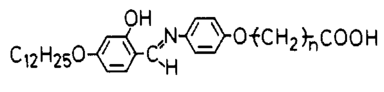
First, several multilayer samples were prepared under the conditions of different surface pressures. Neither the optical absorption spectra nor the long spacings from X-ray diffraction depended on the surface pressure at the multilayer preparation. Moreover, the rates of the thermal decoloration possessed little dependence on the surface pressure.

Second, the multilayers were prepared from the mixed monolayers of DSA and arachidic acid (AA). The monolayers with the DSA/AA mixing ratios of 20/80, 10/90, and 5/95 were spread on a subphase. The mixed multilayers (20–60 layers of Y-type films) could be deposited on quartz plates from every mixed monolayer. As was shown in Figure 5, the same optical absorption peaks were observed in every DSA/AA mixed multilayer as in the pure DSA multilayer. Even in the mixed multilayer with the DSA content of 5 mol %, the peak wavelengths were not affected by the dilution with arachidic acid. Then, we assumed that microphase separation occurred in the mixed monolayers, and therefore, the aggregated structure of DSA molecules in the mixed multilayers turned out to be the same as those in the pure DSA multilayer. The rate constants of the thermal decoloration of the mixed multilayers were exactly the same as that of the pure DSA multilayer.

Then, we finally tried to change the aggregated structures of the SA groups in the multilayers by modification of the chemical structure of the amphiphile. We prepared two amphiphiles in which spacer methylene sequences were inserted between the SA group and the hydrophilic head group. In this case, the aggregated structures of the multilayers were found to depend on the chemical structures of the amphiphiles. The rate constants of the thermal decoloration were also governed by the structures of the amphiphiles. The details of this aspect will be described separately in a subsequent publication.



n = 3 DSA-3
n = 10 DSA-10

In conclusion, the ordered molecular multilayer that consists of an amphiphilic salicylideneaniline derivative could be prepared by the LB method, and reversible photochromism has been detected in the multilayer. The rate of thermal back-reaction was the same order of magnitude as those in crystalline salicylideneanilines, suggesting the aggregated structures in the multilayer was very regular. This work, we believe, gives the first step for the designed control of photochromism in organic solid films by use of the LB technique.

Acknowledgment. We thank Prof. T. Kunitake of Kyushu University for his interest on our work. This work was partly supported by the Grant-in-Aid on Special Project Research for "Organic Thin Films for Information Conversion" from the Ministry of Education, Science, and Culture, Japan.

Registry No. DSA, 111772-61-3; DSA-3, 111793-76-1; DSA-10, 111793-77-2; 4-dodecoxysalicylaldehyde, 111772-62-4; 4-carboxyaniline, 150-13-0.

Use of a Photoreversible Fulgide as an Actinometer in One- and Two-Laser Experiments[1]

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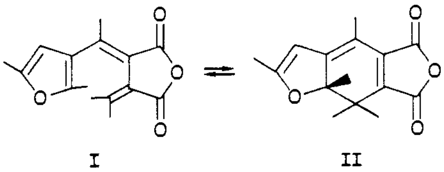
Abstract: The photoreversible fulgide Aberchrome-540 has been tested and developed as an actinometer for one- and two-laser experiments. In the former, the technique allows the determination of extinction coefficients for short-lived reaction intermediates by a method that requires substantially fewer assumptions than other techniques in the literature. In the case of stepwise two-photon processes, the Aberchrome-540 method allows the determination of quantum yields for photoreactions of short-lived reaction intermediates. For this particular application the technique is the only one of its kind.

This report deals with two closely related problems. The first is the development and testing of an actinometer for use in laser photolysis experiments, including its comparison with other available techniques. The second is the development of a technique for the measurement of quantum yields for the photodecomposition of short-lived reaction intermediates. This technique, which is particularly useful in two-laser, two-color experiments, is, to the best of our knowledge, the only one of its kind available at present.

Heller et al. have calibrated fulgide I for use as an actinometer in solution.[3,4] I, which is commercially available under the name of Aberchrome-540, has an absorption maximum at 344 nm ($\epsilon_{344} = 6400$ M^{-1} cm^{-1}). Upon UV irradiation it interconverts to II with a quantum yield of 0.20 in toluene at room temperature (eq 1).



(1)

I II

The forward quantum yield was examined between 313 and 366 nm and found to be wavelength independent.[3] Reaction 1 is photoreversible; for the photobleaching process (i.e., II → I) the quantum yield was found to be temperature and wavelength dependent.[4] In toluene at 21 °C it follows a remarkable linear dependence between 436 and 546 nm, according to eq 2. This

$$\Phi_{II\to I} = 0.178 - 2.4 \times 10^{-4}\lambda \text{ (nm)} \qquad (2)$$

expression leads to $\Phi_{II\to I} = 0.059$ at 494 nm, the absorption maximum for II ($\epsilon_{494} = 8200$ M^{-1} cm^{-1}). We have used this reaction as an actinometer for studies of the photochemistry of short-lived reaction intermediates (e.g., Ph$_2\dot{C}$OH, see following paper in this issue).[5]

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[1] Issued as NRCC-28014.

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[3] Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkin Trans. 2* **1981**, 341.

[4] Heller, H. G., private communication.

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It should be noted that literature extinction coefficients for many short-lived reaction intermediates have shown remarkable fluctuations. Carmichael and Hug recently published an extensive compilation of triplet–triplet absorption spectra[6] and, separately, a least-squares analysis of the reported extinction coefficients.[7] The great majority of reported extinction coefficients are based on relative measurements leading to a ratio of values for two intermediates, one of which is known or can be adequately estimated.[8] Quite frequently, this analysis involves numerous assumptions. Other techniques, such as "total depletion", are subject to a wide range of sources of error (vide infra).

The method developed in this work also leads to a ratio of extinction coefficients, but the reference compound has a well-established extinction coefficient and is not a transient species. In other words, the comparison is made with a reference that can be measured in a regular spectrophotometer, which makes our method essentially an absolute determination.

Experimental Section

Materials. Benzophenone and duroquinone were recrystallized from ethanol before use. Naphthalene was sublimed and then recrystallized from ethanol. 1,2-Di(1-naphthyl)ethane (DNE) was recrystallized from ethanol/methylene chloride. Aberchrome-540 (Aberchromics Ltd., Cardiff, U.K.), valerophenone, methylviologen (ICN), and ruthenium tris(2,2′-bipyridyl) dichloride (ICN) were used as received, as were the solvents (benzene and toluene, spectroscopic grade).

General Instrumentation and Methods. UV–visible spectra were recorded on a HP-8451-A diode array spectrometer. A Perkin-Elmer 8320 gas chromatograph equipped with a 12-m BPI on vitreous silica capillary column was used for GC analyses.

Quantum yields for photocoloration of Aberchrome-540 were determined against the Norrish type II production of acetophenone from valerophenone ($\Phi = 0.30$).[9] Samples of Aberchrome-540 (1.5×10^{-4} M in toluene) and valerophenone (1.5×10^{-2} M in benzene) were deaerated by bubbling nitrogen and irradiated for 1 h with the 313-nm line of a mercury lamp (with a 313-nm interference filter) or with a 308-nm laser (Aberchrome, 30 shots; valerophenone, 60 shots). Product analyses were done by UV–visible spectrometry for Aberchrome-540 and by GC for valerophenone.

Laser Photolysis Measurements. The laser flash photolysis facility and recent modifications required for two-laser experiments have been described in detail.[10,11] A Lumonics TE-860-2 excimer laser with a Xe/HCl gas mixture (308 nm, ~5-ns pulses, ≤20 mJ/pulse), a Molectron UV-24 nitrogen laser (337 nm, ~8-ns pulses, ≤10 mJ/pulse), or a Candela flash-pumped dye laser (Stilbene-420 or Coumarin-503 dyes in 50% aqueous methanol; 100–350 mJ/pulse, ~250-ns pulses) was used for excitation. Most experiments were carried out using a flow system with 7×7 mm^2 quartz cells, with the same cell being used for both the actinometer and the sample. All samples except for Aberchrome-540 were deaerated with a stream of nitrogen.

For the determination of extinction coefficients, solutions of the sample in benzene and of Aberchrome-540 in toluene were prepared with matched optical densities (typically 0.3) at the laser wavelength (308 or 337 nm). The optical density at 494 nm for the Aberchrome was measured as a function of the laser intensity, which was adjusted with a set of calibrated neutral-density filters (evaporated metal on quartz plates). The optical density for the sample was then measured at the triplet–triplet absorption maximum for the sample, again as a function of the laser intensity.

For the photobleaching experiments, solutions of 1,2-di(1-naphthyl)ethane (OD at 308 nm, ≤0.3) and Aberchrome-540 (OD at 308 nm, ~0.55) were used. Two sets of measurements were carried out for each: (1) the optical density for the transient produced by 308-nm excitation was measured at the dye laser wavelength (430 nm) as a function of the 308-nm laser intensity; (2) the amount of bleaching induced by the dye laser was measured at 410 and 494 nm for DNE and Aberchrome-540, respectively, as a function of the 308-nm laser dose.

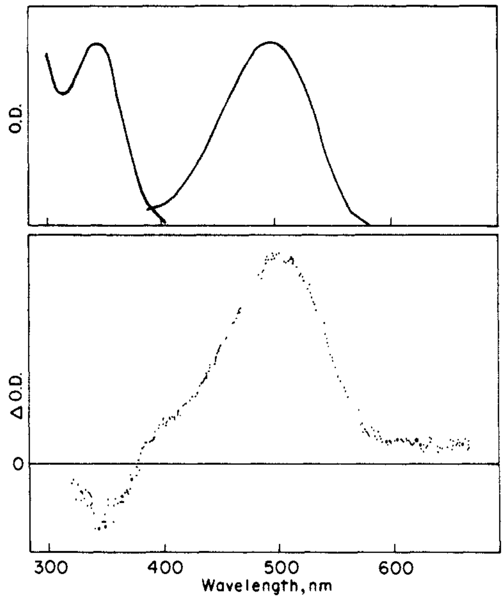

Figure 1. Absorption spectra of I (λ_{max} 344 nm) and II (λ_{max} 494 nm) in toluene (top) and transient absorption spectrum produced by 308-nm excitation of I in toluene (bottom).

Results

(1) Tests of Aberchrome-540 under Laser Irradiation. Several tests were carried out in order to establish that the quantum yield data for Aberchrome-540 reported under conditions of lamp irradiation[3] could be used for laser irradiation. For this purpose, we carried out comparative lamp and laser irradiations of Aberchrome-540 in toluene and of valerophenone in benzene. The latter has been frequently employed as a convenient actinometer for organic photoreactions. Valerophenone undergoes the Norrish type II reaction to yield acetophenone with $\Phi = 0.30$ in benzene at room temperature.[9] Solutions of Aberchrome-540 (1.5×10^{-4} M) in toluene and of valerophenone in benzene (1.5×10^{-2} M) were irradiated at 313 nm by using the corresponding line from a mercury lamp and at 308 nm by using pulses from an excimer laser. These samples had matched initial optical densities at the excitation wavelength, and we assume that there is no wavelength dependence for these reactions between 308 and 313 nm. In the valerophenone samples, the reagent depletion was minimal, and no correction for this effect is needed. However, for the relatively dilute Aberchrome-540 solution (vide infra), significant decoloration in the UV region took place during the irradiation, and eq 3 was used to account for this effect. C_0 and C_t are the concentrations of substrate (Aberchrome-540 in this case) at time zero and time t, and $I_a{}^0$ is the initial absorbed light intensity in einstein per liter per second. Equation 3 is only valid for an optically dilute solution and assumes that form II is transparent at the excitation wavelength. Under these conditions $C_0/C_t = I_a{}^0/I_a{}^t$, where $I_a{}^t$ is the light absorbed at time t.

$$\Phi_{\mathrm{I}\rightarrow\mathrm{II}} = \frac{C_0 \ln (C_0/C_t)}{I_a{}^0 t} \tag{3}$$

Application of eq 3 led to $\Phi = 0.19$ at 313 nm (lamp) and $\Phi = 0.20$ at 308 nm (laser), which led us to conclude that lamp and laser quantum yields of photocoloration for Aberchrome-540 can be regarded as identical. This is not surprising, since II is essentially transparent in the 308–313-nm region. This comparison of lamp and laser irradiation, as well as the reported experiments using lamp irradiation,[3] indicates that the quantum yield for the I → II photoconversion is largely power independent.

Finally, we note that we use more dilute Aberchrome-540 solutions than those recommended by Heller and Langan, who suggest that the solution must absorb all the incident light.[3] This is not possible for transient absorption experiments, which require the excitation beam to penetrate a considerable distance into the solution. Figure 1 (top) shows the spectra of I and II; the latter

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(5) Johnston, L. J.; Lougnot, D. J.; Wintgens, V.; Scaiano, J. C., following paper in this issue.

(6) Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1.

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(8) Bensasson, R.; Land, E. J. *Photochem. Photobiol. Rev.* **1976**, *1*, 163.

(9) Wagner, P. J.; Kelso, A.; Kemppainen, A. E.; McGrath, J. M.; Schott, N. H.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7506.

(10) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.

(11) Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396.

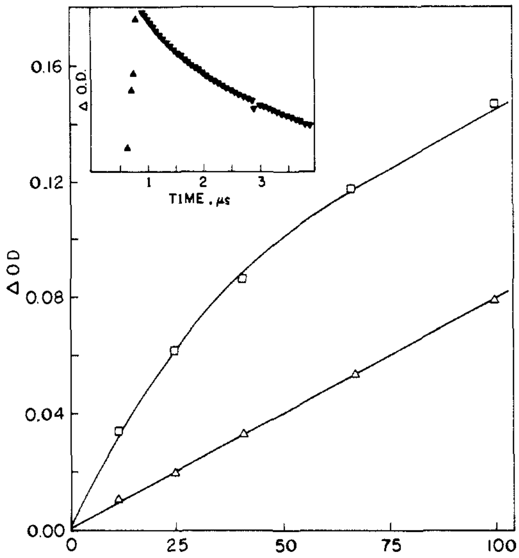

Figure 2. Changes in optical density as a function of 308-nm laser dose for triplet benzophenone in benzene (□, monitored at 525 nm) and II in toluene (Δ, monitored at 494 nm). Inset: A decay trace for triplet benzophenone in benzene monitored at 525 nm.

was produced by photoconversion of I at 350 nm.

(2) Determination of Extinction Coefficients for Short-Lived Species. Aberchrome-540 actinometry was carried out on several reaction intermediates using mostly 308-nm excitation and, in a few instances, 337-nm pulses. These experiments involve three distinct parts: (a) Aberchrome-540 irradiation, (b) sample irradiation, (c) analysis of the data. These are described in three separate subsections.

(a) Aberchrome-540 Irradiation. These experiments were carried out using a flow system, since preliminary work indicated that static samples led to considerable errors due to depletion of I, even if care was taken to stir the sample after every laser shot. The flow rate was selected so as to ensure that a fresh portion of solution would be available to each laser shot (typically ~5 mL/min). Comparative experiments showed identical behavior for deaerated and air-saturated solutions; the latter were used as a matter of convenience. The solutions were typically ~7 × 10^{-5} M. We have found that a minor nonreversible process occurs in addition to reaction 1. This is not surprising, since Heller et al. had already detected this process at 313 nm and had found it to be quite extensive at $\lambda \leq 300$ nm.[3] The irradiated solutions were discarded after use, since photoreversion and recycling led to estimated light doses about 10% lower than those obtained from fresh solutions.

The spectrum of II obtained under conditions of laser irradiation was in full agreement with that obtained by lamp irradiation. Figure 1 (bottom) shows the spectrum obtained with transient spectroscopy techniques. Note that this spectrum records changes in OD (i.e., ΔOD) and, therefore, shows negative segments where bleaching of I occurs.

Irradiation of the Aberchrome-540 actinometer involved a series of experiments in which we measured the change in optical density (at 494 nm) as a function of the laser dose, adjusted with a calibrated set of neutral-density filters. At 100% of the laser dose the energy delivered at 308 nm is typically 10–20 mJ/pulse. Figure 2 shows a representative plot. These plots showed only minor deviations from linearity at high laser doses, an effect that can probably be attributed to significant (15–20%) depletion of I under these conditions. These results are consistent with the monophotonic nature of the phototransformation of reaction 1.

(b) Sample Irradiation. We use as our primary example the case of benzophenone triplets in benzene. All these experiments were carried out in deaerated solutions. While a flow system was not essential in these experiments, it was nonetheless preferred, since it allowed us to use the same reaction cell for both the actinometer and the sample. Aberchrome-540 and sample measurements were always carried out immediately after each other to minimize changes in laser output and/or beam alignment, and the absorptions of the two solutions were carefully matched at the laser wavelength. Benzophenone triplet was monitored at its long-wavelength band, λ_{max} 525 nm.[6] Naturally, the corresponding traces undergo decay in the microsecond time scale (see the insert in Figure 2). The optical density at 525 nm was measured before significant decay took place. The corresponding plot showing the dependence on excitation dose has also been included in Figure 2 and shows marked negative curvature. We note that this curvature is not related to any significant depletion of ground-state benzophenone, since less than 5% of the molecules in the beam path were excited. The effect is the result of a combination of an inner-filter effect by triplet benzophenone (which is a strong absorber at the excitation wavelength)[6] and the recently reported repopulation of ground-state benzophenone via excitation of the triplet.[12]

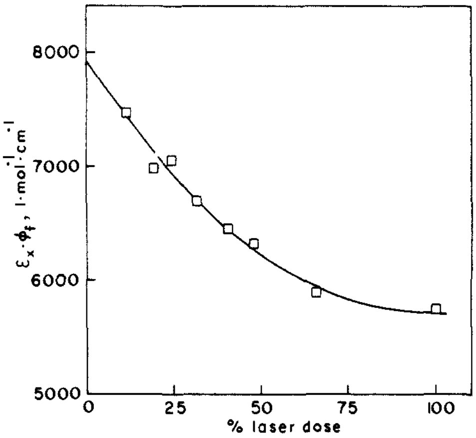

Figure 3. Plot of $\epsilon_x\Phi_f$ as a function of 308-nm laser dose for benzophenone triplet in benzene.

Extinction coefficients for naphthalene, duroquinone, and 1,2-di(1-naphthyl)ethane (DNE) triplets were also measured.[13] The latter was chosen since it has been used (vide infra) as a test compound in our two-laser experiments.

(c) Analysis of the Data. It is clear from the data illustrated in Figure 2 that proper analysis will require extrapolation to low laser doses, to avoid problems of inner-filter effects and ground-state repopulation for benzophenone and of precursor depletion for Aberchrome-540. There are two approaches that we have used. In the first we determine the slope at the origin for plots such as those in Figure 2. It should be noted that the analysis yields the product of the transient extinction coefficient ϵ_x times its quantum yield of formation Φ_f. This product is given by eq 4, where S_x

$$\epsilon_x\Phi_f = (S_x/S_A)\epsilon_A\Phi_A \qquad (4)$$

and S_A are slopes at the origin (see Figure 2) for sample and actinometer, respectively, Φ_A is the quantum yield for actinometer photocoloration (0.20 in toluene at 21 °C), and ϵ_A is the extinction coefficient of II (8200 M^{-1} cm^{-1} at 494 nm). No correction of the type accounted for by eq 3 is necessary, since the data used actually correspond to "zero dose" conditions.

The second approach involves calculating the product $\epsilon_x\Phi_f$ for each pair of actinometer–sample data points and then extrapolating this function to zero light dose. In this case, each product is based on the changes in optical densities rather than slopes, i.e., eq 5.

$$\epsilon_x\Phi_f = (\Delta OD_x/\Delta OD_A)\epsilon_A\Phi_A \qquad (5)$$

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(12) McGimpsey, W. G.; Scaiano, J. C. *Chem. Phys. Lett.* **1987**, *138*, 13.

(13) The quantum yield of intersystem crossing for DNE was not available in the literature. It was determined by the method of Lamola and Hammond, involving the sensitized cis-to-trans isomerization of 1,3-pentadiene: Lamola, A. A.; Hammond, G. S. *J. Chem. Phys.* **1965**, *43*, 2129. The experiments were carried out in benzene using naphthalene as a reference ($\Phi_{ISC} = 0.75$) and using Rayonet RPR-3000 lamps for irradiation. The yield of cis–trans isomerization was determined by gas chromatography. The value obtained for DNE was $\Phi_{ISC} = 0.80$.

Table I. Extinction Coefficient Data in Benzene at Room Temperature

substrate^a	λ_{max}, nm	$\Phi_{ISC}\epsilon^b$	Φ_{ISC}	ϵ^b	lit.[6] ϵ range^b
benzophenone (8)	525	7800 ± 800	1.0	7800	6000–12 000
naphthalene (2)	421	9400 ± 1500	0.75	12 500	11 300–17 500
duroquinone (1)	488	7500 ± 1000	1.0	7500	6950–11 400
DNE (2)	(410)^c	4500 ± 400	0.8	5600	
DNE (2)	430	7000 ± 500	0.8	8700	

^{a}Number of determinations in parentheses. ^{b}In units of M^{-1} cm^{-1}. ^{c}Monitoring wavelength, not λ_{max}.

Figure 3 illustrates a representative plot. Note that ignoring the extrapolation to "zero dose" can lead to very large errors, which largely originate in the sample measurement. This is also a problem with other methods for the determination of extinction coefficients.

We find that if multiple measurements of the same extinction coefficient are to be carried out, the two methods above give essentially the same result; however, when a value is going to be determined only a couple of times, the technique of Figure 3 has some advantages, since it is easier to evaluate visually the actual quality of the data.

The extinction coefficient for benzophenone in benzene at 525 nm was determined six times with 308-nm excitation and twice with 337-nm excitation[14] and led to $\Phi_f\epsilon_{525} = 7800 \pm 800$ M^{-1} cm^{-1}. In this case Φ_f is the quantum yield of intersystem crossing Φ_{ISC}, which for benzophenone is known to be 1.0.[15]

Similar measurements were carried out for naphthalene, duroquinone, and 1,2-di(1-naphthyl)ethane and are summarized in Table I. The values of λ_{max} quoted are those recorded in our laboratory and agree well with literature data.[6] Typical errors with the Aberchrome-540 method are ≤15%. We emphasize that these are realistic error limits; we find that while the literature frequently quotes errors of a comparable magnitude, many of these values actually have much larger error, judging from the dispersion in the published values.[6] Quite frequently, the reported errors reflect little more than reproducibility within two or three measurements. We believe that typical data based on the comparison of transient absorptions, in cases where the power dependence has not been examined, may frequently have as much as 50% error (see the Discussion).

(3) Photobleaching Tests. In order to determine whether the II → I phototransformation would be a suitable reaction to use as an actinometer in our two-laser experiments (vide infra), we carried out several one-laser (dye only) experiments in order to compare our determinations with literature data in at least one example where such comparison was possible.

II was generated by 350-nm irradiation of solutions of I with a CW light source, until a suitable optical density was achieved. Laser photobleaching was induced by 515-nm excitation. As usual, a flow system was employed, and the bleaching was monitored at 494 nm. The procedure employed was much the same as for the photocoloration experiments described in earlier sections. The laser was attenuated with neutral-density filters to check that the photobleaching was linearly dependent on the laser dose.

As a test reaction we have used the reduction of methylviologen (MV^{2+}) by the excited triplet charge-transfer state of $Ru(bpy)_3^{2+}$ generated by 515-nm excitation, i.e., eq 6. The formation of the

$$Ru(bpy)_3^{2+*} + MV^{2+} \rightarrow Ru(bpy)_3^{3+} + MV^{\bullet+} \quad (6)$$

reduced form $MV^{\bullet+}$ was monitored at 600 nm. Using the same approach as in Section 2 and, in this case, matching the optical densities of $Ru(bpy)_3^{2+}$ and II at 515 nm, we obtained $\Phi_f\epsilon = 2760$ M^{-1} cm^{-1}. Introducing the known extinction coefficient for $MV^{\bullet+}$ ($\epsilon = 12000$ M^{-1} cm^{-1})[16] leads to $\Phi_f = 0.23$. At the concentration of MV^{2+} used in these experiments (0.06 M), and using the reported rate constant[17] for reaction 6, we calculate that approximately 99% of the excited states of $Ru(bpy)_3^{2+}$ would be quenched by MV^{2+}. This corresponds then to an electron-transfer efficiency of 0.23. This compares well with values of 0.17–0.30 reported in the literature.[17,18]

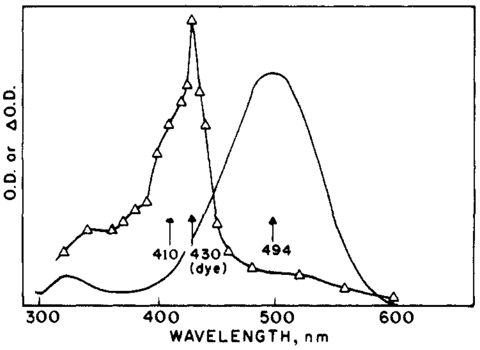

Figure 4. Absorption spectrum of II in toluene (—) and transient absorption spectrum of triplet DNE in benzene (Δ).

The agreement between these values should not be taken as a calibration of the method but rather as an indication that the bleaching of II can indeed yield reliable values.[19]

(4) Actinometry for Two-Laser Two-Color Experiments. In these experiments the yield of a process induced by two-laser pulses is not only a function of the energy delivered by the two lasers but also of the extent of overlap (in space and in time) of the two laser beams. That is, in the extreme situation in which the two beams excite nearby but not overlapping volumes, the yield of the two-photon process will be zero. For this reason, it is critical that the actual actinometer be generated in situ, so that its spatial distribution models adequately the distribution of reaction intermediates encountered in the experiment of interest.

We use as a reversible actinometer the system of reaction 1 and as a test system a benzene solution of DNE. For the latter, UV excitation leads to the triplet state following intersystem crossing (reaction 7), while visible excitation of the triplet (at 430 nm) leads to ground-state repopulation (reaction 8).

$$DNE \xrightarrow{h\nu} \xrightarrow{ISC} DNE^* \quad (7)$$

$$DNE^* \xrightarrow{h\nu'} DNE \quad (8)$$

Reaction 8 is a rather unusual process and deserves some comment.[20] From a practical point of view, excitation of DNE* in benzene leads to its ground state with no apparent involvement of other intermediates. We note that 1-naphthylmethyl radicals would be readily detectable under our experimental conditions.[22]

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(14) The actual values obtained were 6300, 7600, 8400, 7900, 8500, and 8000 M^{-1} cm^{-1} with 308-nm excitation and 9000 and 7400 M^{-1} cm^{-1} with 337-mm excitation. Each value was measured in a completely independent experiment.

(15) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.

(16) Farrington, J. A.; Ledwith, A.; Stam, M. F. *J. Chem. Soc., Chem. Commun.* **1969**, *259*.

(17) Kalyanasundaram, K.; Kiwi, J.; Grätzel, M. *Helv. Chim. Acta* **1978**, *61*, 2720.

(18) The higher value is obtained by assuming that the extinction coefficient for $Ru(bpy)_3^{2+*}$ is small compared with that of the ground state. The lower value assumes an upper limit of 7000 M^{-1} cm^{-1}.[17]

(19) The reported values of ϵ for $Ru(bpy)_3^{2+*}$ must have considerable error, since we observe bleaching at 400 nm where the relative extinction coefficients for the ground and excited states would predict triplet absorption: Bensasson, R.; Salet, C.; Balzani, V. *C. R. Seances Acad. Sci., Ser. B* **1979**, *289*, 41.

(20) In a preliminary report[21] we suggested that the bleaching of triplet DNE could lead to cleavage to produce 1-naphthylmethyl radicals by analogy with a similar reaction of 1,3-di(1-naphthyl)-2-propanone.

(21) Scaiano, J. C.; Johnston, L. J. *Pure Appl. Chem.* **1986**, *58*, 1273.

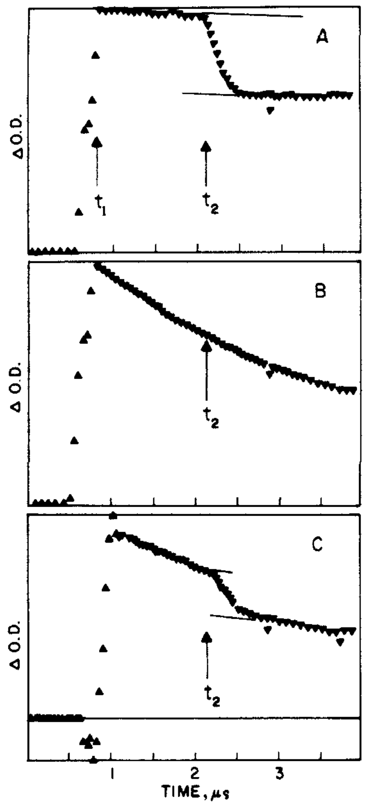

Figure 5. (A) Production of II by 308-nm excitation of I at time t_1 followed by bleaching with a 430-nm laser pulse at t_2 (monitoring wavelength 494 nm). (B) Transient decay trace at 430 nm for triplet DNE produced by 308-nm excitation. (C) Transient decay trace at 410 nm showing the production of triplet DNE by 308-nm excitation followed by bleaching of the signal at time t_2 with a 430-nm laser pulse.

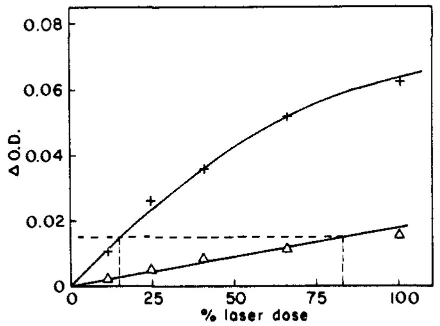

Figure 6. Plots of changes in optical density at 430 nm as a function of 308-nm laser dose for triplet DNE (+) and II (Δ).

Table II. Determination of the Bleaching Efficiency for DNE

	DNE	Aberchrome-540
OD at 308 nm	0.30	0.56
ΔOD_{430} range (NDF)	0.122 (100)	0.020 (100)
	0.022 (11.5)	≤0.005 (11.5)
ΔOD_{430} at t_2 (NDF)	0.072 (100)	0.020 (100)
	0.013 (11.5)	≤0.005 (11.5)
bleach monitored at λ	410 nm	494 nm
ΔOD_λ range at t_2 (NDF)	0.041 (100)	0.060 (100)
	0.006 (11.5)	0.010 (11.5)
bleach range (NDF)[a]	0.013 (100)	0.014 (100)
	0.002 (11.5)	≤0.003 (11.5)
ΔOD_{match} at 430 nm (NDF)	0.020 (16.5)	0.020 (100)
bleach (matched) at λ[a]	0.0030	0.0145
ΔOD^0 at t_2 at λ[b]	0.0100	0.061

[a] See eq 11 and 12. [b] See eq 10.

Product studies[23] do not show formation of any significant yields of products, and the transient phenomena show only bleaching of the T–T absorptions from DNE. The process is characteristic of aromatic solvents, particularly benzene, and is believed to involve energy transfer from an upper excited state of the donor (DNE) to the surrounding solvent molecules. A similar process has been recently reported for benzophenone in benzene.[12]

The object of these experiments is to determine the quantum yield of reaction 8. We emphasize that this is just a "monophotonic" quantum yield, although it refers to the photolysis of a short-lived species rather than a stable precursor. The "two-photon" nature of the process refers only to the need to use the first laser pulse to generate the species of interest.

Just as in the case of single-laser experiments (see Section 2), it is important to match the optical densities of the sample and actinometer. We note however that, in this case, the terms "sample" and "actinometer" refer to the species to be bleached, that is triplet DNE (DNE*) and II generated in situ by 308-nm excitation. These need to be matched at the dye laser wavelength (not at the monitoring wavelength) and at the time of the dye laser pulse. This timing aspect is not important for Aberchrome-540, since II does not decay in the time scale of the experiment, but it is critical for DNE*, which under our experimental conditions has a lifetime of a few microseconds. Figure 4 shows an overlap of the spectra of DNE* and of II with all the relevant wavelengths adequately indicated. Note that this technique requires that the two spectra show some overlap at the dye laser wavelength (i.e., both should absorb at 430 nm in this case). As illustrated in the DNE* example, even a modest overlap is sufficient, although the studies are much easier when the overlap is more extensive than in the case of Figure 4.

Figure 5 (top) illustrates a two-laser experiment monitored at 494 nm showing 308-nm induced I → II photoconversion at t_1, followed by II → I bleaching at t_2. The center figure (B) illustrates a 308-nm-only trace monitored at 430 nm (dye laser wavelength). It is at this wavelength, and at time t_2, that the optical densities need to be matched. However, a two-laser experiment is not possible at this wavelength, because scattered light from the powerful 430-nm pulse is sufficient to cause saturation and/or nonlinear response of the photomultiplier. Thus, the bleaching is determined at a different wavelength and at t_2, and trace C in Figure 5 illustrates the two-laser trace at 410 nm.

Two approaches (or their combination) can be used to achieve absorbance matching at 430 nm: (a) Since for the bleaching experiment matching at 308 nm is not critical, one can adjust the concentrations of sample and actinometer to give matched transient absorbances. However, large differences are not recommended, because they can lead to differences in the spatial distribution of transients. For example, for the traces in Figure 5 the optical densities at 308 nm (7-mm optical path) were 0.30 for DNE and 0.56 for I. Larger differences are unacceptable, as they lead to considerable error. (b) We use a set of calibrated neutral-density filters to adjust the amounts of II and DNE* generated by the 308-nm laser in the same way indicated in section 2. For example, Figure 6 shows the corresponding plots for DNE* and II. Note that at this wavelength the signal from II is relatively weak, and therefore, to achieve appropriate matching it is necessary to run the DNE sample under considerable laser attenuation. By running the bleaching experiments (as in Figure 5) under matched conditions one determines a ΔOD_{bleach} for each sample at the appropriate monitoring wavelength. Of course, if the attenuation required does not correspond to an available laser dose, ΔOD_{bleach} is determined from a plot of the experimental values and interpolation to the adequate laser dose. Table II summarizes the data for one particular experiment. If the magnitude of bleaching for both measurements is small compared with the value of ΔOD at the monitoring wavelength or if the fraction bleached is similar

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(22) Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 6368.

(23) Two identical samples of 0.2 mM DNE in benzene were irradiated with (i) 500–308-nm laser pulses and (ii) 500 pairs of 308-nm plus 430-nm pulses (with a 0.5-μs delay between lasers) by using similar techniques to those described in ref 5. No products (i.e., <1%) were detected by GC for either of the two samples. A very minor amount of an unidentified material was observed by HPLC (UV detection at 254 nm), but this must correspond to ≪1% of the material since it was not detected by GC.

Table III. Photobleaching Quantum Yields at 293 K Obtained in Two-Laser Experiments

species	solvent	λ, nm dye	max	mon	Φ_2	ref
DNE*	benzene	430	430	410	0.021 ± 0.008	this work
$Ph_2\dot{C}OH$	cyclohexane	515	545	550	0.27 ± 0.06	5
benzil*	benzene	488	485	460	0.06[a]	25
benzophenone*	benzene	488	525	535	0.057[a]	13
1,3-di(1-naphthyl)-2-propanone*	benzene	430	430	410	0.06[a]	26
dibromoanthracene*	benzene	467	430	445	0.041[a]	27

[a] Single determination; estimated error ~±0.30%.

for sample and actinometer, then a good approximation to the quantum yield of photobleaching (Φ_2) is given by eq 9, where the

$$\Phi_2 = \frac{\text{bleach}_2}{\text{bleach}_1}\frac{\epsilon_1}{\epsilon_2}\Phi_{II\rightarrow I} \qquad (9)$$

subscripts 1 and 2 refer to Aberchrome-540 and DNE, respectively, at their monitoring wavelengths and the term bleach refers to the optical density change at those wavelengths. Note, however, that the value of $\Phi_{II\rightarrow I}$ refers to the laser wavelength.

A more accurate approach, and a necessary one if the conditions above are not met, is given by eq 10, which is based on the same considerations as eq 3 for CW irradiations, where the superscripts

$$\Phi_2 = \frac{\epsilon_1}{\epsilon_2}\frac{\Delta OD_2^0}{\Delta OD_1^0}\frac{\ln (\Delta OD_2^0/\Delta OD_2^d)}{\ln (\Delta OD_1^0/\Delta OD_1^d)}\Phi_{II\rightarrow I} \qquad (10)$$

"0" and "d" refer to values before and after the dye laser pulse, respectively (eq 9, 10).

$$\text{bleach}_1 = \Delta OD_1^0 - \Delta OD_1^d \qquad (11)$$

$$\text{bleach}_2 = \Delta OD_2^0 - \Delta OD_2^d \qquad (12)$$

For the data in Table II ($\Phi_{II\rightarrow I} = 0.0748$), we obtain Φ_2 values of 0.022 and 0.023 using eq 9 and 10, respectively.

The value of Φ_2 for the photobleaching of DNE* in benzene was measured in four independent experiments and led to $\Phi_2 = 0.021 \pm 0.008$.[24] We note that the error quoted is significantly larger than the standard deviation ($\sigma = 0.004$), but we feel that ca. 30% is a realistic estimation of the errors, that takes into account that the parameters in eq 10 incorporate errors (some of them systematic) that may not be reflected by the standard deviation.

The error limits may be somewhat larger in systems where the transient bleached is not a primary species (e.g., ketyl radical in the following paper).[5] The values can also be considerably more accurate when the spectral overlap between II and the transient in question is better than in our example (e.g., benzil triplet). Table III summarizes various bleaching quantum yields determined by this technique.

It is clear that while our examples involve photobleaching, the same approach can be used to determine quantum yields for product formation. Such an approach yields the product of the quantum yield for transient formation times its extinction coefficient.

Discussion

This work was initially undertaken as a response to the need for suitable actinometers for two-laser experiments involving the photolysis of short-lived reaction intermediates. It soon became evident that an additional benefit of the Aberchrome-540 technique is the possibility of determining the extinction coefficients of short-lived reaction intermediates by a technique that involves a much smaller number of assumptions than those used in the literature.[6] Thus, our technique depends only on the product $\epsilon_A\Phi_A$ for the photoconversion of I into II[28] and on data obtained at low laser doses, i.e., extrapolated to zero laser dose.

The largest single set of transient extinction coefficients in the literature has been reported by Bensasson and Land in an extensive series of papers over a 20-year period.[6,8,29-36] Several of these papers present detailed discussions of the assumptions involved. We will cover here the cases of duroquinone, benzophenone, and naphthalene triplets.

Duroquinone will be discussed in some detail, since the assumptions involved in the determination of its triplet extinction coefficient are similar to those involved in many other determinations using energy-transfer experiments and pulse radiolysis techniques. Most of these are related in various ways to the extinction coefficient of $Ph_2\dot{C}OH$ in water ($\epsilon_{540} = 3220 \pm 600$ M^{-1} cm^{-1}) measured by Land relative to the yield of electrons in the radiolysis of water.[30] A value of 3700 M^{-1} cm^{-1} was estimated in cyclohexane on the assumption that the oscillator strength was solvent independent.[31] The triplet extinction coefficients are then related to the ketyl value by the following method. Triplet benzophenone is generated by pulse radiolysis and yields ketyl radical by hydrogen abstraction from the solvent. The decrease in ketyl yield upon the addition of benzophenone triplet quenchers is then assumed to show a 1:1 correspondence with the number of acceptor triplets formed. A correction for radiolytically generated ketyl radicals that are not formed via benzophenone triplets is also introduced.[31] For naphthalene this analysis led to $\epsilon_{415} = 24\,500$ M^{-1} cm^{-1} in cyclohexane; the value in benzene was estimated as $\epsilon_{425} = 13\,200$ M^{-1} cm^{-1} on the assumption of a solvent-independent oscillator strength. From this it is straightforward to obtain $\epsilon_{490} = 6950$ M^{-1} cm^{-1} for duroquinone triplets by using energy-transfer techniques.[31,32,37] This value compares well with our determination of $\epsilon_{488} = 7500$ M^{-1} cm^{-1}. Our technique does not necessarily improve the value, but rather it reduces quite drastically the number of assumptions involved and makes the value less dependent on potential future revisions in the values adopted for the calculations.

The triplet state of benzophenone in benzene has been the subject of considerable attention, and the "accepted" values generally fall in the 7000–8000 M^{-1} cm^{-1} range.[6] Earlier values include the following: $\epsilon_{532} = 7630$ M^{-1} cm^{-1} obtained by use of the technique discussed in the previous paragraph;[31] $\epsilon_{530} = 7220$ M^{-1} cm^{-1} determined by Hurley et al. on the basis of direct measurement of the energy dose in laser photolysis experiments and extrapolated to zero laser dose;[38] 7200 M^{-1} cm^{-1} determined

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(24) Values of 0.015, 0.026, 0.023, and 0.018 were obtained.

(25) McGimpsey, W. G.; Scaiano, J. C., unpublished results.

(26) Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 5487.

(27) McGimpsey, W. G.; Scaiano, J. C., unpublished results.

(28) The product $\epsilon_A\Phi_A$ has less error than the individual values because of the way Heller obtained them.[3]

(29) The set of extinction coefficients reported by Bensasson and Land is too extensive to try to be exhaustive in this report. Only a few that are relevant to this paper are included in the next few references. These have recently been reviewed in detail.[6]

(30) Land, E. J. *Proc. R. Soc. London, A* **1968**, *305*, 457.

(31) Bensasson, R.; Land, E. J. *Trans. Faraday Soc.* **1971**, *67*, 1904.

(32) Land, E. J. *Trans. Faraday Soc.* **1969**, *65*, 2815.

(33) Bensasson, R. V.; Gramain, J.-C. *J. Chem. Soc., Faraday Trans 1* **1980**, *76*, 1801.

(34) Bensasson, R. V.; Land, E. J.; Truscott, T. G. *Flash Photolysis and Pulse Radiolysis. Contribution to the Chemistry of Biology and Medicine*; Pergamon: Oxford, 1983; Chapter 1.

(35) Amand, B.; Bensasson, R. *Chem. Phys. Lett.* **1975**, *34*, 44.

(36) Lavalette, D.; Bensasson, R. V.; Amand, B.; Land, E. J. *Chem. Phys. Lett.* **1971**, *10*, 331.

(37) This value for ϵ_{490} for triplet duroquinone comes from ref 31 and is apparently a revision of the one originally published in ref 32.

(38) Hurley, J. K.; Sinai, N.; Linschitz, H. *Photochem. Photobiol.* **1983**, *38*, 9.

by ferrioxalate actinometry,[39] where the actinometer was irradiated in situ, although the further reactions in this actinometer could not have been performed at the sample compartment; and 7800 M^{-1} cm^{-1} reported by us. A more extensive compilation, reporting values between 6000 and 12 000 M^{-1} cm^{-1}, has been published by Carmichael and Hug.[6]

The technique of total depletion, or variations on the same principle, has also been applied to the determination of triplet–triplet extinction coefficients. The assumption in this technique is that by increasing the intensity of the exciting pulse it is possible to achieve complete conversion of a small ground-state concentration to the triplet manifold. A wide variety of problems in this technique have been discussed in the literature, including a recent analysis by Carmichael and Hug[40] on the breakdown of this assumption for short laser pulses. Our recent work on ground-state repopulation by triplet excitation implies that, at least in aromatic solvents, the basic assumption of the technique is incorrect.[12] That is, if the photochemical behavior of a system can be represented by eq 13 and 14, one cannot achieve total conversion of A into

$$\mathrm{A} \xrightarrow{h\nu} \mathrm{A}^* \qquad (13)$$

$$\mathrm{A}^* \xrightarrow{h\nu} \mathrm{A} \qquad (14)$$

its triplet state A* but, rather, a short-lived photostationary state will be reached. As pointed out for the cases of benzophenone[12] and DNE (vide supra), reaction 14 involves energy transfer to the solvent. Thus, if the energy of a pulse is increased, eventually one would reach a condition where at the end of the pulse

$$[\mathrm{A}]/[\mathrm{A}^*] = \Phi_{14}\epsilon_{\mathrm{A}^*}/\Phi_{13}\epsilon_{\mathrm{A}} \qquad (15)$$

where Φ_{14} and Φ_{13} are the quantum yields for the reactions specified and the extinction coefficients correspond to the laser wavelength. For benzophenone it is possible to make a semiquantitative analysis if we assume $\Phi_{13} = \Phi_{ISC} = 1.0$,[15] $\Phi_{14} \simeq 0.06$[12] (same as measured at 517 nm in benzene), $\epsilon_A = 70$ M^{-1} cm^{-1}, and $\epsilon_{A^*} \simeq 6700$ M^{-1} cm^{-1} at 308 nm in benzene.[41] Thus, the formation of benzophenone triplet will level off at

$$[\mathrm{A}]/[\mathrm{A}^*] \sim 6$$

That is, only 15% conversion to the triplet could be achieved! While it is clear that the extinction coefficient of benzophenone does not make it an ideal candidate for depletion techniques at $\lambda_{laser} > 300$ nm, the example above exemplifies, nevertheless, how dramatic the role of photochemically induced ground-state repopulation can be.

We turn now to the measurements of quantum yields in the photochemistry of short-lived species. The Aberchrome-540 technique is limited to the wavelength range in which the colored form (II) absorbs. If we use as our wavelength limits the region where ϵ_{II} exceeds 15% of the value at the maximum, this defines a range from 410 to 570 nm. The transient of interest must obviously show absorption somewhere in this region. As illustrated in Figure 6, it is necessary to match the transient optical densities at the laser wavelength for II and the transient of interest. The transient optical density at the laser wavelength is determined by the transient's extinction coefficient at that wavelength, the quantum yield of its formation, the energy dose from the synthesis laser, and the optical density of the precursor. Among these the energy dose can be easily adjusted with neutral-density filters and does not need to be the same for sample and actinometer. If the spectra overlap significantly there is also some room to play with the extinction coefficients, by simply selecting a wavelength where they have convenient values. There is also some flexibility by changing the precursor concentration, but extensive differences here are not recommended. In summary, differences in the $\epsilon\Phi$ products (see eq 5) of up to 1 order of magnitude at the wavelength of the second laser can be readily accommodated, but beyond this point a significant price is paid in terms of precision.

Transient photobleaching quantum yields can be evaluated by using either eq 9 or 10, depending on the relative magnitudes of the photobleaching induced in the sample and actinometer. These magnitudes can be quite different, but the smaller one has to be sufficiently large that an adequate experimental measurement can be carried out. If this is not the case, the dye laser dose can be adjusted with neutral-density filters, although it should be noted that their transmittance enters directly in the calculation of quantum yields.

While in this paper we have dealt exclusively with the quantum yields of transient photoprocesses, the technique can in principle be adopted for use in the determination of quantum yields of products generated in two-laser experiments. The parameter relating transient concentrations and final stable product concentrations is the ratio of the volume irradiated by the laser to the volume in which the products dilute before analysis. The latter is simply the sample volume, and the former can in principle be estimated by comparing optical density changes induced in reaction 1 under conditions of laser irradiation with those measurable in a normal spectrometer *after* laser irradiation.

Finally, in spite of its limitations this technique for the measurement of transient quantum yields has now been used in our laboratory for a wide range of measurements, some of which have been summarized in Table III, and has allowed the first measurements for quantum yields for photoreactions of short-lived transients. A side benefit of the development of this technique has been the calibration and testing of Aberchrome-540 for the determination of extinction coefficients for transients; this new method involves fewer assumptions than other techniques normally used for these measurements.

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[39] Compton, R. H.; Grattan, K. T. V.; Morrow, T. *J. Photochem.* **1980**, *14*, 61.

[40] Carmichael, I.; Hug, G. L. *J. Phys. Chem.* **1985**, *89*, 4036.

[41] The extinction coefficient for triplet benzophenone at 308 nm was estimated from the measured extinction coefficient at 525 nm by comparing the relative signal intensities at 308 and 525 nm.