

Distortion of the Fluorescence Spectrum of Anthracene with Increasing Laser Pulse Excitation Energy

Juan Carlos del Valle,[†] Andrzej M. Turek,[‡] Nikolay D. Tarkalanov, and Jack Saltiel*

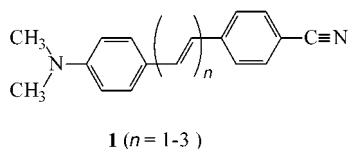
Department of Chemistry, The Florida State University, Tallahassee, Florida 32306-4390

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An anthracene solution in cyclohexane was subjected to continuous 354 nm laser pulse excitation under conditions that lead to amplified spontaneous emission (ASE) laser spikes in strongly fluorescent molecules. Instead of ASE spike development, the fluorescence spectrum of anthracene undergoes distortion that becomes increasingly pronounced with increasing excitation laser-pulse energy (0.10–13 mJ/pulse). On the assumption that the distortion is due to absorption of the fluorescence by transient excited states, an effective transient absorption spectrum is derived that is primarily composed of a combination of the known $T_n \leftarrow T_1$ and $S_n \leftarrow S_1$ anthracene spectra. The filtering of the fluorescence by the $T_n \leftarrow T_1$ absorption is prominently expressed in a splitting of the vibronic band at ca. $23\,500\text{ cm}^{-1}$ as predicted earlier [Weber, M. J.; Bass, M. *IEEE J. Quantum Electron.* 1969, 175–188].

Introduction

The response of solutions of fluorescent molecules to high laser excitation energies often involves cooperative processes in more than a single excited molecule. The appearance of amplified spontaneous emission (ASE) laser spikes from solutions of benzoxazole derivatives exposed to intense laser excitation is an example of nonlinear collective response.^{1,2} A different response is the appearance of a structureless excimer-like emission at the red edge of the normal fluorescence in, for instance, push–pull disubstituted diphenylpolyenes, **1** ($n = 1–3$).^{3–6} Here, a new emitting entity, the bicimer, is postulated



to form through the encounter of two S_1 molecules.^{7,8} A third response was encountered in the case of all-*trans*-1,6-diphenyl-1,3,5-hexatriene (DPH) involving the filtering of the fluorescence due to the build-up of a large singlet excited-state concentration with strong $S_n \leftarrow S_1$ absorption in the region of $S_1 \rightarrow S_0$ emission.⁹

In this paper, we describe the excitation pulse intensity dependence of the luminescence response of a cyclohexane solution of anthracene at 298 K. We establish that, in large part, the observed distortion of the fluorescence spectrum is due to its absorption by transient concentrations of anthracene triplets. This confirms the behavior predicted by Weber and Bass.¹⁰

Experimental Section

Materials. Anthracene (Eastman Kodak, reagent grade) and cyclohexane (spectrophotometric grade) were used as received.

[†]On leave from Departamento de Química Física Aplicada, Universidad Autónoma de Madrid, Cantoblanco 28049, Madrid-España, Spain.

[‡]On leave from Jagiellonian University, Faculty of Chemistry, 30 060 Cracow, Poland.

Measurements. Spectroscopic measurements were made at 298 K on an air-saturated 2.4×10^{-3} M anthracene solution in cyclohexane. Emission spectra were recorded as previously described for ASE measurements² by excitation with a Nd:YAG laser (Spectra-Physics Quanta-Ray DCR-3G), using the third (354 nm) harmonic. Laser pulse repetition was 10 Hz and the pulse duration was 5 ± 1 ns. The output of the Nd:YAG laser was focused to a narrow line horizontally across the sample cell (the cylindrical lens focus distance was 16 cm, and the cell was placed 11–12 cm from the lens). A Moletron L 251 laser dye cell of 0.80 cm optical length was used with oblique windows designed to prevent optical feedback from the windows. The anthracene solution was stirred to minimize secondary processes, such as local heating, from interfering with the experiment. The emission was dispersed by a 300 lines/nm, 0.32 m polychromator (Instruments SA model HR320), detected through an optimally positioned pinhole with an optical multichannel analyzer (EG&G/PAR model 1421), and analyzed with a system processor (EG&G/PAR model 1461/1463). Noise reduction was achieved by operation of the detector in a gated mode synchronously with the Nd:YAG laser. Laser excitation intensities were optically calibrated with a volume-absorbing disk calorimeter (Scientech, Inc., model 36-0001). Emission spectra were not corrected for instrumental nonlinearity. Anthracene photostability was investigated by measuring the absorption spectrum of the solution before and after the laser experiment, using a cuvette of 0.01 cm optical length. Absorption spectra were recorded with the use of a Shimadzu UV-2100 spectrophotometer. Anthracene loss, based on the change in the area of the UV spectrum, was $\sim 4.5\%$ during the course of these measurements, Figure 1.

Data Analysis. Principal component analysis (PCA) calculations were performed on a DELL PRECISION 530 1.4 GHz computer in the MATLAB 6.1 (release 12.1) environment using the Optimization Toolbox version 2.1.^{11,12}

Results and Discussion

Heldt and Heldt observed normal ASE laser spike spectra upon laser pulse excitation of solutions of meso-disubstituted

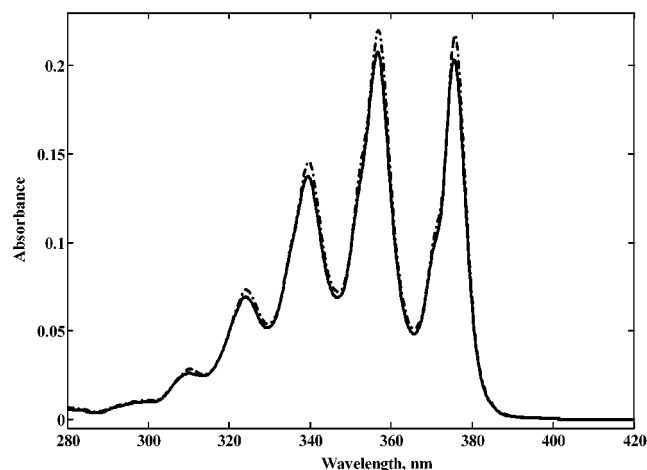


Figure 1. Absorption spectra of anthracene, 2.4×10^{-3} M, in air-saturated cyclohexane, $l = 0.010$ cm, before and after the pulsed laser excitation measurements.

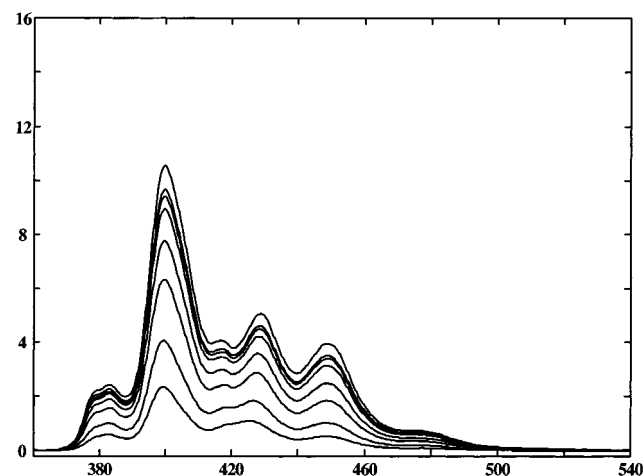


Figure 2. Fluorescence spectra of anthracene, 2.4×10^{-3} M, in air-saturated cyclohexane as the excitation laser-pulse energies are increased (354 nm) from 0.10 to 13 mJ/pulse.

anthracenes that have relatively high fluorescence quantum yields and correspondingly low intersystem crossing yields.¹³ In this work, no ASE response could be elicited upon subjecting an anthracene solution to laser excitation pulses of progressively increasing energy (354 nm, 0.10–13 mJ/pulse). Instead, the shape of the fluorescence spectrum changes systematically as it gains intensity, Figure 2. The fluorescence spectra obtained at the extremes of the excitation pulse energy range, normalized to the same intensity at the most intense band, ~ 400 nm, are shown in Figure 3. The 0-0 band of the fluorescence spectrum is displaced to about 380 nm and is severely self-absorbed because of the high anthracene concentration (the initial absorbance is 18.2 at 375 nm, Figure 1). Viewed as in Figure 3, the intensity ratio of this severely attenuated band to the most intense band at 400 nm appears to be nearly independent of laser excitation power, but the lower intensity bands in the 420–500 nm region seem to undergo subtle red shifts and to gain in relative intensity. This behavior is reminiscent of the spectral response of all-*trans*-1,6-diphenyl-1,3,5-hexatriene (DPH) for which more pronounced filtering of the emission at shorter wavelengths caused by differential $S_n \leftarrow S_1$ self absorption leads to the illusory appearance of bicimer-like fluorescence enhancement of the emission at longer wavelengths on excitation with higher energy laser pulses.⁹ In fact, as in DPH, PCA treatment of the 14 anthracene spectra, obtained for laser pulse

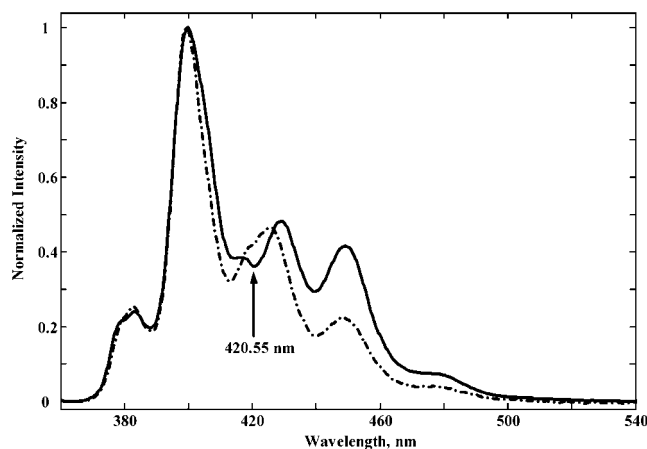


Figure 3. Comparison of anthracene fluorescence spectra obtained with low (0.10 mJ/pulse) and high (13 mJ/pulse) excitation laser-pulse energies.

excitation energies in the 0.10–13 mJ/pulse range, shows that the spectral matrix behaves as a very good two-component system.

Comparison of the spectra in Figure 3 reveals a dip at 420.6 nm in the high excitation energy spectrum that nearly coincides with the λ_{\max} of anthracene's $T_n \leftarrow T_1$ absorption as predicted by Weber and Bass.¹⁰ On the basis of the assumption that appearance of enhanced emission intensity at longer wavelengths is due to preferential absorption by S_1 and T_1 anthracene excited states at the onset of its fluorescence spectrum, an effective transient absorption spectrum was recovered as described in the following paragraph.

Reported $T_n \leftarrow T_1$ and $S_n \leftarrow S_1$ anthracene spectra indicate that no distortion of the fluorescence should occur at $\lambda \geq 449$ nm.^{14–19} The experimental spectra were first interpolated to 0.25 nm wavelength increments, smoothed one time using splines, and baseline corrected. Assuming one-component character for the trailing spectral edge, a search was made for the optimum left-range wavelength limit of the one-component spectral data submatrix. This search was accomplished by tracing the evolution of the ratios of the most significant eigenvalues (ev1, ev2, and ev3 in the order of decreasing magnitude) as a function of the moving left-range wavelength limit of a resulting submatrix. The ev2/ev1 ratio attains a minimum value for 448 nm, and other ratios, such as ev3/ev1 and ev3/ev2, minimize at 450 nm, remarkably close to the onset of $T_n \leftarrow T_1$ absorption. Accordingly, the submatrix consisting of intensities for $\lambda \geq 450$ nm was taken as comprising an undistorted one-component spectral window, as confirmed by comparison with the fluorescence spectrum of a dilute anthracene solution at very low excitation intensity. By matching the intensities of any two of the spectra in Figure 2 in the selected spectral window, a set of very similar difference spectra was obtained having the scaled spectral pattern characteristic for a transient absorption spectrum. To minimize errors, more pronounced for differences between neighboring spectra in the laser power scale, only difference spectra between the spectrum for the lowest pulse excitation energy and each of the spectra for the highest four pulse excitation energies in Figure 2 were employed. The selected difference spectra were then normalized to unit area and factor-analyzed. The first eigenspectrum obtained for this one-component spectral system was taken as the most representative image of the interfering transient absorption spectrum, Figure 4. Despite the choice of the limiting wavelength for the one-component window at 450 nm, the resulting transient absorption spectrum possesses small nonzero absorption values in the 450–

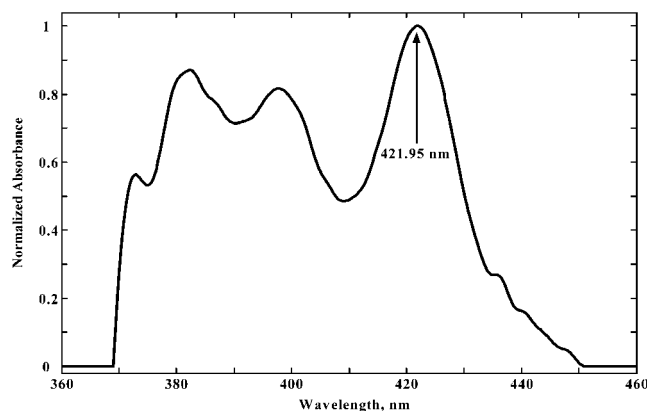


Figure 4. Effective transient absorption spectrum.

452 nm range. This is probably due to the fact that our treatment neglects minor absorbance to lower triplet excited states. In particular, it is well-known, that beginning with the origin at 895 nm of the $T_2 \leftarrow T_1$ transition of anthracene at 298 K in poly(methyl methacrylate) rods, there is a progression of weak absorption bands that extends to shorter wavelengths.^{20,21} The sudden drop in the absorption values on the short wavelength side of the spectrum in Figure 4 occurs at the onset of the fluorescence spectrum where the low fluorescence intensity is severely attenuated by normal self absorption, that is, interference by the $S_1 \leftarrow S_0$ transition. We stress that, because anthracene fluorescence serves as the light source that interrogates transient absorption, meaningful measurements are confined to the 370–490 nm range, Figure 2. Accordingly, the peak at 372 nm is regarded as an artifact of the measurement. The well-resolved bands at 422 and 398 nm correspond nearly exactly to the major two bands in the $T_n \leftarrow T_1$ absorption spectrum of anthracene in cyclohexane,^{14,15,17–19} and the peak at 383 nm is close to a third peak that was observed clearly in the $T_n \leftarrow T_1$ absorption spectra of anthracene in poly(methyl methacrylate),¹⁶ in benzene solution,¹⁸ and in cyclohexane at 77 K¹⁹ but, thus far, discerned only as a shoulder in cyclohexane solution at room temperature.¹⁵ This independent evidence confirms assignment of the 383 nm band as a real feature in the $T_n \leftarrow T_1$ absorption spectrum of anthracene, clearly revealed despite the very high $S_1 \leftarrow S_0$ absorbance in this wavelength region. Relative to the absorbance at $\lambda_{\text{max}} = 422$ nm, the absorbances of the two shorter wavelength bands in Figure 4 are substantially higher than in the published $T_n \leftarrow T_1$ absorption spectrum of anthracene.^{14–19} Additional interference by the underlying broad $S_n \leftarrow S_1$ anthracene absorption¹⁶ must account for much of the discrepancy. The set of experimental spectra in Figure 2 is reproduced quantitatively by applying the effective spectrum in Figure 4 as a filter of progressively increasing optical thickness to the fluorescence spectrum of anthracene for the lowest laser pulse excitation energy (0.10 mJ/pulse, Figures 2 and 3). However, comparison of the 0.10 mJ/pulse spectrum with the fluorescence spectrum of a dilute anthracene solution obtained at very low excitation intensity shows that even at that excitation pulse energy the spectrum is distorted because of transient absorption. The transient absorption spectrum required to distort pure anthracene fluorescence to the shape observed with 0.10 mJ/pulse excitation has an absorbance of 0.21₂ at 422 nm. Filter absorbances at 422 nm increase with laser-pulse energy, reaching a value of 0.56₇ for 13 mJ laser pulses, Figure 5. Because the shape of the filter is independent of laser pulse excitation energy, the ratio of the effective S_1 and T_1 anthracene concentrations that interfere with the fluorescence is likewise independent of laser pulse excitation energy. The buildup of

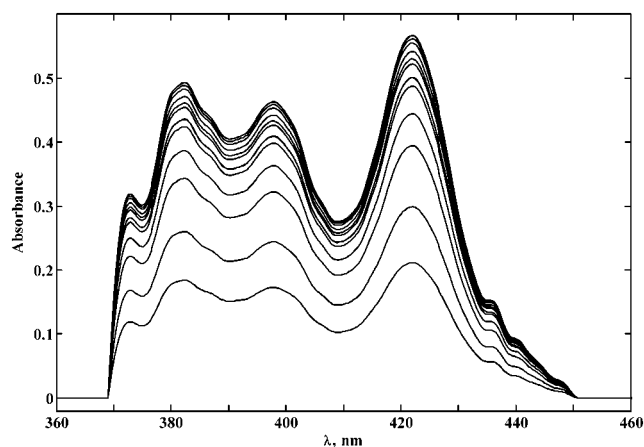


Figure 5. Transient absorption spectra generated at the laser-pulse energies employed in this work.

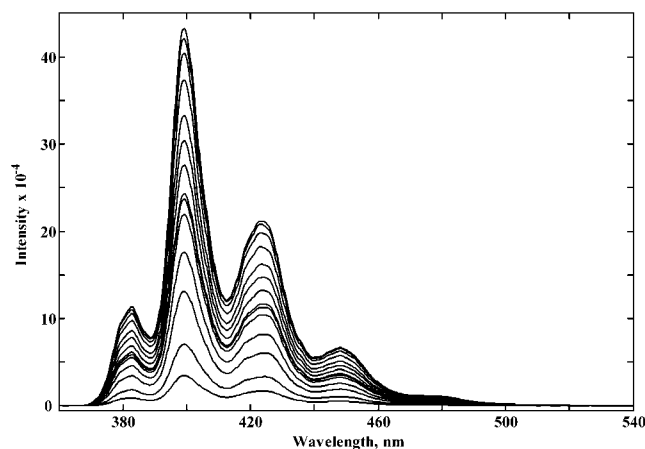


Figure 6. The fluorescence spectra in Figure 2 after correction for transient self absorption.

transient excited-state concentrations implies some diminution of ground-state population (ground-state bleach¹⁸) and a concomitant decrease with increasing pulse energy of the pronounced fluorescence self absorption that is due to overlap of the $S_1 \leftarrow S_0$ absorption spectrum with the onset of the $S_1 \rightarrow S_0$ emission spectrum. Ground-state bleach was neglected in our calculations because, even at the highest pulse excitation energy, the effective triplet concentration is only 2.6×10^{-5} M (on the basis of the absorbance of 0.57 at 423 nm, $\epsilon_{423} = 5.4 \times 10^4$ cm⁻¹ M⁻¹ and an average effective path length $l = 0.4$ cm)¹⁸ and corresponds to only 1.1% bleach. The 4.5% anthracene loss, Figure 1, during the course of these measurements was also neglected. It is no doubt due to the well-known photodimerization and photooxidation reactions, and both photoproducts are transparent at 354 nm.^{22–25}

Correction of each of the experimental spectra in Figure 2 with the corresponding transient absorption spectrum in Figure 5 yields the set of fluorescence spectra in Figure 6. These spectra are identical except for the change in intensity and, aside from ground-state self absorption at the shorter wavelengths, have nearly the same shape as the pure anthracene fluorescence spectrum. A plot (not shown) of transient absorbance at 422 nm, taken from Figure 5, vs laser power reveals a rapid increase up to 3 mJ/pulse and a leveling off at higher pulse energies. Indeed, area ratios of the raw fluorescence spectra in Figure 2 and the corresponding recovered fluorescence spectra in Figure 6 reveal that the loss of fluorescence intensity due to interference by transient absorption rises quickly from 25.8% to 48.1% as the laser energy is increased from 0.10 to 2.74 mJ/pulse and

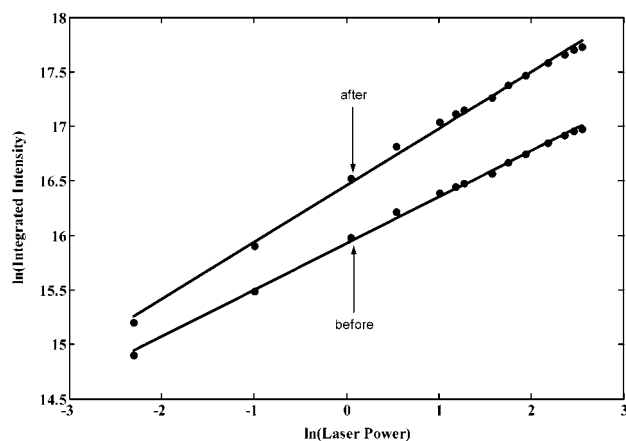


Figure 7. Integrated fluorescence intensity before and after correction for transient self absorption as a function of laser-pulse energy.

then gradually attains a value of 52.7% loss at 12.8 mJ/pulse. The saturation effect in triplet transient absorbance may reflect progressively shorter effective triplet lifetimes with increasing laser-pulse energy due to the enhanced role of bimolecular decay via triplet-triplet annihilation.^{24,26,27} Logarithmic plots of the relative fluorescence intensity before and after correction for transient absorption vs laser-pulse energy are shown in Figure 7. Although restoration of the spectra to their unfiltered shape increases the initial slope (first 4 points) from 0.462 to 0.569, the deviation from unity remains large indicating some unaccounted for energy losses. A similar result was obtained earlier for all-*trans*-1,6-diphenyl-1,3,5-hexatriene.⁹

The $S_1 \rightarrow T_1$ intersystem crossing yield of anthracene in air-saturated hydrocarbon solvents is 0.77.^{27,28} This includes the induced intersystem crossing that accompanies fluorescence quenching by oxygen ($\varphi_f^0/\varphi_f^{\text{air}} = 1.25$ in cyclohexane at 298 K).^{27,32,33} At the high anthracene concentration employed in this work, excimer formation leading to dimer formation decreases the intersystem crossing yield to 0.71 (the rate constant for excimer formation is close to $1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$).^{24,27} No contribution to our measurements is expected from the very short-lived, weakly fluorescent anthracene excimer.²⁹⁻³¹ Oxygen quenching and anthracene self quenching reduce the lowest singlet excited-state lifetime of anthracene from 4.9 to 3.6 ns^{27,32,33} and the lowest triplet lifetime from 0.38 ms (at $2.4 \times 10^{-3} \text{ M}$)³⁴ to 170 ns.^{27,33} The near coincidence between the lifetime of S_1 and the laser pulse width of 5 ± 1 ns may account for its strong involvement in the observed distortion of the fluorescence spectrum. However, the reason meso-disubstituted anthracenes, such as 9,10-diphenylanthracene (DPA), develop well-defined ASE laser spikes under the conditions employed in this study¹³ and anthracene does not must be due primarily to their much lower intersystem crossing yields (for DPA, $\varphi_f^0 = 0.93$ and $\varphi_f^{\text{air}} = 0.70$ in cyclohexane)^{35,36} and the relatively less-important attenuation of their fluorescence by filtering caused by the strongly overlapping $T_n \leftarrow T_1$ absorption spectrum. Even in the case of DPA, it was recognized that the $T_n \leftarrow T_1$ absorption interfered somewhat with ASE laser spike development.¹³ In the case of anthracene, this interference effectively suppresses the development of ASE spikes.

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