolution of 30 ns was derived as well as an accurate determination of the lifetime of the energy-storing species, without the need of convolution techniques.[55]

Shortly thereafter, Eyring and co-workers published a TRTL study of benzophenone quenched by KI and attained ca. 100-ns time resolution using the method of determining τ_T with a constant laser-beam diameter.[18] The authors of this study indicated that it should be possible to time resolve the thermal lens signal down to the τ_a limit, ca. 30 ns for the particular setup used. They also compared TRTL and LIOAS for the same system and concluded that for lifetime estimations the former method is easier to handle and requires no changes in the pump-beam diameter as in previous determinations[55] or complex convolution procedures as in former work.[83] Having a larger dynamic time range (from nanoseconds to milliseconds),[157] TRTL should become more widely applicable, when feasible. This is so provided that ground state and transients are transparent to the probe beam and the sample is clear (no high scattering), as already pointed out.

Further improvements in time resolution (for 1,1-bis(*p*-bromophenyl)ethylene (τ_T = 7.5 ± 0.2 ns was determined) were recently reported by Arnaut, using a ceramic detector and a front-face-type cell.[68]

The τ_T of erythrosin was determined by TRTL and consideration was given to the abnormal signals produced by the absorption of the probe beam by triplets produced in high yield by the pumping laser. The shape and amplitude of this additional signal, superimposed on the normal thermal-lens signal, is governed by the quenching of triplet erythrosin by oxygen.[158] (See section entitled "Singlet Molecular Oxygen, $O_2(^1\Delta_g)$".)

The triplet state of C_{60} (buckminsterfullerene), studied by TRTL, was found to be efficiently populated and decayed essentially nonradiatively to the ground state with τ_T = 49 μs in degassed benzene.[159]

Transient thermal grating with nanosecond pump pulses was used for the first time for the determination of τ_T. The method was fully described, its advantages and disadvantages were compared with other photothermal methods, and it was applied to well-understood systems like benzophenone, quinoxaline, phthalazine, phenazine, and anthracene.[151]

7.3. Triplet Energies

One of the most basic questions in physical organic chemistry is the shape of various potential energy curves in the excited states of simple molecules. Much experimental and theoretical work has been devoted to the connection of geometrical and energetic parameters on upper potential surfaces of stilbene and styrene, for example. Perhaps the most obvious success of LIOAS in this regard is the accurate determination of the relaxed E_T values for various alkenes, as a function of rigidity and substitution. This method now overcomes reliance on low-temperature phosphorescence energy determinations for molecules with known Φ_{isc}.

The relaxed energy of the 1-phenylcyclohexene triplet was the first measured by laser-induced optoacoustic methods.[65] This line of investigation was extended with a report of the relaxed E_T of the stilbenes, several dienes, and some cyano-substituted alkenes to a precision of 8–17 kJ/mol and of 2–4 ns in τ_T, as obtained by deconvolution of signals from a ceramic detector. The effect of cyano substitution was shown by comparison of fumaro- and acrylonitrile, the former compound having a value of E_T 42 kJ/mol lower than that of the latter.[160]

A more complete study was that of Ni et al.,[140] who looked at a rather large selection of alkene triplets and compared their relaxed E_T values to the spectroscopic (unrelaxed) E_T's as measured by oxygen or external heavy atom perturbation. With the time resolution of ca. 20 ns obtained with the front-face reflection cell, the reported precision was often better than 4 kJ/mol for τ_T > 50 ns. These data yield accurate relaxed E_T values which are in many cases, the first direct experimental results. The results provide a consistent picture of E_T lowering through twisting about the double bond, with values ranging from 176 kJ/mol for *cis*-stilbene, to 273 kJ/mol for indene.[140]

The results presented here bear on several important issues in physical organic chemistry. For example, the *trans*-stilbene E_T = 194 ± 4 kJ/mol is 10 kJ/mol higher than that measured by triplet quenching.[161] This upward revision in the relaxed triplet energy shows that the conclusion, the S_0 and T_1 surfaces must cross at 90° twist of the central bond, is unwarranted.

Comparison of the relaxed E_T values for 2,5-dimethyl-2,4-hexadiene with the spectroscopic E_T from O_2 perturbation spectra showed a difference of 29 kJ/mol, suggesting substantially different relaxed T_1 and S_0 geometries. Coupled with the observation that energy-transfer rates from several high-energy donors to this diene have been observed to be lower than those predicted from exothermicity alone, the hypothesis was raised that these lower rates are due to the substantial geometry changes which must take place for the donor or acceptor.[162,163]

These E_T values, when compared to the new Benson group equivalent estimates[164] for the energies of the corresponding 1,2-biradicals, support the hypothesis that the alkene triplets are well modeled by such species.[140] Such a model had been used to successfully predict the activation energy for the isomerization of various alkenes[165] and appears to be even more accurate in predicting the thermodynamic parameters of biradical sites even further removed than vicinal.[166]

Caldwell's investigations into the stability and reactivity of several strained cyclic alkenes produced through the benzophenone sensitized triplet state led to the determination of the E_T's of 1-phenylcyclohexene,[65] 1,3-cycloheptadiene, and 1-phenylcycloheptene.[167] The relaxed E_T value for 1-phenylcycloheptene (221 kJ/mol) was found to be quite similar to that of acyclic styrene derivatives, as expected from the flexibility of the molecule, whereas the 1-phenylcyclohexene E_T was 236 kJ/mol, approximately 15 kJ/mol higher than for the acyclic analog. 1-Phenylcyclopentene has an E_T = 247 kJ/mol reflecting its even greater rigidity with respect to twisting around the double bond. These data can be interpreted in terms of an energy lowering along the triplet potential surface as a function of C=C twist angle. The strain energies of the corresponding metastable trans ground-state species were simultaneously determined or estimated and are presented in the appropriate section.[167]

Further extensions of LIOAS into the field of mechanistic organic photochemistry were reported by examining the values of E_T for α,β-unsaturated cyclic ketones as a function of alkyl substitution pattern.[162,168] These triplets were generated via direct irradiation and are formed with unity efficiency. Analogous to the alkene triplets, a correlation was found between structural rigidity and relaxed E_T. The results also show that the small but real solvent effects on τ_T of such molecules, as detected by transient absorption spectroscopy,[169] are extremely well reproduced in the optoacoustic exper-

Table IV. Relaxed Triplet Energies from Photothermal Measurements[a]

compound	solvent	E_T (kJ/mol)	ref
anthracene	cyclohexane	179 ± 5	140
naphthalene	cyclohexane	249 ± 1	140
benzophenone	acetonitrile	285 ± 1	140
benzophenone	benzene	289 ± 2	68
biphenyl	carbon tetrachloride	280 ± 2	198
styrene	cyclohexane	214 ± 8	140
trans-stilbene	cyclohexane	194 ± 4	140
cis-stilbene	cyclohexane	176 ± 6	140
1,1-diphenylethylene	cyclohexane	218 ± 8	140
1-phenylcycloheptene	methanol	221 ± 5	167
1-phenylcyclohexene	cyclohexane	236 ± 3	140
1-phenylcyclopentene	cyclohexane	247 ± 1	140
2-cyclohexenone	acetonitrile	262 ± 4	168
2-cyclopentenone	cyclohexane	306 ± 5	68
testosterone acetate	acetonitrile	294 ± 3	168
3-phenyl-2-cyclohexenone	acetonitrile	229 ± 1	168
fumaronitrile	acetonitrile	201 ± 13	160
acrylonitrile	acetonitrile	242 ± 17	160
1,3-cyclohexadiene	acetonitrile	213 ± 4	160
buckminsterfullerene (C_{60})	toluene	150 ± 3	172
buckminsterfullerene (C_{60})	benzene	157 ± 4	173
anthanthrone	toluene	155 ± 7	176
anthanthrone	benzonitrile	134 ± 7	176

[a] Errors reflect statistical analysis and not the errors of the underlying photochemical assumptions.

iment. An unsuccessful attempt was made in this study to detect a putative metastable ground state *trans*-2-cyclohexenone which had been implicated in the [2+2] photocycloaddition of 2-cyclohexenone to alkenes,[170,171] although such a species would not have been detectable had its lifetime been similar to that of the triplet state (ca. 25 ns) from which it would logically be derived. E_T and τ_T of 2-cyclopentenone were recently reported as 306 ± 5 kJ/mol and 116 ± 14 ns, respectively, at an enone concentration of 6.0 mM, corresponding to a sample absorbance of 6×10^{-4} at the excitation wavelength.[68] This E_T value was previously unmeasurable due to sensitivity problems.

Two groups recently used photothermal techniques to determine the value of E_T for C_{60} (buckminsterfullerene). Using PAC, values of 150 ± 3 kJ/mol in toluene[172] and 157 ± 4 kJ/mol in benzene[173] resulted, in agreement with bracketed values determined previously[174] and similar to the value (170 kJ/mol) determined from low-temperature phosphorescence.[175] From the high Φ_Δ value and the lack of fluorescence, the authors concluded that $\Phi_{isc} = 1$. Terazima et al.[173] additionally investigated the T–T absorption spectrum which displays a large maximum at 750 nm.

Lower limits for E_T of anthanthrone in toluene and benzonitrile were determined using LIOAS to be 155 ± 7 kJ/mol and 134 ± 7 kJ/mol, respectively. These values represent lower limits since $\Phi_{ic} = 0$ was assumed. On the basis of the values of $\Phi_f = 5 \times 10^{-3}$ and 2×10^{-3} determined in toluene and benzonitrile, respectively, a value of $\Phi_{isc} = 1$ (within the experimental error of the LIOAS measurements) could be assumed.[176]

Table IV gives a list of relaxed E_T values determined by photothermal methods.

8. Reactive Intermediates

The application of photothermal techniques to the measurement of the properties of reactive intermediates other than excited states is beginning to become widespread. Radicals, biradicals, ion pairs, radical ion pairs, and carbenes have been studied by these types of techniques. As long as the yields are known with some accuracy, the energies and lifetimes of these species can be obtained from an equation analogous to eq 12. This is often the only method which can give this information, since optical detection is frequently inapplicable to these species.

8.1. Radicals and Biradicals

Di-*tert*-butyl peroxide photolysis, the chain-initiating reaction in numerous radical studies, was investigated using TRTL. Rates of hydrogen abstraction reactions by di-*tert*-butoxyl radical with toluene and cyclohexane were determined to be 7×10^4 and 3.6×10^5 M^{-1} s^{-1}, respectively.[177] These radical pairs live for microseconds and the associated decays do not contribute to the prompt thermal signal.

Laser-induced photoacoustics was first used to study radical processes by Rothberg et al.[97] in an analysis of the hydrogen atom abstraction from aniline by benzophenone triplet, initially producing the radical ion pair, which decays to the radical pair within the instrumental response time. The heat of reaction to form this radical pair was found to be 192 ± 21 kJ/mol, agreeing with the calculated enthalpy of reaction, 188 kJ/mol. This paper, containing a thorough presentation of the relevant general theoretical derivation, also pointed out the useful range of detection in the short- and long-lived species cases. Several problems with this early work have been recognized. Formation of $O_2(^1\Delta_g)$ as energy-storing species, an efficient process for several of the calibration compounds used,[15] was overlooked. In addition, the relatively high laser fluences used (100 μJ) raise the question of two photon processes, which were shown to be operative in thermal lensing studies of benzophenone.[98]

The energy (272 ± 12 kJ/mol) and lifetime (85 ± 10 ns) of the triplet 1,4-biradical obtained from the intramolecular hydrogen abstraction in valerophenone, as well as the enthalpy of reaction (75 ± 25 kJ/mol) for the Norrish type II photocleavage of valerophenone to acetophenone and propene were determined in a study from Peters' laboratory.[83] In this paper the authors presented for the first time the technique of deconvolution of the experimental (E(t)) wave from the transducer (T(t)) wave in order to obtain the lifetimes of the transient species of interest. Later on the methods of deconvolution have been refined to a high degree.[67,68]

Another paper from this group described the determination of the O–H bond enthalpy of phenol, by first measuring the quantum yield of *tert*-butoxy radical formed upon 337-nm excitation of *tert*-butyl peroxide and then by the measurement of the heat released upon reaction of this radical with phenol.[178] The value obtained, 353 ± 4 kJ/mol, is in good agreement with a quoted value of 362 kJ/mol.[179] The applicability of photothermal methods to complex reaction schemes was demonstrated, providing that the system is independently characterized with respect to yields of luminescence, intersystem crossing, and formation of various products.[178]

Griller and co-workers also began investigations aimed at the determination of Hammett substituent effects in homolytic bond dissociation energies, using LIOAC to probe the O–H bond dissociation energies in para-substituted phenols.[180] Their value for the bond dissociation energy for phenol agrees very well with the value given above.[178] The bond dissociation energies for their series of substituted compounds correlate well with both σ^+ and the bimolecular rate constants for hydrogen abstraction by *tert*-butoxyl, suggesting that the substituent effects reflect the variations in bond strengths, as opposed to the polar contributions to the transition state.[180]

Scaiano's group, in their series of publications investigating two-color, two-photon chemistry, used LIOAC to determine Φ_f of diphenylmethyl radical as 0.31.[181] Additionally, they introduced a new calorimetric standard for the internal calibration of synthesis-probe type photoacoustic experiments. This is 1-(chloromethyl)naphthalene, which gives rise to 1-naphthylmethyl radical in high yield upon 308 nm photolysis.[182] This use of a short-lived intermediate formed during the first ("synthesis") pulse and excited by the second ("photolysis") pulse meets the general requirements for photoacoustic standards (see "Calorimetric References") and is neatly generated in situ.

Further investigations of radical processes were made by Burkey et al.,[57] using an experimental procedure adapted from that of Peters. The quantum yield of free *tert*-butoxy radicals produced upon photolysis of *tert*-butyl peroxide in carbon tetrachloride was measured as 0.71, in contrast to the value in benzene (0.84).[178] The value $\Phi = 0.71$ was further used to determine the bond strengths of the Sn–H bond in tri-*n*-butyltin hydride (308 ± 8 kJ/mol), the allyl C–H bond in 1,4-cyclohexadiene (305 ± 8 kJ/mol), and the secondary C–H bond in diethyl ether (387 ± 8 kJ/mol).[57] The quantum yield for the photolysis of diphenyl disulfide in isooctane was reported as 0.18, indicating that a cage effect is not operating in the system. The heat of formation of *tert*-butoxytriphenylphosphoranyl radical was determined as 130 kJ/mol, providing a detailed enthalpy profile for the formation of this species from the addition of *tert*-butoxyl radical to triphenylphosphine, and eventually leading to triphenylphosphine oxide. Difficulties arising from absorption of light by the reactants were described.[57]

The C–H bond dissociation enthalpy of benzoyl chloride was measured using triethylsilyl radical as the hydrogen abstractor.[183] The photoinduced dissociation of *tert*-butyl peroxide initiated the reaction. The results (371 ± 11 kJ/mol) confirmed previously established literature[184] and disagreed with a reported lower enthalpy value,[185] which would have assigned the benzoyl radical as possessing a resonance stabilized electronic structure. This is apparently not the case.

The triplet 1,3-biradicals cyclopentane-1,3-diyl and 2-isopropylidenecyclopentane-1,3-diyl, derived from the triplet sensitized photolysis of the corresponding diazenes, were studied using PAC.[166] For the first time, the lifetimes and the heats of formation of these spectroscopically invisible (nonconjugated) biradicals were directly determined in solution. Several interesting differences were observed between these two compounds, including a factor of 3 longer lifetime for the 2-isopropylidene compound (with some unknown contribution from bimolecular reactions supposed) and a larger measured exothermicity (54 kJ/mol) for ring closure of the 2-alkylidenyl biradical to the more strained, substituted bicyclopentane. However, these reactions require a triplet sensitizer, and unknown side reactions can introduce serious distortions as was discussed by the authors. In this work, mention was made to the possible contribution to the photoacoustic signal from the volume change associated with the release of molecular nitrogen during the photolysis. This phenomenon (see section entitled "Molecular Volume Changes") should yield a large apparent value of the prompt heat released.[166]

Pentadienyl and 3-substituted pentadienyl radicals, generated by *tert*-butoxyl hydrogen abstraction of 3-substituted 1,4-pentadienes, were studied using PAC. The C3–H bond dissociation energies of these highly stabilized radicals (tertiary or diallyl) were not found to vary significantly as H was replaced by methyl at C3 (321 kJ/mol). Replacement of H by OH reduced this value to 289 kJ/mol.[186]

Poston and Harris' investigation of hydrogen abstraction by benzophenone triplet from ethanol in carbon tetrachloride solution was carried out using PBD. Influences on the signal due to absorption into upper singlet states of benzophenone were discussed, along with the feasibility of determining properties of the triplet, even in the case that triplet–triplet absorption takes place.[41] The derived bond dissociation energy of the C–H bond of benzhydrol (364 ± 8 kJ/mol) was recently questioned by Arnaut and Caldwell,[187] who studied the more informative hydrogen abstraction from benzhydrol by triplet benzophenone using PAC. This reaction yields two ketyl radicals, providing $\Delta H_f = 22$ kJ/mol for this species, and allowing the calculation of the benzhydrol C–H bond dissociation energy as 315 ± 6 kJ/mol in a straightforward way through a thermodynamic cycle.[187]

The formation of 1,4-biradicals produced prior to photodimerization of cyclopentenone was the first such study of precycloaddition biradicals by PAC. This compound undergoes efficient self-quenching at the concentrations which were previously required to provide adequate signal for the PAC experiment, precluding a determination of the E_T value for cyclopentenone, although allowing the study of triplet biradical formation.[162] E_T of cyclopentenone was recently reported as 306 ± 5 kJ/mol after substantial improvements to the experimental apparatus.[68] Since it was not possible to separate the contributions of the two isomeric biradicals (head-to-head vs head-to-tail) formed upon the enone self-quenching reaction, their concentration-weighed energy was reported as 196 ± 7 kJ/mol, in excellent agreement with values calculated for such species using Benson group additivity rules.[165] The lifetimes of the biradicals averaged 37 ns, in agreement with the lifetime of a transient detected in a kinetic absorption experiment, with maximum at 250 nm.

The first photothermal study on radical recombination of photodissociated species in solution (iodine radicals) was performed by Zhu and Harris.[38a] A theoretical model was developed to describe the time dependence of the diffraction signals from the transient thermal grating and rate constants on the order of 2×10^{10} M^{-1} s^{-1} were obtained for the recombination of out-of-cage iodine atoms in various alkanes. The enthalpy of the recombination was estimated from the ratio of the amplitudes of the diffraction transients.[38a] This work has been extended to the study of Br_2 photodissociation in CCl_4, initiated by 432-nm excitation. A quantum yield of 0.12 ± 0.01 for this process was determined, with a rate constant for nongeminate recombination similar to that for I atoms.[38b]

8.2. Other Photochemical Intermediates

The first study of carbenes was carried out by Simon and Peters, who examined triplet diphenylcarbene formed with a quantum yield of 0.78 from the UV photolysis of diphenyldiazomethane in benzene. The heat of reaction determined in this study was -50 ± 8 kJ/mol, in contrast to the endothermic heat of reaction of triplet methylene carbene (138 kJ/mol). This same product was studied in ethanol, a solvent in which the singlet carbene undergoes an insertion reaction to give a diphenylmethyl ethyl ether, with a heat of reaction of -226 ± 8 kJ/mol.[188]

LaVilla and Goodman published a series of papers in the general area of carbenes and subsequent reaction products, using PAC to great advantage. An initial study was of the ylides formed upon reaction of acetone and acetonitrile with methylene carbene, generated from the photolysis of diazomethane. The heats of formation of the ylides were determined to be 19 kJ/mol for the acetone ylide and 296 kJ/mol for the acetonitrile ylide, although the errors were very large (40 kJ/mol) and the determinations were complicated by side reactions and volume change contributions, due to the evolution of molecular nitrogen. The lifetime determinations were more reliable, being 55 ± 5 ns and 117 ± 9 ns for the acetone and acetonitrile ylides, respectively.[189] The lifetime of the latter ylide was measured as a function of fumaronitrile concentration, and a bimolecular rate constant of $(2.3 \pm 0.9) \times 10^9\ M^{-1}\ s^{-1}$ was derived,[189] in agreement with a literature value.[190]

The thermochemistry of singlet carbenes and their reaction products was further investigated as a function of carbene substituent (phenyl vs methoxy, fluoro vs chloro vs bromo).[191] The data were compared to MNDO calculations of the heats of formation and reaction of the carbenes with methanol. The discrepancies (the measured values were 48–126 kJ/mol lower than those calculated) were ascribed to (1) solvation of the carbene, although the heat of formation of the carbenes was measured to be essentially the same in acetonitrile and heptane, suggesting that this phenomenon was not important, (2) an unresolved reaction volume change, which should be positive for the formation of the carbene from the corresponding diazo compound, resulting in an apparently low heat of formation of the carbene, or (3) incorrect MNDO enthalpies for the carbene and diazirine.[191]

The 1,2-hydrogen shift rearrangement of alkylchlorocarbenes was also studied by LaVilla and Goodman, with the aim of clarifying the activation barrier for such processes. The heats of formation of methyl-, ethyl-, and isopropylchlorocarbenes were measured, along with a temperature-dependent lifetime determination of the methylchlorocarbene (the only carbene studied with a lifetime amenable to time resolution by PAC), which revealed an activation energy, E_a ca. 20 kJ/mol, for the rearrangement to chloroethene. The lifetime of this carbene at 295 K in heptane was measured as 740 ± 80 ns.[192]

Product and quenching studies of this reaction by tetramethylethylene (TME) indicated the presence of another pathway for the formation of vinyl halides involving an excited state forming the vinyl halide rapidly (in less than 10 ns) and with relatively high quantum yield (0.33 and 0.41 for chloro and bromo methyl carbene, respectively). Thermal formation of the vinyl halide in the presence of TME did not involve this additional pathway. Such experiments show the utility and versatility of photothermal techniques in the study of spectroscopically invisible species, when combined with classical product studies.[193]

This group is continuing intensive experimentation in this area, as evidenced by recent papers on the thermodynamics of the formation of pyridinium ylides from carbenes[194] and on the heat of formation and reaction of dimethoxycarbene with several alcohols.[195] This latter work used the strength of several spectroscopic approaches, making interesting findings. The dimethoxy carbene was found to be the most stable studied, but at the same time the most reactive toward methanol. The authors offered an interpretation based on different OH insertion mechanisms, which contribute according to the stability of the carbene. Relatively unstable carbenes have electrophilic character and were suggested to react primarily with the hydroxylic oxygen, while the stabilized, nucleophilic carbene could react more rapidly with alcohols via proton transfer. These two cases would define the two extremes of classical OH insertion transition states.[195]

9. Energy Transfer

There are, in principle, three types of energy transfer processes which may be considered in this section: electronic–vibrational intramolecular, electronic–electronic intermolecular, and vibrational–translational intermolecular processes. The theories covering the latter process, mostly applied to gas-phase studies and therefore not reviewed here, have been summarized elsewhere and the treatment can be readily extended to the liquid phase.[14,42] Jacobs provided a reliable numerical scheme for treating the effects of compressibility, diffusive and viscous effects, and energy transfer on flows, combined in a cylindrical container.[196] The programs developed were applied to gas-phase studies by Barker and Toselli with good agreement.

Intramolecular electronic-vibrational energy transfer has not been widely investigated by photothermal techniques, with the exception of a recent study on CALI (chromophore-assisted laser inactivation) as applied to nonfluorescent dyes bound to bovine serum albumin (BSA).[106] The 2.6% difference between the heat evolved after absorption by malachite green (100% prompt heat) and malachite green bound to BSA (97.4%) was determined not to be due to reaction volume changes, changes in emission yield, or oxygen quenching, but attributed to a slightly enhanced intersystem crossing to a long-lived triplet or to other metastable species.

Although intermolecular electronic energy transfer has been used in photothermal experiments as a way to produce excited states of molecules of interest, this type of energy transfer in liquid phase as a subject of study in its own right has not received a great deal of attention with these techniques, especially in the liquid phase. An early application of PAS with monochromatic light to study the energy transfer from benzene to biacetyl in the gas phase, was reported by Kaya, Harshburger, and Robin. Direct excitation of biacetyl at wavelengths longer than 443 nm led to production of its triplet state, with subsequent slow decay to the ground state, whereas direct irradiation with higher energy light, or energy transfer from benzene preferentially populates the T_2 state of biacetyl, rapidly decaying to the ground state. Acoustic detection made the identification of this $T_2 \rightarrow S_0$ pathway possible, since optical detection had not been able to confirm the existence of this upper triplet state.[4]

The significance of isooptoacoustic points, in direct analogy to isosbestic points, and their use for energy transfer studies, was discussed in a paper by Schneider and Coufal on PAS experiments.[197] Intermolecular electronic energy-transfer processes alter the optoacoustic results, i.e., the spectra are no longer the simple superposition of the two individual optoacoustic spectra. For mixtures of two species with quantum yield of nonradiative transition which are low for the donor and high for the acceptor, the amplitude of the PAS signal may be higher than for solutions of the donor alone. Although this precludes the determination of the mole fractions of species present in the solution by PAS alone, the addition of nonfluorescing acceptor molecules can be used to enhance the detection of molecules with low yield for the radiationless processes.[197]

Electronic energy transfer between benzophenone triplet and biphenyl was investigated with PBD. The direct-energy-transfer rate and E_T values of donor and acceptor were estimated, as well as the reverse-energy-transfer rate. The forward rate constant was measured as $(5.8 \pm 0.9) \times 10^8\ M^{-1}\ s^{-1}$, which is 1 order of magnitude slower than diffusion controlled in carbon tetrachloride, slower than expected for a donor–acceptor pair separated by only 8 ± 2 kJ/mol, as determined in this study.[198] These results were, however, in accord with the previous estimation of the steric contributions to the entropy change upon triplet formation of biphenyl.[199] The reverse-energy-transfer rate was measured as $(1.6 \pm 0.8) \times 10^8\ M^{-1}\ s^{-1}$.[198] The larger error in this rate constant was due to the uncertainty in the lifetime of the donor. Indeed, the reverse-energy-transfer rate was admitted to be probably too large, considering the reported values of k_{for}/k_{rev}, which range from 7[200] to 23.[201]

Terazima and Azumi studied electronic energy transfer between the upper triplet states of 2-acetylphenanthrene and the ground state of biphenyl using TRTL.[202] The observation of a slow-rising component of the signal confirmed the formation of the triplet state of the energy acceptor, biphenyl. Comparison of the magnitude of this slow-rising component with that of the fast-rising component yielded an energy-transfer yield of 0.85 ± 0.11. Back energy transfer in this experiment could not be quantified, but was not considered to be efficient at the 2-acetylphenanthrene concentration of 0.02 mM. It was also pointed out that the sensitivity of this method is limited by the maximum measurable value of the ratio of the fast-rising to the slow-rising signals. This parameter is related to the E_T gap between donor and acceptor: the smaller the gap, the less sensitive the method becomes. The method is not recommended for acceptors with triplet lifetimes shorter than 100 ns.[202]

10. Singlet Molecular Oxygen, $O_2(^1\Delta_g)$

One of the most common modes of formation of singlet molecular oxygen, $O_2(^1\Delta_g)$, in fluid phase is through sensitization by energy transfer from donor triplet states. Although this is in general an efficient process with quenching constants, $k_q > 10^9\ M^{-1}\ s^{-1}$, it has been demonstrated that quenching does not occur solely by energy transfer resulting in the formation of $O_2(^1\Delta_g)$ with unity efficiency.[15,203-205]

The accurate determination of Φ_Δ, the quantum yield of $O_2(^1\Delta_g)$ formation, has become an important task in order to evaluate the efficiency of the energy-transfer process. This is especially so in view of the search for better sensitizers for use in photodynamic therapy, in which this reactive species is believed to play a predominant role,[206] but also in order to understand the molecular factors underlying the efficiency of the energy-transfer process between the sensitizers and $O_2(^3\Sigma_g^-)$.

After energy transfer from the triplet state and in the absence of any chemical acceptor, $O_2(^1\Delta_g)$ decays by predominantly nonradiative means, with only a small fraction ($<10^{-3}$) relaxing by a radiative transition with emission maximum at 1270 nm.[207,208] Thus, a study of the formation and relaxation of $O_2(^1\Delta_g)$ using photocalorimetric techniques is particularly appropriate. However, in some of these systems, long-lived radicals may be produced which can also act as energy-storing species.

The lifetime of $O_2(^1\Delta_g)$, τ_Δ, ranging from 4 μs in H_2O to several ms in some chlorinated solvents,[109] is long enough to neatly separate the slow and prompt heat release.

In the great majority of cases the sensitizers under study are triplet states. However, $O_2(^1\Delta_g)$ which might be produced by quenching of a singlet excited-state [provided that $E_T - E_S > E_\Delta$ and the $O_2(^3\Sigma_g^-)$ concentration is large enough to quench the short-lived singlet] will add to the stored energy. The possible role of this process should be carefully checked in each case. In what follows, the quenching of triplets is treated in detail.

In the presence of enough O_2 to quench all sensitizer triplet states, the only species storing energy for a time longer than the heat-integration time of the experiment is $O_2(^1\Delta_g)$ and eq 1 changes slightly to give eq 18.

$$E_a = \Phi_f \cdot E_f + \alpha \cdot E_a + \Phi_\Delta \cdot E_\Delta \tag{18}$$

The energy stored is now the product of the molar energy content of $O_2(^1\Delta_g)$, E_Δ = 94.1 kJ/mol[209] times Φ_Δ.

On the basis of these concepts, TRTL was applied to the determination of Φ_Δ and of τ_Δ. Itoh and co-workers developed the technique in order to evaluate the latter with high accuracy.[210,211] Values as short as ca. 1 μs were obtained from the slow-decay part of the thermal lensing signal. Chartier et al. applied the method to determine τ_Δ values in water as well as in micellar solutions.[158]

Rossbroich et al. used the fast and slow parts of the lens signal (eq 8) in order to determine absolute values of Φ_Δ for various sensitizers.[16] The same approach was employed to derive Φ_Δ values for hematoporphyrin.[212] Both TRTL and time-resolved phosphorescence detection (TRPD) were used for the detection of $O_2(^1\Delta_g)$ in order to evaluate the molecular factors determining the ability of several molecules to produce $O_2(^1\Delta_g)$. In the presence of enough O_2 to quench all triplet states and for a series of aromatic hydrocarbons, ketones, and quinones, the highly polarizable n,π* triplet states have a low value of $\Phi_\Delta/\Phi_{isc} = S_\Delta = 0.3 \pm 0.05$ and a quenching rate constant by O_2, k_q, increasing sharply with the triplet energy, while for the aromatic π,π^* the values are $S_\Delta = 0.91 \pm 0.1$ and $k_q = (2 \pm 0.5) \times 10^9$ M^{-1} s^{-1}, one-ninth of the diffusional rate constant, independent of its triplet energy.[15]

In order to explain these results, the only mechanism considered to compete with the production of $O_2(^1\Delta_g)$, upon collision of $O_2(^3\Sigma_g^-)$ with the triplet state, was the $O_2(^3\Sigma_g^-)$ induced triplet→singlet intersystem crossing of the sensitizer. The scheme including the nine possible spin substrates of the intermediate exciplex between the triplet state and $O_2(^3\Sigma_g^-)$ was used (see the discussion in Saltiel and Atwater),[213] including transitions between the charge-transfer states derived from these exciplexes. These charge-transfer states had been already postulated in connection with triplet states quenching by $O_2(^3\Sigma_g^-)$ by Garner and Wilkinson.[204] No other transient needed to be considered in any of the systems analyzed, since the lens signal showed no further slow dissipation after the decay of $O_2(^1\Delta_g)$. This contrasted with the proposed formation of 1,4-biradical intermediates during the quenching of triplet states of aromatic ketones by $O_2(^3\Sigma_g^-)$.[205]

Φ_Δ for 4-thiouridine was evaluated in deuterated water and in acetonitrile.[103] The value of $S_\Delta = 0.7$ in both solvents, derived from a combination of LIOAS and TRTL measurements of the triplet yield and of Φ_Δ, was taken as indicative of a π,π^* character for the lowest triplet state of the rare nucleoside, on the basis of the above mentioned relationship between the S_Δ value and the electronic structure of the sensitizer.[15]

For C_{60}, Terazima et al.[173] determined a value of $\Phi_\Delta = 1$, independent of excitation wavelength (excitation with 340 and 532 nm), using the slow and fast parts of the TRTL signal. This result, which indicates that Φ_{isc} is also unity [quenching of the excited singlet to yield $O_2(^1\Delta_g)$ can be neglected in this case], is in contrast to the previous postulation of an internal conversion channel for this molecule.[174]

The now widely used method of TRPD for the determination of Φ_Δ affords only relative values, since it essentially consists of measuring the intensity of the near-IR emission by $O_2(^1\Delta_g)$, $I_\Delta = A'\cdot\Phi_\Delta\cdot k_r\cdot\tau_\Delta$. I_Δ is, in addition to Φ_Δ, proportional to k_r, the radiative constant of $O_2(^1\Delta_g)$ in a particular solvent and to τ_Δ through an instrument constant A'. Gorman et al. used TRTL for the determination of absolute Φ_Δ values (in addition to τ_Δ values) for the same sensitizer in cyclohexane and in benzene.[214] With these values and the I_Δ values derived from TRPD they unambiguously showed that k_r for $O_2(^1\Delta_g)$ is solvent dependent, as had been already shown utilizing a different approach by Scurlock and Ogilby.[215]

The low values of k_r and τ_Δ for $O_2(^1\Delta_g)$ in water hamper the measurements of the IR luminescence of this species in aqueous medium. As already discussed, the photothermal methods also yield low signals in water, due to the low value of the ratio β/C_p (eq 10). By incorporating the sensitizers in reverse micelles, Redmond found an increased signal when using TRTL, LIOAC, and TRPD, due to the increase in the value of β in the bulk of the micellar solution, for both photothermal methods, and in an increase in the value of k_r for $O_2(^1\Delta_g)$ for the luminescence method. A value of $\Phi_\Delta = 0.8$ was thus determined by TRTL and by LIOAC for rose bengal included in the micelles, with signals increased 5–6 times with respect to those in neat water.[102]

11. Electron Transfer

The study of electron-transfer reactions has become increasingly important in the last ten years, and some (although relatively few) investigations in this area have been carried out with the help of photothermal methods.

Goodman and Peters studied specific salt effects on the energies of benzophenone anion–alkali metal cation contact ion pairs, reporting a decrease in energy upon going from the reference benzophenone–DABCO contact ion pair (217 kJ/mol) and a noncomplexing cation, tetra-*n*-butyl ammonium perchlorate (217 kJ/mol), to sodium perchlorate (199 kJ/mol), to lithium perchlorate (195 kJ/mol).[216] Taking into account the previously reported uncertainties from this laboratory (10–12 kJ/mol),[65,160] the differences in energies derived in this work are roughly the same as the experimental error. Therefore, although the gain in energy of approximately 20 kJ/mol upon formation of an alkali metal interaction, as compared to the interaction with DABCO, is genuine, the authors wisely avoided drawing conclusions about differences in the sodium and lithium ion values, considering that the measurements were not absolute, rather reflected the differences between ion interaction with solvent and with benzophenone anion.[216]

Whitten and co-workers[217] studied the metastable radical pair formed upon reaction of the excited state of β-lapachone, an *o*-quinone, and triethylamine. Although this rather complicated system was not completely characterized at the time of the publication, the experimenters were able to correlate some results from NMR and ESR experiments with the results from PAC. The semireduced *o*-quinone was formed in wet (3% H_2O) benzene through oxidation of triethylamine and was indefinitely stable at room temperature. The behavior of the radical pair was affected by the quinone concentration. A secondary electron transfer to produce enamine and semi or fully reduced quinone species was postulated.[217]

PAC was used to probe the Marcus inverted region with respect to charge recombination and charge-shift reactions for the electron-transfer reaction between either cyanoanthracene or *N*-methylacridinium and a series of alkyl benzenes. The quantum yields of separated ions formation were in excellent agreement with those measured by transient absorption spectroscopy. The decrease in reverse-electron-transfer rates with increasing exothermicity is more pronounced for charge-shift reactions (in which no net charge change takes place) than for charge-recombination reactions (in which two ions yield two neutral species), most likely due to a smaller solvent reorganization energy term for the charge-shift reactions.[218] This was in contrast to previous predictions.

The influence of solvent polarity on the radiationless deactivation of intramolecular exciplexes formed between excited pyrene and indole or between excited pyrene and triethylamine was studied using LIOAS and transient absorption spectroscopy. Both sets of results suggest, contrary to former interpretations, that internal conversion is an important decay process of the exciplexes and that it becomes more important with increasing solvent polarity. This result was rationalized in terms of current theories describing electron transfer since the radiationless decay process of the exciplexes is the charge recombination reaction.[219]

LIOAS was used to determine the relative energy stored by the ion pairs formed after absorption of a laser pulse by photosystem I (PS I) and photosystem II (PS II) particles isolated from *Synechococcus* sp. and with lifetimes longer than the heat-integration time, 1.4 μs.[104] The photoproducts formed within this time, i.e., the states P^+-$700A_1^-$ for PS I and Z^+P-$680IQ_A^-$ for PS II, were found to be associated with a relative energy storage of 0.83 ± 0.08 and 0.65 ± 0.07, respectively. Several conclusions about the thermodynamics of both systems were drawn with these data. For PS II with closed reaction centers (saturated with respect to their ability to perform photosynthesis) a fraction of 5% of the absorbed energy stored for a time longer than 1.4 μs was attributed to the formation of triplet P-680 by charge recombination.[104] A similar study with intact cells of *Rhodospirillum rubrum* S_1 revealed that the relative energy stored by P^+-$880IQ_A^-$, the photoproduct formed in the reaction center of this bacterium within the specified heat-integration time (1.4 μs), was 0.44, considerably smaller than that found previously for PS II from *Synechococcus* sp. (vide supra).[220] This was a surprising result, in view of the similarities between the bacterial photosystem and PS II. In this same work the quantum yield of triplet production by charge recombination in closed reaction centers was found to be $\Phi_{cl}^T = 0.50 \pm 0.15$.[220] In spite of the complexity of the reaction centers, in each of these cases the reaction under study was well defined thanks to the wealth of optical studies which offered a clear identification of the energy-storing species within the particular observation time, i.e. the heat-integration time.

12. Metastable Ground-State Molecules

Reversible ring opening, geometrical isomerizations, and keto–enol tautomerizations are some examples of photoinduced reactions producing a ground-state metastable isomer of a stable parent compound that have been studied using photothermal methods.

Several photochromic reactions in the crystalline and adsorbed (on silica gel) states were studied by PAS. The absorption spectra and decay lifetimes of short-lived photochromic species were recorded.[221]

Since the betaines formed by photoinduced ring opening of several [1,8-*a*]dihydroindolizines have a lifetime longer than ca. 1 μs, PAS with modulation frequency of 30 Hz and a gas-coupled microphone was employed in order to study the energy stored by the reaction as a function of the substitution pattern. Zinc tetraphenylporphyrin in the presence of oxygen (to quench all triplet states) was used as the calorimetric reference. A direct correlation was observed between the rate constants for the decay of the betaines and the respective energy storage. In other words, betaine lifetimes are determined by their energy content, which makes the indolizine–betaine system not well suited for solar-energy storage.[5]

Cyanine dyes were the object of several LIOAS studies. The laser dyes 3,3′-diethyloxadicarbocyanine iodide (DODCI) and 3,3′-diethylthiadicarbocyanine iodide (DTDCI), used for pulse operation and as saturable absorbers in mode-locking techniques, produce metastable photoisomers (P) which return to the stable ground state (N) with rate constants at room temperature in ethanolic solutions $k = 7.7 \times 10^2\ s^{-1}$ and $4 \times 10^3\ s^{-1}$, respectively.[105,222,223]

With the spectral overlap of N and P taken into account, a simple numerical model was developed including the four differential equations describing the kinetic behavior of the concentrations of the four species (N, P, N*, and P*) involved and a fifth equation describing the time behavior of the heat produced by all radiationless processes in the system. With this model, the fluence-dependent value of α (eq 11), after microsecond laser excitation with various wavelengths, was fitted to the experimental points. Several kinetic and thermodynamic parameters were extracted for the case of excitation of N and, in the case of DODCI, for pulsed excitation of P during photostationary equilibrium between N and P.[105,222,223]

For DODCI, the absorption spectrum of P was calculated with great accuracy, especially in the spectral region strongly overlapping with the spectrum of N. The energy content of P was measured as 154 ± 30 kJ/mol. For this dye the LIOAS results support a model in which, opposite to the case of N*, P* deactivates mainly by internal conversion to P, without passing through the twisted state.[105,222] This conclusion was later confirmed by Rentsch et al.[224] and by Zhu and Harris,[63f] and implies that the back-photoisomerization P→N has a very low yield.

The evaluation of the photophysical parameters for the photoisomerization of DTDCI was less precise due to the much stronger overlap of the absorption spectra of N and P. In this case the spectrum of P was deduced with great precision from the LIOAS data but no definitive conclusion about the deactivation channel of P* could be reached. A very low value for the energy stored by P (14 ± 14 kJ/mol) was deduced for DTDCI[223] which contrasts with the larger value obtained for DODCI (vide supra).[222]

During these studies, isooptoacoustic points[197] were used in order to derive spectroscopic properties of the species involved. In systems involving more than just two species (e.g., a four-level system like DODCI or DTDCI), the lack of dependence of the normalized heat emission on the laser fluence does not necessarily imply the lack of an additional species absorbing in the system. Extended isooptoacoustic spectral regions (for which $\alpha_i \cdot \sigma_i$ = constant, with α = fraction of heat dissipated promptly (eqs 1 and 11) and σ = absorption cross section) may be present resulting in non-fluence-dependent heat emission.[222,223]

More recently, laser-induced anharmonic thermal grating was used for the study of the photoisomerization of two cyanine dyes, 3,3′-diethyloxatricarbocyanine iodide (DOTCI) and 1,3,3,1′,3′,3′-hexamethylindotricarbocyanine iodide (HITCI). In order to explain the anomalous excitation-fluence dependence of the diffraction efficiency observed for both dyes, a general numerical method calculating the diffraction from anharmonic thermal grating[225] was applied.[226] Due to the high photon densities used, at least two nonlinear absorption processes contributed simultaneously to the formation of higher order thermal grating in each dye solution, namely saturation of the ground-state absorption and excited-state absorption. These were also the processes leading to nonlinear fluence dependence of the optoacoustic signals in the case of DODCI and DTDCI.[105,222,223] On the basis of the measured refractive intensities of the various grating harmonics and by using the above mentioned numerical method, the different photophysical parameters for DOTCI and HITCI were extracted. The conclusion was that for the former, ground-state saturation and strong excited-state absorption explained the anomalies, while for the latter, photoisomer absorption might also play a role.[226]

Merocyanine 540, a cyanine dye undergoing isomerization to yield a photoisomer which returns to the stable form with a lifetime of 11 ms at room temperature in ethanol, was also studied by LIOAS, in addition to several other methods.[227] The value of the product $\Phi_{st}{\cdot}E_{st}$ was measured which, combined with the value of Φ_{st} derived from the saturation method in transient absorption spectroscopy, yielded a value for the molar energy stored by the isomer of $E_{st} = 124 \pm 13$ kJ/mol. However, should photochemical back-isomerization be important within the 15 ns of the laser pulse, this value of Φ_{st} would represent an upper limit. By using the same value for the product $\Phi_{st}{\cdot}E_{st}$ and an energy level for the photoisomer just below the first excited singlet of the stable state, a lower limit of $\Phi_{st} = 0.32$ was obtained.[227]

LIOAS studies with nanosecond excitation of the open tetrapyrrole compounds biliverdin dimethyl ester[59] and phycocyanobilin dimethyl ester[228] led to the conclusion that, from the two families of conformers coexisting in solution for each compound, only the more stretched conformer(s) photoisomerize to yield metastable species, returning thermally to the stable state in several nanoseconds. This conformationally selective photoisomerization takes place with a relatively large quantum yield which was calculated, neglecting the possible photochemical back-isomerization of the photoisomer. Should this process take place, the values of Φ_{st} would again constitute upper limits. Since the photoisomer absorption spectrum strongly overlaps that of the thermodynamically stable state (no transient absorption spectrum can be detected for these compounds), in order to solve this question, LIOAS measurements should be performed with few picosecond or femtosecond excitation, thus avoiding the excitation of the metastable isomers within the laser pulse.[81]

The role of the ^1A_g state in the trans–cis photoisomerization of stilbene was clarified by two-photon fluorescence and TRTL studies. Although this work was based on multiphoton absorption, its conclusions bear on the participation of the various states of stilbene in its general photochemical behavior.[229]

Brennan and Caldwell determined the enthalpy of isomerization E_{ct} of *cis*-1-phenylcycloheptene to the strained *trans*-1-phenylcycloheptene and of 1,3-cycloheptadiene to *cis,trans*-1,3-cycloheptadiene. According to the authors, the value $E_{ct} = 121 \pm 13$ kJ/mol obtained for the former isomerization indicates that the degree of strain associated with the seven-membered ring is considerably less than in the six-membered ring. (E_{ct} for 1-phenylcyclohexene was measured as 187 ± 20 kJ/mol by PAC.[65]) For the heptadiene a value $E_{cc\text{–}ct}$ in the range 155–192 kJ/mol was estimated, although it was not completely certain that the heat storage observed should be assigned to the formation of the cis,trans isomer.[167] The uncertainty quoted largely reflects that for the quantum yield of isomerization used for the calculation.

The intermediate in [2 + 2] photocycloadditions of alkenes to 2-cyclohexenones was suggested to be a highly twisted, trans isomer of the ground state enone.[171] PAC experiments gave no indication of such a species, which, however, would not have been detectable should its lifetime be close to that of its precursor, the twisted triplet enone (ca. 25 ns).[168]

LIOAC was used to determine the enthalpy of the trans to cis photoisomerization of 1,3-diphenyltriazene in toluene and in methanol. The fact that the cis to trans back thermal isomerization was faster in alcohols, when the energetics were less favorable, was attributed to a change in mechanism involving solvent-assisted isomerization. The authors postulated the participation of two hydrogen-bonding solvent molecules in the transition state in hydrogen bonding media which accelerates the isomerization rate.[230]

The enthalpy difference between the enol and keto forms of 7-hydroxyquinoline was determined by TRTL to be 41 kJ/mol in the ground state, while the activation energy for the proton back-transfer in the excited-singlet manifold was derived to be ca. 50 kJ/mol. This indicates that the excited state of the compound exists mainly in the enol form.[231]

The photostability of 3-phenyl-1,2-dihydronaphthalene with respect to possible ring opening was analyzed using LIOAS and the heat release compared to that by 2-phenylidene and stilbene. The large flexibility of the excited 3-phenyl-1,2-dihydronaphthalene allowing for rapid distribution of the absorbed energy was considered responsible for the lack of photoreaction.[232]

13. Metal–Ligand Bond Strengths

The difficulty of obtaining accurate metal–ligand bond strengths has hindered the prediction of reactivities and stabilities of metal clusters, although the introduction of photoacoustic techniques in this field has made some progress, notably in the field of Cr-carbonyl chemistry. The question of contributions to the acoustic wave due to molar volume changes (already treated in a previous section), which arises when considering reactions in which the number of particles changes (e.g., for a CO splitting reaction) has not been generally addressed by workers in this field.

Peters' group did the initial study in this area, reporting the M–CO bond enthalpies for single carbonyl dissociation from Cr, Mo, and W hexacarbonyls in ethanol and cyclohexane, but the high laser fluences used in these experiments were found to yield incorrect results.[233] A subsequent paper reported a corrected value of the Cr–CO bond enthalpy (113 kJ/mol in heptane, reflecting a 42 kJ/mol stabilization due to the heptane–$Cr(CO)_5$ interaction), as well as the bond strengths of several other typical chromium ligands. The latter values were determined by detecting the amount of heat released as the transient heptane ligand of the initially created (heptane)chromium pentacarbonyl species was displaced by a more stable ligand.[234] These experiments were later extended to the study of bond energies of pyridine derivatives, in which steric effects influence the observed enthalpy of activation and enthalpy of displacement of heptane.[235]

By using the photolysis of $Mn_2(CO)_{10}$ as a reaction of interest, PAC was used to investigate the energy of the Mn–Mn bond in this compound.[236] This reaction results in cleavage of both the Mn–Mn bond and one of the Mn–CO bonds, both processes occurring within 25 ps with quantum yields estimated as 0.3 and 0.1, respectively.[236] Use of higher quantum yields for these processes, as previously reported[237] yielded results which were judged inconsistent with independent chemical evidence.[238] The Mn–Mn bond strength was reported in this study as 159 ± 21 kJ/mol, not including the 42 kJ/mol uncertainty in the assumed ΔH_{coord} for $[Mn_2(CO)_9]$ in hexane (20–60 kJ/mol), or the uncertainty in the Mn–CO enthalpy 150 ± 8 kJ/mol.[239]

Burkey used similar methods in a study of the enthalpies of ligand exchange between aliphatic amines and $Cr(CO)_6$.[240] In this work the contributions of the hydrogen bonding arising between coordinated and free amine (15–20 kJ/mol) to the overall reaction enthalpies were considered and the effects could be separated, isolating in this way the enthalpic differences due to steric effects of the various ligands. The equilibrium constants for hydrogen bond formation were found to decrease with steric restriction, an effect not reflected in the enthalpies of hydrogen bonding, suggesting that entropy is the controlling factor. Bulkier amines were found to increase endothermicity of the Cr–ligand bond formation, indicating a stronger effect than the increased basicity of substituted amines. Insights into the nature of the transition state for solvent displacement by ligands were gained and it was suggested that participation of solvent in the transition state for solvent displacement may depend on the steric properties of the incoming ligand.[240]

Recent work from this group focused on the strengths of metal–alkane (agostic) bonds in Cr, Mo, and W pentacarbonyl species. A difference of 12 kJ/mol between the enthalpies of CO dissociation in heptane (114 ± 5 kJ/mol) and cyclohexane (101 ± 3 kJ/mol) led the authors to conclude that a stronger agostic bond is formed with the purely secondary CH-containing alkane.[241] Burkey also examined the replacement of CO in hexacarbonyls and two aromatic organometallic complexes by triethylsilane, finding a range of binding enthalpies for triethylsilane of 88–118 kJ/mol, compared to 38–55 kJ/mol for alkanes. This narrow range of enthalpies, in contrast to the 76 kJ/mol variation found in metal–CO bonds, and the endothermic, parallel reactivity for these ligands suggest that metal–silane bonding resembles metal–alkane interactions more than metal–CO interactions. The metal–silane enthalpies were measured for the first time in this work and exemplify the large impact of PAC in this field over the last few years.[242]

Examination of the quantum yields of CO substitution in Cr(CO)L in neat ligand solution (cyclohexane, benzene, and 1,2-dichloroethylene) and in dilute perfluorodecalin solutions of the ligands strongly suggests that the interaction of the chromium pentacarbonyl with the fluorocarbon is weaker than with the ligand.[243] These results, combined with viscosity data and variation in excitation wavelength, support a proposed model of cage effect processes in these species.[244] The major conclusion was that cage recombination of CO is enhanced by a factor of ca. 200 for the perfluorodecalin solutions, while the cage escape rate is retarded by a factor of only about 6.

Bond dissociation energies for the photoinduced amino ligand hydrolysis in Cr complexes of 138 kJ/mol for $Cr(NH_3)_6^{3+}$ and 100 kJ/mol for $Cr(NH_3)_5Cl$ were reported.[154] The heats of reaction measured in this study have large errors due to uncertainties in Φ_{isc} and product yields.

The relative stability of transition-metal complexes of strained olefins over that of their unstrained counterparts has been demonstrated by the results obtained using PAC for the metal–olefin dissociation energies (ΔH_{diss}) in (*cis*-cyclooctene)chromium pentacarbonyl and (*trans*-cyclooctene)chromium pentacarbonyl. A value of $\Delta H_{diss} = -59.9 \pm 4$ kJ/mol was determined for the former, while for the latter $\Delta H_{diss} = -81.6 \pm 10$ kJ/mol resulted.[245] These results are in agreement with the previously reported difference in stability of *cis*- and *trans*-cyclooctene.[246]

Dissociation energies of Mn–L bonds (for L = tetrahydrofuran, −67 ± 6 kJ/mol; L = acetone, −73 ± 4 kJ/mol; L = *cis*-cyclooctene, −102 ± 10 kJ/mol; L = Bu_2S, −120 ± 10 kJ/mol) were determined for photogenerated $CpMn(CO)_2$–L (Cp = cyclopentadiene) complexes by PAC.[247] A study utilizing a tethered ligand giving cyclic products via a ligated solvent intermediate has also been reported.[248] PAC was used to determine the heat of the ring-closure reaction. Closure of the four-membered ring was 59 kJ/mol endothermic, in contrast to the five- and six-membered rings which were 11 and 7 kJ/mol, respectively. This was attributed to strain energy of the four-membered ring.[248]

Metal–hydrogen bond strengths of silicon[249] and germanium[250] were determined by Griller's group, in efforts to understand factors influencing the strength of M–H bonds in such compounds. In the case of Ge, various alkyl and aryl substitutions did not appreciably influence the bond dissociation energies (331–345 kJ/mol) as compared to the literature value for GeH_4 (346 kJ/mol).[251] Similar conclusions were reached for the Si–H bond strengths, with the exception of tris(trimethylsilyl)silane, which showed a 46 kJ/mol reduction in the Si–H bond strength, compared to triethylsilane (377 kJ/mol). The former compound was suggested as a free radical reducing agent, as alternative to tributyltin hydride. In both papers, small corrections were applied to account for attack of the *tert*-butoxyl radical on methyl and methylene hydrogens of the silane, as opposed to the dominant mode of reaction, i.e., abstraction of the Si–H.[249]

The thermochemistry of d^8–d^8 binuclear metal complexes was studied using PAC.[252] The triplet state participates in hydrogen and halogen transfer reactions with substrates RX, forming a radical pair. The heats of the atom transfer reactions were determined for the $Pt_2(P_2O_5H_2)_4^{4-}$ system. Its triplet energy in methanol was found to be 236 ± 7 kJ/mol. With the assumption that the radicals were formed with unity efficiency, the atom-transfer reaction enthalpy was extracted from the data. The decay of the radical apparently involves breakage of two bonds, the Pt–X bond and the Pt–Pt bond. Thus, the authors made a simplifying assumption about the Pt–Pt bond dissociation energy, setting it equal to the triplet energy of $Pt_2(P_2O_5H_2)_4^{4-}$. This treatment provides a range of $Pt_2(P_2O_5H_2)_4^{4-}$–X dissociation energies in the range 443 (for Cl) to 370 kJ/mol (for Br).[252]

14. Conclusions

In order to follow the heat evolution in a solution after excitation by a light pulse, several techniques have been developed which detect the induced changes in pressure or in temperature (the latter in general by means of the refractive index change). These techniques are amplitude-modulated photoacoustic spectroscopy, PAS, with time resolution limited to the millisecond range, laser-induced optoacoustic spectroscopy, LIOAS (also called laser-induced optoacoustic calorimetry, LIOAC or photoacoustic calorimetry, PAC), time-resolved thermal lensing, TRTL, and photothermal beam deflection, PBD. With LIOAS, LIOAC, PAC, TRTL, and PBD the time resolution is limited to few nanoseconds, independent of the laser-pulse time width. A somewhat better time resolution is achieved with the front-face arrangement and deconvolution techniques, than with the right-angle arrangement.

Subnanosecond time resolution has been obtained by photothermal experimental arrangements involving more than one ultra-short laser pulse absorbed by the sample, like pump-probe and thermal grating methods which, however, are constrained to solutions of high optical quality (the same is valid for TRTL and PBD).

With all these techniques, the kinetics and energetics of reactions involving various types of photogenerated metastable short-lived species in solution have been studied covering a large time range between ca. 10 ps to several milliseconds or longer. The species studied include singlet and triplet states, radicals, biradicals, carbenes, ion pairs, as well as metastable ground-state molecules. In all cases properties otherwise not accessible by other methods were derived. In addition, for some systems, information on molecular movements concomitant with the photochemical reaction has been derived from these experiments.

The very high sensitivity of the photothermal techniques permits their use in order to monitor reactants or products in chemical reactions involving species at low concentrations or with low absorbance, in particular expanding the time scale for study of fast bimolecular reactions.

The choice of a particular photothermal technique depends on the properties of the particular system under study including optical quality, concentration range, time range, and absorption spectra of ground and metastable species.

The possibility of obtaining, by the application of photothermal methods, information complementary to well-established techniques, like transient absorption and emission, explains the growing interest in the use of photothermal methods by scientists working on systems with participation of various types of transient species.

15. Symbols, Acronyms, and Abbreviations

List of symbols, acronyms, and abbreviations used throughout the review, unless otherwise specified in special cases

A	absorbance
c_p	specific heat capacity
C_p	molar heat capacity at constant pressure
cw	continuous wave
$E_a = E_l \cdot (1 - 10^{-A})$	molar energy absorbed
E_f	molar energy of the fluorescing state
E_l	molar energy of the laser pulse
E_p	molar energy stored by a long-lived product = E_{st}
E_{st}	molar energy stored by a long-lived product = E_p
E_T	molar triplet energy
E_Δ	molar energy of singlet molecular oxygen
H	maximum amplitude of the optoacoustic signal
ISC	intersystem crossing
k	thermal conductivity
LIOAC	laser-induced optoacoustic calorimetry = PAC
LIOAS	laser-induced optoacoustic spectroscopy
n	number of einsteins in a laser pulse
n	refractive index
$O_2(^1\Delta_g)$	singlet molecular oxygen
p	pressure in the medium
p'	pressure immediately after the laser pulse
PAC	photoacoustic calorimetry = LIOAC
PAS	photoacoustic spectroscopy, generally applied to amplitude-modulated photoacoustics with gas-coupled microphone detection
PBD	photothermal beam deflection (laser-induced)
R	radius of the laser beam : halfwidth at $1/e$ of maximum beam amplitude
T	temperature
TRPD	time-resolved phosphorescence detection of near-IR emission
TRTL	time-resolved thermal lensing
V	volume
v_a	sound velocity in the medium
α	fraction of absorbed energy dissipated into the medium as prompt heat
$\beta = 1/V \cdot \partial V/\partial T$	cubic expansion coefficient
ΔV_{con}	volume change due to a molecular conformational change = ΔV_r
ΔV_r	volume change due to a molecular reaction
ΔV_{th}	volume change due to heating of the medium
Φ_f	fluorescence quantum yield
Φ_{ic}	internal conversion quantum yield
Φ_{isc}	intersystem crossing quantum yield

Φ_{st}	quantum yield of the processes storing energy for a time longer than the time resolution of the experiment
Φ_Δ	quantum yield of generation of $O_2(^1\Delta_g)$
ρ	density $\propto 1/\upsilon_a^{1/2}$
ρ'	density immediately after the laser pulse
$\tau_a = R/\upsilon_a$	acoustic transit time
$\tau_a' = 2R/\upsilon_a$	effective acoustic transit time
τ_1	laser pulse time width
τ_T	triplet lifetime
$\chi = [\beta/(\rho \cdot C_p)] \cdot MW$	thermal expansitivity (MW = molecular weight)

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