

RELAXATION DYNAMICS OF THE FIRST EXCITED ELECTRONIC SINGLET STATE OF AZULENE IN SOLUTION

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An upper limit to the relaxation time of the first excited electronic singlet state (S_1) of azulene in cyclohexane has been determined for two excitation frequencies. The lifetimes of S_1 excited by single picosecond duration optical pulses of frequency 18910 cm^{-1} and 16000 cm^{-1} are $\lesssim 1\text{ ps}$ and $\lesssim 2\text{ ps}$ respectively.

1. Introduction

The use of picosecond duration optical pulses for the study of the dynamics of ultrafast relaxation processes in excited electronic states of large molecules in the condensed phase is a topic of current interest. The much discussed aromatic hydrocarbon, azulene, is particularly attractive for experimental study of rapid relaxation from the first excited electronic singlet state (S_1) for several reasons.

First, fluorescence from S_1 is extremely weak (quantum efficiency $\eta_F(S_1) \approx 10^{-6}$ [1]). This weak quantum efficiency together with the calculated radiative decay rate $k_F(S_1) \approx 1.3 \times 10^6\text{ s}^{-1}$ [2] leads to an extremely short fluorescence lifetime $\tau_F(S_1) = k_F^{-1} \eta_F \approx 0.8 \times 10^{-12}\text{ s}$. Very rapid nonradiative relaxation processes must transfer the energy from S_1 to triplet states (intersystem crossing) or to the ground state (S_0) (internal conversion). Second, azulene has a modest fluorescence quantum yield from the second excited singlet (S_2) to S_0 ($\eta_F(S_2-S_0) \approx 0.031$ [3]). This anomalous behavior probably results from the large energy gap between S_2 and S_1 (14000 cm^{-1}). The non-radiative decay rate k_d from S_2 is slower than normally expected for dye molecules [4] ($k_d(S_2) = k_F(S_2) [\eta_F^{-1}(S_2) - 1] \approx 7 \times 10^8\text{ s}^{-1}$ [3]).

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2. Experimental

The fluorescence from S_2 permits simple picosecond probe techniques to directly study the lifetime of the molecules in S_1 . An intense light pulse excites the molecules into a definite Franck-Condon state of S_1 . A delayed probe pulse transfers excited molecules into a higher singlet state (S_n). The time-dependent excited state absorption of the probe pulse is monitored by observing the $S_2 \rightarrow S_0$ fluorescence.

Previous measurements with picosecond pulses using this technique report lifetimes in S_1 about five to ten times larger than the calculated fluorescence lifetime [5,6]. We report in this paper measurements that agree with the fluorescence calculations and the results of two very recent experimental efforts**. Three distinct experiments using different excitation frequency combinations are reported in this paper.

(A) In the first experiment the energy (population) lifetime of S_1 is determined with identical excitation and probe frequency $\nu_g = 18910\text{ cm}^{-1}$ and approximately equal pump and probe pulse intensity. The experimental configuration we use here is the well-known triangular arrangement employed for two-photon fluorescence measurement of pulse widths. The colliding short pulses produce a bright spot of fluorescence

** We learned of independently obtained results on S_1 relaxation in azulene by two groups [7,8] after completion of our work.

upon a weaker fluorescence trace, where two-step absorption (one photon from each pulse) is possible. The lifetime of S_1 is then calculated from width of the fluorescence profile, together with the known optical pulse widths.

(B) In the second experiment, two different excitation and probe frequencies were used: $\nu_g = 18\,910\text{ cm}^{-1}$ and $\nu_r = 16\,000\text{ cm}^{-1}$. The experimental configuration employed was an adjustable optical delay line which permitted the variation in temporal separation between the excitation and probe pulse as they propagated nearly collinearly through the azulene cell. The fluorescence produced by each pulse pair was monitored with a high gain photomultiplier.

(C) An attempt was made in the third experiment to measure the vibrational relaxation within S_1 by using a delay line arrangement and the excitation frequency $\nu_g = 18\,910\text{ cm}^{-1}$ and the probe frequency $\nu_{IR} = 9455\text{ cm}^{-1}$. This measurement was not successful due to a very small excited state absorption cross section at these frequencies.

In all of our experiments, we used a mode locked Nd-glass laser [9]. Single picosecond pulses were selected from the mode locked pulse train with an electro-optic shutter. The single light pulses were amplified in a Nd-glass amplifier to an energy of $E_L \approx 3\text{ mJ}$. The pulses had a duration $\Delta t_L \approx 5\text{ ps}$ (fwhm) and a spectral width of $\Delta\tilde{\nu}_L \approx 3\text{ cm}^{-1}$ (fwhm).

3. Results

A. Lifetime measurement with identical excitation and probe frequency

In this measurement two light pulses at equal frequency $\nu_g = 18\,910\text{ cm}^{-1}$ collide in an azulene sample and the fluorescence trace is measured. Each beam generates fluorescence light by two-step absorption. In the overlap region and in the spatial domain where the excitation has not decayed out of the S_1 state the crossing beams are more strongly absorbed and a bright fluorescence spot is observed. We employed the conventional triangular configuration shown in fig. 1 [10]. A saturable absorber (DC) (linear transmission $T_0 = 0.1$) was used to remove possible background and reduce the infrared pulse width by about 20% [11]. The second harmonic pulse at $18\,910\text{ cm}^{-1}$ was gener-

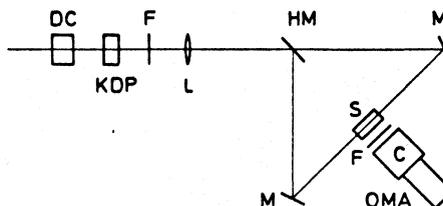


Fig. 1. Experimental arrangement for measurement of two-step fluorescence profiles in azulene and two-photon fluorescence profiles in 9,10-DPA. DC saturable absorber cell, KDP second harmonic generation, HM 50% mirror, F filters, L lens, M mirrors, S sample cell, C camera, OMA optical multi-channel analyzer.

ated in the KDP crystal. An optical multichannel analyser (OMA) was used in place of the conventional photographic film to record the traces. The resolution of our detector system is limited to 0.3 ps. The signal to background contrast ratio was found to be in the range between 2.8 and 3 in good agreement with the theoretical value of 3. The decay time of excited state absorption, τ_g , was determined by measuring the fluorescence profile width obtained in azulene by two-step absorption and by comparing with the fluorescence profile width obtained in 9,10-diphenylanthracene by two-photon absorption. In 9,10-DPA there are no real electronic states near the green excitation frequency. Since the laser frequency $\nu_g = 18\,910\text{ cm}^{-1}$ reaches far into higher excited singlet states, even if the molecules have relaxed down to the lowest vibrational states in S_1 ($\nu \approx 14\,000\text{ cm}^{-1}$), the diminishing of the excited state absorption indicates that the excited molecules have decayed out of the S_1 -state, either to the ground state (internal conversion) or to triplet states (intersystem crossing). (Negligible excited state absorption from the ground state of S_1 seems unlikely; see discussion below.) The decay time of excited state absorption τ_g therefore determines the lifetime of the molecules in the S_1 -state which were excited to a vibronic state in S_1 , $18\,910\text{ cm}^{-1}$ above the ground state.

This experiment consisted of collecting over 60 fluorescence traces each, in 9,10-DPA and azulene. We used concentrations of 10^{-3} M/l in cyclohexane for both substances. Fig. 2 shows histograms of the measured fluorescence profile widths in 9,10-DPA and azulene. The important points to notice here are (1) the similarity between the distribution of the pulse widths for both substances; (2) the fact that the short-

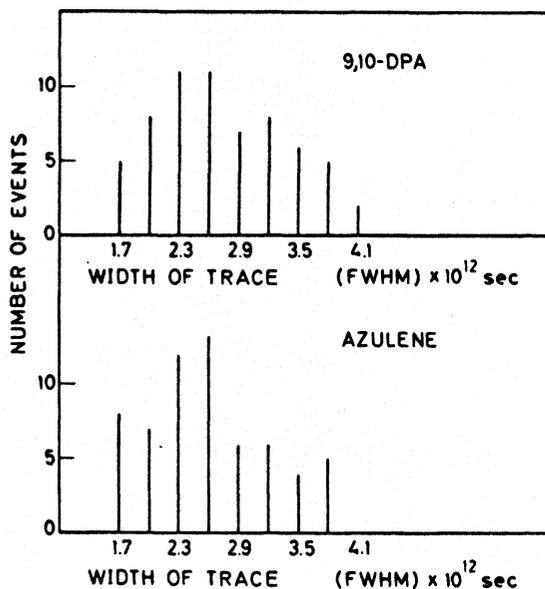


Fig. 2. Histograms of measured fluorescence profile widths produced in 9,10-DPA and azulene.

est fluorescence profiles were, in both cases, 1.7 ps in duration.

We find that the average widths of the fluorescence traces in azulene and 9,10-DPA were 2.6 and 2.7 ps, respectively. In the case of azulene the width of the trace represents the convolution of pulse duration t_p and decay time τ_g , while in the case 9,10-DPA the pulse duration t_p is directly measured. No broadening of the fluorescence traces in azulene is observed. This fact implies that τ_g is remarkably shorter than the average pulse duration t_p . The shortest convolution times observed were 1.7 ps. Assuming in these cases a real pulse width of $t_p \geq 1$ ps we find a decay time $\tau_g \leq 1$ ps [6].

B. Lifetime measurement with delayed probe pulse

The decay of excited state absorption after preparation of the system with nearly equally intense light pulses at $\nu_r = 16000 \text{ cm}^{-1}$ and $\nu_g = 18910 \text{ cm}^{-1}$ was measured observing S_2-S_0 fluorescence with a photomultiplier. With a variable optical delay the arrival of the green light was scanned over a time range of ca. 15 ps. As long as the green pulse arrived at the sample earlier than the red pulse, the green pulse acted mainly as the exciting pulse while the red pulses monitored the excited state population by ex-

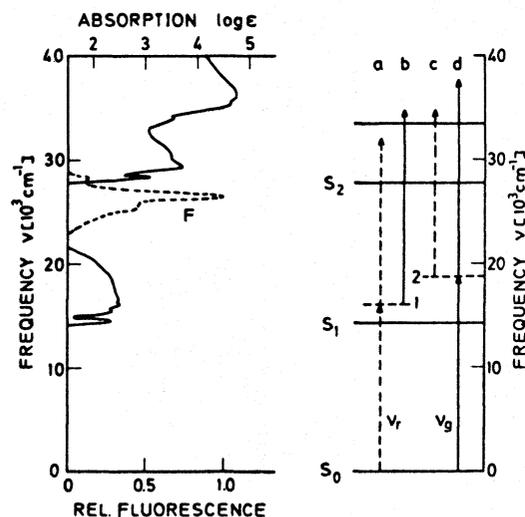


Fig. 3. Energy level diagram for electronic states of azulene together with absorption and fluorescence spectrum. ϵ is the decadic molar extinction coefficient. The arrows and the levels (1) and (2) indicate the excitation scheme: (a) two-step absorption of red pulse at $\nu_r = 16000 \text{ cm}^{-1}$; (b) excitation with red pulse and probing of excited state absorption with green pulse at $\nu_g = 18910 \text{ cm}^{-1}$; (c) excitation with green and probing with red pulse; (d) two-step absorption of green pulse.

cited state absorption (route c in fig. 3). In cases where the green pulse arrived later than the red pulse, the function of the two pulses exchanged (route b). Both pulses themselves contribute to the excited state absorption and subsequent S_2-S_0 fluorescence by two-step absorption (routes a and d). The occurring four excitation processes are depicted in fig. 3 together with the absorption and fluorescence spectrum of azulene dissolved in cyclohexane.

The excitation routes (a) and (d) generate a background fluorescence signal and do not contribute to decay time measurements. The excitation process (c) determines the decay time τ'_g of excited state absorption of the red light pulse and therefore monitors the lifetimes of molecules in the S_1 -state with the initial state at position (2) (see below). Approximately the same time as in the previous section (A) is measured. The transition route (b) measures the decay time τ_r of excited state absorption of the green light pulses and thereby determines the lifetime of molecules in the S_1 -state prepared to position (1).

The experimental arrangement employed is de-

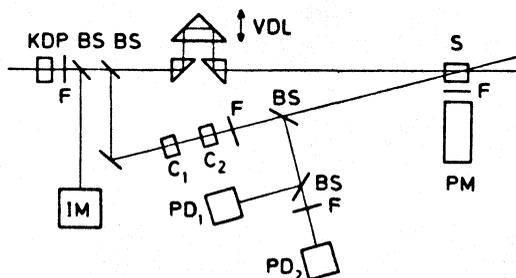


Fig. 4. Experimental arrangement for lifetime measurement with delayed probe pulse. KDP second harmonic generation, IM intensity measurement, BS beam splitters, F filters, PD₁₋₂ photodetectors, C₁₋₂ ethanol cells, VDL variable delay line, S azulene sample cell, PM photomultiplier.

picted in fig. 4. The second harmonic pulse is generated in the KDP crystal and split into two parts by a beam splitter (BS). The red pulse generated in two separated ethanol cells is suitably filtered and enters the cuvette (S) containing 0.001 molar azulene in cyclohexane. The green pulse that is transmitted through the beam splitter enters the cuvette along a different path that contains a variable delay. The fluorescence is detected with a lens and filter system and a high gain photomultiplier that view the sample 90° to the excitation direction.

The intensity of the second harmonic pulse was measured with a two-photon absorber [12] (IM) while the energy of the red pulse selected by a beam splitter (BS) was determined in a photodiode (PD₁). The intensity and energy of the light pulses was needed for normalizing the measured fluorescence signals. With another filter F and the photodiode PD₂ it was verified that no higher order Stokes light was generated.

The two-step absorption routes (a) and (d) of fig. 3 reduce the signal to background ratio. It may be shown that the peak signal to background ratio occurs when each of the two pure frequency absorptions contribute equally to the background fluorescence. This criteria was satisfied in our experiment. The peak signal to background ratio depends upon the various ground state and excited state absorption cross sections. The minimum peak signal to background ratio of 2 occurs in the case when all four excited state absorption cross sections are equal and the excitation frequencies are non-degenerate. The peak signal to background ratio would be large if one excited state absorption cross section were dominant. Our data suggest that, for the two excitation frequencies employed here ($\nu_g = 18910 \text{ cm}^{-1}$,

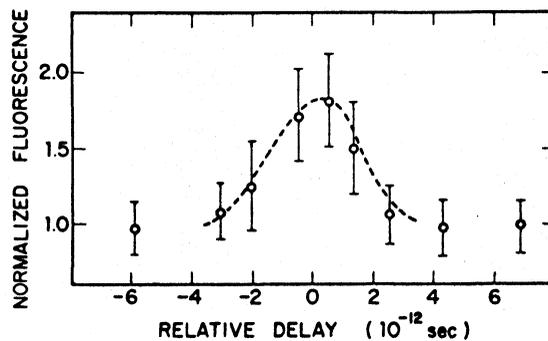


Fig. 5. Normalized fluorescence as a function of delay of the green pulse with respect to the red pulse. Negative delay corresponds to τ'_g decay while positive delay corresponds to τ_r decay.

$\nu_r = 16000 \text{ cm}^{-1}$), no single excited state absorption cross section dominates.

The measured fluorescence profile (fig. 5) as a function of the temporal separation between the green and red picosecond pulses is normalized with respect to the sum of the fluorescence due to the two pure frequency two-step absorption processes discussed above. The normalizing term is determined from the measured pulse intensities and the measured fluorescence efficiency curves.

The data peak at 1.8 times the background signal level near zero relative delay and decay to the background level in less than 2.5 ps for both positive and negative delay. The position of zero relative delay was determined by an independent measurement and is accurate to within 2 ps. Shot-to-shot fluctuations in the intensity of the green pulse with respect to the red pulse account for the slight deviation of the measured peak signal to background ratio from the optimum. Each data point contains at least 20 individual laser shots. The principal sources of scatter in the data are due to photomultiplier gain fluctuations and pulse width fluctuations from shot to shot.

The measured fluorescence profile width (fwhm) of 3.5 ps is consistent with the average pulse width of the second harmonic derived from the uncompressed infrared laser pulse. The left part follows the decay time τ'_g , while the right part follows the decay time τ_r . Within the accuracy of the measurement, both lifetimes seem to be equal, although a slight asymmetry in the fluorescence profile admits the possibility that τ'_g and τ_r may differ. The agreement of the measured curve with the expected pulse duration indicates that both

relaxation times are very short. An upper limit of $\tau < 2$ ps can be easily concluded from the data.

C. Attempts to measure vibrational decay in the S_1 -state

At this point we would like to discuss an alternative choice of excitation frequencies that would measure vibrational relaxation within S_1 . A compelling case can be made for the choice of a pump pulse at $18\,910\text{ cm}^{-1}$ and a probe pulse at 9450 cm^{-1} . We note that the infrared radiation is not absorbed by S_1 , and S_2 is not reached by a direct two-photon absorption. By choosing appropriate intensity values for the green and infrared light pulses one would expect that the rate of the green-infrared two-step absorption dominates the rate of the green-green two-step absorption. This is the technique reported by Rentzepis [5] in an early effort to measure the azulene S_1 relaxation time. In our experiments, the intensity parameters of the exciting and probing pulses could not be varied in such a way as to result in a tolerable signal-to-background ratio. We measured the fluorescence from azulene excited with coincident green and infrared pulses (orthogonal linear polarizations). Measurements were made over a wide range of green intensities ($I_g = 2 \times 10^6 - 2 \times 10^8\text{ W/cm}^2$) and high infrared intensities up to $I_{IR} = 5 \times 10^8\text{ W/cm}^2$. We found that the pure green-green two-step fluorescence always dominates the much weaker green-infrared two-step fluorescence. We estimate the S_1-S_2 excited state absorption cross section for the infrared to be smaller than the S_1-S_n excited state absorption cross section for the green by a factor of $I_g/I_{IR} \approx 2 \times 10^6/5 \times 10^8 \approx 4 \times 10^{-3}$. The highest infrared intensities were limited to $I_{IR} \lesssim 10^9\text{ W/cm}^2$ by third harmonic generation in the pure solvent that is absorbed by the azulene and appears as S_2-S_0 fluorescence. The lowest green intensities employed corresponded to photoelectron counting limit of detection of our lens photomultiplier system.

4. Discussion

We now turn to a discussion of the physical decay mechanisms that contribute to the measured relaxation rates. There are three possibilities that can explain

the decay of excited state absorption: (i) relaxation out of the S_1 -state by internal conversion to the ground state S_0 (ii) transfer from the S_1 -state to triplet states by intersystem crossing (iii) vibrational decay within the S_1 -state to a temporal equilibrium position from where excited state absorption is small. Our measurements cannot distinguish between these three processes. The process of internal conversion and intersystem crossing should occur while the molecules are vibrationally decaying down within the S_1 -state. The relaxation of the molecules out of the S_1 -state by internal conversion and/or intersystem crossing is in agreement with the calculated S_1 -fluorescence lifetime from quantum efficiency measurements [1]. A change of excited state absorption of the probe pulse cannot be excluded when the molecules relax down within the S_1 -band [13]. The calculated S_1 -fluorescence lifetimes excludes a significant accumulation of population in the equilibrium position of the S_1 -band.

5. Conclusions

The results obtained here clearly indicate a very rapid relaxation time for two widely spaced vibronic levels in the first excited electronic singlet state of azulene. The lifetime $\tau_g \lesssim 1$ ps of the vibronic levels excited by a single $18\,100\text{ cm}^{-1}$ picosecond pulse is considerably shorter than previously thought to be the case. The lifetime of vibronic levels excited by a $16\,000\text{ cm}^{-1}$ single picosecond pulse was determined to be $\tau_r \lesssim 2$ ps. These results allow us to set new limits for relaxation from the first excited electronic singlet of a complicated dye molecule.

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