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Steady-state absorption rate models for use in relaxation rate studies with continuous laser excited photothermal lens spectrometry †

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This paper examines the solutions of kinetic rate equations for prediction of the photothermal lens signals under irradiance conditions that can lead to optical saturation or bleaching. The relaxation kinetics resulting from forcing excited state populations in multiple levels by high excitation irradiance continuous lasers is examined and irradiance-dependent photothermal lens signals are predicted. The analyses described in this paper are based on simple kinetic models for optical excitation and subsequent excited state relaxation. Dark-state relaxation is assumed to be extremely fast compared to limiting kinetics resulting in simplified excited state models. Kinetic models are derived for two, four and five active level molecular systems. Gaussian laser beam profiles are assumed and time dependent photothermal lens signals are calculated. Models account for excitation laser profile, thermal relaxation of the spatially and temporally distorted heating rate distribution resulting from nonlinear absorption, and metastable state relaxation. This heating rate is used to calculate the temperature change distribution and subsequently the optical elements needed to model the experimental photothermal signals.

Introduction

Energy transfer can be studied by time-or phase-resolved spectrometry, by excited state quenching, or by forcing excited state population with optical excitation.¹ Time-resolved spectroscopy studies have been very successful in mapping out energy dispersion in excited state relaxation. In the later, excited states are produced by pumping the ground state to specific excited states. Optical and physical properties of these excited states may then be deduced by the relaxation competitive with optical excitation.

Some of the requirements for excited state relaxation studies are that species under study have excited states that are accessible through optical pumping, have ground and/or excited populations that can be monitored with sufficient sensitivity, and have an energy level system can be observed on the time-scales of the relaxation. Taken in total, these requirements often necessitate the use of ultrafast lasers, with high instantaneous irradiances, and high concentration samples. The high irradiances can result in bleached or saturated absorption; population in multiple excited states; and may cause nonlinear effects that mask or alter relaxation signals. High concentration samples may be needed to overcome weak signals. The higher concentrations may result in problems due to excited state dimer formation and self-quenching.

Alternatively, low irradiance optical excitation may be used to study excited state relaxation by continuously forcing population of excited states while monitoring the change in sample absorption.²⁻⁴ Coupled with high sensitivity detection, such as photothermal spectrometry,⁵ this optically forced competitive rate technique can result in similar information without expensive high speed measurement equipment and without as many complicating nonlinear effects. In some regards, this technique is similar to competitive kinetic techniques used in the study of chemical kinetics. However, the rate of excited state population is controlled by varying the optical excitation irradiance. When

the excitation rate becomes competitive with relaxation, ground state population is depleted, and the excitation rate changes. The rate of excitation can be monitored using photothermal spectrometry even when the ground state population is bleached since each transition ultimately results in heat production. So photothermal spectrometry has an advantage over absorption spectrometry in this regard.

In fact, photothermal spectroscopy has many characteristics that make it a useful tool for energy transfer studies.⁵ It has high sensitivity, reducing the concentration requirements for species that are not fluorescent. Signals result from changes in the refractive index of the sample. The refractive index changes are due mostly to temperature changes resulting from optical energy dispersion as heat. And although other effects can alter the refractive index and serve to complicate signal interpretation, these are usually minor perturbations and can be accounted for.^{6,7} Photothermal spectrometry signals are proportional to absorbed optical energy or power. Light absorption increases the temperature which, in turn, changes the refractive index of the sample. The refractive index change is monitored by one of several optical methods. The fact that signal magnitudes are proportional to excitation irradiance has led to the use of powerful laser excitation sources with small focused beams.

Irradiances produced by even weak laser sources can result in nonlinear sample absorption when focused to small spot sizes. Bleaching of the ground, absorbing state is very common when using focused laser sources. The propensity for an absorber to bleach is often characterized by the bleaching irradiance, E_s (W m^{-2}). The bleaching irradiance is related to the optical absorption and relaxation parameters by $E_s = h\nu/\sigma\tau$, where $h\nu$ (J) is the photon energy, σ (m^2) is the absorption cross section, and τ (s) is the time required for a molecule to recycle to the ground state. E_s is the irradiance at which a significant fraction of the population is in excited states. A molecule with a high charge transfer or π - π^* transition may have a molar absorption coefficient of $10000 \text{ M}^{-1} \text{ cm}^{-1}$ at 400 nm. The corresponding absorption cross-section is about $\sigma = 4 \times 10^{-21} \text{ m}^2$ and the photon energy is $h\nu = 5 \times 10^{-19} \text{ J}$. Metastable triplet state lifetimes or organic dyes are typically in microsecond or longer

† Dedicated to Professor Silvia Braslavsky to mark her great contribution to photochemistry and photobiology particularly in the field of photothermal methods.

timescales. For a metastable state lifetime of 10 μs , the $10^4 \text{ M}^{-1} \text{ cm}^{-1}$ species has bleaching irradiance would be 12 MW m^{-2} . While this may seem high, it is easily obtained with modest focused lasers. For example, this irradiance can be obtained by focusing a 20 μW laser to a spot with a 1 μm radius.

With nonlinear absorption so easily obtained with even modest laser power, it is no wonder that absorption was found rather early in the development of photothermal spectrometry. The paper by Twarowski and Klinger presented a theory for modeling of photothermal lens signals produced by multiphoton absorption and then applied the theory to interpreting benzene multiphoton absorption data.⁸ Use of photothermal spectrometry for time-resolved energy transfer studies was also recognized early on. Flynn and coworkers used time-resolved photothermal lens spectrometry to measure vibrational state relaxation.^{9,10} Trevor, Barker and Rothen derived a model of photothermal lens spectrometry used to interpret electronic state relaxation.¹¹ Terazima *et al.*^{12,13} and others^{14–17} used time-resolved photothermal spectroscopy to measure triplet relaxation rates and triplet state energy of a variety of species in condensed phases. Optical bleaching has often been observed and noted.^{2–4,18–20}

From an analytical perspective, nonlinear absorption results in measurement errors that are difficult to detect and account for.^{21–24} Detection requires apparatuses that simultaneously measure photothermal signals and excitation laser irradiance or power. The data are recorded as a time series and subsequently displayed, empirically modeled, and/or analyzed. Data are most useful when the excitation laser irradiance is varied over a substantial range. Because photothermal spectrometry is sensitive to alignment errors in the overlap of excitation and probe laser beams, attenuation schemes that do not produce beam offset or deflection are required. In addition, laser mode variations that occur over time or pulse-to-pulse can mask underlying nonlinear effects. Laser mode control is often a prerequisite to obtaining data useful for nonlinear diagnostics. Knowledge of the nonlinear response can help in design of analytical procedures that are accurate. In addition, semiempirical models of nonlinear sample response can be used as a tool for increasing analytical information. For example, individual components of gas mixtures have been identified and quantitatively measured using semiempirical modeling of nonlinear absorption at a single wavelength.²⁵

On the other hand, measurement and modeling of the nonlinear absorption can result in physical insight and important quantitative information regarding the excited states of the species under study. Bleaching is a common nonlinear effect that occurs in measuring condensed phase solutions of organic dyes.²⁶ Bleaching occurs when the analyte has long-lived excited metastable states, *i.e.*, a triplet state. Excited state populations affect the absorption, primarily by depleting the ground state, and secondarily by optical absorption. The absorption coefficient of the excited state may be larger or smaller than the ground state. Comparison of modeled absorption and relaxation processes to experimental observation has resulted in the determination of excited state absorption cross section and relaxation rate constant information on a number of organic dyes.^{2–4}

In this paper, kinetic rate expressions typical of molecular dye molecules in solution are solved for continuous and gated or chopped irradiance conditions. The theoretical focal length of the photothermal lens element resulting from this excitation is subsequently found. The thermal lens focal length is inversely proportional to analytical signals. Signals predicted from continuous and gated or chopped experiments on two-level systems are first examined and compared. The means to calculate the signal developed in this section are then applied to more complex excited energy state systems. The theoretical irradiance-dependent photothermal lens signals are then calculated in order to predict the range of values that may be measured using

the rate-competitive continuous excitation method to study excited state relaxation dynamics and excited state photoprocesses.

Results and discussion

The main steps involved in modeling the photothermal lens signals produced by nonlinear absorption were perhaps best outlined by Twarowski and Klinger in their paper describing the use of photothermal lens spectrometry to measure multiphoton absorption cross-sections.⁸ This procedure was expanded to continuous laser excited photothermal lens spectrometry, as well as other photothermal techniques, in ref. 5. The same steps may be used to determine signals for other nonlinear absorption effects. Moreover, the temperature change profiles can be used to determine the effect of nonlinear absorption in other photothermal spectrometry experiments, such as photothermal interferometry and deflection, and even photothermal diffraction. The steps are:

1. Determine number density or relative concentration of all states of the species during excitation.
2. Determine energy or power absorbed by each state during irradiation.
3. Calculate the temperature change resulting from the absorbed energy.
4. Determine the strength of the optical elements produced by the photothermal effect from the irradiance-dependent energy or power absorbed.

The first step requires a model of the excited states and how these excited states connect to one another. Kinetic rate models can be found in the literature regarding organic dye photochemistry. The excited state model is a set of coupled differential rate expressions that must be solved under the experimental irradiance conditions. Most relaxation processes are first- or pseudo-first-order, at least in the high dilution limit, and analytical solutions for the number densities can usually be obtained for constant-irradiance conditions. Solutions can also be obtained if the time-scales for excitation and relaxation are very different. For example, in cases of pulsed laser excitation where the pulse duration is either much shorter or much longer than relaxation times, the rate expressions can be simplified by using steady-state approximations or by removing slower relaxation rate processes.

Numerical integration must be used when analytical solutions cannot be obtained. Integration requires a model for the time-dependent irradiance. The integrated irradiance-dependent signal changes with the temporal profile of the excitation laser pulse.^{23,24,27} A good measurement of the time-dependence of the excitation pulse is required. Laser pulses are generally exponential, for gas lasers, or Gaussian, for flash lamp or Q-switched lasers. Only the case of constant irradiance is considered in the present paper.

Two-level system

Consider the case of a two-level system with no excited state absorption shown in the energy level diagram in Fig. 1. Results from this simple two-level system may apply to species with

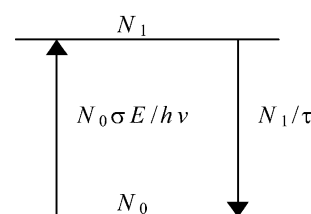


Fig. 1 A simple energy level diagram showing with optical excitation and relaxation. The excitation rate of excitation is $N_0 \sigma E / h \nu$. Relaxation is characterized by a general relaxation time constant, τ .

vibrational quantum states or background states that are not optically coupled. An example is charge transfer transitions of metal complexes. The excited state is at energy of $h\nu$ (J) above the ground state and relaxes with time-constant, τ (s). The differential equations for this case are

$$\begin{aligned}\frac{dN_0(t)}{dt} &= -\frac{E\sigma}{h\nu}N_0(t) + \frac{1}{\tau}N_1(t) \\ \frac{dN_1(t)}{dt} &= \frac{E\sigma}{h\nu}N_0(t) - \frac{1}{\tau}N_1(t)\end{aligned}\quad (1)$$

$N_0(t)$ and $N_1(t)$ (m^{-3}) are number densities in the ground and excited states respectively, E (W m^{-2}) is the optical irradiance, σ (m^2) is the cross section absorption of a photon with energy, $h\nu$ (J), h (J s) is Planck's constant and ν (s^{-1}) the optical frequency. Cases where stimulated emission needs to be considered, e.g., gas phase absorption, is considered in references 23, 24 and 27, and will not be addressed herein. The number density solution for this simple system being irradiated with at constant irradiance is

$$\begin{aligned}N_0(t) &= \left(\frac{N_{\text{total}}}{\left(\frac{E\sigma}{h\nu} + 1\right)}\right) \left\{ 1 + \frac{E\sigma}{h\nu} \exp\left[-\frac{t}{\tau}\left(\frac{E\sigma}{h\nu} + 1\right)\right] \right\} \\ N_1(t) &= \frac{N_{\text{total}}\left(\frac{E\sigma}{h\nu}\right)}{\left(\frac{E\sigma}{h\nu} + 1\right)} \left\{ 1 - \exp\left[-\frac{t}{\tau}\left(\frac{E\sigma}{h\nu} + 1\right)\right] \right\}\end{aligned}\quad (2)$$

Approximations may be used to simplify the kinetic models and give physical insight regarding relaxation processes. The cases of short-pulsed excitation and continuous excitation are given below.

Short pulse excitation

For short-pulsed laser excitation, excited state relaxation is often slow compared to the rate for optical excitation. This situation is typically valid when using ultra-short pulsed, ps to fs lasers. In this instance, the excited state concentration initially populated by the excitation laser is calculated based on an exponential law using the ratio of the integrated optical irradiance, $H(r)$ (J m^{-2}), assumed to be cylindrically symmetric with r being radius, to the integrated irradiance for ground state bleaching, H_s (J m^{-2})

$$H_s = \frac{h\nu}{\sigma}\quad (3)$$

The excited population subsequently relaxes, perhaps *via* metastable intermediate states, but with an overall relaxation time of τ . This is the simplest case of optical bleaching. The excited state energy density is a function of integrated irradiance, which, in turn, has the spatial dependence of the excitation laser beam.

For a short laser pulse relative to τ

$$\begin{aligned}\lim_{\tau \rightarrow \infty} N_0(r) &= N_{\text{total}} \exp\left[-\frac{H(r)}{H_s}\right] \\ \lim_{\tau \rightarrow \infty} N_1(r) &= N_{\text{total}} \left(1 - \exp\left[-\frac{H(r)}{H_s}\right]\right)\end{aligned}\quad (4)$$

N_{total} is the number density in ground in excited states. The later limit implies that the excitation is shorter than excited state

relaxation. Later, the implication will be that the excited state relaxes faster than thermal diffusion or acoustic relaxation times. $H(r)$ is radius-dependent the integrated irradiance given as $t_{\text{pulse}}E(r)$ where t_{pulse} is the pulse duration, $E(r)$ is irradiance, and r (m) is radius. Experimentally, $H(r)$ is determined by integrating the instantaneous irradiance over the temporal excitation profile. The excitation laser beam is Gaussian with a radial-dependent integrated irradiance of

$$H(r) = \frac{2Q_0}{\pi w^2} \exp\left(-\frac{2r^2}{w^2}\right)\quad (5)$$

Q_0 (J) is total pulse energy and w (m) is the electric field radius. Although the beam waste radius changes along the direction of propagation, it is assumed that the sample path length is less than the confocal distance. In addition, it is assumed that the optical transmission is nearly 100%.

In this instance, integration of the absorption due to the ground state population yields an energy density equivalent to the excited state population density, N_1 . The absorbed energy is directly proportional to the excited state number density. Since each transition requires the absorption of one photon, the energy density is, $U(r) = h\nu N_1(r)$ (J m^{-2}). The formula for the radius-dependent energy density $U(r)$ (J m^{-3}) resulting from an energy of $h\nu$ (J) being absorbed by each molecule is

$$U(r) = h\nu N_{\text{total}} \left[1 - \exp\left(-\frac{H(r)}{H_s}\right)\right]\quad (6)$$

Power series expansion easily performed using a power series of standard Gaussian functions yields

$$U(r) = -h\nu N_{\text{total}} \sum_{m=1}^{\infty} \frac{1}{m!} \left(-\frac{H_0}{H_s}\right)^m \exp\left(-\frac{2mr^2}{w^2}\right)\quad (7)$$

Here, $H_0 = 2Q_0/\pi w^2$ (J m^{-2}) is the integrated irradiance of the pulsed Gaussian excitation laser. Because of ground state bleaching, the initial excited state energy density is no longer a Gaussian, but is flattened due to optical bleaching. As illustrated in Fig. 2, optical bleaching distorts the energy density profile over that of the Gaussian excitation profile. This must be taken into account when calculating the photothermal, and even photoacoustic, spectrometry signals.

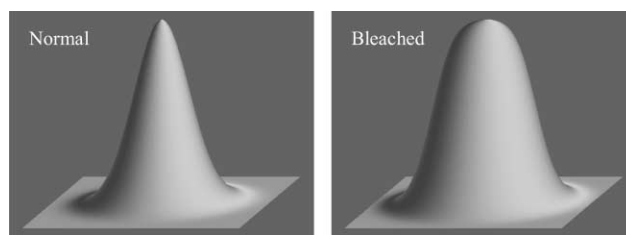


Fig. 2 Spatial energy densities resulting from excitation at energies both less than, labeled “Normal”, and four times that required for bleaching. The spatial distortion in the excited state profile alters the measured photothermal signal strength over that of the unperturbed Gaussian profile.

The resulting signal is a superposition of terms resulting from each Gaussian element. Each element in the $U(r)$ series is a Gaussian with a beam waist radius w^2/m . Since the pulsed-laser excited photothermal lens signal resulting from a Gaussian beam is well known, this fact may be used to find the photothermal lens signal. Each Gaussian element produces a time-dependent lens with focal length, f (m), in the photothermal lens experiment. The inverse focal length is, in turn, proportional to the signal for a typical optimized apparatus.

The relative time-dependent thermal lens strength for low absorbance sample, *i.e.*, low transmission loss, and instantaneous excited state relaxation is⁵

$$f^{-1}(t) = \left(\frac{dn}{dT} \right) \frac{8Q_0\alpha_0 l}{\pi\rho C_p w^4} \frac{1}{(1 + 2t/t_c)^2} \quad (8)$$

In this equation, α_0 (m^{-1}) is the exponential absorption coefficient, l (m) is the sample pathlength, assumed to be shorter than the confocal length of the laser beam, ρ (kg m^{-3}), is the sample density, and C_p ($\text{J kg}^{-1} \text{K}^{-1}$) is the sample heat capacity. The characteristic time constant is $t_c = w^2/4D_T$, where D_T ($\text{m}^2 \text{s}^{-1}$) is the thermal diffusion constant for the sample. The refractive index differential with respect to temperature (dn/dT) (K^{-1}) relates temperature change to refractive index. Assuming that the sample pathlength is much shorter than the confocal length of the laser beam is effectively the same as assuming beam waste radius does not change through the sample.

Applying this to the series expansion of the energy density results in the time-dependent signal resulting from optical bleaching

$$f^{-1}(H_0, t) = - \left(\frac{dn}{dT} \right) \frac{4h\nu N_{\text{total}} l}{\rho C_p w^2} \sum_{m=1}^{\infty} \left(-\frac{H_0}{H_s} \right)^m \left(\frac{1}{m!} \right) \frac{m}{(1 + 2mt/t_c)^2} \quad (9)$$

This solution applies only to the cases where the excitation laser has a rectangular time profile, for example, in chopped continuous laser excitation. Results for exponential-shaped pulses like those found in TEA lasers have been reported.^{23,24,27}

The initial ($t = 0$) integrated irradiance-dependent signal is

$$f^{-1}(H_0) = \left(\frac{dn}{dT} \right) \frac{4N_{\text{total}} h\nu l}{\rho C_p w^2} \left(\frac{H_0}{H_s} \right) \exp \left(-\frac{H_0}{H_s} \right) \quad (10)$$

The initial integrated irradiance-dependent photothermal lens signal is a gamma (Erlang) distribution for optical bleaching. The integrated irradiance dependent signal predicted by this equation is illustrated in Fig. 3. It is interesting to note that the initial signal first increases, then decreases with increasing excitation energy. This is because bleaching flattens the initial

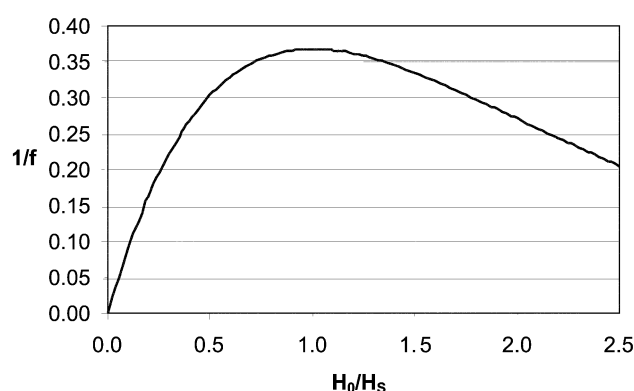


Fig. 3 Predicted pulsed-laser excited photothermal lens signal for a two-level system and rectangular excitation pulse time profile. H_0 is the integrated irradiance of the laser pulse and H_s is the integrated irradiance required to bleach the ground state. It is assumed that stimulated emission does not occur and the ground and excited states are not coherently coupled. The short-time inverse focal length of the photothermal lens ($1/f$) is plotted relative to the relative integrated irradiance. The decrease in the photothermal lens strength, and thus signal, at high relative integrated irradiances is due to the flattening of the initial temperature change profile.

temperature change distribution. The photothermal lens strength is proportional to the second derivative of the temperature change with respect to radius. The flattened temperature change distribution apparently diminishes this derivative. On the other hand, thermal diffusion will cause the second derivative of the temperature change to increase, even for a “top hat” irradiance profile.

Two-level system with continuous irradiation

The solution for the ground state population for continuous chopped-continuous laser excitation is easily obtained by either using the steady state assumption, *e.g.*, setting the time derivatives in eqn. (1) equal to zero and subsequently solving for N_0 , or by taking the infinite time limit of the time-dependent solutions in eqn. (2). In either case

$$N_0 = N_{\text{total}} \frac{1}{1 + E\sigma/h\nu} \quad (11)$$

The steady-state populations in the optically coupled ground and excited states are used to determine the excitation laser irradiance-dependent absorption coefficient, $\alpha(E)$, based on the bleaching irradiance, E_s , through

$$\alpha(E) = \alpha_0 \left(\frac{1}{1 + E(r)/E_s} \right) \quad (12)$$

$\alpha_0 = N_{\text{total}}\sigma$ (m^{-1}) is the exponential absorption coefficient in the absence of bleaching. The bleaching irradiance for the two-level system is E_s (W m^{-2}) defined here as

$$E_s = \frac{h\nu}{\sigma\tau} \quad (13)$$

The irradiance for Gaussian profile laser excitation is

$$E(r) = \frac{2\Phi_0}{\pi w^2} \exp(-2r^2/w^2) \quad (14)$$

Φ_0 (W) is the laser beam power. Substitution of the Gaussian irradiance profile into the power loss equations followed by a binomial expansion results in

$$P(r) = -\alpha_0 E_s \sum_{k=0}^{\infty} \left(-\frac{E_0}{E_s} \right)^{k+1} \exp(-2(k+1)r^2/w^2) \quad (15)$$

The constant, $E_0 = 2\Phi_0/\pi w^2$ (W m^{-2}) is the Gaussian beam irradiance, and has been substituted for simplicity. This power distribution is distorted relative to the excitation beam profile. The distortion is similar to that shown in Fig. 2.

As in the pulsed laser excitation case, the signal is assumed to be proportional to the inverse focal length of the photothermal lens. The inverse focal length is in turn deduced from the result for an ideal case where there is no distortion of the spatial power distribution. Since the power distribution is a sum over Gaussian terms. Continuous Gaussian laser excitation of a linear absorbing sample produces a time-dependent photothermal lens with an inverse focal length of

$$f^{-1}(t) = \left(\frac{dn}{dT} \right) \frac{E_0\alpha_0 l}{2\kappa} \frac{1}{1 + t_c/2t} \quad (16)$$

In this equation, κ ($\text{W m}^{-1} \text{K}^{-1}$) is the thermal conductivity of the sample and is related to the thermal diffusion coefficient through $\kappa = \rho C_p D_T$. The characteristic time constant is still $t_c = w^2/4D_T$. Since each term in the power series expansion is Gaussian, the time-dependent thermal lens is

$$f^{-1}(t) = -\left(\frac{dn}{dT}\right) \frac{E_s N_{\text{total}} l}{2\kappa} \sum_{k=1}^{\infty} \frac{(-E_0/E_s)^k}{1 + t_c/2kt} \quad (17)$$

The maximum inverse focal length, occurring times, t , much longer than t_c , can be obtained from the limit. For long irradiation times, each time-dependent term, $1 + t_c/2kt$, approaches unity, and the binomial series can be contracted. The resulting irradiance-dependent inverse focal length is

$$f^{-1}(\infty) = \left(\frac{dn}{dT}\right) \frac{E_0 \alpha_0 l}{2\kappa} \frac{1}{1 + (E_0/E_s)} \quad (18)$$

The photothermal lens signal for this case is illustrated in Fig. 4. In this case the photothermal signals increases with increasing irradiance to a limiting value of

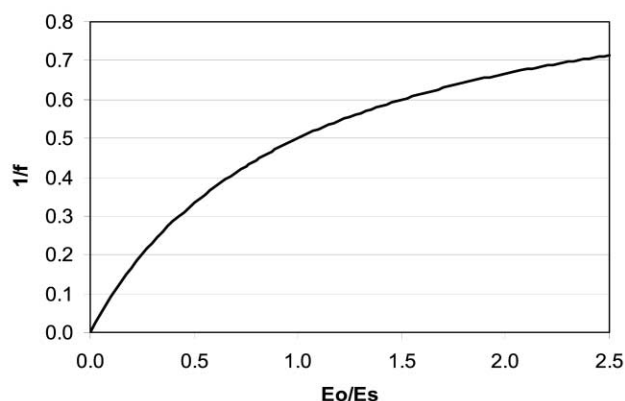


Fig. 4 Predicted continuous-laser excited photothermal lens signal for a two-level system and rectangular excitation time profile. E_0 is the irradiance of the laser beam and E_s is the irradiance required to bleach the ground state. The long-time inverse focal length of the photothermal lens ($1/f$) is plotted versus relative irradiance. The leveling off of the photothermal lens strength at higher irradiances is due to the combined effect of bleaching and distortion in the power distribution. Thermal diffusion still produces a finite signal even when the irradiance is far from that needed to bleach the ground state.

$$\lim_{E_0 \rightarrow \infty} f^{-1}(\infty) = \left(\frac{dn}{dT}\right) \frac{E_s \alpha_0 l}{2\kappa} \quad (19)$$

This limit has been observed in practice since excited state absorption typically causes the signal to increase with increased excitation irradiance.

Multiple-level models for molecular dyes

Although insight into the way bleaching affects the photothermal lens signal may be obtained by examining the simple two-level systems, more extensive models are needed to describe energy level dynamics of common colored substances. A more realistic energy level diagram is shown in Fig. 5. In this model, excited singlet, S, and triplet, T, states may absorb energy. Optical excitation is to states favored by Frank–Condon overlap or otherwise allowed. Excited states are assumed to be decoupled from the excitation source though fast dark or background state coupling, or vibrational relaxation out of the initially-populated Frank–Condon states.²⁸ Coupling and relaxation is assumed to occur much faster than stimulated emission or subsequent excitation in condensed phases. Coherent depopulation effects are not modeled.²⁹ On the other hand, stimulated emission may occur in fluorescent species, especially in the gas phase. This is not modeled in this paper, but could be included as an additional term in the rate expressions given below.

In the study of organic and even inorganic dye molecule photophysics, species are commonly modeled as three-level systems with fast intersystem crossing rates (ISC) from the S_1

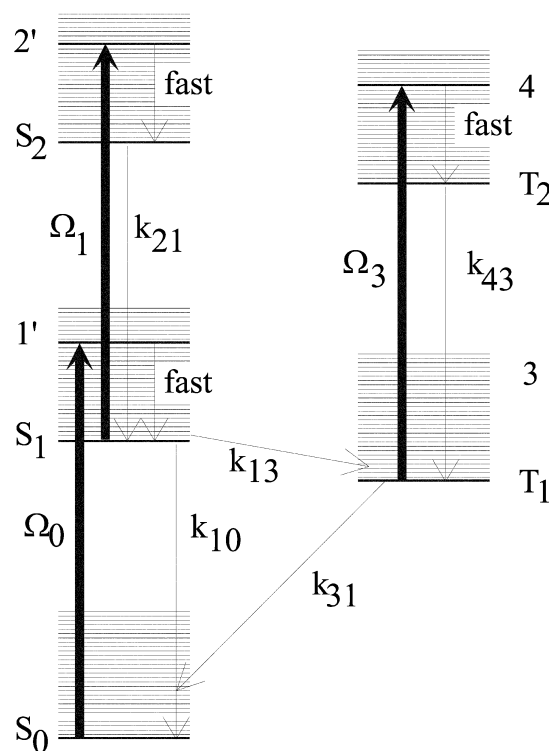


Fig. 5 Energy level diagram for a dye molecule including excited singlet and triplet state absorption. The rate constants and optical excitation rate constant connect the electronic states. There is not optical coupling between singlet and triplet states. Optical bleaching of the ground state and the first excited singlet and triplet states may occur.

state. In these cases, excited state perturbations from $S_1 \rightarrow S_2$ and $T_1 \rightarrow T_2$ absorptions are thought to be minor. However, we have found that $T_1 \rightarrow T_2$ absorptions can be significant at high irradiance^{2,3} and molecules with potentially significant $S_1 \rightarrow S_2$ absorption have more recently been described.³⁰

In the model proposed here, optical excitation is initially from the singlet S_0 to the S_1 state with an optically driven rate with a constant, Ω_0 (s^{-1}). Vibrationally excited S_1 molecules rapidly relax to the lowest vibronic state from which return to the ground S_0 state through fluorescence and internal conversion mechanisms, with an overall first-order rate constant of k_{10} (s^{-1}). Intersystem crossing to the lowest triplet, T_1 , with rate constant k_{13} (s^{-1}) also occurs. The triplet relaxes to the ground state through phosphorescence and inverse intersystem crossing with an overall rate constant of k_{30} (s^{-1}). The lowest triplet state may also absorb radiation to be excited to T_2 with rate constant, Ω_3 . Relaxation from the excited T_2 triplet returns molecules to T_1 with a first order rate constant of k_{43} (s^{-1}). Similarly, the first excited singlet, S_1 , may absorb light, populating the second excited singlet, S_2 , with a rate constant of Ω_1 . The higher singlet level can return to S_1 with first order rate constant k_{21} (s^{-1}). The kinetic equations for this model are

$$\begin{aligned} \frac{dN_0(t)}{dt} &= -\Omega_0 N_0(t) + k_{10} N_1(t) + k_{30} N_3(t) \\ \frac{dN_1(t)}{dt} &= \Omega_0 N_0(t) - \Omega_1 N_1(t) - k_{13} N_1(t) - k_{10} N_1(t) + k_{21} N_2(t) \\ \frac{dN_2(t)}{dt} &= \Omega_1 N_1(t) - k_{21} N_2(t) \\ \frac{dN_3(t)}{dt} &= k_{13} N_1(t) - \Omega_3 N_3(t) - k_{30} N_3(t) + k_{43} N_4(t) \\ \frac{dN_4(t)}{dt} &= \Omega_3 N_3(t) - k_{43} N_4(t) \end{aligned} \quad (20)$$

$N_0(t)$, $N_1(t)$, $N_2(t)$, $N_3(t)$, and $N_4(t)$ (m^{-3}) are number densities in S_0 , S_1 , S_2 , T_1 and T_2 , respectively, $\Omega_0 = E\sigma_0/h\nu$ and $\Omega_1 = E\sigma_1/h\nu$ (s^{-1}) are the irradiance-dependent rate-constants for singlet state excitation and $\Omega_3 = E\sigma_3/h\nu$ (s^{-1}) is the rate constant for triplet excitation. σ_0 , σ_1 and σ_3 (m^2) are the cross sections for absorption by S_0 , S_1 and T_1 , respectively. Excitation rate constants are assumed to be first order and so irradiance may not be time dependent.

The rate equations can easily be solved under steady-state conditions. Steady-state number densities may be obtained from either time-dependent solutions or by assuming that the number density rates of change are zero. The time-dependent solutions are complicated because of the number of states and rate constants. The steady-state solution is used here since steady-state will be reached on time scales on the order of triplet state lifetimes. Triplet lifetimes are typically at most on the order of milliseconds, while chopping times used in photothermal lens spectrometry are typically on the order of seconds or tens of seconds. This greatly simplifies the resulting analysis.

Steady-state number densities for the five-state model are

$$\begin{aligned} N_0 &= N_{\text{total}}(k_{10} + k_{13})k_{21}k_{30}k_{43}/K \\ N_1 &= N_{\text{total}}k_{21}k_{30}k_{43}\Omega_0/K \\ N_2 &= N_{\text{total}}k_{30}k_{43}\Omega_0\Omega_1/K \\ N_3 &= N_{\text{total}}k_{13}k_{21}k_{43}\Omega_0/K \\ N_4 &= N_{\text{total}}k_{13}k_{21}\Omega_0\Omega_3/K \\ K &= (k_{10} + k_{13})k_{21}k_{30}k_{43} + \Omega_0(k_{30}k_{43}(k_{21} + \Omega_1) + k_{13}k_{21}(k_{43} + \Omega_3)) \end{aligned} \quad (21)$$

The denominator, K , is the same in each of the number density expressions. It is interesting to note that some numerators and the denominator are second order in irradiance. There may be conditions, e.g., specific combinations of rate constants, where absorption may appear to be second order in irradiance.

As with the two-level system, the photothermal lens signal equation are found by first, determination of the power absorbed by the ground, P_0 , and first excited singlet, P_1 , and triplet states, P_3 , then second, finding the inverse photothermal lens focal length. For example, the power absorbed by the ground state is $P_0 = E(r)\sigma_0N_0$. The optical powers absorbed by these three states are

$$\begin{aligned} P_0 &= N_{\text{total}}E(r)\sigma_0((k_{10} + k_{13})k_{21}k_{30}k_{43}/K) \\ P_1 &= N_{\text{total}}E(r)\sigma_1(k_{21}k_{30}k_{43}\Omega_0/K) \\ P_3 &= N_{\text{total}}E(r)\sigma_3(k_{13}k_{21}k_{43}\Omega_0/K) \\ K &= (k_{10} + k_{13})k_{21}k_{30}k_{43} + \Omega_0(k_{30}k_{43}(k_{21} + \Omega_1) + k_{13}k_{21}(k_{43} + \Omega_3)) \end{aligned} \quad (22)$$

The irradiance-dependent signal is formulated and may subsequently be used to determine rate parameters by analysis of experimental data. Each power term can be expressed as a function of the radius-dependent excitation irradiance. For example,

$$\begin{aligned} P_0 &= N_{\text{total}}E(r)\sigma_0((k_{10} + k_{13})k_{21}k_{30}k_{43}/K) \\ K &= (k_{10} + k_{13})k_{21}k_{30}k_{43} + \\ &\quad \frac{E(r)\sigma_0}{h\nu} \left(k_{30}k_{43} \left(k_{21} + \frac{E(r)\sigma_1}{h\nu} \right) + k_{13}k_{21} \left(k_{43} + \frac{E(r)\sigma_3}{h\nu} \right) \right) \end{aligned} \quad (23)$$

Each power term can also be expanded as a power series. For example, that due to the ground state absorption is

$$P_0(r) = N_{\text{total}}E(r)\sigma_0 \sum_{k=0}^{\infty} A_k E^k(r) \quad (24)$$

The A_k are irradiance independent expansion coefficients. The sum is over Gaussian-like terms, each with a beam waist radius of w^2/k , and each resulting in a time-dependent inverse focal length of

$$f_0^{-1}(t) = \left(\frac{dn}{dT} \right) \frac{N_{\text{total}}\sigma_0 l}{2\kappa} \sum_{k=0}^{\infty} A_k \frac{E_0^{k+1}}{1 + t_c/2(k+1)t} \quad (25)$$

E_0 (W m^{-2}) is the Gaussian excitation laser beam irradiance defined as $2\Phi_0/\pi w^2$. Φ_0 (W) is power. This, plus the two other equations, describing heating due excited singlet and triplet states, are summed together to calculate the total time-dependent photothermal lens signal.

At times long relative to t_c , the time-dependent denominator is unity, and the inverse focal length is simply

$$f_0^{-1}(\infty) = \left(\frac{dn}{dT} \right) \frac{N_{\text{total}}E_0\sigma_0 l}{2\kappa} \sum_{k=0}^{\infty} A_k E_0^k \quad (26)$$

This results in a photothermal lens signal components proportional to

$$\begin{aligned} f_0^{-1}(\infty) &= \left(\frac{dn}{dT} \right) \frac{N_{\text{total}}E_0\sigma_0 l}{2\kappa} \left(\frac{(k_{10} + k_{13})k_{21}k_{30}k_{43}}{K} \right) \\ f_1^{-1}(\infty) &= \left(\frac{dn}{dT} \right) \frac{N_{\text{total}}E_0^2\sigma_0\sigma_1 l}{2\kappa h\nu} \left(\frac{k_{21}k_{30}k_{43}}{K} \right) \\ f_3^{-1}(\infty) &= \left(\frac{dn}{dT} \right) \frac{N_{\text{total}}E_0^2\sigma_0\sigma_3 l}{2\kappa h\nu} \left(\frac{k_{13}k_{21}k_{43}}{K} \right) \\ K &= (k_{10} + k_{13})k_{21}k_{30}k_{43} + \\ &\quad \frac{E_0\sigma_0}{h\nu} \left(k_{30}k_{43} \left(k_{21} + \frac{E_0\sigma_1}{h\nu} \right) + k_{13}k_{21} \left(k_{43} + \frac{E_0\sigma_3}{h\nu} \right) \right) \end{aligned} \quad (27)$$

The inverse focal lengths are due to absorbance from S_0 , S_1 and T_1 states, respectively. Each of these transitions have bleaching irradiances which are inversely proportional the rate of return to lower states. Bleaching irradiances may be deduced from the expressions given above, or by finding the appropriate relaxation times from the energy level diagram in Fig. 5. In particular, the bleaching irradiance for the S_1 and T_1 levels are

$$E_{S,1} = \frac{h\nu}{\sigma_1} k_{21} \quad E_{S,3} = \frac{h\nu}{\sigma_3} k_{43} \quad (28)$$

Applying these definitions results in the simplification

$$\begin{aligned} f_0^{-1}(\infty) &= \left(\frac{dn}{dT} \right) \frac{N_{\text{total}}E_0\sigma_0 l}{2\kappa} \left(\frac{k_{13}k_{30}}{K} \right) \\ f_1^{-1}(\infty) &= \left(\frac{dn}{dT} \right) \frac{N_{\text{total}}E_0\sigma_0 l}{2\kappa} \left(\frac{E_0}{E_{S,1}} \right) \left(\frac{k_{21}k_{30}\phi_r}{K} \right) \\ f_3^{-1}(\infty) &= \left(\frac{dn}{dT} \right) \frac{N_{\text{total}}E_0\sigma_0 l}{2\kappa} \left(\frac{E_0}{E_{S,3}} \right) \left(\frac{k_{13}k_{43}\phi_r}{K} \right) \\ K &= k_{13}k_{30} + \phi_r \frac{E_0\sigma_0}{h\nu} \left(k_{30} \left(1 + \frac{E_0}{E_{S,1}} \right) + k_{13} \left(1 + \frac{E_0}{E_{S,3}} \right) \right) \end{aligned} \quad (29)$$

The triplet quantum yield is defined as

$$\phi_T = \frac{k_{13}}{k_{10} + k_{13}} \quad (30)$$

Photothermal lens signals will be proportional to the sum of the inverse focal lengths from the three absorptions. The total inverse focal length is

$$f^{-1}(\infty) = \left(\frac{dn}{dT} \right) \frac{N_{\text{total}} E_0 I}{2\kappa} \left(\frac{k_{13} k_{30} + (E_0 / E_{S,1}) k_{21} k_{30} \phi_T + (E_0 / E_{S,3}) k_{13} k_{43} \phi_T}{k_{13} k_{30} + \phi_T \frac{E_0 \sigma_0}{h\nu} [k_{30} (1 + E_0 / E_{S,1}) + k_{13} (1 + E_0 / E_{S,3})]} \right) \quad (31)$$

Three-level system

The optical bleaching characteristics of most molecules can be described with a three level system. In this case it is assumed that absorption rates out of S_1 and T_1 are not large enough to cause bleaching in these states. Without excited state bleaching, $E_{S,1}$ and $E_{S,3}$ are both large compared to the excitation irradiance, E_0 . The total inverse focal length equation is

$$f^{-1}(\infty) = \left(\frac{dn}{dT} \right) \frac{N_{\text{total}} E_0 I}{2\kappa (1 + E_0 / E_{S,0})} \left(\sigma_0 + \left(\frac{k_{30}}{k_{13} + k_{30}} \right) \sigma_1 E_0 / E_{S,0} + \left(\frac{k_{13}}{k_{13} + k_{30}} \right) \sigma_3 E_0 / E_{S,0} \right) \quad (32)$$

Ground state bleaching irradiance was defined as

$$E_{S,0} = \frac{h\nu}{\sigma_0} \frac{k_{13} + k_{10}}{k_{13} + k_{30}} k_{30} \quad (33)$$

The T_1 - S_0 relaxation rates are slow compared to the ISC and IC rates for most species. In this case k_{30} is small compared to k_{13} . The saturation irradiance is

$$E_{S,0} = \frac{h\nu}{\phi_1 \sigma_0} k_{30} \quad (34)$$

The inverse focal length is simply

$$f^{-1}(\infty) = \left(\frac{dn}{dT} \right) \frac{N_{\text{total}} E_0 I}{2\kappa} \frac{\sigma_0 + \sigma_3 E_0 / E_{S,0}}{1 + E_0 / E_{S,0}} \quad (35)$$

It is apparent that the first term, proportional to σ_0 , accounts for the ground state absorbance while the second term, proportional to σ_3 , is due to triplet absorption.

The above result is similar to the expression used earlier to model bleaching a series of organic dye molecules.^{3,4} As shown in that study, a more accurate expression may be formulated by taking into account the power lost through fluorescence and phosphorescence emission. A heat yield term is useful for this purpose.⁵ The heat yield is the amount of absorbed energy or power that is recovered as heat, and thus contributes to the photothermal signal. The effective heat loss due to fluorescence is

$$Y_H^{(S)} = 1 - \phi_f \frac{\nu_f}{\nu} \quad (36)$$

ϕ_f is the fluorescence quantum yield and ν_f is the mean optical frequency of the fluorescence emission. The increase in S_1 - S_0 relaxation rate due to fluorescence emission is simply accounted for in an increased k_{10} rate constant.

Using the heat yields we obtain an inverse focal length formula generally useful for modeling bleaching for organic dye molecules that may have fluorescence or phosphorescence emission

$$f^{-1}(\infty) = \left(\frac{dn}{dT} \right) \frac{N_{\text{total}} E_0 I}{2\kappa} \frac{Y_H^{(S)} \sigma_0 + Y_H^{(T)} \sigma_3 E_0 / E_{S,0}}{1 + E_0 / E_{S,0}} \quad (37)$$

The triplet state heat yield, $Y_H^{(T)}$, is defined similarly to that for the singlet.

This equation gives the characteristic irradiance dependent responses illustrated in Fig. 6. At low irradiance, the slope of the line is proportional to the singlet absorbance. As the relative irradiance is increased, the slope changes to the excited triplet state absorbance. Analysis of irradiance dependent photothermal lens signals using this model has resulted in the determination of the ground and triplet state absorption cross sections, as well as the triplet relaxation rate constant.^{2,4}

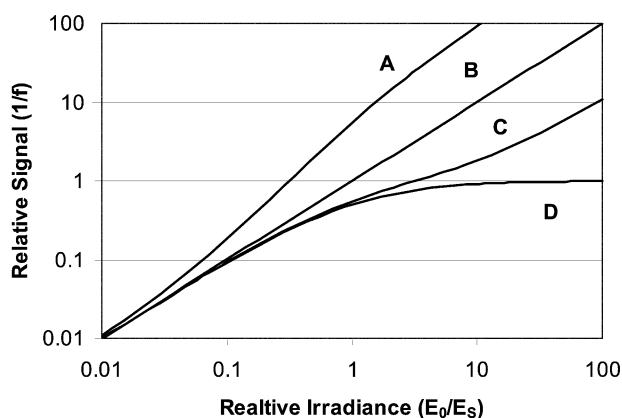


Fig. 6 Relative photothermal lens signals ($1/f$) as a function of relative excitation irradiance (E/E_s) for the three-level model with relative triplet state absorption cross sections of A: $\sigma_3 = 10\sigma_0$, B: $\sigma_3 = \sigma_0$, C: $\sigma_3 = 0.1\sigma_0$, and D: $\sigma_3 = 0$. The singlet and triplet heat yields are unity.

Four-level system

In some of our experimental studies, we observed a diminished signal in high irradiance conditions where all of the molecules were in triplet states. This bleaching that was attributed to T_1 bleaching. We attributed this to bleaching of the T_1 state through high irradiance T_1 - T_2 excitation. This is another special case of the general five-level model. In this instance, we neglect S_1 - S_2 photobleaching for simplicity. In contrast, S_1 bleaching or even a signature indicative of S_1 absorption has not been observed to date. However, differences between triplet and excited singlet state absorption and bleaching is subtle.

Again assuming that the T_1 - S_0 relaxation rate is very slow, k_{30} is small compared to k_{13} , the inverse focal length is

$$f^{-1}(\infty) = \left(\frac{dn}{dT} \right) \frac{N_{\text{total}} E_0 I}{2\kappa} \frac{\sigma_0 + \sigma_3 E_0 / E_{S,0}}{1 + E_0 / E_{S,3} (1 + E_0 / E_{S,3})} \quad (38)$$

The saturation irradiances for the ground singlet and triplet states are the same as those given above, and repeated here for clarity.

$$E_{S,0} = \frac{h\nu}{\phi_1 \sigma_{01}} k_{30} \quad E_{S,3} = \frac{h\nu}{\sigma_3} k_{43} \quad (39)$$

Of course for cases where k_{30} is not small compared to k_{13} , can be modeled using the equation for the five-level system.

An example of the predicted photothermal lens signal is shown in Fig. 7. For these calculations, the triplet saturation irradiance was set at $E_{s,3} = 10^4 E_{s,1}$. This is reasonable given the relaxation rate constant dependence in eqn. (39). T_1 – S_0 relaxation times are as long as milliseconds, but typically in the range of microseconds. On the other hand T_2 – T_1 relaxation times should be just as fast as other excited state internal conversions, typically nanoseconds or less.

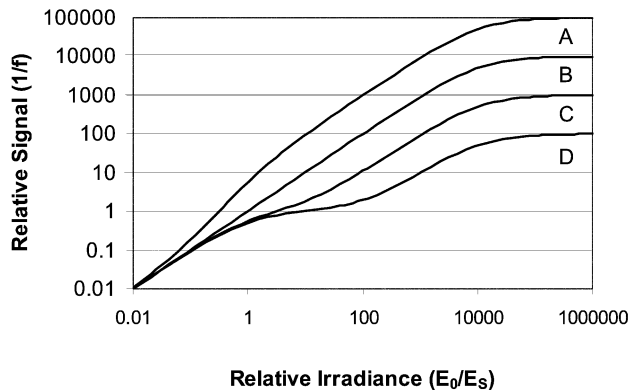


Fig. 7 Predicted photothermal lens signal with both ground and excited triplet state bleaching as a function of the irradiance relative to the ground state bleaching irradiance. The triplet state bleaching irradiance is 10^4 larger than that for ground state bleaching in all cases shown here. The difference curves represent different triplet state absorption cross sections; A: $\sigma_3 = 10\sigma_0$, B: $\sigma_3 = \sigma_0$, C: $\sigma_3 = 0.1\sigma_0$, and D: $\sigma_3 = 0.01\sigma_0$.

The effect of ground state bleaching is observed at around a relative irradiance of $E_0/E_s = 1$. At this point the relative signal shifts, reflecting the change from dominant singlet to triplet state absorption. There is a leveling off of signal at $E_0/E_s = 10^4$ due to triplet state bleaching. Irradiances beyond this, while still resulting in a photothermal lens signal, will not increase the signal.

Summary

The effect of photobleaching on the photothermal spectroscopy signal can be significant. The rate expressions for two- and five-level systems were solved under the assumption of steady-state irradiance and long-time behavior, *i.e.*, after transient changes in the excited state populations. Equations describing the inverse focal length of the photothermal lens were derived for several important limits. In particular, the three-level system was shown to have a limiting inverse focal length equivalent to those found previously when the rate of triplet relaxation was assumed to be much shorter than any other rate and excited singlet state absorption could be neglected. These are essentially the same requirements used to derive the equations from the time-dependent solution used in the previous study.

In addition, results of the three-level system were found for the case where the triplet relaxation was not considerably slower and were the singlet absorption can take place. This new result may be applicable to modeling the optical bleaching in molecular systems with fast response time or thought to have significant excited singlet absorption.

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