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An Analytic Model for the Determination of Excited State Parameters from Pump-probe Measurements

by Timothy M. Pritchett, Andrew G. Mott,
Michael J. Ferry, and Robert C. Hoffman

ARL-TR-3327 **September 2004**

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REPORT DOCUMENTATION PAGE

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1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED (From - To)
September 2004	Final	October 2002 to March 2004

4. TITLE AND SUBTITLE
An Analytic Model for the Determination of Excited State Parameters from Pump-probe Measurements

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Timothy M. Pritchett, Andrew G. Mott, Michael J. Ferry and Robert C. Hoffman

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army Research Laboratory
ATTN: AMSRD-ARL-SE-EO
2800 Powder Mill Road
Adelphi, MD 20783-1197

8. PERFORMING ORGANIZATION REPORT NUMBER
ARL-TR-3327

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Research Laboratory
2800 Powder Mill Road
Adelphi, MD 20783-1197

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

In order to completely and accurately characterize the materials whose nonlinear optical response makes them good candidates for use in eye and sensor protection applications, one must measure not only the absorption and refraction cross-sections of the various quantum energy levels involved in the optical absorption process, but also the decay rates of these states. This can be accomplished in a single experiment using time resolved pump-probe techniques. In a pump-probe experiment, a strong pump pulse excites a sample of the material under investigation, and one measures the transmittance of a weak probe as a function of time. In a double pump-probe experiment, two pump pulses excite the sample sequentially. The first pulse populates various molecular excited states, while the second induces transitions whose rates depend on the various populations and cross-sections. As in a single pump-probe experiment, one measures the sample transmittance of a weak probe beam or pulse as a function of time, from which one can infer the relevant excitation and decay rates. Parameter values are obtained by fitting a theoretical model to the experimental data, a procedure that may be carried out with particular ease if the model has an analytic solution. We describe the most complete model for the normalized probe transmittance that may still be solved analytically.

15. SUBJECT TERMS
Pump-probe measurements, optical nonlinearities in organic materials

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE	UL	12	Timothy M. Pritchett
Unclassified	Unclassified	Unclassified			19b. TELEPHONE NUMBER (*Include area code*) (301) 394-0332

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

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1. Introduction

The absorption of energy from an intense laser pulse propagating through a medium redistributes the molecules of the medium among the ground state and various excited states. In general, these states differ significantly in their intrinsic ability to absorb and refract optical radiation. Thus, population redistribution typically results in a transient alteration in the bulk optical properties of the medium. By monitoring the manner in which the medium's optical properties evolve in time, one can infer not only the intrinsic optical properties of the various molecular states, but also the rates at which these states decay as the material relaxes back to its initial, unperturbed state. The monitoring may be accomplished using a second laser pulse (the probe), generally much weaker than the first (the pump).

Pump-probe techniques using a single fast (sub-nanosecond) pump pulse have long been used to measure the lifetimes and absorption cross-sections of the excited singlet states (*1*). Swatton (*2*) pioneered use of a second picosecond pump pulse in an effort to obtain additional information about the triplet excited states. These states are inaccessible directly from the ground state and for this reason are not significantly populated until some time *after* the arrival of the initial laser pulse. By choosing the time delay between the two pump pulses to be on the order of the crossing time between the singlet and triplet manifolds, Swatton succeeded in measuring various photophysical parameters of both singlet and triplet excited states simultaneously. This is extremely important, since the triplet states play a dominant role in determining the nonlinear optical absorptive properties of many of the most promising materials for eye and sensor protection applications. More recently, McEwen and coworkers (*3*) employed a similar double pump – probe technique using a pair of nanosecond pump pulses and a continuous wave probe beam to measure the photophysical parameters of a series of porphyrin compounds.

Nonlinear absorption in a wide variety of organic dyes is well described by a model consisting of five vibrational-rotational bands: a singlet ground state, two singlet excited states, and two triplet excited states (*4*). The arrangement of the various bands is shown in figure 1. Parameter values are obtained by fitting a theoretical model to the experimental data, a procedure that may be carried out with particular ease if the model has an analytic solution. Unfortunately, the rate equations comprising the five-band model admit no such analytic solution and must be solved numerically. The simplified model presented here yields an analytical expression for the normalized transmittance of a CW probe in the presence of a strong pump pulse.

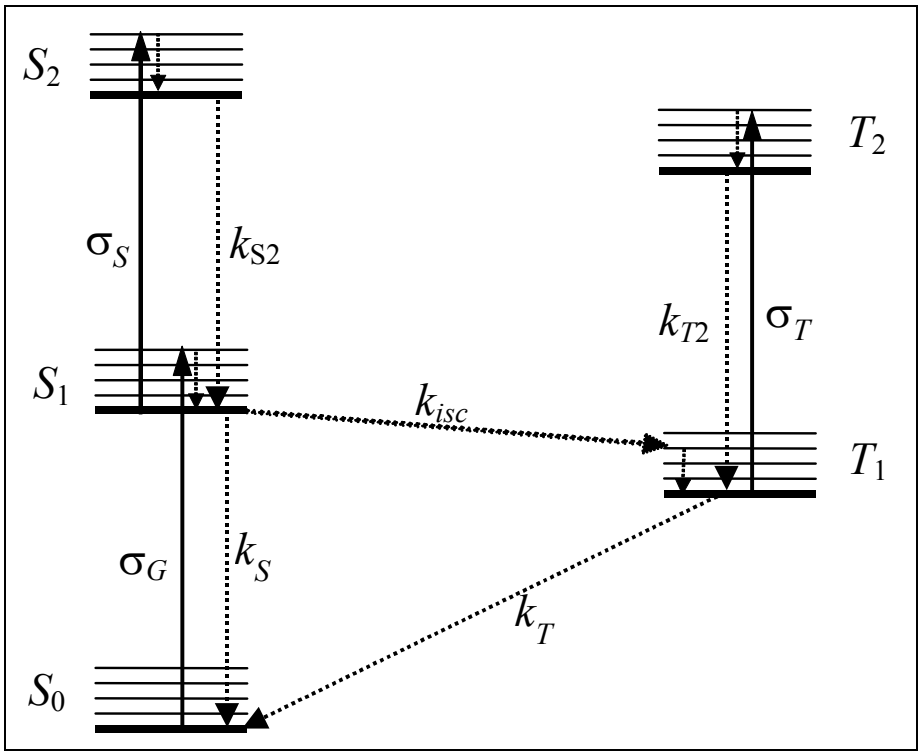

Figure 1. The five-band model. The σ's are absorption cross sections; the *k*'s are rate constants for the indicated transitions among the various bands.

2. The Model

The pump and probe propagate along the *z*-axis through a sample of thickness *L*. Both are spatially Gaussian $TEM_{0,0}$-mode beams; their spot radii are, respectively, w_{pump} and w_{probe}. The probe is a continuous wave source while the pump is Gaussian in time. We approximate the pump by the temporally clipped Gaussian with irradiance

$$I(t,r,z) = \begin{cases} I_{Peak}(r,z)\, e^{-(t/\tau)^2}, & -t_\varepsilon < t < t_\varepsilon \\ 0, & \text{otherwise} \end{cases}. \tag{1}$$

The on-axis pump fluence at the input face of the sample is then

$$F(t,0,0) = \frac{2E}{\pi\, w_{pump}^2} \begin{cases} 0, & t \le -t_\varepsilon \\ \frac{1}{2}(1-\varepsilon) + \frac{1}{2} erf[t/\tau], & -t_\varepsilon < t < t_\varepsilon \\ (1-\varepsilon), & t \ge t_\varepsilon \end{cases}, \tag{2}$$

where *E* is the total energy delivered by an unclipped pump pulse, ε is fraction of that energy contained in the omitted tails, *erf*[*x*] is the Gaussian error function, τ is the HW(1/*e*)M temporal pulse width, and $t_\varepsilon = \tau\, erf^{-1}[1-\varepsilon]$.

In order to obtain a set of rate equations that may be solved analytically, we replace the five-band model with a three-band effective model consisting of a ground state and two excited states of equal spin multiplicity. The model is illustrated in figure 2. We assume that the decay from the

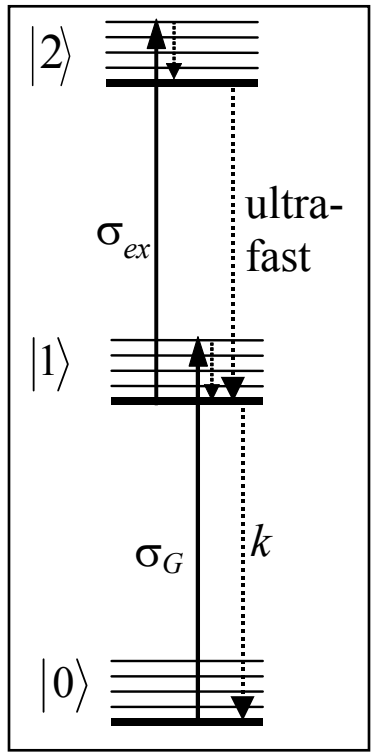

Figure 2. Three-band effective model.

second excited state is so rapid that the population of this state is always negligible. We further assume that the lifetime k^{-1} of the first excited state is sufficiently long ($k\tau << 1$) that we may neglect the effects of the decay from this state during the interval $-t_\varepsilon < t < t_\varepsilon$ in which the pump irradiance is non-zero. The fraction of X of the absorbing molecules in the first excited band then evolves according to

$$\frac{\partial X}{\partial t} = \frac{\sigma_G}{h\nu}(1-X)\,I \tag{3a}$$

in the presence of the pump ($-t_\varepsilon < t < t_\varepsilon$) and according to

$$\frac{\partial X}{\partial t} = -kX \tag{3b}$$

during the subsequent refractory period ($t \geq t_\varepsilon$). Here, σ_G is the ground state absorption cross-section, which is related to the linear absorption coefficient α_0 and the number density N_0 of absorbing molecules by $\alpha_0 = N_0\,\sigma_G$; ν is the frequency of the pump radiation; h is Planck's constant; and I the pump irradiance. Both pump and probe irradiances attenuate according to

$$\frac{dI}{dz} = -N_0\left(\sigma_G(1-X) + \sigma_{ex}X\right)I\,, \tag{4}$$

where σ_{ex} is the absorption cross-section of the excited band.

Introducing the saturation fluence $F_S = h\nu/\sigma_G$, we assume that $F(t=\infty, r=0, z=0)$, the total pump input fluence on-axis, is sufficiently small that the more stringent of the following conditions is satisfied:

$$\frac{1}{2}\left(\frac{\sigma_G}{\sigma_{ex}} - 1\right)\frac{F(\infty,0,0)}{F_S} << 1 \qquad \text{or} \qquad \frac{F(\infty,0,0)}{F_S} << 1 \tag{5}$$

With these assumptions, the normalized transmittance of the probe beam is

$$\frac{P(t)}{P_{Linear}(t)} = 1 - \left(\frac{\sigma_G}{\sigma_{ex}} - 1\right)\frac{1-e^{-\alpha_0 L}}{1+\left(\frac{w_{probe}}{w_{pump}}\right)^2}\frac{F(t,0,0)}{F_S} \times \begin{cases} 1, & t < t_\varepsilon \\ e^{-k(t-t_\varepsilon)}, & t \geq t_\varepsilon \end{cases}. \tag{6}$$

It is straightforward to generalize (6) to the case of multiple pump pulses.

3. Experimental Validation of the Model

In order to validate the model, we conducted a series of pump-probe measurements on a 1-mm sample of 1.39-mM C_{60} in toluene. C_{60} was chosen for this study because its triplet yield is close to unity; in such a material, the actual decay rate of the lowest-lying triplet band should show close agreement with the decay rate of the first excited band in the model. The sample was pumped with 9-ns (FWHM) pulses from a Continuum Powerlite 7000 frequency-doubled, injection-seeded, single-longitudinal-mode Nd:YAG laser operating at a repetition rate of 10 Hz. The experiment employs a 514-nm, continuous-wave probe beam from a Lexel 95 Ar^+ laser. Telescopes set the spot sizes of the pump and probe beams at the sample at 150 μm and 42.5 μm, respectively. The two beams are aligned collinearly and have orthogonal polarizations. After the two beams pass through the sample, the probe is separated from the pump using a polarizer. The probe beam is then focused onto a fast, sensitive Nu-Focus photodiode by a 75-mm lens. An Edmund Scientific notch filter for 514 nm blocks any residual scattered pump light from reaching the probe photodiode. Figure 3 shows the data (gray dots) from two such measurements, one extending over temporal range of 70 ns and the other over 1.75 μs. In each case, the pump pulse delivered 2.85 μJ. The solid black line indicates the predictions of the model, computed from equation (6).

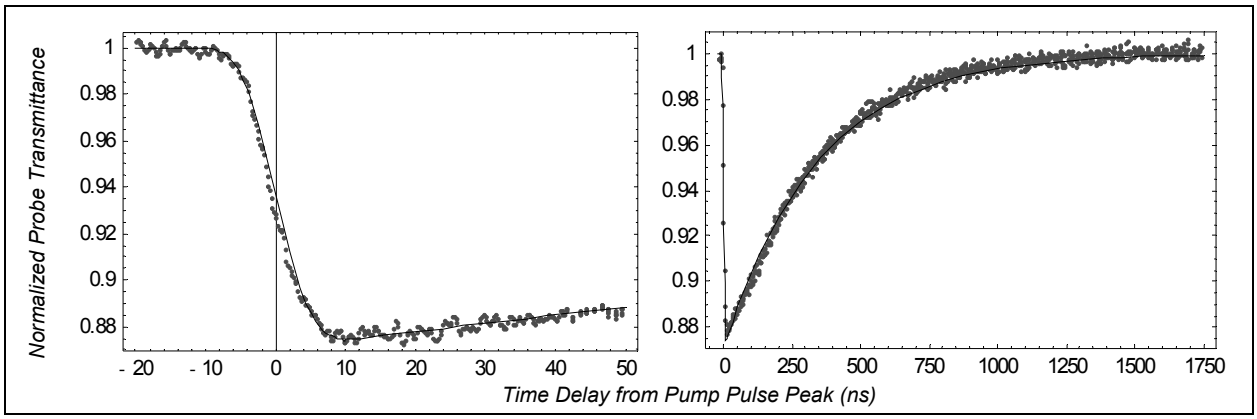

Figure 3. Normalized transmittance of a 7-mW CW probe by a 1-mm sample of 1.39-mM C_{60} in the presence of a 9-ns FWHM, 2.85-μJ pump pulse, focused to a spot of radius 150 μm. The probe spot radius is 42.5 μm.

4. Analysis and Conclusions

An independent measurement using a spectrophotometer yielded a value of 2.57 cm^{-1} for α_0, the linear absorption coefficient of the sample, corresponding to a ground state absorption cross-section σ_G of 3.1×10^{-18} cm^2. For the purposes of the calculation, we set $\varepsilon = 0.01$, i.e., we assume that the clipped pulse posited by the model contains 99% of the energy delivered by the pump pulse used in the experiment. The theoretical curves shown in figure 3 were generated by choosing the parameters σ_{ex} and k to give the best fit to the experimental data. The resulting "best fit" value of 1.7×10^{-17} cm^2 for the excited state absorption cross-section σ_{ex} in the model agrees extremely well with value of 1.6×10^{-17} cm^2 quoted in [4,5] for the absorption cross-section of the first singlet excited state of C_{60}. Likewise, the "best fit" value of $(340\ ns)^{-1}$ for the excited state decay rate k shows excellent agreement with the rate of decay from the lowest-lying triplet state in C_{60} to the ground state, reported in [6] as $(330 \pm 25\ ns)^{-1}$ in air-saturated benzene solution. The experimental pump pulse energy corresponds to a fluence ratio $F(\infty, 0, 0) / F_S$ of 0.13, so the conditions of (5) are satisfied.

In summary, we have presented a simple, analytic model for the normalized transmittance of a weak CW probe in the presence of a (relatively) strong pump pulse in the low fluence regime. Because it neglects excited state decay for the duration of the pump pulse, the model would be expected to provide best results in the limit of short (picosecond) pump pulse widths. Nonetheless, the predictions of the model show excellent agreement with the results of an experimental pump-probe study of C_{60} employing 9-ns pump pulses.

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