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Excitation-Wavelength-Dependent Structure in the Fluorescence Spectra of B_u States of Diphenylpolyenes

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Experiments have used a tunable picosecond laser to study evolving fluorescence spectra of 1,8-diphenylocta-1,3,5,7-tetraene (DPO) in hexane solution at room temperture. The spectra recorded synchronously (±20 ps) with the irradiation event are analysed in terms of the time-integrated spectra, spectra obtained through a delayed gate, resonance Raman signals and fluorescence from the second excited singlet state. Data are presented to show the dependence of the $S_2 \rightarrow S_0$ spectrum on the excitation wavelength. The spectra clearly show that vibrational relaxation is incomplete on the timescale of the S_2 lifetime. On the other hand, the spectral bands show little tendency at room temperature towards line-narrowing effects. This indicates that the rate of molecular site relaxation is at least comparable to the lifetime of the S_2 state under these conditions.

1. INTRODUCTION

In recent years, several reports have appeared in the literature of spectrally resolved fluorescence from higher excited states of aromatic molecules. In fact, given the advantages of pulsed laser technology, upper state fluorescence has been shown to be a quite general phenomenon. It has been used in our laboratory to obtain information about subpicosecond relaxation between excited states and as an intramolecular "upconversion" probe in the study of very weakly fluorescent lowest excited singlet states.[1,2] For example, it has been possible to determine the relaxation time of the lowest excited singlet state (^1A_g) of biphenylene by pulse-sequenced excitation of the fluorescence from a state higher in energy than S_1.[3] In this way, it

was possible to detect the fluorescence in a region of the spectrum free from background radiation—no reliable record of biphenylene S_1 fluorescence had been reported, but our observation of the upper state fluorescence signal provided an indirect route to the measurement of the S_1 lifetime.

It has also recently been shown that the fluorescence spectra of upper excited singlet states of a polynuclear aromatic hydrocarbon, such as 3,4,9,10-dibenzpyrene (DBP), are a sensitive function of excitation wavelength.[1] In fluid solution at 300 K, the degree to which higher vibronic states can be selected is chiefly limited by inhomogeneous broadening. However, the spectra show clear evidence of fluorescence line-narrowing, which we attribute to molecular site selection. This, in turn implies that the excited state lifetime is substantially less than the relaxation time for the molecular site in fluid solution. The best resolved spectra so far obtained show maximum homogeneous linewidths in the upper state spectra of about 150 cm^{-1}. This is consistent with estimates, based on quantum yield measurements, of lifetimes as short as 40 fsec.

Since the spectra are sensitive to the excitation wavelength, particularly in terms of their Franck–Condon profiles, it is clear that the states populated by consecutive two-photon absorption relax electronically before significant vibrational relaxation takes place.

A detailed study was carried out for DBP in which the fluorescence spectra were integrated, corrected for the S_1 absorption spectrum, and normalized to account for variation of the irradiating laser intensity with wavelength.[1] The result was a clear observation that the fluorescence quantum-efficiency for a higher excited state depends on the excess vibrational energy. That is, exciting within a given absorption band, the quantum-efficiency maximized at the absorption origin, falling by more than a factor of 2 as higher vibrational levels were excited.

Other factors come into play in considering the relaxation between electronically excited states, in particular the role of selective coupling of vibrational modes in the two states and, in the case of higher states than S_2, competition for the excitation energy between different lower states and its effect on the lifetimes and quantum yields of the various states involved. For example, we have presented evidence of specific vibrational coupling in the molecule 1,2,5,6-dibenzanthracene[4] and of specific electronic coupling in the molecule 3,4,9,10-dibenzpyrene.[1]

One of these factors (competition between lower electronic states) can be effectively eliminated by making accurate measurements on the S_2 state. However, because of the small $S_2 \rightarrow S_1$ energy gap, it is necessary to consider once again direct, one photon excitation. The major disadvantage originally encountered when the upper singlet state fluorescence spectra were first being explored was that single-photon population of the upper state created difficulties through the relatively large amount of scattered light generated at or near the irradiation wavelength. To all intents and purposes this served to mask upper state fluorescence, and two-step methods, in our case consecutive two-photon absorption, were adopted.[5,6]

However there is with S_2 states an additional problem in the presence of relatively intense S_1 fluorescence in the same region of the spectrum. Fortunately using optical gating techniques, it is possible to eliminate more than 99% of scattered light having duration 1 ns and longer, preserving enough sensitivity for upper state fluorescence detection. Within the past couple of years we have shown that, in the molecules DBP and DPO, the S_2 fluorescence is an essential part of the time-evolving fluorescence spectrum.[7,8]

In the present paper we report the completion of an important missing stage in the earlier experiments. That is, we are now able to make linear measurements of the fluorescence spectra of sub-picosecond states using variable excitation wavelengths. In this way, we are in a position to produce spectra of the kind originally generated by the consecutive two-photon approach, except with an absolute, linear intensity calibration (i.e., the $S_1 \rightarrow S_0$ fluorescence, which appears on the same spectrum).

2. PICOSECOND FLUORESCENCE SPECTROMETER (Figure 1)

The experiments reported here required a highly stable, high-power source of tunable, near-ultraviolet pulses which were of sufficiently short durations to resolve a subpicosecond fluorescence spectrum from nanosecond background fluorescence. For this purpose, an anti-resonant ring mode-locked YAG laser was used as the oscillator, generating stable trains of pulses about 25 ps in duration.[9] The output from such a laser also has a particularly stable transverse mode structure for a high-power oscillator. An external amplifier further

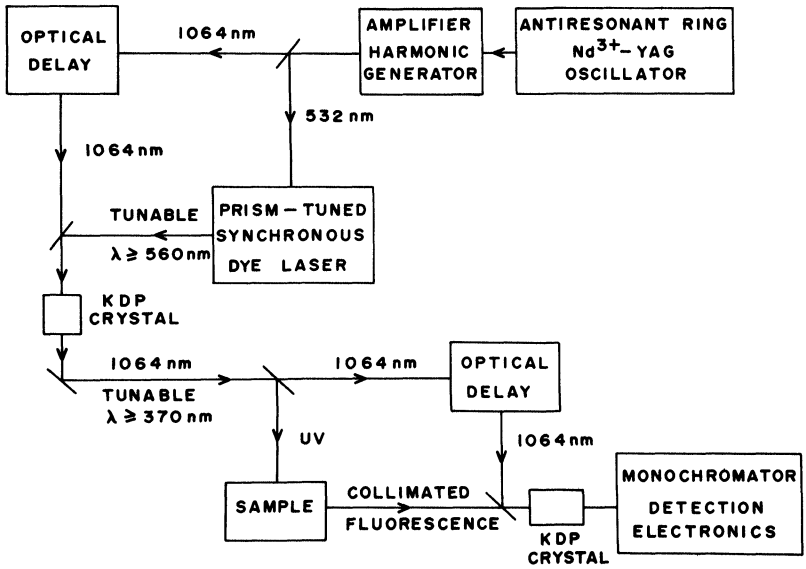

FIGURE 1 Block diagram of the picosecond fluorescence spectrometer. The repetition rate of the laser was 10 p.p.s., and the irradiation intensity at the sample was approximately 5 μJ per square mm, in a pulse of less than 30 ps duration.

boosted the power prior to the dye laser pumping stage. (Note: a regenerative amplifier technique was also available, capable of delivering 10 ps pulses,[10] but higher power was available, given two laser heads, from the configuration described above.) As will be seen, the slight loss of time-resolution was justified, since the considerably higher photon fluxes allowed the S_2 experiments to proceed with tunable radiation.

The dye laser used for these experiments was pumped transversely in a Hansch-type arrangement. However, tuning was accomplished by a pair of equilateral prisms and the cavity length was optically synchronized with the master YAG oscillator. Operated in this mode, the dye laser gave excellent power, tunability and bandwidth in the spectral region of interest from 560 to 700 nm (30% conversion from 532 nm; 50 μJ per pulse; <3 cm^{-1}). As the laser operated in heavily gain-saturated mode, pulse-durations were <30 ps.

The dye laser output was collimated, and synchronized with the residual 1064 nm pulses. The two were then passed together into a

phase-matched KDP crystal where the sum-frequency was generated. This gave efficient (about 15%) conversion to tunable radiation in the range 360–420 nm. The overall response function of the apparatus was about 40 ps, as measured from the FWHM of the transient fluorescence of the lowest ^1B_u state of DPO.

After the up-conversion process, the infrared fundamental was once more split from the tunable radiation by a dichroic beam splitter. For most of our experiments, a 90° irradiation-detection geometry was used to minimize spurious signals from the irradiation source and from resonance enhanced Raman scattering. Emitted fluorescence from the sample was gated by frequency up-conversion, using the 1064 nm pulses, and the resulting signal processed by a gated integrator. A simple autotracker optimized the upconversion angle during scans of the spectra.

3. EMISSION FROM THE LOWEST ^1B_u STATE OF DPO

DPO has in common with many polyenes that its lowest excited electronic singlet state is of A_g symmetry, so that direct S_0 to S_1 transitions are weak.[11] It has been shown that the residual strength of such transitions depends on the energy gap between this state and the ^1B_u state lying relatively close by. (Also, for such a molecule in fluid solution, the C_{2h} point group assignment can only be an approximation as has recently been pointed out by Goldbeck *et al.*[12]) In the terminal diphenyl substituted polyenes, the ^1B_u and $^1A_g^*$ states are almost at the same energy in the butadiene derivative while in longer chain members, the separation gradually increases. It has also been shown that the ^1B_u state energy is very sensitive to the solvent polarizability. In turn, this factor affects the vibronic coupling between the two electronic states, as manifested in the solvent dependent fluorescence radiative lifetimes of, for example, diphenylhexatriene (DPH).[13] Similar solvent effects probably affect the rate of radiationless transfer between the two electronic states, both in an absolute sense, and also in terms of specific couplings between vibrational modes in the two states.

Our major interests in the DPO case are first to observe and characterize fluorescent transitions from the ^1B_u state to the ground state ($^1A_g^\circ$), in order to study the effects of excitation level on the

relaxation time between the two states. Second, we wish to exploit the ultrafast second singlet state to probe conformational relaxations in this important class of flexible molecules.

In an early publication,[8] we showed good evidence for a short-lived transient fluorescence in DPO, which we assigned to the ^1B_u state on the basis of lifetime and some features of the spectrum. At the time, although we used less than 15 psec time resolution, only a single wavelength was used for irradiation (354.7 nm). Moreover, this wavelength excited the molecule about 6000 cm^{-1} above the origin of $^1A_g^*$ and about 3000 cm^{-1} above the origin of ^1B_u. As the fluorescence spectrum of a subpicosecond state depends on the excitation conditions *even in fluid solution*, excitation at such high excess energies leads to spectral congestion. Thus, the experiment using 354.7 nm irradiation does not yield high-quality spectral data about the ^1B_u state of DPO. In fact the assignment of the transient feature to the ^1B_u state was only possible on the basis of solvent shift measurements, following ref. 13.

In the earlier work,[8] we measured the decay time of the $S_2(^1B_u)$ state of DPO to be about 0.4 ps. In view of the considerable excess energy, this is probably less than the decay time under longer wavelength excitation conditions. Thus, this state exhibits intermediate behavior between that of a typical long-lived electronic state (in which vibrational and molecular site relaxation are complete well within the fluorescence decay time) and a state of much higher energy. In the latter case, as we have shown in several publications, electronic relaxation is much faster than vibrational and molecular site relaxation, even at 300 K in hexane. Hence, the fluorescence spectra exhibit Franck–Condon profiles which depend strongly on the excitation conditions and which exhibit fluorescence "line-narrowing".[1] In these cases, the narrowing is limited by the intrinsic decay time of the state, typically greater than 100 cm^{-1} for 50 fsec lifetimes. Thus, from this standpoint, the S_2 state of DPO is important to study as it opens up new avenues into competitive processes on the 0.1–1 ps timescale.

Figure 2 shows a sequence of gated fluorescence spectra for DPO, for different excitation wavelengths. Figure 3 shows reference absorption and (time-integrated) fluorescence spectra. As may be seen, the spectra are indeed different for different excitation wavelengths, which appears to confirm that the state relaxation time is shorter than the time required for vibrational relaxation. However, because of the

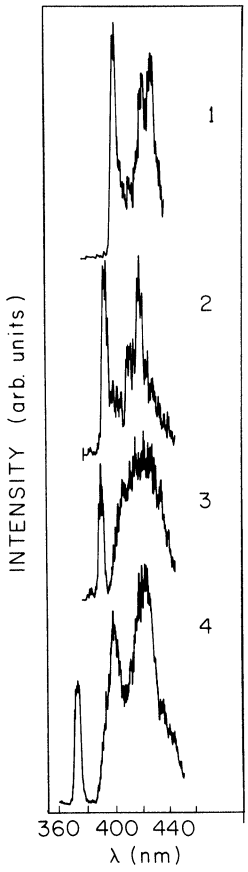

FIGURE 2 Sequence of fluorescence spectra gated synchronously with the irradiation event. From top to bottom, the irradiation wavelengths were: 400, 394, 390 and 372 nm. For the top three traces the 90° irradiation geometry was used, and the laser peak was unattenuated. This indicates a very low level of scattered light. For the bottom trace, recorded earlier, a front-surface irradiation-detection configuration was used, which necessitated attenuation of the laser line. These spectra were artificially attenuated by a mirror reflectivity at wavelengths >430 nm.

width of the spectral bands, it is not possible to exclude partial vibrational relaxation. In particular, structure is observed in the fluorescence spectrum when excitation is into the origin region (near 395 nm), or into the region of the first broad vibronic peak (near

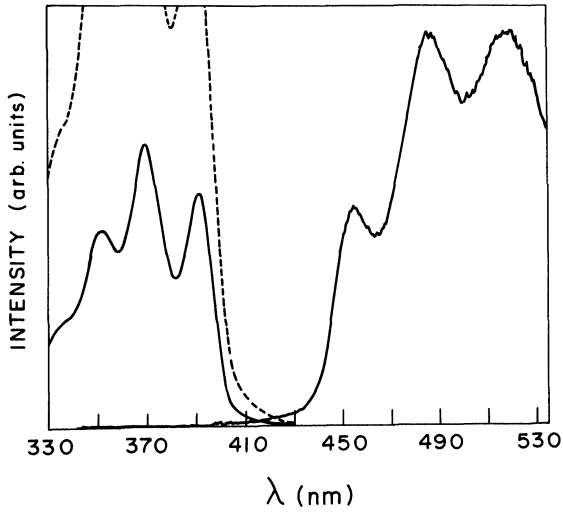

FIGURE 3 Absorption and emission spectra of DPO, measured in hexane at room temperature.

370 nm). Excitation into an intermediate position gave rise to a featureless broad band, maximizing near 420 nm. As the recent paper of Ikeyama and Azumi[14] showed through work in octane at 77 K, DPO exhibits a simple vibrational progression in the S_2 absorption spectrum, having two components: 1680 cm^{-1} and 1200 cm^{-1}. Similarly, the $S_1 \rightarrow S_0$ emission spectrum has the same two components, now 1580 cm^{-1} and 1190 cm^{-1}, which have also been observed in the Raman spectrum.[15]

In fluid solution at 300 K, the absorption lines are considerably inhomogeneously broadened, but the persistence of residual vibrational structure implies inhomogeneous widths of from 500–1000 cm^{-1}. Now, excitation into the region either of the electronic origin or of one of the principal vibrational bands effectively selects a small distribution of molecular sites. This selectivity is apparent from the structured emission spectrum. (Strictly, these will be doubled in the region of 370 nm due to the presence of two principal vibrational frequencies.) However, excitation at some intermediate position, such as with 390 nm, excites two extreme kinds of site: high-energy sites containing molecules excited into their origins and low-energy sites

containing molecules undergoing vibronic transitions. This has the result of erasing any structure through spectral congestion.

The structure seen in Figure 2 has three components: scattered laser radiation, resonance-enhanced Raman scattering, and true vibronic structure of the $S_2 \rightarrow S_0$ transition. First, it is probable that, although resonance fluorescence was a common feature of the consecutive two photon experiments, in the present data the feature at the excitation wavelength is due to scattered laser radiation. This conclusion was reached on the basis of experiments carried out at high resolution.

In view of the nearly 3000 cm^{-1} separation between the electronic origins of the ^1B_u and $^1A_g^*$ states, it is natural to investigate the high-frequency edge of the "normal" fluorescence spectrum to determine whether the ^1B_u fluorescence is detectable. (It is to be noted that the fluorescence gating approach actually *reduces* the signal by about 200 times as a result of the low gating efficiency. The $S_1 \rightarrow S_0$ fluorescence decreases by a further factor of 100 due to the short gate.) Figure 4 presents two spectra, comparing the amplified

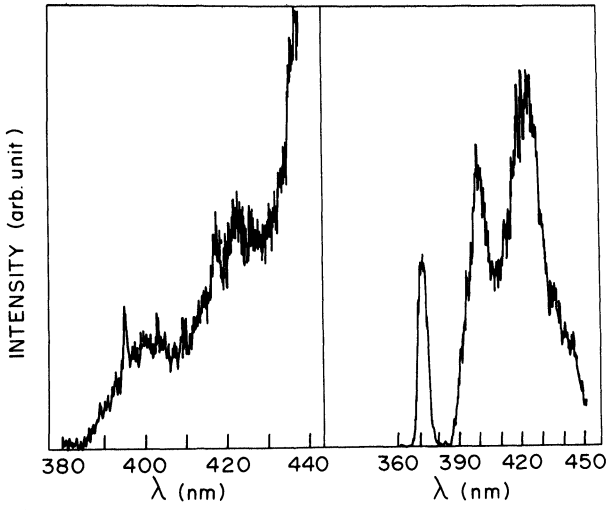

FIGURE 4 Fluorescence of DPO in hexane at 300 K excited by 372 nm radiation. LHS-time-integrated spectrum showing two broad bands and some weak Raman structure superimposed on the blue edge of the $S_1 \rightarrow S_0$ fluorescence. RHS-gated spectrum from which the $S_1 \rightarrow S_0$ fluorescence has been reduced about 50 times relative to the $S_2 \rightarrow S_0$ signal. The intensity in the LHS spectrum was about 1% of that of the $S_1 \rightarrow S_0$ origin band at 452 nm. This is consistent with an S_2 lifetime of about 0.5 ps.

high-frequency edge of the time-integrated fluorescence with the synchronously gated spectrum. As can be seen, there is a good correspondence between the positions of bands near 400 nm and 425 nm in the two spectra. In addition, there is a weak resonance Raman line on the time integrated spectrum which is not prominent on the gated spectrum due to the reduced spectral resolution. Thus, we can definitely confirm that the $S_2 \rightarrow S_0$ spectrum is observable on the high-frequency edge of the normal fluorescence spectrum, although it is partially masked by inhomogeneous broadening of the $S_1 \rightarrow S_0$ transition.

Resonance Raman features were commonly observed in the spectra taken at moderately-high resolution (30 cm^{-1}). The stronger of the two lines observed was centred around 1580 cm^{-1}, and was superimposed on the "$\Delta\nu = 1$" band of the $S_2 \rightarrow S_0$ spectrum. A weaker line became observable on excitation into the S_2 origin—its separation was about 1190 cm^{-1} from the irradiation line. The intensity of the Raman (and scattered laser) features was considerably increased by using a front-surface irradiation and collection geometry. For the purpose of the data in Figure 2, a 90° geometry was used, with horizontal polarization of the laser almost eliminating scattered light of that polarization. The $S_2 \rightarrow S_0$ emission, on the other hand was not linearly polarized and, although of reduced intensity, was effectively isolated from scattered light by this procedure.

It was also observed that the ratio of the prominent 425 nm feature in the S_2 fluorescence and that of the 452 nm feature in the S_1 fluorescence varied with the excitation wavelength. Although the data need to be refined further, it is apparent that the effective quantum efficiency for S_2 fluorescence is greater by about a factor of three when excited into the origin (395 nm) as opposed to the region of the first principal vibronic band (372 nm). The potential consequences of this in terms of the influence of excess vibrational energy on internal conversion will be the subject of a forthcoming paper.

The question of molecular site relaxation on the timescale of the decay time of the S_2 state remains to be resolved. There appears for certain irradiation wavelengths to be a definite improvement in the spectral structure over the absorption spectrum, for example, but a separate study is necessary to examine the dependence of the $S_2 \rightarrow S_0$ spectra as a function of solvent viscosity. Further, a more detailed, higher resolution study of the contribution of resonance Raman

scattering to the spectrum is necessary for accurate quantitative analysis and fluorescence quantum yield evaluations. However, the present indications are that for the most part, the Raman features contribute only a small fraction of the intensity.

We may conclude that the $S_2 \rightarrow S_0$ fluorescence of DPO has been observed to behave in a number of ways like a typical, ultrashort-lived state. (Unlike the related case of DPH, the S_2 state is not thermally reactivated from S_1).[16] However, it promises to be a valuable source of information about other processes such as intramolecular energy redistribution and molecular site relaxation.

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