Pure & Appl. Chem., Vol. 63, No. 2, pp. 289–299, 1991.
Printed in Great Britain.

206922209100032

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

ORGANIC CHEMISTRY DIVISION
COMMISSION ON PHOTOCHEMISTRY*

MOLAR ABSORPTION COEFFICIENTS OF TRANSIENT SPECIES IN SOLUTION

Prepared for publication by

R. BONNEAU[1], IAN CARMICHAEL[2] and G. L. HUG[2]

[1]L.A. 348 du C.N.R.S., Université de Bordeaux I, 33405 Talence Cedex, France
[2]Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556, USA

*Membership of the Commission during the period (1987–1989) this report was prepared was as follows:

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The Commission acknowledges the contributions of the following scientists who acted as members of the working party on this project or who otherwise commented on various drafts of this manuscript and made valuable contributions:

R. Bensasson; R. S. Hubig; M. A. J. Rodgers; J. C. Scaiano.

Molar absorption coefficients of transient species in solution

INTRODUCTION

When chemical systems are monitored by optical absorption, molar absorption coefficients are the physical observables that are central to any quantitative analysis of the experiments. Stable systems and systems that change slowly, while remaining homogeneous, present no particular problems, but transients can be troubling to analyze precisely. Transient species have been monitored extensively by absorption in the last few decades in conjunction with the wide-spread use of flash photolysis [1] and pulse radiolysis. [2] The current work will be concerned with transients produced by photolytic methods. The best characterized molar absorption coefficients of these transients are those associated with triplet-triplet transitions. [3]

In the first part of this paper, the experimental conditions required to get accurate and significant absorbances will be examined, along with some corrections to be used when the ideal conditions are not achieved. With some techniques, such as those involving transient changes of the refractive index of the solution induced by the absorption of the transient species (mirage effect, light diffraction by transient induced gratings, etc.), it is often quite difficult to calculate the corresponding value of the absorbance with reasonable accuracy. The second part of the paper will be devoted to the various methods which may be used for measuring, calculating or evaluating the concentration of the transient species. The third and last part of the paper has a list of the absorption coefficients of several transient species which are proposed as reference materials. These may be used to check experimental setups or as references in relative measurements. The list of transients is mainly confined to excited triplet states.

I. GENERAL CONSIDERATIONS

The determination of the molar absorption coefficient (ε) of any species requires a knowledge of the concentration (c) of that species and the true *absorbance* (A) of that species along an optical pathlength (l). For a *transient species*, the absorbance and the concentration must refer to the same physical space within the optical cell and to the same *time*. Then, provided that the transverse distribution of the transient species is homogeneous and the solution isotropic, the molar absorption coefficient is given by the simple relation

$$\varepsilon = \frac{A}{c\,l} . \tag{1}$$

In nearly all cases, the absorbance is computed from

$$A = \log_{10} \frac{E_p^0}{E_p} , \tag{2}$$

where E_p^0 and E_p are the transmitted photon fluxes in the absence and presence, respectively, of the transient species.

II. EXPERIMENTAL CONSIDERATIONS

The determination of the true absorbance (A) requires that a number of conditions are fulfilled:

a) The analytical beam should be only transmitted or absorbed, with little or no reflection or scattering. This is usually not a severe problem.

b) The measured photon fluxes, E_p^0 and E_p, should be exclusively those of the analytical beam. Scattered excitation light, fluorescence, or other luminescence should be negligible during the measurement. This may be a real difficulty when studying the excited singlet of highly fluorescent compounds or species with a decay time not much longer than the duration of the excitation pulse. In many cases, the problem can be solved either by recording separately the fluorescence (or the luminescence) signal for correcting the transient absorption signal or by extrapolation to "zero" time of the curve $E_p = f(t)$ based on a kinetic analysis of the unperturbed part of the decay. When the rise time of the transient is not much shorter than its decay time, the extrapolation procedure must be made according to the equation given in section 3.1.2 of reference 4.

c) The response curve (signal amplitude/photon flux) of the analytical system should be known and should, ideally, be linear. The response needs to be checked in general. This is especially important when the optical transmission of the sample is monitored by an attenuation of a probe pulse (the technique commonly used in the subnanosecond time range).

d) The response time of the analytical system (detector, amplifiers, oscilloscope or transient recorder, etc.) and/or the duration of the probe pulse must be much shorter than the decay time of the transient. If not, corrections must be applied.

e) The absorbance due to any species other than the ones under investigation must be known at the selected wavelength and time of measurement.

f) The excited volume must completely overlap the analyzed volume. This may be a problem in some experiments using laser flash photolysis. One example is when a laser beam of low-energy, high-power pulses is focussed to a point the size of a millimeter or less. Several effects can distort the expected excitation path. For instance, this path can be modified by self-focussing; in addition on such tight focussing, it must be remembered that the excitation path is governed by the λ-dependence of the focal lengths of the lenses in the optical system. Another example is when a cell with a large length/diameter ratio is used and the analyzing beam is poorly collimated. Special care must be paid to reject any analyzing light traveling in the walls of the cell which can act as an optical fiber. The consequences of a bad overlap, a method for testing the quality of the overlap, and the corrections to be applied when a perfect overlap cannot be achieved were discussed by Bazin and Ebbesen. [4]

g) Problems arising from polarization effects must be considered when lasers are used for the excitation if the delay between the excitation and the analysis is of the same order as the time for rotation of the investigated molecule. The rotation time can be roughly estimated from the molecular size and the viscosity of the solvent.

h) The transverse distribution of the transient species should be homogeneous in the analyzed volume. Usually, this condition cannot be strictly fulfilled, only approximated when experimental conditions are carefully chosen.

The condition (h) can often be approximated in conventional flash photolysis. This happens when the photolysis cell is symmetrically excited by at least two flash tubes and when these flash tubes are used in conjunction with an efficient chamber for diffusing the light. In addition, the absorbance of the photolyzed solution needs to be low in the wavelength region of the exciting light.

In laser flash photolysis it is extremely difficult to get a homogeneous distribution of the transient species because of the attenuation of the laser beam as it propagates in the solution being excited. This creates a concentration gradient either along the axis of the analytical beam (colinear arrangement) or perpendicular to it (crossed-beam arrangement). This effect can be minimized by keeping the absorbance of the solution at the excitation λ as low as possible (0.1 over the relevant dimension of the analyzed volume is the recommended maximum). In addition, when a crossed-beam arrangement is used, the excitation beam can often be more tightly focussed (still keeping the focal point behind the cell, away from the incident light) so that the reduction in exciting photons as the beam passes through the sample is partially matched by a reduction in the beam's cross section, which keeps the beam's photon flux relatively high all along the excitation path.

The spatial distribution of the energy in a cross section of the laser beam also causes an inhomogeneous distribution of the transient. The beams of multimode lasers usually contain "hot spots". It is practically impossible to calculate a correction factor between the measured absorbance and the absorbance that would be obtained with the same amount of transient distributed homogeneously. Solid-state lasers can have particularly bad hot spots. Bundles of optical fibers, known as scramblers, have been used to partially overcome this problem. Single-mode lasers give a nonuniform photon distribution which is, in most cases, more or less Gaussian or ring shaped. For such a distribution a correction factor can be mathematically evaluated, provided the profile of the photon flux is measured (with a photodiode array, for instance).

Corrections to be applied to account for some special cases of inhomogeneous excitation have been studied by J. W. Boag. [5] Using computers, it is now possible to calculate correction factors in most cases provided that the profile of the energy distribution is reproducible. It should be noticed that the uncertainty in the absorption coefficient due to inhomogeneities greatly depends on the method used to estimate the concentration of the transient species. These methods are examined in the following section.

III. METHODS

The various methods used to evaluate the concentration of a transient species all rest on a few basic principles and fall into the following types of measurements:

A) The transient species is formed, with a known yield, from another species, the concentration of which is known or can be measured.

B) The transient species is converted, with a known yield, into another species, the concentration of which is measured or calculated.

C) The transient's concentration is evaluated from kinetic measurements.

D) The transient's concentration is directly measured by a method other than electronic absorption spectroscopy.

A. Methods using a precursor

The precursor from which the transient is formed with a known yield may be either the ground state or the excited singlet of the investigated compound or the triplet state of a standard compound used as a sensitizer.

A1. Ground state depletion [6]

In this case the precursor is the ground state of the parent molecule of the transient.

If, at some time (t) after the excitation, the ground state (G) has been converted only into the transient species (T), then the concentration of T equals the ground-state depletion, namely

$$[T] = \Delta[G] = [G]_0 - [G] . \tag{3}$$

If there is, in the range of the ground-state absorption, a wavelength λ_1 accessible to analysis where the transient does not absorb, then the absorbance change at time t and wavelength λ_1 is $\Delta A(\lambda_1) = -\varepsilon_G(\lambda_1)[T]\,l$. At any wavelength, λ_2, within the transient's absorption band, $\Delta A(\lambda_2) = \{\varepsilon_T(\lambda_2) - \varepsilon_G(\lambda_2)\}[T]\,l$, and thus

$$\varepsilon_T(\lambda_2) = \varepsilon_G(\lambda_2) - \varepsilon_G(\lambda_1)\frac{\Delta A(\lambda_2)}{\Delta A(\lambda_1)} . \tag{4}$$

Limitations, Advantages and Disadvantages

As long as the above conditions are satisfied, this method is simple and can be used for any type of transient species: excited singlet states, triplet states, radicals, radical ions, ground states of metastable products, etc.

Obviously, if the chemical yield of conversion is not unity, i.e. some products (P) are present in the solution at time t, then corrections must be made. The corrections may be quite simple or tedious depending on the absorption properties of P. But the yield of conversion must be known in all cases.

The main disadvantage is that it is impossible in many cases either to find a convenient wavelength where G is the only absorbing species or even to know whether or not such a wavelength exists. Several methods have been proposed that partially overcome this difficulty. They are founded either on the expected shape of the absorption spectrum of T or on the assumption that fine-structured absorption spectra of G and T are not likely to present sharp peaks at the same wavelength. Such considerations have been previously discussed. [3,7]

A2. Total depletion or saturation [8]

When a transient's absorbance, ΔA_T, is plotted against the energy of excitation E, the ΔA_T vs. E curve eventually reaches a region of nonlinearity [9] at high values of E. If the high-energy behavior of this curve tends to a plateau value, $\Delta A_{T,\,max}$, it is assumed that this plateau corresponds to a complete conversion of the initial ground state G into the transient T. Then $[T] = [G]_0$, and

$$\varepsilon_T = \frac{\Delta A_{T,\,max}}{[G]_0\,l} . \tag{5}$$

Limitations, Advantages and Disadvantages

This method is of course limited to cases where T and G are the only species present in the solution at the time chosen for measuring the absorbance; any intermediate between G and T must be entirely converted into T. This may require some delay between excitation and analysis, and the transient may decay appreciably during that time. Therefore, when the decay time of T is not much longer than its rise time, corrections must be applied either by extrapolation to "zero" time or by a mathematical analysis of the curve $[T] = f(t)$.

A major disadvantage is that many other sources of an apparent saturation are possible, for example reabsorption of the excitation by excited states and transient species or (especially in laser flash photolysis) multiphotonic processes, biphotonic ionization, etc.

When the quantum yield (ϕ_T) of formation of T is not unity, the duration, τ_p, of the excitation pulse must be much longer than the lifetime, τ_X, of any precursor of T in order to allow a complete conversion by successive recycling and reexcitation. For instance, the relation, [10]

$$\tau_p > \frac{2\tau_X}{\phi_T} , \tag{6}$$

must hold for T being a triplet and X being the excited singlet. Equation 6 contains an important limitation when using a laser flash photolysis technique.

A3. Actinometry

In this case, the relevant precursor is the excited state of the photolyzed compound. Its concentration, [E*], is calculated from N_{abs}, the number of photons absorbed in the analyzed volume, V. The concentration of the transient is then given by

$$[T] = \phi_T [E^*] = \phi_T \frac{N_{abs}}{V} . \quad (7)$$

Depending on the experimental setup, there are several methods for determining N_{abs} and V.

With conventional flash photolysis, V is usually equal to the effective volume of the cell. N_{abs} is determined by filling the cell with an actinometer that has an absorption spectrum that must match as closely as possible the absorption spectrum of the investigated compound in both shape and absorbance over the whole spectral range of excitation. The actinometer can be any standard chemical actinometer that has been proven to give reliable results under flash-photolysis conditions. For instance, the ferrioxalate actinometer has proven to be usable [11] even in nanosecond laser flash photolysis. The main difficulty for actinometry in conventional flash photolysis is to match the absorbance over a large spectral range.

This is not a problem in laser flash photolysis because of the monochromaticity of the excitation. The number of photons absorbed in the analyzed volume can be calculated from the absorbance of the sample solution at the excitation wavelength and the energy of the laser pulse entering the cell. This energy can be measured, through the optical system (lenses, diaphragms,...) used for the measurements of the transient absorption, with a calibrated joulemeter or with a convenient actinometer such as ferrioxalate or Aberchrome-540. The cross-section of the excitation beam must be well defined (diaphragms) and precisely known. When chemical actinometers are used, their concentration must be high enough to ensure a total absorption of the excitation. This method is quite sensitive to problems arising from inhomogeneities in the excitation and from absorption by species other than the ground state.

Limitations, Advantages and Disadvantages

Several conditions must be fulfilled for the method to give reliable results:

a) The decay time of the transient species must be much longer than its growing-in time (duration of the excitation pulse + complete conversion of any intermediate precursor of the transient).
b) The excitation is assumed to be homogeneous over the volume V.
c) The quantum yield, ϕ_T, of formation of T must be known.
d) N_{abs} must be the number of photons absorbed by the ground state of the parent compound. Corrections accounting for absorption by the solvent, the reactants, etc. are trivial. However, it may be much more difficult to take into account the absorption of the excitation beam by the transient itself or by some other species, kinetically intermediate between the initial ground state and the investigated transient.

A4. Relative actinometry [12]

A closely related method (often called Relative Actinometry) uses two cells that have been matched in $A(\lambda_{ex})$, where λ_{ex} is the excitation wavelength. One cell contains the reference compound, and the other cell contains the precursor of the transient under investigation. The reference transient has a known ε_R and is produced with a known yield (ϕ_R), from the reference compound. A comparison of the absorbance (ΔA_T) of the investigated transient with the absorbance (ΔA_R) of the standard transient can be used to calculate the desired molar absorption coefficient

$$\varepsilon_T = \frac{\Delta A_T \phi_T}{\Delta A_R \phi_R} \varepsilon_R . \quad (8)$$

A recent [13] method using a chemical actinometer, Aberchrome-540, appears to give good results. This method is essentially a relative measurement, but this actinometer has the advantage that it does not involve yet another transient.

Limitations, Advantages and Disadvantages

With conventional flash-photolysis the main difficulty is to match the absorbance of the two cells over a large excitation spectral range. In laser flash photolysis, this method gives more reliable results than the straightforward actinometry method since it largely compensates for problems with excitation inhomogeneities. Furthermore, it is no longer a problem to match the absorbance of the solutions of the standard and investigated compounds since the excitation is confined to a well-defined wavelength. However, care must be taken to maintain a photon flux of excitation that is sufficiently low to prevent any saturation of absorbance.

A5. Energy transfer from a standard [14]

In this case, the precursor must be an excited state of a compound (X), most often the triplet state, whose molar absorption coefficient (ε_X) for some transition at wavelength λ_X is well known. This sensitizer is selectively excited either by flash-lamps (with convenient and efficient filters) or by pulses from a suitable laser. The overall measurement is done in a series of steps. In a first experiment, the sensitizer alone is excited, and the transient absorption ΔA_X is measured at wavelength λ_X. In a second experiment, the compound under investigation (the triplet quencher) is added to the solution of sensitizer, and the concentration of the quencher is adjusted so that it is large enough to quench every sensitizer triplet. The transient absorption ΔA_T due to the triplet of the investigated molecule at a wavelength λ_T is measured after excitation of the mixture by a light pulse with the same energy as in the first experiment.

In ideal cases, the concentration of the triplet transient, $[T] = \Delta A_T / (\varepsilon_T l)$, equals the concentration of the sensitizer triplet, $[^3X^*] = \Delta A_X / (\varepsilon_X l)$. Equating the two expressions and rearranging leads to

$$\varepsilon_T = \varepsilon_X \frac{\Delta A_T}{\Delta A_X} . \tag{9}$$

Limitations, Advantages and Disadvantages

This method has been developed (and is mainly used) for determining molar absorption coefficients of triplet transients with the advantage of not requiring a knowledge of the quantum yield of triplet formation. It can be extended to any transient species that is produced from the triplet of the investigated molecule, as long as that transient's yield is known. Since the absorbances of the transients are compared in two experiments that are conducted under the same experimental conditions, the method minimizes the problems arising from excitation inhomogeneities which frequently plague laser flash photolysis (however see limitations e and f below).

The method is limited to studies in fluid solutions where the acceptor and sensitizer molecules can diffuse and encounter. In order to get reliable results from this method, additional limitations need to be imposed (or corrections need to be made):

a) The excitation should be given only to the sensitizer.

b) In the second experiment (when exciting the mixture), there must be some delay, depending on the acceptor concentration, between the excitation and the absorbance measurement to allow the completion of the energy-transfer process. Whenever possible, the acceptor concentration, [Q], should be large enough so that the decay of the acceptor triplet (or monitored product) can be neglected during that delay, namely

$$k_{et}[Q] \gg \frac{1}{\tau_X} , \tag{10}$$

where k_{et} is the quenching rate constant and τ_X is the lifetime of the acceptor triplet (or monitored product). If not, corrections must be made. [3,14]

c) The triplet of the sensitizer must be quantitatively quenched by the acceptor. Therefore the triplet energy of the sensitizer must be higher than that of the acceptor (reversible energy transfer must be avoided). Also for quantitative transfer, both the sensitizer triplet lifetime, τ_{sen}, and the concentration, [Q], of the acceptor must be sufficiently large, namely

$$k_{et}[Q] \gg \frac{1}{\tau_{sen}} . \tag{11}$$

d) When the acceptor concentration cannot be made large enough to fulfill the conditions in eqns 10 and 11, a complete kinetic treatment of the system is needed to get significant ε values. Difficulties in obtaining sufficient concentrations of the quencher may be exacerbated if the acceptor can absorb part of the excitation. Additional limitations on [Q] may be due to other common reasons (solubility, secondary reactions, etc.).

e) The measured transient absorbances should be of the same order of magnitude.

f) The changes in the energy of the exciting pulse, which may be required when the values of ε_X and ε_T are very different, should be obtained by using calibrated attenuators and not by changing the operating conditions of the laser source since this usually changes the energy distribution in the laser beam.

This method, which is widely used, rests on the assumption that the quenching of the sensitizer triplet proceeds only by energy transfer. This is probably valid in most cases where the lowest level of the triplet state of the sensitizer is sufficiently above the triplet levels of the acceptor triplets. However when choosing a sensitizer, molecules that have chemically reactive triplet states should be avoided. In particular, a reversible elementary reaction, such as electron transfer, can give efficient quenching without producing any detectable stable product. Even when sensitizers are chosen with their redox potentials in mind, there remains an uncertainty in the efficiency of the energy transfer which may be alleviated if concordant results can be obtained when two different sensitizers are used.

B. Methods by conversion into a product

In these methods, the concentration of the transient species is deduced from the concentration of one of its products. A knowledge of the transient-to-product yield is an essential component of these methods. The product may be an excited state, a radical, or a stable photoproduct of either the investigated compound or another compound added as an indicator.

B1. Energy transfer to a standard [14]

This method is quite similar to the one described as "Energy Transfer from a Standard" but now the parent molecule of the transient is the sensitizer, and the standard compound is the acceptor. In practice, the investigated transient is an excited state, usually a triplet state. As with Method *A-5*, this method can be extended to other was a variant of this technique. The standard was the benzophenone ketyl radical (formed from the benzophenone triplet) which was formed in competition with energy transfer to the investigated triplet.

The experiments are conducted in a same fashion as those in Section *A-5*. First, the transient absorbance, ΔA_T, of the sensitizer alone is measured at a wavelength, λ_1. Second, the transient absorbance, ΔA_X, of a solution containing both the sensitizer and acceptor is measured at a wavelength, λ_2, where the molar absorption coefficient (ε_X) of the standard triplet state is known. Assuming complete and quantitative conversion of the triplet transient into the triplet of the standard, the molar absorption coefficient of the compound under investigation is given by

$$\varepsilon_T = \varepsilon_X \frac{\Delta A_T}{\Delta A_X} . \tag{12}$$

Limitations, Advantages and Disadvantages

See those mentioned for the "Energy Transfer from a Standard".

B2. Chemical conversion

In this method, the concentration of the transient of interest is determined by measuring the concentration of either a stable compound or another transient species, produced with a known yield from the transient under investigation. This transformation can be a chemical reaction which may be either intramolecular or induced by an added reactant. For instance:

a) The concentration of a semi-reduced radical RH·, known to disappear exclusively by dismutation into two stable molecules R and RH_2, will be equal to twice the concentration of the RH_2 produced. The amount of RH_2 can be measured by any convenient analytical method.

b) The concentration of an excited state M*, reacting with an added molecule RH_2 to give the radicals MH· + RH· with a yield ϕ, can be obtained by measuring the concentration of RH· and dividing it by ϕ.

Limitations, Advantages and Disadvantages

The method can be applied to any type of transient species, from long-lived excited singlets to metastable, strained ground states. Short-lived and very unreactive species are the exceptions. There are many possible reactant partners for the transients, and they can be used in a very large range of concentrations, provided that they do not absorb the excitation light. In some cases (i.e. the monitored product is a stable species produced with a low yield), it may be useful to submit the sample to a number of excitation pulses before measuring the concentration of the product. Under these circumstances, it is necessary to check to be sure that there is no significant change in the behavior of the system between the first and last excitations.

When the monitoring of the concentration of the standard species cannot be confined to the volume monitored for the transient's optical absorption or when macroscopic diffusion may have occurred during the time of the chemical conversion, the excitation must be uniform over the entire volume of the cell. Uniform irradiation is usually not attained in laser flash photolysis.

The main difficulty of the method is the determination of the chemical conversion yield which, in many cases, can only be roughly approximated.

C. Methods founded on a kinetic analysis

These methods are based on calculations of the transient concentration as a function of the competition between its kinetics of formation and decay.

C1. Steady state method

A steady-state concentration of the transient is obtained when its rate of decay, $[T]/\tau_T$, equals its rate of formation, $\phi_T I_{abs}$. In these expressions, I_{abs} is the quantity of photons absorbed in the monitored volume (in units of einstein / L · s), ϕ_T is the quantum yield of formation of the transient, and τ_T is the transient's lifetime (in seconds). Then, if ϕ_T is known, the steady-state concentration,

$$[T]_{ss} = \tau_T \phi_T I_{abs} , \tag{13}$$

can be calculated by measuring τ_T and I_{abs}.

Limitations, Advantages and Disadvantages

To get a measurable stationary absorption of the transient, the lifetime must be long. For instance, the method was used for triplet states in glassy solutions, with τ_T in the second range, but it can be applied to other long-lived transients (τ_T > 1-100 ms depending on the photon flux of excitation) such as unstable ground states.

The method, in the simple form given above, rests on several assumptions. First, the parent ground state and the transient are the only species present in significant amounts. Second, the transient decays according to a first-order kinetics. Third, the depletion of the parent ground state must be negligible. Fourth, the transient should not absorb the excitation light; this can be checked by testing the linearity of the absorbance of the transient as a function of I_{abs}.

C2. Kinetic method

The concentration of the transient is still the steady-state concentration under a constant photon flux of excitation, but this value is derived from the kinetics of the build-up of the transient. Under certain conditions, which will be given below, the set of differential equations describing this build-up can be solved to give

$$[T]_{ss} = [G]_0 \left(1 - \frac{\tau_r}{\tau_T}\right), \tag{14}$$

where $[G]_0$ is the initial concentration of the parent ground state, τ_T is the lifetime of the transient, and τ_r is the rise time of its exponential growth.

Experimentally, the excitation light is rapidly turned on, and the growth of the transient absorption is recorded. The build-up curve is fit with an exponential growth which determines τ_r. After this absorption has reached a plateau value (ΔA_{ss}), the excitation light is suddenly turned off. The decay of the transient is recorded and fit with an exponential decay which determines τ_T. The transient's molar absorption coefficient can then be computed as

$$\varepsilon_T = \frac{\Delta A_{ss}\ \tau_T}{[G]_0\ l\ (\tau_T - \tau_r)}. \tag{15}$$

Limitations, Advantages and Disadvantages

The major advantage of this method is that the molar absorption coefficient of the transient is obtained from four accurately measurable quantities. It does not require knowledge of the quantum yield of formation of the species or knowledge of the molar absorption coefficient of a standard.

The absorption of the transient in the steady-state regime must be rather large (at least 100 times the detection limit) in order to make possible a precise determination of τ_r and τ_T by an analysis of the growth and decay parts of the curve $\Delta A = f(t)$. As in the Steady State Method, this is only possible with intense excitation sources, with very long-lived transients decaying according to a first-order kinetics, and with systems where any photochemical degradation is negligible.

An additional limitation is that there must be no long-lived precursor of the transient. Otherwise it is intuitively clear, that the meaning of τ_r will be changed, and also that the approximations needed to derive the simple expression for ε_T are no longer justified. The full kinetic treatment of a system where the transient is a triplet and the precursor an excited singlet is given elsewhere. [3,7] This treatment may be easily translated into other cases (i.e. a triplet precursor and an unstable isomer ground state as the transient).

C3. Partial saturation method

This method makes use of the nonlinearity (transient absorption vs. exciting pulse energy) which is observed when the energy of the excitation pulse is so large that a significant fraction of the ground state of the parent molecule is converted into the transient.

If this nonlinearity is due exclusively to the decreasing absorption of the excitation by the ground state (i.e. the transient itself does not absorb the excitation light) and if the concentration of any intermediate between the parent ground state and the transient is negligible at any time during the excitation process, then the set of differential equations accounting for the population of the transient and the depopulation of the ground state gives [16]

$$[T] = [G]_0 \left(1 - \exp\{-\alpha H_p \phi_T\}\right), \tag{16}$$

where α = 2303 ε_G , with ε_G being the molar absorption coefficient of the ground state at the excitation wavelength. H_p is the number of photons per unit area (in units of einstein cm^{-2} when ε_G is in units of L mol^{-1} cm^{-1}, note that 2303 contains a conversion factor of 1000 cm^3 L^{-1}). The transient absorption is given by

$$\Delta A_T = \varepsilon_T [G]_0\ l\ (1 - \exp\{-\alpha H_p \phi_T\}) = M(1 - \exp\{-N H_p\}). \tag{17}$$

Curve fitting techniques are then used for determining the M and N coefficients, and the molar absorption coefficient can be calculated as

$$\varepsilon_T = \frac{M}{[G]_0 \, l} \, . \tag{18}$$

When the product ($\alpha H_p \phi_T$) is very small, the expansion of the exponential may be limited to the first-order term. Such a truncated expansion gives a linear relation between ΔA_T and H_p with a coefficient proportional to the product $\phi_T \varepsilon_T$. Within this approximation, this method reduces to the actinometric method discussed above.

Limitations, Advantages and Disadvantages

One advantage of this method is that it gives independently ε_T and ϕ_T. In addition, even though the energies of excitation needed to reach the nonlinear region are usually fairly high, they are much lower than those required to obtain total depletion. This decreases the probability of multiphotonic processes which are usually to be avoided. The main limitations are:

a) The molar absorption coefficients of the parent ground state and of the transient at the excitation wavelength(s) have to be appropriate. The first one must be large (so that the initial concentration of the ground state can be small but still allow appreciable depletion using excitation pulses of "reasonable" energies), and the second must be zero (or very small) in order to prevent absorption of the excitation by the transient.

b) The presence of any intermediate or side product which can accumulate during the population of the transient can cause problems. This would destroy the basic assumption that the transient and the parent ground state are the only species present in the system. In addition, such additional species could absorb a fraction of the excitation. There is always at least one intermediate to be considered: either the excited singlet when the transient is a triplet or some precursor excited state when the transient is a radical or an unstable photoproduct. Even when the transient is the lowest excited singlet, an unrelaxed excited singlet can be considered as an intermediate. The rate of decay of this intermediate must be much faster than its rate of formation which depends on the photon flux of the excitation. The complete kinetic treatment of a system with an excited singlet intermediate and a triplet transient gives the conditions required when using this method. [17]

c) Since the method uses curve-fitting techniques, the accuracy of the determination of the M and N parameter may be questionable when the number of measured couples (ΔA_T, H_p) is limited or when the saturation phenomena are not clearly pronounced.

D. Direct measurement of the transient concentration

In some cases, it is possible to measure simultaneously (or under similar excitation conditions) the UV-visible absorption of the transient and also its concentration by an independent analytical technique. The determination of ε_T is then straightforward.

For instance ESR may be used to measure the concentration of radicals or triplet states. A difficulty in this method is that the ESR signal measures the total amount of the transient but it is extremely difficult to excite homogeneously a sample located in an ESR cavity.

When a transient is formed from a precursor (or decays into a product) by nonradiative processes, it is often possible to measure its concentration by calorimetry using time-resolved photothermal methods. These methods consist of (1) measuring the amount of heat released during the transient's formation (or decay) and (2) measuring the difference between the energy levels of the transient and its precursor (or product). Up to now, this technique has been used to determine the energy levels from the concentration and heat measurements, and has a time resolution ranging from picoseconds to tens of microseconds. Thus it could be used for many excited states decaying in this time range or for radicals and unstable products formed in this time range.

IV. REFERENCE MATERIALS

There is a need for compounds (or systems) that produce transients having both known yields and well-determined molar absorption coefficients. Calibrated molar absorption coefficients are needed in several methods (Relative Actinometry, Energy Transfer, and Chemical Conversion) of measuring unknown ε values of other compounds. Even when some other method is used, a reference can be useful in checking the experimental setup or the methodology used. However this kind of test does not automatically validate the results obtained if the spectroscopic, photophysical and photochemical properties of the investigated system are different from those of the reference material (and usually they are different). Therefore a large number of *reference transients* is needed to cover the wide range of transient species differing in their nature, their lifetime, the wavelength of excitation of their parent ground state, etc.

Triplet states are probably the most useful *reference transients* because the "Energy Transfer Methods" are among the most widely used, sometimes in combination with another method such as a subsequent chemical

conversion. A large number of reference triplets with various triplet energies and convenient spectral properties would be required to make possible the use of these methods in as many cases as possible. Unfortunately, even though ε values have been reported for the triplet-triplet absorption of hundreds of compounds, [3] only a few of these compounds may be considered as useful references because they have been the matter either of many concordant measurements or of specially designed experiments. These compounds are listed in the Table 1.

The compounds listed in Table 1 are some of the most widely measured triplet absorptions. In columns two and three are values for these compounds in benzene and cyclohexane. Most of these values come from the extensive least-squares fit of Bensasson and Land [18]. Great care was taken in these measurements to provide benchmark results. Over the years these values have held up quite well when compared to molar absorption coefficients obtained by methods other than the energy transfer technique which Bensasson and Land employed. The other two values listed in these columns comprise a recent [19] measurement of the benzophenone triplet which indicates a slight modification of the original Bensasson-Land value of (7680 L mol^{-1} cm^{-1}) and a recent measurement of *all-trans*-retinol. [20] This and other polyenes are listed since they have proven to be a useful class of energy acceptors because of their low triplet energies and because of their relatively high absorption coefficients.

These decadic molar absorption coefficients in benzene and cyclohexane are the values we recommend for use whenever the corresponding compound and solvent are used. As a note of caution, the aromatic hydrocarbons should be avoided as references whenever alternatives are possible. The triplet-triplet absorption peaks of these compounds are often very sharp. Unless the monitoring light is very monochromatic and at exactly the right wavelength it will not be possible to reproduce the proper conditions to get the correct molar absorption coefficients.

Although the compounds with molar absorption coefficient values in columns two and three cover a wide range of triplet energies, the list is not very extensive and the number of solvents is limited to two. There is a good deal of variation in the measurements of different solvents. However there is also a good deal of variation of measurements between laboratories. [21] Except in very few cases, there are not enough measurements in the literature to simply average results from a number of laboratories. The pool of values can be greatly increased if solvent effects are ignored, which is justified on the basis that variations between laboratories are of the same order as variations between solvents. [21] Using this assumption and a least-squares technique in the spirit of the original

TABLE 1. Decadic molar absorption coefficients (L mol^{-1} cm^{-1}) and associated λ's (nm)

Triplet States & Ketyl Radical	Benzene Solution[a]	Cyclohexane Solution[a]	Statistical[b] Benzene	Statistical[b] Non-benzene
2′-Acetonaphthone	10500 (430)	-	-	-
Acridine	24300 (440)	31500 (432)	25400‡ (440)	-
Anthracene	45500 (430)	64700 (422)	49800‡ (430)	61900 (430)
Benz[*a*]anthracene	20500 (490)	28800 (480)	19800‡ (490)	26200 (490)
Benzophenone[c]	7220 (532)	-	7870‡ (525)	6250 (525)
Biphenyl	27100 (359)	42800 (361)	25000‡ (360)	37000 (360)
β-Carotene	-	-	-	187000 (515)
all-trans-C_{17}-aldehyde[d]	-	-	63000 (430)	52000 (440)
9,10-Diphenylanthracene	-	-	14500 (445)	15600 (445)
all-trans-1,6-Diphenyl-1,3,5-hexatriene	-	-	105000 (420)	114000 (420)
Diphenylketyl	-	3700 (542)	-	-
all-trans-1,8-Diphenyl-1,3,5,7-octatetraene	-	-	178000 (440)	198000 (440)
2-Methylnaphthalene	-	-	-	30600 (420)
Naphthalene	13200 (425)	24500 (415)	14400‡ (415)	24100 (415)
Phenanthrene	15700 (492)	25200 (482)	15600‡ (490)	26800 (490)
Pyrene	20900 (420)	30400 (412)	20900‡ (415)	-
1-Pyrenecarbaldehyde	-	-	20100 (440)	18400 (440)
all-trans-Retinal	-	-	58400 (450)	69300 (450)
all-trans-Retinol[e]	-	80000 (405)	-	-
2,3,5,6-Tetramethyl-1,4-benzoquinone	6950 (490)	5330 (490)	7030‡ (490)	6310 (490)
N, N, N′, N′-Tetramethyl-1,4-phenylenediamine	12200 (605)	-	12200‡ (620)	17000 (620)
Xanthone	-	-	5300 (610)	6480 (605)

‡ These particular statistical results for benzene solutions are included only for comparison to the values in the "Benzene Solution" column which are the recommended ones.

[a] Reference 18, [b] reference 21, nominal wavelengths are in parentheses, [c] reference 19, [d] *all-trans*-5-Methyl-7-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4,6-heptatrienal, [e] Benzene solution value from reference 20.

Bensasson-Land treatment, almost the entire pool of measured molar absorption coefficients comes into play in determining the ε-value for a particular compound. The mechanism of such a coupling is through the relative measurements where reference ε's are used to measure unknown ε's. Decadic molar absorption coefficients from a least-squares procedure are listed in the last two columns of Table 1. One solvent effect had to be factored into the analysis. Benzene-like solvents had to be treated separately from the other solvents to get results that were in agreement with the results in columns two and three.

The values in the last two columns can be used as secondary references. Values in the "Statistical Benzene" column can be used for the compounds whenever there is no corresponding ε value in column two. The values in the last column can be used whenever the solvents are neither benzene or cyclohexane.

† The work at Notre Dame was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-3144 from the Notre Dame Radiation Laboratory.

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