PERIODICA POLYTECHNICA SER. CHEM. ENG. VOL. 45, NO. 2, PP. 93–109 (2001)

CONCENTRATION-MODULATED ABSORPTION SPECTROSCOPY AND THE TRIPLET STATE: SATURATION EFFECTS IN LONG-LIVED TRIPLETS

W. Jeremy JONES,* Christopher SHAW,* Daniel THOMAS,*
András GROFCSIK** and Miklós KUBINYI**

* Department of Chemistry,
University of Wales Swansea, Singleton Park,
Swansea, SA2 8PP, UK.
E-mail: w.j.jones@swansea.ac.uk
**Department of Physical Chemistry,
Budapest University of Technology and Economics,
H–1521 Budapest, Hungary
Chemical Research Center,
Hungarian Academy of Sciences,
P.O. Box 17, H–1525 Budapest, Hungary

Received: December 2, 2002

Abstract

The theory and technique of the pump and probe method of Concentration Modulated Absorption Spectroscopy (COMAS) has been extended to species with high triplet yields. In the experiments erythrosin B and rose bengal have been applied as model compounds. Using continuous wave laser sources and a modulated pump beam the large COMAS signal expected from the formation of long-lived triplets is shown to be dramatically reduced as a result of strong saturation effects. A gain expression is derived which takes into account such saturation effects and which describes satisfactorily the interaction of coinciding focused Gaussian pump and probe beams with the sample solution. Based on this theory, singlet and triplet concentration profiles in the focal region in the sample can also be evaluated. Such a treatment will be of value in modelling the refractive index gradients that arise from the differing molecular polarisabilities of singlet and triplet molecular species and from the energy conversion of electronic excitation to heat.

Keywords: triplet, xanthene dyes, photoinduced absorption/bleaching.

1. Introduction

Studies of the absorption spectra of organic dye molecules using the methods of UV/Visible spectroscopy are largely dominated by the changes which occur between the ground and excited electronic states of the same spin multiplicity. Investigation of absorption transitions from excited states is very much more difficult because level populations of excited states are frequently depleted by rapid radiative or non-radiative decay processes to the ground state and to any intermediate energy states in the system. Particularly important in these energy decay processes are the long-lived lowest-lying triplet states which frequently occur between the first excited singlet state and the ground state. It is well-known that the presence of such long-lived triplets can play a very important role in a range of photophysical processes and frequently triplet quenchers are employed to shorten the lifetimes of these states.

Because of the intrinsic interest and importance of the triplet states, besides the various conventional methods which have been developed for their study, of which flash photolysis and luminescence spectroscopy have proved to be particularly successful examples [1], [2], many other techniques have been developed in recent years including e.s.r. spectroscopy (see for example references [3], [4]) and optically detected magnetic resonance (ODMR, references [5], [6]). Other methods for studying triplets employ measurements of secondary effects caused by the absorption of light. Most such methods utilise the heating effect caused by non-radiative relaxation following optical excitation and decay into the triplet. Photo-acoustic and thermal lens spectroscopy have already gained wide acceptance and have proved to be very sensitive methods for analytical applications, frequently in circumstances where conventional spectroscopic methods have proved to be inadequate [7], [8], the spread of these techniques being markedly facilitated by the use of laser light sources. The simplest of the various thermal lens techniques uses one laser beam to provide the route both for sample excitation and the means of probing the heat produced, while significant improvements have been achieved by using separate laser sources for ‘pump’ and ‘probe’ beams.

The more typical pump/probe experiment monitors the changes in the transmitted power of the probe beam as a result of the perturbations to the optical characteristics of the sample caused by the pump beam, rather than the indirect beam defocusing and beam deflection behaviour which lie at the heart of photothermal methods. The transmission of a probe laser through a sample (a) is diminished as a result of absorption by excited state species created by absorption of pump photons (photo-induced absorption); (b) is increased due to stimulated emission and the reduced absorption arising as a result of depopulation of the ground state (photo-induced bleaching); thus the observed change in transmission depends on the relative magnitudes of the absorption cross-sections of ground and excited states. Where absorption of pump photons leads eventually to population of an intermediate triplet state the methods of photo-induced absorption and photo-induced bleaching can also provide information on the properties of the triplet state, information which usually cannot be obtained by other less direct methods. The role of the lowest-lying triplet state in various spectroscopic processes is already well known, but its impact on the phenomena of photo-induced absorption and photo-induced bleaching is less well characterised. Recent studies from this research group have attempted to lay the foundation for the methods of photo-induced absorption and photo-induced bleaching on a formal quantitative footing in a technique termed Concentration-Modulated Absorption Spectroscopy (COMAS) [9], [12]. The present paper describes the extension of these COMAS methods to take into account the dramatic changes which occur to the probe transmission when significant triplet formation occurs in condensed phase systems. The detailed experimental studies on solutions of erythrosin B, rose bengal and eosin y will be presented in a separate paper [13].

The effect outlined below may occur in any photothermal experiment as an unwanted side effect and may have to be considered in the quantitative treatment of thermal lens experiments. Interestingly, it is only recently that scientists dealing with thermal lens spectroscopy have recognised the significance of this effect. At first this effect was regarded as an ’error’ or ’abnormal signal’ in thermal lens spectroscopy [14]–[16]. Theoretical treatments are given by CHARTIER and BIALKOWSKI [17], [18] and by TERAZIMA and co-workers [19]–[22]. The latter authors distinguish between a ’population lens’ and transient absorption, both being superimposed on the normal thermal lensing signal. In our COMAS measurements we try to avoid the thermal lens signal in order to study the transient absorption signal independently.

2. Concentration-Modulated Absorption Spectroscopy

The term COncentration-Modulated Absorption Spectroscopy (COMAS) describes succinctly the process which occurs when a modulated flux of pump laser photons perturbs the state concentrations of an absorbing chromophore. Laser radiation may be characterised by a well-defined flux of photons flowing through identifiable regions of space. The absorption of such photons in a defined volume produces a measurable change in the concentrations of state, the lower state concentration being diminished and the higher one increased by this perturbation, the net change as a function of time being determined by the subsequent history of the system. This change is monitored by measuring the transmission of a probe laser, whose power is kept sufficiently low to avoid further significant changes to the populations. The quantitative basis of this method of studying absorption spectroscopy was laid in a series of papers describing its application with mode-locked picosecond laser systems [9]–[11] and high frequency (10 MHz) modulation methods. However, its generality is substantially greater than its application with rapid repetition rate pulsed laser systems, and the theory was modified for use with continuous wave lasers and variable frequency modulation methods [12]. It is this latter aspect of COMAS which is of relevance to the study of photo-induced absorption/bleaching in systems containing significant triplet formation.

Many studies of lifetimes of excited singlet states have been carried out with mode-locked picosecond lasers [23], monitoring that fraction of the excited state population which reverts *directly* to the ground electronic state rather than via the triplet state. For that fraction of the ground state which is repopulated via the triplet state, however, mode-locked laser systems have no advantage over c.w. lasers because of the slow time scale of the recovery of the state populations as a result of long triplet lifetimes. Under such circumstances there are many benefits to be derived from the use of c.w., rather than mode-locked lasers, and from variable frequency modulation methods that can be matched in time to the recovery rate of the ground state concentration repopulated via the triplet.

In order to study the saturation effects on COMAS signals, model experiments have been carried out on xanthene dyes, erythrosin B and rose bengal in dilute

($\sim 10^{-6}$ M) solutions in ethanol and ethylene glycol. The experimental arrangement for which the theory outlined below is developed is shown in *Fig. 1A*. Both the pump and probe beams are produced by c.w. lasers, the pump being of longer wavelength. An electrooptic modulator/polariser combination produces either sine wave or square wave modulation of the intensity of the pump beam. The two beams are made coincident and focused into the sample cell, following which they are separated and the probe beam is sent to a photodiode detector. The signal is processed by a phase sensitive detector locked to the frequency of modulation.

The co-ordinate system used in the theoretical treatment is shown in *Fig.1B*.

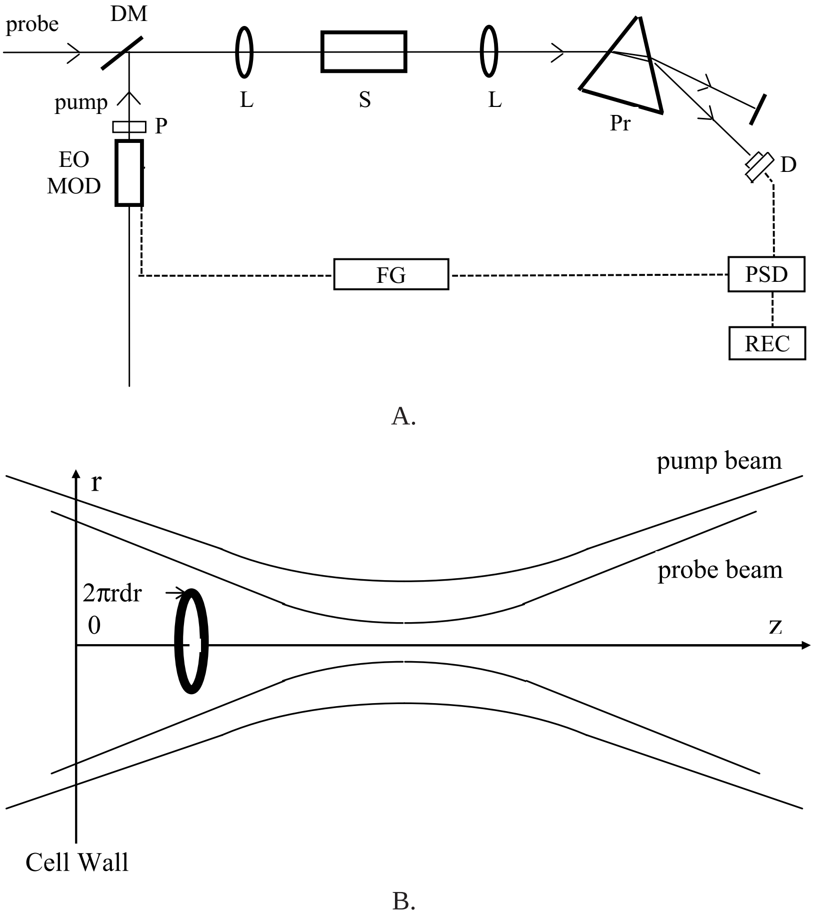

Fig. 1. (A) Schematic diagram of the c.w. COMAS experiments. DM - dichroic mirror; L – lens; S – sample; Pr – prism; D – detector; FG – function generator; EO MOD – electrooptic modulator; P – polariser; PSD – phase sensitive detector; REC – recorder. (B) The co-ordinate system used in the theoretical treatment.

With a modulation frequency f the measured fractional increase of the transmission of the probe laser, the 'gain' (attenuated absorption), using the modulated-pump/unmodulated-probe COMAS method for a two-level system of broad absorption features, is given by the standard gain expression [12]

$$G^{\mathrm{st}} = \frac{n\pi \cdot \sigma_p \cdot \sigma_{pr} \cdot N_1^e \cdot i_p}{\lambda_m \cdot k_2} \cdot F, \tag{1}$$

when different wavelength pump and probe lasers with absorption cross-sections σ_p and σ_{pr} are set to different parts of the ground state absorption band. This expression is analogous to *Eq.* (28) of reference [12] except for:

(i) the replacement of σ^2 in that publication by $\sigma_p \cdot \sigma_{pr}$, the product of pump and probe absorption cross-sections;
(ii) the fact that the probe is of shorter wavelength than the pump so that the concentration perturbation of the ground state only is interrogated, as a result of which the 'gain' is effectively halved; and
(iii) the replacement of λ by the mean wavelength of the two lasers λ_m in the medium of refractive index n. In *Eq.* 1 N_1^e is the unperturbed equilibrium concentration of the chromophore in its ground state, which is equal to the equilibrium population difference $N\Delta^e$ $(= N_1^e - N_1^e)$ for electronic transitions, i_p is the average flux of modulated pump photons incident on the sample per second, and k_2 $(= 1/\tau_2)$ is the rate of re-population of the ground state from those levels populated by the pump laser.

The decay function F of *Eq.* (1) is given by

$$F = \frac{1}{\left[1 + (2\pi f/k_2)^2\right]^{1/2}}. \tag{2}$$

Eq. (1) presupposes that the fractional increase of the probe transmission in each region of space has been integrated over the whole region of space in which gain is created.

When *Eq.* (1) is employed to evaluate the gain for fluorescent dyes in solution it is found that where no intermediate electronic states exist and for excited electronic state lifetimes in the range 1–10 ns the measured gain values agree broadly with the values predicted by *Eq.* (1) using known values for the various parameters involved. Where efficient inter-system crossing to a low-lying triplet level occurs, however, it is the lifetime of the triplet which controls the rate of re-population of the ground state and k_2 in *Eqs.* (1) and (2) is replaced by k_T $(= 1/\tau_T)$ the rate constant of the decay of the triplet [12], [24]. Since triplet lifetimes can be 4–5 orders of magnitude longer than those of the singlet from which they are populated, k_T can be 10^4 s^{-1} or smaller and G^{st} can approach unity, far from the conditions for which the gain expression of *Eq.* (1) was determined. With such long-lived triplets, in the focal zone, ground state singlet species are excited via pump (and probe) laser during the early stages of the pump modulation cycle into the triplet sink, ground state population is diminished dramatically so that little further absorption of the pump laser occurs later in the pump modulation cycle, and the gain saturates at a value far below that predicted by *Eq.* (1). The dramatic effects of this saturation process were discovered during early studies of erythrosin B and rose bengal in dilute solutions in ethanol and ethylene glycol. *Fig.* 2 shows a plot of the ratio of the experimentally measured gain, $|G_{\mathrm{exp}}|$, to the standard ‘gain’, $|G^{st}|$, (calculated using known parameters in *Eq.* (1)) versus the standard gain as abscissa. The experimental data points represent: rose bengal in ethylene glycol – open circles; rose bengal in ethanol – filled circle; erythrosin B in ethylene glycol – open squares; erythrosin B in ethanol – closed squares. Although the samples and solvents are different in many respects, the nature of the problem (*i.e.* triplet saturation) is thought to be the same in each case so that the form of the plot of *Fig.* 2 for these different samples is felt to be justified. The data of *Fig.* 2 were evaluated at the low frequency limit ($f \ll k_T$ in *Eq.* (2)), the triplet lifetime being evaluated by fitting the experimentally measured gain values versus the modulation frequency according to *Eq.* (2) (see inset to *Fig.* 2). Since the calculated relative gain data cover a range of approximately two orders of magnitude they are plotted in *Fig.* 2 on a log/log format and although they exhibit a marked scatter, there is a clear cut correlation establishing the convergence of the observed gain to that expected for low gain conditions ($\log ||G_{\mathrm{exp}}||G^{st} \approx -0.6$, see later). This behaviour is symptomatic of the type of saturation behaviour described above.

It is apparent from *Fig.* 2 that even under conditions of very low pump and probe laser powers, where relatively low gain values are to be expected, there are still significant deviations between calculated and measured values of the probe laser gain. Avoidance of this discrepancy between observed and calculated gain values by reducing pump and probe laser powers proves to be extremely difficult to achieve for systems with long-lived triplet states.

In practice it was found that problems arising from the wholesale conversion of ground singlet state molecules into the triplet could be avoided by enlarging the beam radii in the sample, leaving the only problems to be resolved as (*i*) those associated with the evaluation of the theoretical gain for confocal parameters (defined as $2n\pi w_o^2/\lambda$) substantially greater than the absorption path, and (*ii*) the appropriate gain expressions employed where both singlet and triplet species give rise to significant absorption of pump and probe lasers. These aspects of the theoretical treatment of the probe laser gain in triplet-forming systems are considered in detail below.

3. Concentration-Perturbation and Triplet Formation

In considering the influence of a modulated pump laser on the time-varying concentrations of singlet and triplet states it is convenient to consider the kinetic scheme displayed in *Fig.* 3. This scheme includes triplet absorption but does not include either the reverse intersystem crossing or any chemical reactions of the triplet molecules.

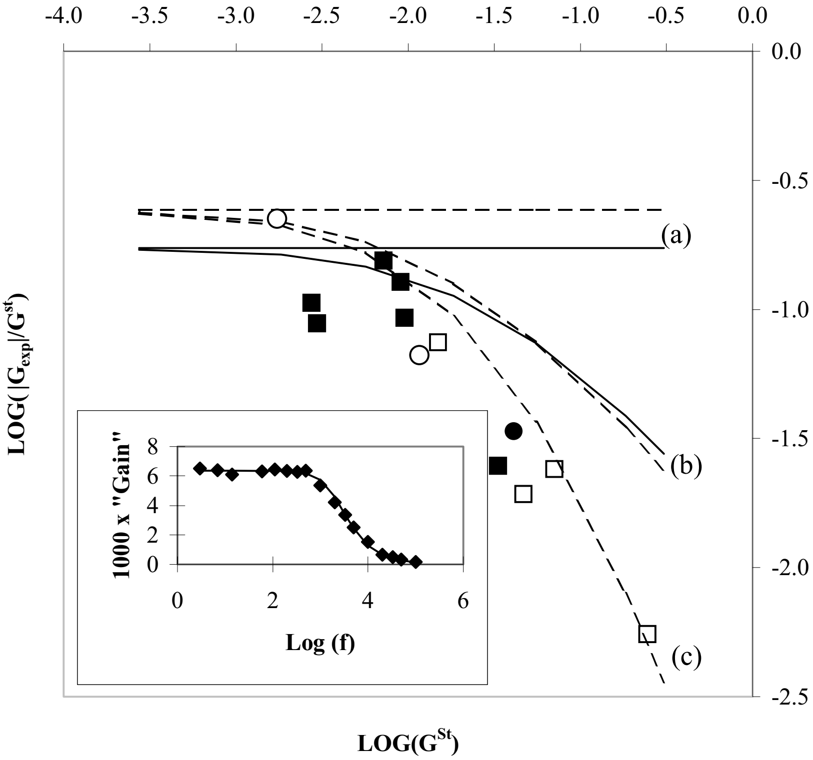

Fig. 2. The variation of the experimental to standard (*Eq.* (1) gain ratios versus the standard gain values for erythrosin B and rose bengal in solutions in ethanol and ethylene glycol. The data points are fitted by theoretical expressions which take account of the non-integer α and β values : (a) without pump or probe saturation effects; (b) pump laser saturation only (*Eq.* 14); (c) with pump (*Eq.* 14) and probe (*Eq.* 7) saturation. The broken lines employ the constants for erythrosin B; the solid lines are calculated for rose bengal. The inset to this diagram shows a typical temporal gain versus modulation frequency (f) decay curve.

(The former of these two effects will be considered later in this paper and the latter effects will be discussed separately [13].)

When an infinitesimally low flux of photons $i_p(r, z, t)$ of an axially symmetric laser beam falls on radial element $2\pi r \cdot \mathrm{d}r$ at longitudinal position z of a sample between time t and $t+\mathrm{d}t$ in the pump modulation cycle (*Fig.* 1*B*), the decrease of the flux of photons due to sample absorption is given by

$$-\frac{\mathrm{d}i_p(r, z, t)}{\mathrm{d}z} = {}^S\sigma_p \cdot N_1(r, z, t) \cdot i_p(r, z, t), \qquad (3)$$

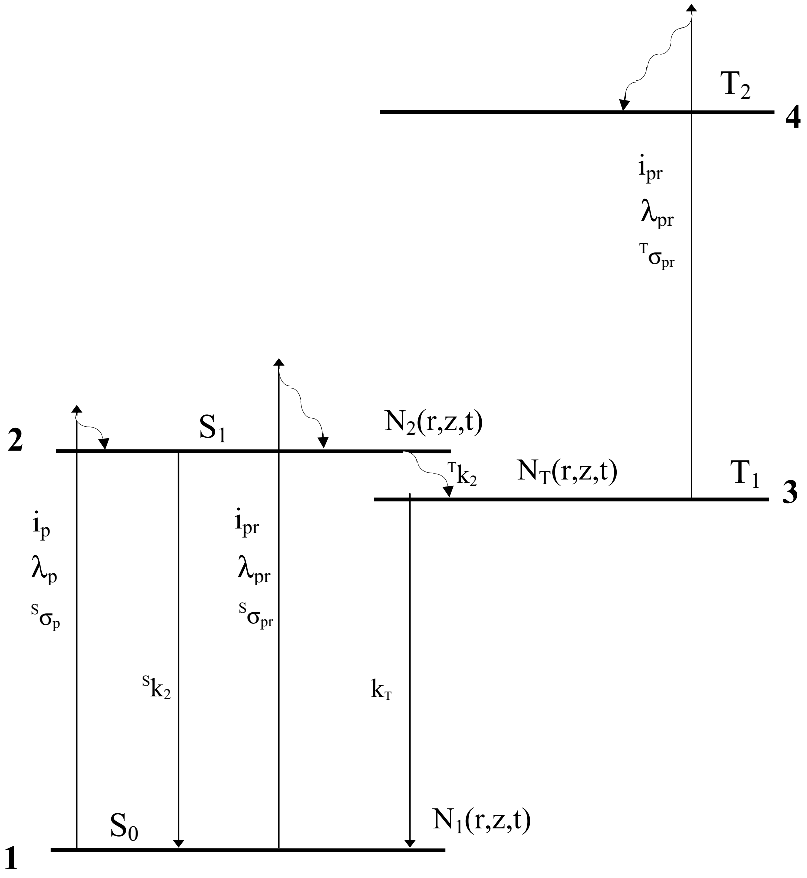

Fig. 3. The energy level scheme and associated spectroscopic and kinetic parameters employed to model the singlet-triplet excitation processes. S_0 and S_1 refer to ground and first excited singlet states, T_1 and T_2 to the corresponding triplet states. i, λ and σ refer to the incident photon flux, the radiation wavelength and the absorption cross-section, respectively, for the pump (subscript p) and probe (subscript pr) lasers. $N(r, z, t)$ refers to the appropriate state concentration at radial position r and longitudinal position z of the radiation profile at time t.

$^S\sigma_p$ being the absorption cross-section from the ground singlet state at the pump laser wavelength.

For a Gaussian laser beam the radial flux of photons is given by [12]

$$i(r, z, t) = \frac{4r}{w^2(z)} \cdot \exp[-2r^2/w^2(z)] \cdot i(z, t) \cdot \mathrm{d}r, \tag{4}$$

where $w(z)$ is the beam radius at position z, and $i\ (z,t)$ is the average number of photons incident upon the sample between t and $t+$ dt.

Since this change $di_p(r,z,t)$ in the number of pump photons corresponds to the number of molecules excited from S_0 to S_1 in volume of space $2\pi r\cdot \mathrm{d}r\cdot \mathrm{d}z$ at position z (*Fig. 1B*), the decrease in the ground singlet concentration in this spatial element at time t can be easily expressed. The flux of pump laser photons in any time interval dt is expressible as $i_p(\mathrm{z,t}) = \mathrm{i}_p(\mathrm{z}) \cdot \mathrm{f(t)} \cdot \mathrm{d}t$, $f(t)$ being the form of the modulation function applied to the pump laser.

It is assumed in this treatment that since the lifetime of the lowest triplet is very long in comparison with the lifetimes of all higher singlet and triplet states, the population of such higher energy states remains extremely low, and in particular $N_2(r,z,t) = 0$, so that

$$N_1^e \approx N_1(r,z,t) + N_T(r,z,t). \tag{5}$$

After setting up the kinetic equations for $\frac{dN_1}{dt}$, $\frac{dN_2}{\mathrm{d}t}$ and $\frac{\mathrm{d}N_T}{\mathrm{d}t}$, and considering the assumptions above, we obtain

$$\frac{dN_1(r,z,t)}{dt} = k_T \cdot N_1^e - k_T \cdot N_1(r,z,t) -$$

$$\alpha \cdot {}^S\sigma_p \cdot N_1(r,z,t) \cdot \frac{2}{\pi w_p^2(z)} \cdot \exp(-2r^2/w_p^2(z)) \cdot i_p(z) \cdot f(t), \tag{6}$$

where $\alpha\ (= {}^Tk_2\ /\ ({}^Sk_2 + {}^Tk_2))$ is the fractional efficiency for triplet formation from S_1, ${}^Sk_2$ and ${}^Tk_2$ being the rate constants for the decay processes from level 2 to the ground singlet and the lowest triplet state, respectively.

Eq. (6) can readily be rearranged to a form which is near identical to the type of expression derived (*Eqs.* 8a and/or 8b of reference [12]) in the original treatment of the modulated concentrations of ground state species created using a c.w. laser modulated by function $f(t)$. The differences between the two treatments arise from:

(i) the present evaluation of the ground state population only (and not the population difference $N\Delta(= N_1 - N_2)$ between Levels 1 and 2, since here the probe laser of higher frequency than the pump only interrogates changes in the population of Level 1);
(ii) the fact that only fraction α of excited singlet species transfer to the triplet; and
(iii) the replacement of k_2 by the triplet decay constant k_T.

Since the form of the temporal evolution of the concentration in Level 1 in region of space (r,z) is identical to that of our previous study [12], it is not necessary to pursue the complex time behaviour of that treatment here. One can accept that the time-dependent probe gain generated in each region of space has precisely the same form as that derived in our previous study, namely a ‘gain’ expression modified by the function F of *Eq.* (2) for a sine wave modulated pump beam.

The aspect which is of particular relevance to this study is the magnitude of the gain signal generated in each region of space (and the resulting overall gain) as a result of the kinetic processes identified above. In evaluating the maximum gain signals, which may be generated at low modulation frequencies, it is convenient to calculate the steady state concentration $N_1^{SS}(r,z)$ and $N_T^{SS}(r,z)$ of ground state singlet and excited triplet species, from *Eq.* (6), which result when each region of space (r,z) is illuminated by continuous pump laser radiation for times long compared with the triplet lifetime. With $f(t)=1$ *Eq.* (6) is readily integrated to yield the steady state concentrations:

$$N_1^{SS}(r,z) = N_1^e\left[1-\frac{b(r,z)\cdot i_p(z)}{k_T\left(1+\frac{b(r,z)\cdot i_p(z)}{k_T}\right)}\right] \quad = \quad N_1^e\cdot\frac{k_T}{(k_T+b(r,z)\cdot i_p(z))}, \tag{7}$$

and

$$N_T^{SS}(r,z) = N_1^e\cdot\left[\frac{b(r,z)\cdot i_p(z)}{k_T\left(1+\frac{b(r,z)\cdot i_p(z)}{k_T}\right)}\right] = N_1^e\cdot\frac{b(r,z)\cdot i_p(z)}{(k_T+b(r,z)\cdot i_p(z))}., \tag{8}$$

with

$$b(r,z) = \alpha\cdot{}^S\sigma_p\cdot\frac{2}{\pi w_p^2(z)}\cdot exp\left[-\frac{2r^2}{w_p^2(z)}\right].$$

The model described above does not include the possibility of reformation of excited singlet species from the lowest triplet. In the case of eosin y the so-called e-type delayed fluorescence is caused by emission arising from this process. Incorporation of this process into the above theory leads to the replacement of k_T in *Eqs.* (7) and (8) by k_T^*, where $k_T^* = [k_T + (1-\alpha)]\cdot{}^2k_T$, ${}^2k_T$ being the rate constant for reformation of excited singlet species from the ground triplet. Because k_T^* contains only constants this modification does not change the basic theory, which now continues as below.

4. Concentration Probing

Since the probe laser is unmodulated, its transmission through region of space (r,z) at the low frequency (steady state) limit may be derived by the Beer-Lambert relationship from *Eqs.* (7) and (8), allowing for the fact that both singlet and triplet species absorb, as

$$-\frac{\mathrm{d}i_{pr}^{SS}(r,z)}{\mathrm{d}z} = {}^{S}\sigma_{pr}\cdot N_1^{SS}(r,z)\cdot i_{pr}(r,z) + {}^{T}\sigma_{pr} N_T^{SS}(r,z)\cdot i_{pr}(r,z),$$

yielding:

$$-\frac{\mathrm{d}i_{pr}^{SS}(r,z)}{\mathrm{d}z} = N_1^{e}\cdot {}^{S}\sigma_{pr}\left\{1-\frac{\beta\cdot b(r,z)\cdot i_p(z)}{(k_T+b(r,z)\cdot i_p(z))}\right\}\cdot i_{pr}(r,z), \tag{9}$$

where $\beta\ (=\ ({}^{S}\sigma_{pr}\ -\ {}^{T}\sigma_{pr})\ /\ {}^{S}\sigma_{pr})$ is the fractional difference in the cross-sections for absorption by the triplet and the ground singlet states.

Introducing the appropriate expressions for $b(r,z)$ and $i_{pr}(r,z)$, assuming both pump and probe lasers have the same spatial profiles $(w_p(z) = w_{pr}(z) = w(z))$, and integrating radially, yields:

$$-\frac{\mathrm{d}\ln i_{pr}^{SS}(z)}{\mathrm{d}z} =$$

$$N_1^{e}\cdot {}^{S}\sigma_{pr}\left\{1-\int_{u=0}^{\infty} 2\alpha\beta\cdot{}^{S}\sigma_p\cdot i_p(z)\cdot\frac{e^{-2u}\cdot\mathrm{d}u}{[k_T\pi w^2(z)+2\alpha{}^{S}\sigma_p\cdot e^{-u}\cdot i_p(z)]}\right\}, \tag{10}$$

where $u = 2r^2/w^2(z)$.

Under very weak focusing conditions and low pump absorption, the second term in the denominator of the integrand of *Eq.* (10) may be neglected and this equation may be integrated algebraically over the whole focal zone to yield the steady state probe transmission in the presence of the pump laser. Hence, by comparison with the probe transmission in the absence of the pump (see [12]), the probe gain expression G (modified by the frequency dependent function F of *Eq.* 2) is given as:

$$G = \frac{n\pi\alpha\beta{}^{S}\sigma_p{}^{S}\sigma_{pr}N_1^{e}i_p(0)}{\lambda_m k_T}\cdot F, \tag{11}$$

where $i_p(0)$ is the average flux of modulated pump photons incident per second on the sample. Comparing this equation with *Eq.* (1), it can be clearly seen that the effects outlined above lead to the introduction of two factors, α and β in the numerator, and to the replacement of k_2 by k_T.

Because of the appearance of the triplet decay term k_T in the denominator, even under mild focusing conditions and low pump powers, the predicted gain can become unmanageably large for longer triplet lifetimes. This difficulty can be overcome, while still retaining measurable probe signals, by using larger spot radii to avoid significant fractions of the available ground state molecules being converted to triplets (even by the low power unmodulated probe laser). Use of a large spot radius w_o, however, brings in its train certain difficulties due to the marked increase of the confocal parameter ($2n\pi w_o^2/\lambda$, where λ is the vacuum wavelength and n is the refractive index of the medium), which can be significantly greater than the cell length. The expected gain under these circumstances is evaluated numerically by integrating *Eq.* (9) over the length of the cell, L, to yield the low-frequency-limit gain, G , for modulation frequencies approaching zero (i.e. F=1), as:

$$G = \frac{i^*_{pr}(L) - i_{pr}(L)}{i_{pr}(L)} = \exp\left\{ \int_{z=0}^{L} N_1^{eS} \sigma_{pr} \cdot \beta \left[1 - \frac{\ln(1 + B(z))}{B(z)} \right] \mathrm{dz} \right\} - 1, \quad (12)$$

where $B(z) = \dfrac{2\alpha^S \sigma_p}{k_T \pi w_p^2(z)} \cdot i_p(0) \cdot \exp\left[-N_1^{eS} \sigma_p \cdot z \right]$, and $i_{pr}(L)$ and $i^*_{pr}(L)$ are the transmitted probe fluxes in the absence and in the presence of pump laser radiation, respectively. The exponential factor in the expression for $B(z)$ allows for sample absorption as the pump laser propagates through the cell.

The beam radius $w(z)$ at distance z inside the cell is obtained for a Gaussian beam from the expression:

$$w^2(z) = w_o^2 \left[1 + \left(\frac{\lambda(z - z_o)}{n \pi w_o^2} \right)^2 \right], \quad (13)$$

where z_o is the distance of the beam focus from the entrance to the cell.

The effect of increase in the spot size on the calculated low-frequency gain is displayed in *Fig. 4* which plots, for a series of w_o values, the calculated G values as a function of z_o, the position of the focus in relation to the front surface of a 1 cm cell. In order to avoid saturation problems related to significant triplet formation, the triplet lifetime in these calculations was set to 10 ns, far shorter than would realistically be expected for these states. Other constants in these calculations were similar to those determined for erythrosin B, one of the dye molecules studied in detail.

Fig. 4 shows that for the lowest displayed focal spot sizes the maximum low-frequency gain, relative to the ‘gain’ value given by *Eq. (11)*, with $\alpha = 1$ and $\beta = 1$ approaches unity (and contours effectively the 1 cm cell profile). With increase in w_o the relative gain diminishes and the profile as a function of displacement of z_o from the cell centre flattens, reflecting to the increase in the confocal parameter, $2n\pi w_o^2\lambda$, where the major part of the gain is created.

Eqs. (1) and (11) are only applicable when the confocal zone is totally contained within the cell, and k_T (k_2) is fairly high so that no saturation effects occur. Otherwise a fuller treatment derived from the original expression (9) is necessary. To maintain generality, and consider that it is frequently difficult to employ pump and probe lasers with the same beam diameters, the gain in most practical situations

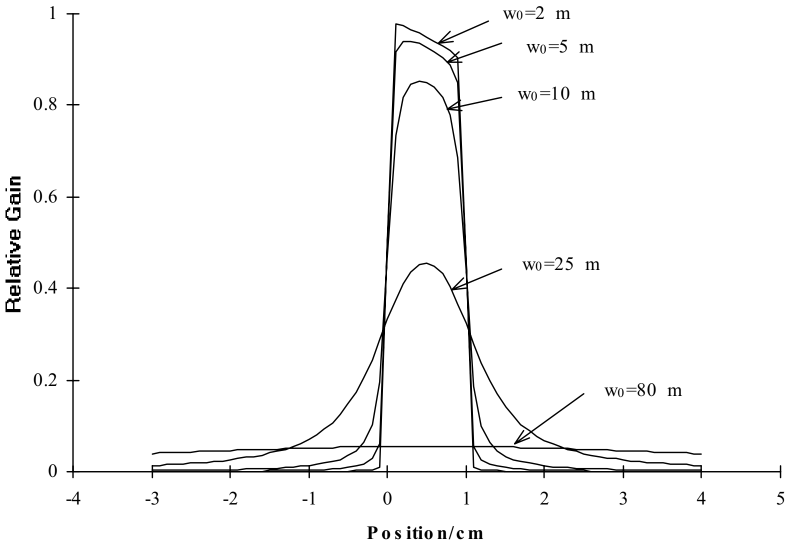

Fig. 4. Variation of the calculated low-frequency gain (*Eq.* (12)) with position of the focus, measured from the front surface of the 1 cm cell. The data are normalised to unity by dividing the calculated gain values by the standard gain expression of *Eq.* (1). Data are displayed for spot sizes w_0 of 2, 5, 10, 25 and 80 μm. To avoid the effects of pump/probe saturation data are evaluated with $k_T = 10^8\ \mathrm{s}^{-1}$. The effect of significant pump absorption is shown by the decay of the gain with position near the maximum of the gain profile (clearest for the 2 μm data).

is derived by integration of *Eq.* (9) with different pump and probe diameters, $w_p(z)$ and $w_{pr}(z)$, having a common focus as:

$$G = \left\{ \left\{ \exp \left[N_1^{e} \cdot {}^{S}\sigma_{pr} \cdot \beta \int\limits_{z=0}^{L} \int\limits_{u=0}^{\infty} \frac{B(z)\cdot v \cdot \exp\left[-u\,(1+v)\right]}{(1 + B(z)\cdot \exp(-u))} \mathrm{d}u\mathrm{d}z \right] \right\} - 1 \right\} \cdot F, \tag{14}$$

where $u = \frac{2r^2}{w_p^2(z)}$, $v = \frac{w_p^2(z)}{w_{pr}^2(z)}$ and $\beta = \frac{({}^{S}\sigma_{pr} - {}^{T}\sigma_{pr})}{{}^{S}\sigma_{pr}}$.

Because of the complexity of this expression, only numerical integration is possible.

The global data, presented in *Fig.* 2, were derived for different solutes (erythrosin B and rose bengal) in dilute ($\sim 10^{-6}$M) solution in ethanol and ethylene glycol under tight focus, extreme-saturation conditions, with a range of different focal spot diameters in the vicinity of 5–10 μm and very similar pump powers. The discrepancies between the measured and calculated gain (or loss) values, as reflected by the ordinate values of *Fig.* 2, are so extreme that they clearly cannot be attributed to uncertainties in the known absorption cross-sections, spot sizes or triplet lifetimes: all of these parameters are in any case incorporated so far as possible into the calculated gain values, and hence should be allowed for in evaluating the ratio G_{exp}/G^{st}. Clearly the difficulties of gain saturation considered above play a significant role in accounting for the discrepancy of up to two orders of magnitude between measured and expected gain values. That triplet saturation alone cannot account for the observed discrepancy is apparent from *Fig.*2, which shows that even for non-saturation conditions ($G^{st} \sim 10^{-3}$) the gain converges to $\sim 25\%(\log_{10}(G_{\mathrm{exp}}/G^{st}) = -0.60)$ of the expected value. This convergence of the ratio to a value of ~ -0.6 is ascribed to the influence of triplet absorption and to the non-quantitative conversion of excited singlets into triplets (i.e. α is less than 1). The two horizontal lines (a) show the influence of these processes on the gain calculated from *Eq.* (14) with α and β values and with absorption cross sections appropriate to those derived from the analysis of the erythrosin B and rose bengal data, as well as with a large k_T to eliminate the effects of triplet saturation. The fact that *Eqs.* (12) and (14) account correctly for the form of the decrease of the G_{exp}/G^{st} ratio as the calculated gain G^{st} (obtained from the simplest theory [12] using *Eq.* (1)) increases is apparent from the pair of lines (b) in *Fig.*2. The broken (erythrosin B) and solid (rose bengal) curves of *Fig.* 2 were evaluated using the spectroscopic constants (${}^{s}\sigma_p$ and ${}^{s}\sigma_{pr}$) for these species in ethanol with appropriate α and β values from the fuller analysis of reference [13], with $w_o = 10\mu$m and an average power of 1.8 mW, typical of the conditions employed for the studies displayed in *Fig.* 2. The expected variations in the calculated gain from that based on the simplest theory (*Eq.* (11)) were derived by changing the triplet lifetime from 0.1 μs to 170 μs (k_T from 10^7 to 6,000 s^{-1}) in *Eq.* (14). A further curve (c) shows the additional influence of probe saturation on the calculated gain. This curve takes into account the diminishing singlet concentration caused by the presence of a constant level of probe laser radiation on the sample using *Eq.* (7). This effect is only taken into account for erythrosin B, since probe saturation is markedly less significant for rose bengal as a result of its very much smaller absorption cross section at the probe wavelength.

Comparison of the experimental data points displayed in *Fig.*2 with the various curves calculated on the basis of the theory outlined above serves to confirm the essential validity of the present treatment. It is worth to briefly note the rather unexpected observation of the effects of probe saturation on the measured gain values. As normally investigated experimentally, this effect would not be considered since the probe is generally kept very much lower in intensity than the pump, and occurs on the high frequency side of the absorption band, where the absorption cross sections are very much lower, and hence it would be less likely to generate significant saturation effects. In spite of these factors, however, probe saturation clearly has a significant influence, as shown by *Fig.* 2, a result, no doubt, of the localisation of the saturating effects of the probe laser in those spatial regions where the probe intensity is highest. Account was taken of this effect in *Fig.*2 by evaluating the residual singlet concentration at the centre of the focused beam with a probe power of $\sim$ 0.35 mW, typical of the probe powers employed for the majority of these studies. With the inclusion of the effects of triplet–triplet absorption and the saturation effects produced by the pump and probe lasers the theory developed above provides a very satisfactory explanation of the discrepancy of more than two orders of magnitude between the gain measured experimentally and that, which would have been expected on the basis of the very simplest gain theory.

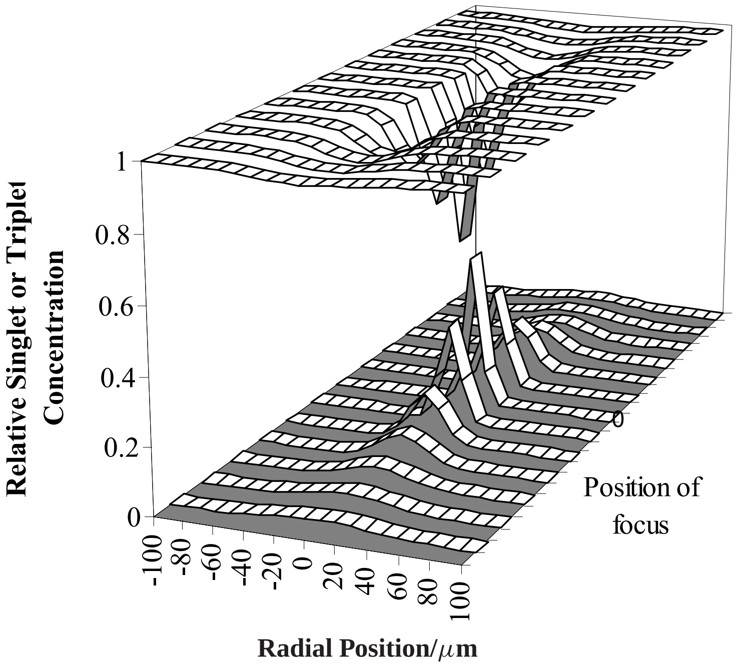

Fig. 5. Variations of the relative singlet and triplet concentrations with position near the focus of a continuous-wave laser beam. The spectroscopic parameters employed (*Eqs.* 7 and 8) are appropriate to erythrosin B in ethanol at a probe wavelength of 488 nm and a concentration of 10^{-6} M (see text), with w_0 = 10 μm, k_T = 13,100 s^{-1} and i_p = 0.1 mW. The concentration variations are plotted every 10 μm radially and every Rayleigh parameter ($\sim$ 0.9 mm) longitudinally.

As an illustration of the dramatic effects of saturation produced by the lasers, *Fig.* 5 shows a typical example of the steady state singlet and triplet concentrations calculated at various positions on the intensity profiles of the laser beams. This diagram shows that for the spectroscopic constants appropriate to a species such as erythrosin B in ethanol ($^S\sigma_{pr} = 7.41 \cdot 10^{-17}$ cm^2 molecule^{-1} at 488 nm, k_T = 13,100 s^{-1}) some 46 % of the ground state singlet molecules are converted into triplets at the maximum of the focused laser intensity profile (w_o = 10 μm) for as little as 0.1 mW c.w. probe power incident on the sample. Clearly, these concentration variations in localised excitation regions will have a significant influence on the absorption of pump laser photons, and hence on the probe gain. This effect will become very much more dramatic for greater absorption cross-sections, longer triplet lifetimes, and higher pump and probe powers. Without taking these concentration perturbations into account there is little hope for obtaining a quantitative interpretation of the time- and space-varying transmission characteristics of pump and probe lasers in these studies of photo-induced absorption and bleaching.

5. Conclusion

The theory developed in this paper satisfactorily explains the discrepancy of more than two orders of magnitude between measured probe ‘gains’ in pump-probe studies of systems generating significant triplet formation as compared with those which would be expected on the basis of the simpler theoretical picture of continuous wave COMAS [12]. The theory provides detailed estimates of the absolute concentrations of singlet and triplet molecules in localised regions of space based on known (or evaluated) spectroscopic constants, including absorption cross sections of singlet and triplet molecules and pump and probe laser intensity profiles. These laser absorption processes generate the concentration and refractive index gradients that drive other processes such as transient induced gratings, thermal blooming and photothermal deflection spectroscopy. As a result, these concentration profiles will be of value in modelling refractive index profiles of laser excited processes in condensed phases arising from internal energy conversion of electronic excitation to heat; and in generating the electronic contributions to the localised refractive index arising from the molecular polarisabilities of singlet and triplet molecular species created by laser excitation.

Acknowledgement

This research was supported by the Engineering and Physical Sciences Research Council, the Hungarian Scientific Research Foundation (under contract number T 025561) and the Hungarian Ministry of Education (contract number 0340/1997), to all of whom we are greatly indebted.

References

[1] WILD, U. P., *Characterization of Triplet States*, in *Topics in Current Chemistry*, **55**, (1975), pp. 1–48.

[2] GILBERT, A. – BAGGOTT, J., *Essentials of Molecular Photochemistry*, Blackwell Science Ltd., Oxford, (1991).

[3] KAKUHO, S. – SEKI, K. – YAGI, M., Time-resolved electron paramagnetic resonance study of the lowest excited triplet states of trans-cinnamic acid and trans-cinnamate anion, *Chem. Phys. Lett.*, **277**, (1997), pp. 326–330.

[4] PASIMENI, L. – HIRSCH, A. – LAMPARTH, I. – MAGGINI, M. – PRATO, M., Transient EPR studies of excited triplet states in polyadducts of C60 and bis(ethoxycarbonyl)methylene *J. Amer. Chem. Soc.*, **119**, (1997), pp. 12902–12905.

[5] SCHMIDT, J. – VAN DER WAALS, J. H., Optical detection of zero-field transitions in phosphorescent triplet states, *Chem. Phys. Lett.*, **2**, (1968), pp. 640–642.

[6] CLARK, R. H. (Ed.), *Triplet State ODMR Spectroscopy, Techniques and Applications to Biophysical Systems*, John Wiley & Sons, New York, (1982).

[7] INGLE, J. D. Jr. –Crouch, S. R., *Spectrochemical Analysis*, Prentice-Hall, London, 1988.

[8] BIALKOWSKI, S. E., *Photothermal Spectroscopy Methods for Chemical Analysis*, John Wiley & Sons, New York, (1996).

[9] LANGLEY, A. J. – BEAMAN, R. A. – BARAN, J. – DAVIES, A. N. – JONES, W. J., Concentration-modulated absorption spectroscopy, *Opt. Lett.*, **10**, (1985), pp. 327–329.

[10] LANGLEY, A. J. – BEAMAN, R. A. – DAVIES, A. N. – JONES, W. J., Concentration- modulated absorption spectroscopy I, *Chem. Phys.*, **101**, (1986), 117–125.

[11] BEAMAN, R. A. – DAVIES, A. N. – LANGLEY, A. J. – JONES, W.J., Concentration-modulated absorption spectroscopy II. Temporal variation of gain, *Chem. Phys.*, **101**, (1986), pp. 127–132.

[12] MALLAWAARACHCHI, W. – DAVIES, A. N. – BEAMAN, R. A. – LANGLEY, A. J. – JONES, W. J., Concentration-modulated absorption spectroscopy IV. The use of continuous-wave lasers, *J. Chem. Soc., Faraday Trans.* **83**, 2, 1987, pp. 707–722.

[13] JONES, W. J. – THOMAS, D. – GROFCSIK, A. – KUBINYI, M., Concentration-modulated absorption spectroscopy and the triplet state: Photoinduced absorption/bleaching in erythrosin B, rose bengal & eosin y, to be published.

[14] TERAZIMA, M. – HORIGUCHI, M. – AZUMI, T., Limitation of absorbance measurements using the thermal lens method, *Anal. Chem.*, **61**, (1989), pp. 883–888.

[15] CHARTIER, A. – GEORGES, J. – MERMET, M., Limitation of the thermal lens method in fluorescence quantum yield measurements, *Chem. Phys. Lett.*, **171**, (1990), pp. 347–352.

[16] ECKER, A. – GEORGES, J. – MERMET, J. M., Influence of the operating mode of the excitation laser in thermal lens spectrometry of erythrosin in water, *Appl. Spectrosc.*, **46**,(1992), pp. 577–580.

[17] CHARTIER, A. – BIALKOWSKI, S. E., Accurate measurements of organic dye solutions by use of pulsed photothermal deflection spectroscopy, *Anal. Chem.*, **67**, (1995), pp. 2672–2684.

[18] CHARTIER, A. – BIALKOWSKI, S., Optical bleaching in continuous laser-excited photothermal lens spectrometry, *Appl. Spectrosc.*, **55**, (2001), pp. 84–91.

[19] TERAZIMA, M. – HIROTA, N., Population lens in thermal lens spectroscopy, *J. Phys. Chem.*, **96**, (1992), pp. 7147–7150.

[20] TERAZIMA, M. – HARA, T. – HIROTA, N., Population lens in thermal lens spectroscopy. 2. Probe wavelength dependence and a new method for subtracting the transient absorption from the thermal lens signal, *J. Phys. Chem.*, **97**, (1993), pp. 10554–10560.

[21] TERAZIMA, M. – HARA, T. – HIROTA, N., Separation of transient absorption and population lens effect from the 'thermal lens' signal, *J. Phys. Chem.* **97**, (1993), pp. 13668–13672.

[22] TERAZIMA, M. – HIROTA, N., Rise profile of the thermal lens signal: Contribution of the temperature lens and the population lens, *J. Chem. Phys.* **100**, (1994), pp. 2481–2486.

[23] FLEMING, G. R., *Chemical Applications of Ultrafast Spectroscopy,* Oxford University Press, Oxford, 1986.

[24] CZARNIK-MATUSEWICZ, B. – GRIFFITH, R. – JONES, P. F. – JONES, W. J. – MALLAWAARACHCHI, W. – SMITH, G., Concentration-modulated absorption spectroscopy. Lifetime Measurements of the ^{2}E state of Cr^{3+} in a ruby crystal, *J. Chem. Soc., Faraday Trans. 2,* **843**, (1988), pp. 1867–1873.