

order solution yields the quasisteady VV equilibrium distribution after initial rapid adjustment. The first-order solution for $\phi_r^{(1)}$ describes the secular adjustment of this equilibrium distribution to a first-order (of ϵ) VV nonequilibrium distribution due to energy addition or removal by VT transitions. Because the first moment equation indicates the secular adjustment, it may be better⁴ obtained directly from the first-order equations [Eq. (2.8) of Ref. 1] by multiplying by r and summing all the equations to a certain level k . Since the VV terms in the first moment equation drop out automatically, Eq. (5.1) of Ref. 1 will again be obtained. This first-order first moment equation describes exactly the change of total number of vibrational quanta for the zeroth-order level populations and is independent of the first-order solution of the level populations. However, it is obvious that the approximation involved in this first moment equation is to the first order of ϵ which is proportional to $P_{10}/P_{0,1,1,0}$, i.e.,

$$\frac{d}{dt} \sum_{r=0}^k r n_r - \frac{d}{dt} \sum_{r=0}^k r n_r^{(0)} = \epsilon \frac{d}{dt} \sum_{r=0}^k r n_r^{(0)} \phi_r^{(1)} + \dots, \quad (5)$$

where $n_r^{(0)}$ and $\phi_r^{(1)}$ refer, respectively, to the zeroth-order solution and first-order correction to the population of level r [see Eq. (2.6) of Ref. 1].

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Double-Photon Absorption and Delayed Fluorescence of Some Aromatic Hydrocarbons in Solution*

J. F. VERDIECK AND A. W. H. MAU

Department of Chemistry, University of Michigan,
Ann Arbor, Michigan 48104

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The utility and importance of laser irradiation in studying photophysical processes result from the

possibility of exploiting three distinct modes of excitation—double-photon absorption into a singlet state, direct excitation of singlet with second-harmonic light, and direct excitation of triplet states with the laser fundamental—each from a short (30–100 nsec), intense (10^{25} photon/cm²·sec) pulse. This usefulness has been well demonstrated in the case of crystalline anthracene by the elegant study of Singh *et al.*,¹ and in a few cases for solution phase.^{2,3}

We have observed double-photon absorption (hereafter, DPA) in ethanol solutions of anthracene, 9,10-dichloroanthracene, 9,10-diphenylanthracene, and phenanthrene. In addition we have observed delayed fluorescence for each of the molecules in solution and the decay times measured. The dominant mode of excitation and energy transfer responsible for the delayed fluorescence was determined from the fluorescence intensity dependence on the laser intensity. This dependence is quartic in laser intensity if the triplet state is populated by way of DPA excited singlet, and quadratic if the triplet is populated by direct absorption of the fundamental.¹

Degassed samples, carefully purified in both solute and solvent, were excited with a focused, Q-switched ruby laser operated at 1 pulse/sec. The delayed fluorescence was separated in time from the prompt fluorescence and the incident laser scatter with a single-disk chopper. The mandatory tests for DPA (intensity dependence of the fast fluorescence on laser intensity, coincidence with laser pulse, and correct fluorescence spectrum) were made and confirmed.

Table I lists the results of the intensity dependence studies as the slope of logarithm of fast fluorescence intensity versus logarithm of laser intensity (abbreviated as slope I_{FF}/I_L in the table) and a similar function for the delayed fluorescence (slope I_{DF}/I_L). The estimated error in these numbers, which are rarely observed to be precisely integral, is 25%. Also listed are the decay times, τ_{DF} , for the delayed fluorescence. Estimated uncertainty is 10%. The decay was found to be exponential over the range measured (greater than two lifetimes). Literature values for the singlet and triplet energy levels are shown for convenience in correlating the suggested mechanisms for producing the delayed fluorescence. Note that DPA is found for all the molecules listed as shown by the intensity

TABLE I. Data for delayed fluorescence and double-photon absorption for $10^{-3}M$ solutions in ethanol.

	τ_{DF} (msec)	Slope I_{FF}/I_L	Slope I_{DF}/I_L	E_S (cm ⁻¹)	E_T (cm ⁻¹)
Anthracene	0.85	2.1	2.8	26 600 ^a	14 790 ^c
9,10-Dichloroanthracene	0.21	2.0	2.4	24 800 ^a	14 080 ^c
9,10-Diphenylanthracene	1.4	1.8	2.4	25 400 ^a	14 290 ^d
Phenanthrene	0.22	1.9	3.5	28 890 ^b	21 730 ^b

^a I. B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules* (Academic, New York, 1965).

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dependence of the fast fluorescence. Previously phenanthrene was thought not to exhibit DPA.³

We infer from Table I that laser-induced delayed fluorescence in dichloroanthracene and diphenylanthracene arises from the direct excitation of the triplet. This is reasonable, viewing the triplet energies shown for these molecules. Phenanthrene delayed fluorescence results from the indirect route of DPA into the singlet followed by intersystem crossing to the triplet. This is expected since the triplet lies some 7000 cm^{-1} above the laser energy of 14 400 cm^{-1} . The anthracene delayed fluorescence apparently results from mixed direct triplet and DPA singlet excitation, at least over the limited range of laser intensity available to us which is slightly more than one decade.

The delayed fluorescence decay times are in good agreement with values obtained by conventional methods,⁴ except for that of anthracene which is about one-half the value measured by Parker. As Parker has shown, low values for the decay time may result either from impurity quenching⁵ or from high rates of light absorption.⁶

Direct singlet excitation with laser second-harmonic light was used to verify the decay times of delayed fluorescence and to determine a rough comparison of quantum yields of the fast and delayed fluorescence. When the intensity of the second-harmonic light was adjusted to give the same fast fluorescent intensity as produced by DPA, negligible delayed fluorescence was observed for dichloroanthracene and diphenylanthracene, which further verifies direct triplet excitation as the dominant mechanism for laser-fundamental-induced delayed fluorescence.

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Photochemical Reduction of Thionine and Other Thiazine Dyes by CO(II)EDTA Complex in a Heterogeneous System

G. S. SINGHAL AND E. RABINOWITZ

Chemistry Department, State University of New York at Albany, Albany, New York 11203

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The photochemical reaction between thionine and Fe^{2+} in water-ether emulsion was studied by Mathai and Rabinowitch,¹ that between methylene blue and Fe^{2+} , by Frackowiak and Rabinowitch.² The leuco dye

TABLE I. Extraction of leucothionine into ether after 10 min of illumination as function of pH.^{a,b}

pH	% extraction of leuco dye	Absorbance at 380 nm due to Co(III)EDTA formed during illumination ^c	Concentration of Co(III)EDTA formed
3.5	3	0.17	$1.3 \times 10^{-4} M$
4.0	17	0.14	$1.1 \times 10^{-4} M$
4.9	45, 53 ^d , 68 ^e	0.17	$1.3 \times 10^{-4} M$
5.5	57	0.17	$1.3 \times 10^{-4} M$
6.4	68	0.14	$1.1 \times 10^{-4} M$
7.5	75	0.14	$1.1 \times 10^{-4} M$
7.9	71	0.15	$1.2 \times 10^{-4} M$

^a Thionine, $2 \times 10^{-3} M$; Co(II)EDTA, $2 \times 10^{-3} M$.

^b Acetate buffer used up to pH 4.0; phosphate buffer at higher pH.

^c Measured in a 5-cm-long absorption cell after extraction of thionine into butyl alcohol.

^d After 1 h illumination.

^e After 3 h illumination.

formed in light is extracted into ether and prevented from reacting back with Fe^{2+} .

The ferro-ferri system does not permit working at $\text{pH} > 4$, while the concentration of water-soluble, neutral leuco-dye molecules increases with pH. Srinivasan and Rabinowitch³ found that photoreduction of thiazine dyes can be studied up to pH 7.0 by using Co(II)EDTA complexes as reductants.

This study deals with optimum conditions for extraction of the leuco dye in this system.

Thionine (Harle Co.), methylene blue (Merck & Co.), toluidine blue (Allied Chemicals), methylene blue NN (Allied Chemicals) and methylene green (Allied Chemicals) were purified by two recrystallizations from ethyl alcohol. Disodium salt of EDTA (reagent grade, Hack Chemical Co.) was purified according to Walcher.⁴ Cobaltous nitrate (Fisher Certified) was used without further purification. Solutions $2 \times 10^{-2} M$ were prepared by mixing stoichiometric amounts of cobalt(II) nitrate with slightly smaller amounts of EDTA. A slight deficiency of EDTA was used to make certain that no free EDTA remained in solution.

To determine the efficiency of extraction, the required amounts of a phosphate-buffered aqueous dye solution ($2 \times 10^{-3} M$) and Co(II)EDTA ($2 \times 10^{-3} M$) were placed in a cylindrical cell (6 cm long, 3 cm in diameter) and kept at $10^\circ \pm 1^\circ \text{C}$. Argon, purified with

TABLE II. Percent extraction of leucothionine into ether as function of the volume of the latter.^a

Volume of the ether phase in cubic centimeters	5	9	11	15	20	25
% Extraction of the leuco dye	21	60	64	68	73	80

^a pH = 6.4; 10 min illumination [thionine] = $2 \times 10^{-3} M$; [Co(II)EDTA] = $2 \times 10^{-3} M$; volume of the aqueous phase, 15 cc.