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Removal of Coherent Coupling Artifact in Ground-State Recovery Experiments: Malachite Green in Water-Methanol Mixtures

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Wavelength-tunable pulses from a synchronously pumped cavity-dumped dye laser were compressed by using an optical fiber. The resulting 250-fs pulses were used to study ground-state recovery in malachite green solutions. The coherent coupling artifact was removed from the data by an antisymmetrizing procedure, and the resultant signals were deconvoluted in the usual manner. The ground-state recovery times are compared with data from nonlinear optical studies, and the lack of a viscosity dependence in water-methanol mixtures is discussed in terms of solvent steric effects.

Introduction

The simplest type of time-resolved pump-probe experiment is one in which both pump and probe pulses are derived from the same laser pulse. A strong pulse is used, for example, to bleach a ground-state absorption, and a weak delayed replica of the pump pulse is used to monitor the decay of the bleaching. This type of ground-state recovery experiment, in principle, has excellent time resolution since pump and probe pulses are derived by beam splitting and there is no timing jitter between them. Unfortunately the use of identical pump and probe pulses introduces a distortion around zero time delay which is called the coherence coupling artifact or the coherence spike.^{1,3} This artifact arises from the coherent interaction of the two light fields with the molecular system. If the dephasing time is short compared with the pulse duration, the coherence spike contains only information about the light fields;¹⁻⁶ if the dephasing time is comparable to the pulse duration, the coherence spike also contains information about the dynamics of the molecular system. This latter case is discussed in detail elsewhere.⁶ Thus, the coherence spike distorts the signal around zero time, making a simple deconvolution of the measured signal with the second-order autocorrelation function of the laser pulses impossible. One alternative is to fit only the experimental data for delay times much greater than the pulse width. This procedure has the twin disadvantages of substantially lowering the possible time resolution and of confining fitting to the region of the measurement where signal to noise is at its worst. In this paper we show how to remove the coherence artifact from the data and then apply standard deconvolution methods to extract accurate decay times. Our technique is based on the work of Palfrey et al.⁷ along with our own procedures developed for the deconvolution of fluorescence decay data.^{8,9}

As an example of the technique, we present ground-state recovery data for the triphenylmethane dye malachite green [(PhN(CH₃)₂)₂Me⁺(Ph)] in water-methanol mixtures. Data were taken with a synchronously pumped dye laser whose pulses were compressed from about 2 ps to 350 fs by means of an optical fiber and grating compressor.¹⁰ Although the width of our pulses is much less than the decay times under study, the compression techniques often leave rather long, low-intensity wings on the pulse. These wings, if not accounted for with a deconvolution procedure, can lead to inaccurate decay times. The reason for study of malachite green was twofold. Firstly, there have been a number of recent measurements, in both time and frequency domain,¹¹⁻¹⁵ of the ground-state recovery of malachite green in water. These measurements have given a range of lifetimes, and it is not presently clear whether time and frequency domain studies are in accord. Secondly, the ground-state recovery times of the triphenylmethane dyes in alcohol solvents follow a (viscosity)^{2/3} dependence. The model for the radiationless decay of the excited singlet to the ground state involves rotation of the phenyl rings toward an equilibrium geometry displaced from that in the ground

state.¹⁶⁻¹⁸ It is proposed that the internal conversion rate is much higher near the equilibrium geometry of the excited state (presumably because of the energy gap law) and the viscosity dependence of ground-state recovery arises simply from the solvent frictional effect in resisting the phenyl ring motion. A theoretical model for radiationless processes involving large-amplitude motion but having *no* intramolecular potential barrier was recently developed by Bagchi et al.^{19,20} However, before applying such a model to the triphenylmethane (TPM) dyes, it is necessary to ensure that viscosity is the major controlling factor—as it is, for example, in stilbene and diphenylbutadiene.²¹⁻²⁴ Recently Gillbro and Sundström suggested a solvent steric effect was important in determining the ground-state recovery rates.²⁷ Since water and methanol have quite different sizes, the present data should allow a test of this proposal. It should also be noted that malachite green appears to have only a single ground-state conformer, in contrast to a number of other TPM dyes.^{17,25-27}

- (1) von Jena, A.; Lessing, H. E. *Appl. Phys.* **1979**, *19*, 131.
- (2) Ippen, E. P.; Shank, C. V. "Ultrashort Light Pulses"; Shapiro, S. L., Ed.; Springer-Verlag: West Berlin, 1977.
- (3) Vardeny, Z.; Tauc, J. *Opt. Commun.* **1981**, *39*, 396.
- (4) Heinz, T. F.; Palfrey, S. L.; Eisenthal, K. B. *Opt. Lett.* **1984**, *9*, 359.
- (5) Wherrett, B. S.; Smirl, A. L.; Boggens, T. F. *IEEE J. Quantum Electron.* **1983**, *QE-19*, 680.
- (6) Balk, M.; Fleming, G. R., submitted to *J. Chem. Phys.*
- (7) Palfrey, S. L.; Heinz, T. F.; Eisenthal, K. B. Technical Digest—Topical Meeting on Ultrafast Phenomena, 1984 Monterey, CA; Optical Society of America.
- (8) Petrich, J. W.; Chang, M. C.; McDonald, D. B.; Fleming, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 3824.
- (9) Cross, A. J.; Fleming, G. R. *Biophys. J.* **1984**, *46*, 45.
- (10) Nikolaus, B.; Grischkowsky, D. *Appl. Phys. Lett.* **1983**, *43*, 3.
- (11) Erskine, D. J.; Taylor, A. J.; Tang, C. L. *J. Chem. Phys.* **1984**, *80*, 5338.
- (12) Song, J. J.; Lee, J. H.; Levenson, M. D. *Phys. Rev. A* **1978**, *17*, 1437.
- (13) Saikan, S.; Sei, J. *J. Chem. Phys.* **1983**, *79*, 4146.
- (14) Trebino, R.; Siegman, A. E. *J. Chem. Phys.* **1983**, *79*, 3621.
- (15) Ippen, E. P.; Shank, C. V.; Bergman, A. *Chem. Phys. Lett.* **1976**, *38*, 611.
- (16) Forster, Th.; Hoffman, G. *Z. Phys. Chem.* **1971**, *75*, 63.
- (17) Sundström, V.; Gillbro, T.; Bergström, H. *Chem. Phys.* **1982**, *73*, 439.
- (18) Cremers, D. A.; Windsor, M. W. *Chem. Phys. Lett.* **1980**, *71*, 27.
- (19) Bagchi, B.; Fleming, G. R.; Oxtoby, D. W. *J. Chem. Phys.* **1983**, *78*, 7375.
- (20) Bagchi, B.; Singer, S.; Oxtoby, D. W. *Chem. Phys. Lett.* **1983**, *99*, 225.
- (21) Rothenberger, G.; Negus, D. K.; Hochstrasser, R. M. *J. Chem. Phys.* **1983**, *79*, 5360.
- (22) Velsko, S. P.; Fleming, G. R. *J. Chem. Phys.* **1982**, *76*, 3553.
- (23) Courtney, S. H.; Fleming, G. R. *Chem. Phys. Lett.* **1984**, *103*, 443.
- (24) Keery, K. M.; Fleming, G. R. *Chem. Phys. Lett.* **1982**, *93*, 322.

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Experimental Section

Apparatus. Cavity-dumped synchronously pumped dye laser pulses compressed by the method of Grischkowsky et al.¹⁰ were used for both pump and probe in our ground-state recovery measurements. An argon ion laser (Coherent, Innova 10) was actively mode-locked with the radio-frequency source from a Coherent Model 468 mode-locker driver. The mode-locked ion laser pulses of ~ 100 -ps fwhm were produced with a repetition rate of 76 MHz and an average power of 800 mW and synchronously pumped a cavity-dumped hybrid dye laser. The cavity-dumping rate was 3.8 MHz (Coherent Model 7200 cavity dumper). The dye laser contained both a rhodamine 6G gain jet and a DODCI saturable absorber jet. The saturable absorber jet enables significantly shorter pulses to be obtained from the cavity-dumped laser (autocorrelation fwhm of < 3 ps), while maintaining good power (35 mW at 3.8 MHz) and broad tunability (570–630 nm).

The cavity-dumped dye laser pulses were coupled to an IT-T-1605 single-mode polarization-preserving optical fiber with a Nikon 20 \times plan achromat microscope objective. The use of this particular objective (20 \times , numerical aperture 0.4) at approximately 1 m from the dye laser cavity dumper resulted in transmission of $> 60\%$ of incident power through objective and fiber, effectively optimizing the match between fiber parameters (numerical aperture and effective core diameter) and focused beam parameters (cone angle and focused beam waist). The spectrally and temporally broadened and linearly chirped pulses were recollimated with a Swift 60 \times objective. Pulse compression yielding autocorrelations of ~ 350 -fs fwhm was achieved by using a holographic diffraction grating with 2400 lines/mm and $\sim 75\%$ diffraction efficiency in first order (American Holographics) along with a right angle prism. The average power of the compressed pulses was typically 5 mW (1.3 nJ/pulse). The compression factor of 8 is less than the theoretically predicted factor of 20–25^{29,30} for a fiber of optimum length. To minimize the wings in the pulses, our fiber was significantly longer (3.75 m) than the theoretically predicted optimum length (1.5 m) for our pulse characteristics.

The experimental arrangement was similar to that of Ippen et al.¹⁵ The pump and probe polarizations were parallel. Rotating the probe polarization 54.7° from the pump gave identical results indicating that rotational diffusion occurred on a time scale that was slow with respect to that of the malachite green ground-state recovery. In order to minimize thermal effects, the sample was flowed through either a standard dye laser nozzle or a 100- μ L pipet. With the pipet, flow rates of 11 m/s could be attained. The pump and probe beams were focused into the sample with a 2.5-cm focal length lens. The probe beam was spatially filtered to remove any contributions from scattered pump light and recollimated with a lens into a EG&G photodiode. The photodiode output was sent to a EG&G PARC 124A (117 differential preamp) lockin amplifier which was referenced to the 500-Hz frequency at which the pump beam was mechanically chopped. Voltage-to-frequency conversion and storage and display of the lockin signal were carried out by an IBM 9000 microcomputer. Malachite green (Eastman C1264) was used without further purification. Methanol–water solutions were made with deionized distilled water and analytical grade methanol.

Data Analysis. Although the compressed pulses were much shorter than the measured decay times (350 fs vs. 1–2 ps), low-intensity wings of the pulse distorted the decay significantly, requiring deconvolution of the measured curve and the pulse

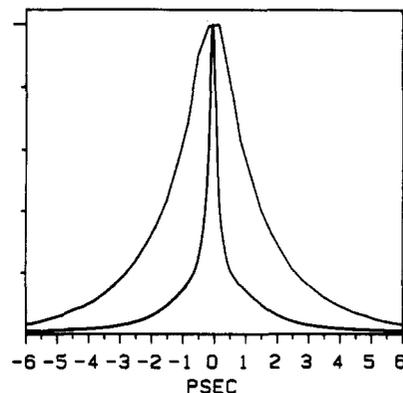


Figure 1. Autocorrelations of compressed (350-fs fwhm) and uncompressed (3-ps fwhm) pulses.

autocorrelation. Straightforward deconvolution over the entire decay range is not possible, however, because of the coherent coupling artifact around $\tau = 0$. In order to extract the true molecular response from the distortions introduced both by the pulse shape and coherence effects, we have used the method developed by Palfrey et al.⁷ and Heinz et al.⁴ Briefly, for slightly noncollinear, copropagating beams, in the small signal limit, the observed signal as a function of delay time can be written as a sum of the terms:

$$S(\tau) = \gamma(\tau) + \beta(\tau) \quad (1)$$

For times long compared with the dephasing time,⁶ the first term corresponds to the convolution of the system response with the intensity autocorrelation of the pulse:

$$\gamma(\tau) = \int_{-\infty}^{\infty} G(t+\tau) R^i(t) dt \quad (2)$$

$G(t)$ is the second-order autocorrelation of the laser pulse, and $R^i(t)$ is the incoherent molecular response. The second term, again assuming rapid dephasing (and unchirped pulses), is given by

$$\beta(\tau) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \text{Re} [E(t) E^*(t-\tau)] R^c(t-t') \text{Re} [E(t') E^*(t'-\tau)] dt' dt \quad (3)$$

$E(t)$ is the complex electric field envelope, and $R^c(t)$ is the coherent molecular response. Note that $\beta(\tau)$ is symmetric with respect to delay. Thus, antisymmetrization of $S(\tau)$ will produce a function, S_a , from which the coherent coupling artifact is absent:

$$S_a(\tau) = \frac{1}{2}[S(\tau) - S(-\tau)] = \frac{1}{2}[\gamma(\tau) - \gamma(-\tau)] \quad (4)$$

The antisymmetrized curve may also be written as a single convolution

$$S_a(\tau) = \int_{-\infty}^{\infty} G(t+\tau) R_a(t) dt \quad (5)$$

where $R_a(t)$ is the antisymmetrized form of the molecular response function:

$$R_a(t) = \frac{1}{2}[R^i(t) - R^i(-t)] \quad (6)$$

$R^i(t)$ may be recovered from $R_a(t)$ by multiplying by a step function, $\theta(t)$:

$$R^i(t) = 2\theta(t) R_a(t) \quad (7)$$

To extract accurate relaxation times from our data, we have antisymmetrized our data traces about $\tau = 0$ and fit the antisymmetrized convolution of a single exponential with the pulse autocorrelation to each trace. This was done by using the finite-difference Marquardt–Levenberg algorithm which minimized the sum of the squares of the residuals (fitted points minus data points) by varying the decay time and a proportionality constant.^{32,33}

(25) Lewis, G. N.; Magel, T. T.; Lipkin, B. *J. Am. Chem. Soc.* **1942**, *64*, 1774.

(26) Gomes de Mesquita; MacGillavry, C. H.; Eriks, K. *Acta Crystallogr.* **1965**, *18*, 437.

(27) Sundström, J.; Gillbro, T. In "Applications of Picosecond Spectroscopy to Chemistry"; Eisinger, K. B., Ed.; Reidel: Dordrecht, The Netherlands, 1984; NATO ASI Ser. C, Vol. 127.

(28) Hirsch, M. D.; Mahr, H. *Chem. Phys. Lett.* **1979**, *60*, 299.

(29) Doust, T. *Chem. Phys. Lett.* **1983**, *96*, 522.

(30) Magde, D.; Windsor, M. W. *Chem. Phys. Lett.* **1974**, *24*, 144.

(31) Tomlinson, W. J.; Stolen, R. H.; Shank, C. V. *J. Opt. Soc. Am. B* **1984**, *1*, 139.

(32) Levenberg, K. *Quant. Appl. Math.* **1944**, *2*, 164.

(33) Marquardt, D. W. *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431.

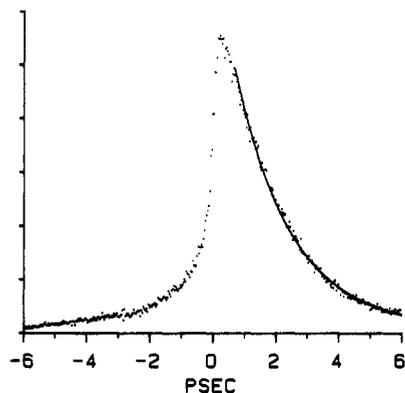


Figure 2. Simulated γ function with noise ($\gamma(\tau) = \int_{-\infty}^{\infty} G(t+\tau) R^i(t) dt$, where $R^i(t)$ is a single-exponential decay with time constant 1.2 ps). The solid line is the best fit single exponential with time constant 1.8 ps.

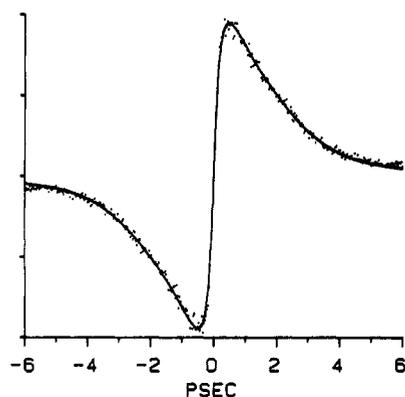


Figure 3. Antisymmetrization of simulated γ function. The solid line is the best fit antisymmetrized convolution of a single exponential with pulse autocorrelation. True decay time (1.2 ps) is recovered.

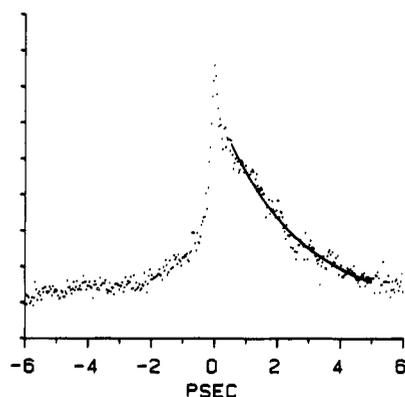


Figure 4. Typical measured decay trace, with dc offset. The coherence peak is apparent. The solid line is the best fit single exponential with a time constant of 2.45 ps.

Results

Figures 2 and 3 demonstrate the need for deconvolution. A simulated function is produced by convoluting a typical pulse autocorrelation with a single-exponential material response function with a decay time of 1.2 ps. The solid line is a single-exponential fit to the trace, with a decay time of 1.8 ps. Similar results are obtained when a simulated β function (coherence peak) is added. In each of these cases, the antisymmetrization procedure (Figure 3) recovered the true decay time to within 20 fs. This error arose from noise included in the simulations. Fitting the actual data shows similar effects. Figure 4 shows a typical experimental trace. The coherence peak is apparent. The solid line, a single exponential plus a constant background, is the best fit to the data over the range indicated. The decay time of the exponential is 2.45 ps. The antisymmetric deconvolution procedure produces a best fit (Figure 5) indicating a decay time of 1.25 ps. The difference between single-exponential and deconvoluted fit

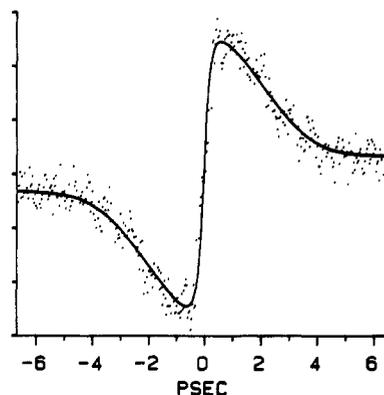


Figure 5. Antisymmetrization of typical decay (see Figure 4). The solid line is the best fit antisymmetrized convolution of a single exponential with the appropriate autocorrelation. Recovered decay time: 1.25 ps.

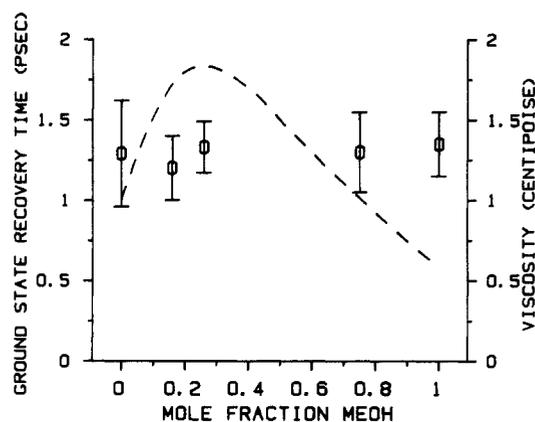


Figure 6. Ground-state recovery times and viscosities vs. mole fraction of methanol for methanol-water mixtures. No evidence for any correlation between recovery times and viscosity is observed.

times is somewhat larger than that of the simulations due to slightly larger wings on the pulse. In all cases, deconvolution shortened the best fit decay times.

By reconvoluting the pulse autocorrelation with extracted decay time, thereby reconstructing γ , and subtracting it from the measured decay, it is possible to extract the β term. The width of the extracted peak (210 fs) is approximately half the width of the autocorrelation of the pulse, indicating that the compressed pulses are approximately a factor of 2 from the transform limit.

It should be noted that β , which is symmetric in the case of instantaneous dephasing, acquires some slight asymmetry for finite dephasing times. This effect is much smaller than the scatter in our data and does not affect the significance of our results. The antisymmetrized recovery times as a function of mole fraction of methanol for several methanol-water mixtures are presented in Figure 6. The dashed line represents the viscosity of the methanol-water mixture. It has been generally observed in studies of TPM dyes that the recovery times and the quantum yields of fluorescence are proportional to $\eta^{2/3}$, where η is the viscosity of the solution.^{16,27-30} In this case, however, it can be seen that, to within experimental error, the recovery time of malachite green is insensitive to viscosity.

Discussion

The fluorescence lifetimes and quantum yields and the ground-state recovery times of the TPM dyes have undergone a great deal of study. In general, these quantities have been found to be proportional to the viscosity, η , raised to a power ranging roughly between 1/3 and 2/3. For a brief compilation of these results, see Bagchi et al.¹⁹ A prime motivation for the present study was that the values for the ground-state recovery time of malachite green in MeOH ($\eta = 0.6$ cP) have generally been found to be larger than those obtained for malachite green in H₂O ($\eta = 1.0$ cP). These times have been obtained by a variety of methods, however, the usually at the limit of resolution of the

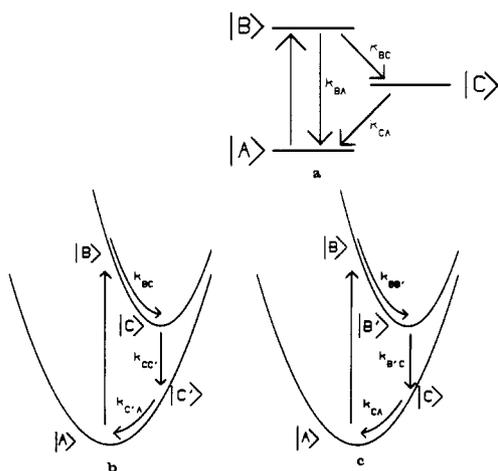


Figure 7. (a) Three-level scheme used to interpret ground-state recovery and polarization spectroscopy experiments. States $|A\rangle$ and $|B\rangle$ correspond to ground and first excited states, respectively. The decay rates correspond to the definitions of Song et al.¹² as follows: $k_{BA} = \gamma_a$, $k_{BC} = \gamma_b$, $k_{CA} = \Gamma_a$. (b and c) Possible assignments of the states of the three-level model to a potential diagram including viscosity-dependent distortion coordinate. See text for further details.

experiments. This result is in contrast to the above observation and in apparent variance with the explanation that the rate of recovery is governed by the rotation of the phenyl rings toward the excited-state equilibrium geometry which may then lead to a significant enhancement in the rate of internal conversion.

Our recovery times for malachite green in MeOH are not, however, greater than those in water. In fact, we obtain the intriguing result that the ground-state recovery times are, within experimental error, the same for MeOH, H₂O, and MeOH–H₂O mixtures. In other words, the recovery time is constant over a range of viscosity from 0.6 to 1.8 cP. This suggests that some factor other than the bulk solvent property of viscosity is responsible for retarding the phenyl group rotation and hence decreasing the rate of internal conversion. A possible explanation for this phenomenon is that the lone-pair oxygen electrons of the water or methanol interact strongly with the empty p orbital of the malachite green cation. The presence of solvent molecules relatively tightly bound to either side of the solute thus hinders phenyl ring rotation.

A good test of this explanation is to study the recovery times of a TPM dye as a function of viscosity in several solvents by varying the temperature. If solvent viscosity is the only factor influencing the recovery time, then the recovery time at a given viscosity should be the same for any two solvents. Sundström and Gillbro³⁴ have constructed such an isoviscosity plot for ethyl violet in various alcohols. They found, for example, that the recovery time was greater when the solvent was ethanol than when it was methanol for a given value of the viscosity. Further study in solvents which are less likely to interact with the empty p orbitals of the TPM dyes but of similar viscosity (e.g., a comparison of CHCl₃ with MeOH both with $\eta = 0.6$) should help to elucidate the particular nature of the solvent–solute interaction occurring in this system.

(34) Sundström, V.; Gillbro, T. *J. Chem. Phys.* **1984**, *81*, 3463.

The dynamics of malachite green in water have been investigated in the frequency domain by several groups.^{12–14} The polarization spectroscopy studies of Song et al.¹² and Trebino and Siegman¹⁴ when corrected for saturation³⁵ give decay times of 1.2 ± 0.1 and 1.2 ± 0.3 ps, respectively. Saiken and Sei¹³ also using polarization spectroscopy find 0.7 ps. This value is identical with that reported by Siegman before the saturation correction is applied,³⁵ and so it appears that a decay time of 1.2 ps represents the best single-exponential lifetime from the frequency domain studies. If both ground-state recovery and polarization spectroscopy are interpreted via the three-level scheme shown in Figure 7a, both techniques should give identical decay times. The width of the resonance peak in polarization spectroscopy and the time constant for ground-state recovery both reflect the slowest rate or rates in the repopulation of the ground state. It thus appears that our time-resolved measurement of 1.29 ± 0.33 ps for malachite green in water is in excellent agreement with the nonlinear spectroscopic studies. The identification of the measured rate with one (or more) of the rates shown in Figure 7a depends on the interpretation of level $|C\rangle$ as either the conformationally relaxed S₁ state (Figure 7b) or as a vibrationally and conformationally unrelaxed ground state (Figure 7c). A kinetically equivalent alternative to the suggestion in Figure 7c is that $|C\rangle$ corresponds to another excited state S_x.¹⁷ If we assume that $|C\rangle$ does not emit (Figure 7c), then the fluorescence lifetime measurement of Stavola et al.³⁶ of 2 ± 1 ps implies that the 1.2 ps corresponds to k_{BC} , rather than k_C (Γ_a) as assumed by Song et al.¹² In terms of Figure 7c k_{BC} is a composite of $k_{BB'}$ and $k_{B'C}$. On the other hand, if $|C\rangle$ fluoresces, then the 1.2 ps corresponds to k_{CA} (a composite of $k_{CC'}$ and $k_{C'A}$ in Figure 7b). In their study Saiken and Sei assumed that the measured time corresponded to $k_{CC'}$ (Figure 7b) or $k_{B'C}$ (Figure 7c). Without a complete spectral study it does not seem possible to decide between these alternatives at present.

If the model of Bagchi et al.¹⁹ applies to malachite green, then a simple kinetic picture may not be adequate. In this model the system is in general quite far from equilibrium and the probability of remaining on the excited-state surface does not decay exponentially. At low viscosities, however, the decay does become exponential after an initial rapid decay.¹⁹ Attempts to fit our data to a double-exponential decay resulted in convergence to two identical decay times. Trebino and Siegman,¹⁴ however, found in a three-laser, induced-grating study that their data could not be fit well by a single exponential but was well fit by a double-exponential fit of the form $0.9 \exp[-t/(0.78 \pm 0.10 \text{ ps})] + 0.1 \exp[-t/(7.4 \pm 3.0 \text{ ps})]$ or by a uniform range of exponentials extending from 0.34 ± 0.04 to 7.2 ± 3.0 ps.

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Registry No. Malachite green, 569-64-2; methanol, 67-56-1.

(35) Siegman, A. E. In "Applications of Picosecond Spectroscopy to Chemistry"; Eisenthal, K. B., Ed.; Reidel: Dordrecht, The Netherlands, 1984; NATO ASI Ser. C, Vol. 127.

(36) Stavola, M.; Mourou, G.; Knox, W. *Opt. Commun.* **1980**, *34*, 404.