THE FLUORESCENCE LIFETIMES OF CARBONYL DERIVATIVES OF AZULENE SHOWING DUAL EMISSION

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Summary

The lifetimes of the fluorescences $S_1 \to S_0$ and $S_2 \to S_0$ of three carbonyl derivatives of azulene were investigated by means of a single-photon counting apparatus using laser excitation pulses of 250 ps duration. The S_1 lifetimes are observed to correlate with the energy gap. The S_2 lifetimes are smaller than 50 ps, in qualitative agreement with expectations based on the large decrease of the $S_2 \to S_1$ energy gap relative to that of azulene. No evidence was found for a significant participation of triplet states in the deactivation of both singlet states. Spectral data indicate that the carbonyl group interacts only very weakly with the azulene chromophore, the main effect being a shift of the S_1 state towards higher energies.

1. Introduction

The kinetics of the second excited electronic state S_2 of azulene and its derivatives have been investigated by a number of workers [1 - 4]. However, little is known about the decay behaviour of the first excited electronic state S_1 of the azulene moiety. This is mainly because the emission $S_2 \to S_0$ of azulene and many simple derivatives is characterized by a moderately large quantum yield — 0.03 in azulene [1] — and a lifetime in the nanosecond region, allowing its investigation by means of conventional techniques using nanosecond flashlamps. The emission $S_1 \to S_0$, however, possesses a very short lifetime and a quantum yield of the order of 10^{-6}. It has therefore become accessible to kinetic studies only with the advent of short-pulse lasers. Recent concurrent studies [5 - 7] have established that the lifetime of the S_1 state of azulene is about 2 ps. The low temperature fluorescence spectrum of the $S_1 \to S_0$ transition has been recorded using laser excitation [8] in order to overcome the problems caused by the extremely low intensity.

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The ultrafast decay of the S_1 state of azulene remains one of the most interesting problems in photophysics. Selective variation of molecular parameters by means of substitution may be one way of elucidating the detailed mechanism of the anomalously fast internal conversion $S_1 \leadsto S_0$.

The intensity of the emission $S_1 \to S_0$ and concomitantly the lifetime of S_1 are significantly increased on raising the energy of the S_1 state by proper substitution. This has been achieved by Eber *et al.* [9] by attaching carbonyl substituents to the azulene chromophore. The compounds obtained exhibit dual fluorescence. Lifetimes and quantum yields of the two emissions of two such compounds have been determined [10]. The results indicate that the change in the lifetime related to a change in the energy gap is much larger for the S_1 state than for the S_2 state.

Since the energy gap dependence of the internal conversion $S_1 \leadsto S_0$ of azulene systems may present the unique opportunity of comparing two internal conversion processes within the same chromophore (the energy gap dependence of the S_2 decay kinetics has been investigated by Murata *et al.* [1]), we decided to reinvestigate the decay behaviour of the two lowest excited electronic states of suitable azulene derivatives showing dual fluorescence. A recently developed single-photon counting apparatus [11] employing a mode-locked argon ion laser as the excitation source enables us to investigate the kinetics of weak emissions. The excitation pulse width of 250 ps affords a significant improvement of temporal resolution compared with nanosecond flashlamp excitation such as that used in previous work [10]. Furthermore, several laser lines can be used for excitation whereas near-UV N_2 lamps do not allow the selective excitation of the S_1 state.

2. Experimental

The fluorescence lifetime apparatus and the deconvolution method have been described in detail elsewhere [11]. A mode-locked argon ion laser (Coherent Radiation model 52) emitting a train of 250 ps pulses separated by 8.71 ns served as the excitation source. The 5145 Å laser line was frequency doubled by an ammonium dihydrogen phosphate crystal placed in a Coherent Radiation model 440 UV generator. The samples were contained in thin sealed-off quartz tubes degassed by repeated freeze–thaw cycles and were placed in an Oxford DN 704 cryostat, the temperature of which could be stabilized within the range from 77 K to room temperature. The fluorescence decay curves were measured at several emission wavelengths with a spectral resolution of 15 Å. In all cases there was no evidence of a change in fluorescence lifetime with a change in wavelength.

In principle, exponential decays characterized by a time constant a few times smaller than the excitation pulse width can be deconvoluted. The decay times obtained in this manner, however, should be expected to be accurate only when a relatively large fluorescence quantum yield, as for instance in cyanine dyes, brings about short measurement times and a

good signal-to-noise ratio. Under such favourable circumstances we expect to be able to investigate lifetimes down to about 50 ps using 250 ps pulses.

Based on the photon counting technique emission spectra were recorded on a home-built computer-controlled luminescence spectrometer. It was equipped with a cooled RCA C 31 034 photomultiplier. The samples used were the same as those employed for the lifetime measurements. Absorption spectra were obtained using a Beckman Acta V spectrometer.

The three compounds studied are shown in Fig. 1. 1-Trichloroacetyl-azulene (III) was synthesized according to the method described by Anderson and Anderson [12]. Compound I was of unknown origin. Compound II was a gift from Dr. G. Eber and Dr. S. Schneider, Munich. Prior to sample preparation the compounds were purified by chromatography on alumina. Their purity was checked using high pressure liquid chromatography. The solvents were purified according to standard procedures.
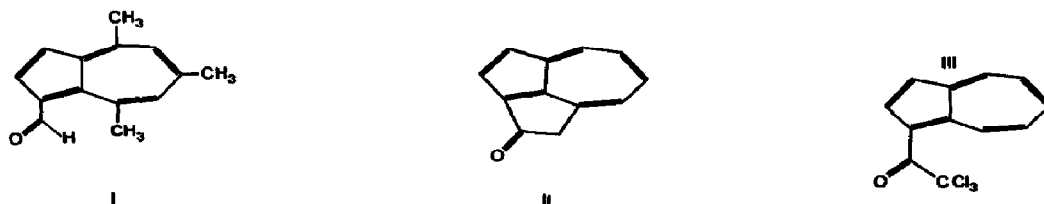

Fig. 1. Structures of the carbonyl derivatives of azulene investigated.

3. Results

3.1. Spectra

With respect to the shapes of the transition bands and their relative intensities the absorption spectra of the three carbonyl compounds investigated still very much resemble that of the parent compound azulene. This is in marked contrast with the strong effect of carbonyl substitution on the electronic spectrum of the naphthalene chromophore. In all three cases the only photophysically important consequences of substitution seem to be a hypsochromic shift of the $S_1 \leftarrow S_0$ transition and a bathochromic shift of the $S_2 \leftarrow S_0$ transition. Thus the energy gap S_1-S_0 is increased relative to that of azulene whereas the gap S_2-S_0 is decreased, bringing about the appearance of dual fluorescence emission [9]. The transition $S_1 \leftarrow S_0$ is subject to a solvatochromic blue shift of roughly a thousand wavenumbers on going from aliphatic solvents to ethanol. Eber et al. [10] have attributed this to the change in the dipole moment direction associated with the transition. The vibrational structure is not as well resolved in polar solvents.

The absorption spectrum of compound II in n-hexane is shown in Fig. 2. It agrees well with the spectrum recorded in 3-methylpentane by Eber et al. [10]. The vibrational structure and the intensity of the S_1 absorption band are strikingly similar to those observed in azulene. The insensitivity of the
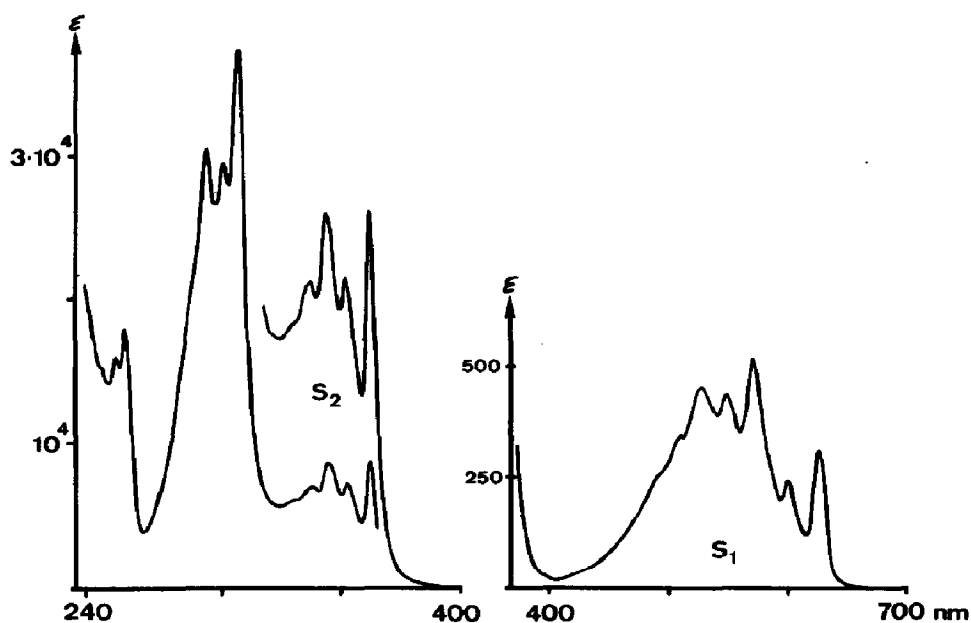
Fig. 2. The absorption spectrum of compound II in n-hexane at room temperature.

S_1 absorption band shape with respect to substitution at the azulene chromophore seems to be a general feature. It is also observed in the spectra of several simple derivatives [1, 4] which show only a shift of the energy of the S_1 state. The spectrum of the transition $S_2 \leftarrow S_0$, however, is altered to a degree that is dependent on the position of the substituent but is very little dependent on the nature of the substituent [4]. Substitution at the 1 position, i.e. at the five-membered ring, leads to an increase in the intensity of the 0—0 band. Correspondingly, the S_2 absorption band observed in this work is characterized by a typical vibrational structure very closely resembling that found in 1,3-dihaloazulenes [4].

The absorption spectra of compounds I and III are not as well resolved. We attribute this to the larger mobility of the carbonyl groups in compounds I and III relative to the mobility of the carbonyl group in compound II. Nevertheless the same spectral features are observed.

The fluorescence emissions $S_2 \rightarrow S_0$ and $S_1 \rightarrow S_0$ of compounds I and II recorded at 77 K are shown in Figs. 3 and 4. The spectra of compounds II and III have been reported by Eber et al. [9, 10] with lower resolution, blurring the vibrational structure completely. In agreement with their findings, we observe a gradual decrease in the intensity of the $S_1 \rightarrow S_0$ fluorescence with increasing temperature whereas the intensity of the $S_2 \rightarrow S_0$ fluorescence is essentially independent of temperature.

In contrast with the behaviour reported for several simple halogenated derivatives of azulene [4], the carbonyl compounds do not show an appreciable decrease in the linewidth of the fluorescence bands on lowering the temperature. The emission bandwidth is much larger than, and independent of, the spectral bandwidth of the exciting beam (15 Å in the spectra
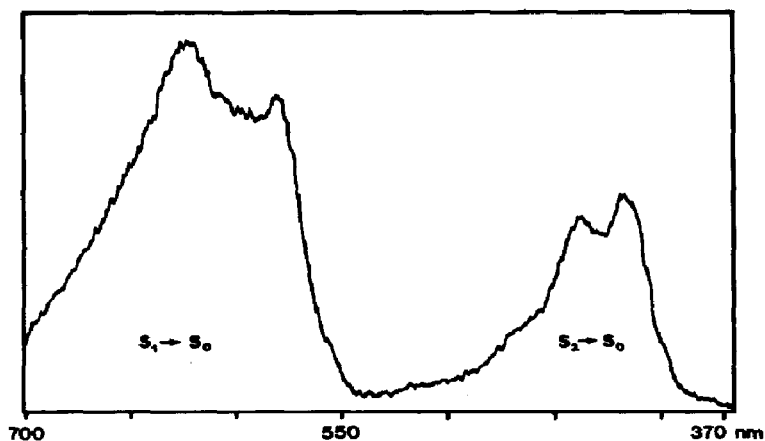
Fig. 3. The fluorescence spectrum of compound I in ethanol at 77 K. Excitation into S_2 at 355 nm.
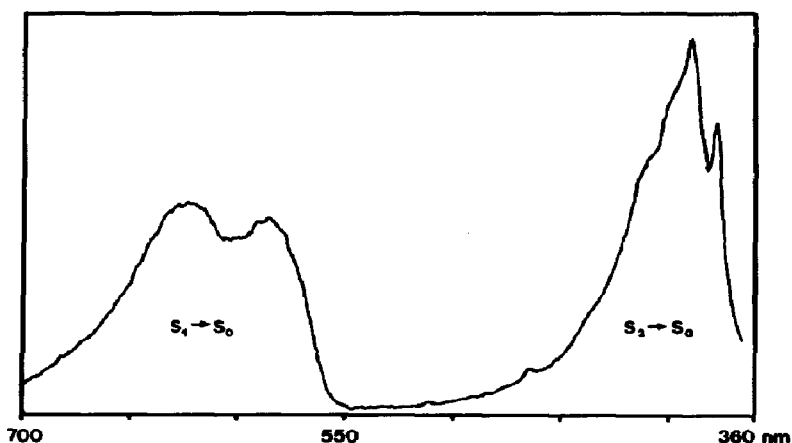

Fig. 4. The fluorescence spectrum of compound II in ethanol at 77 K. Excitation into S_2 at 356 nm.

shown). Neither did we succeed in elucidating a more detailed vibronic structure by embedding the substances in frozen n-alkanes (Shpolskii matrices).

3.2. Fluorescence lifetimes

Excitation into S_1 by means of the 5145 Å laser line yields a fluorescence $S_1 \rightarrow S_0$ which is identical with the emission observed on exciting into S_2 (see Figs. 3 and 4). For all three compounds the decay of the fluorescence $S_1 \rightarrow S_0$ follows a single exponential behaviour. Figure 5 shows the experimental emission decay curve obtained from compound I in ethanol. It also shows the excitation pulse shape obtained from Rayleigh-scattered light and the computer evaluation.

The lifetimes of the fluorescences $S_1 \rightarrow S_0$ turned out to be much shorter than we expected on the basis of the results of the previous study [10]. Our results are summarized in Table 1. The weakness of the emissions
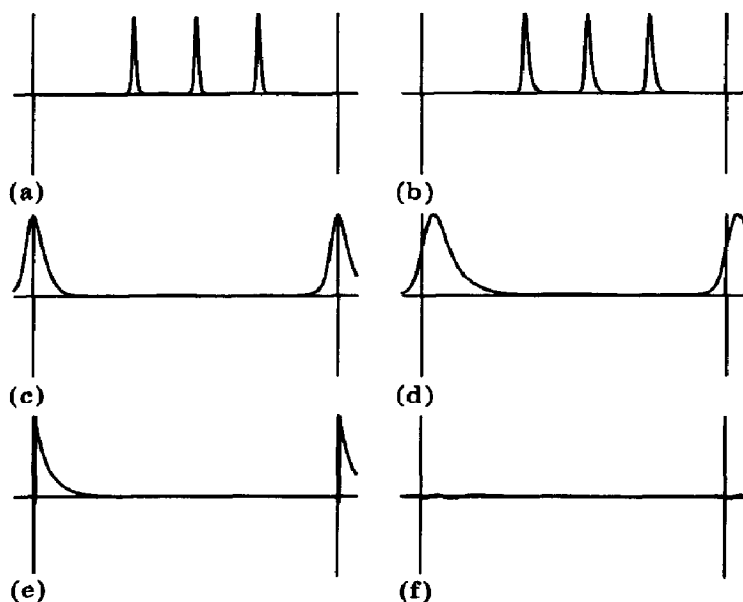
Fig. 5. The decay of the $S_1 \rightarrow S_0$ fluorescence of compound I in ethanol at 77 K, excited into S_1: (a) excitation pulse at 5145 Å (experimental data, 1024 data points); (b) fluorescence decay curve monitored at 5785 Å (experimental data, 1024 data points); (c), (d) Figs. 5(a) and 5(b) mapped onto the standard pulse interval; (e) single exponential decay curve; (f) deviation from single exponential behaviour. The lifetime obtained from these data is 400 ps.

TABLE 1

Experimental lifetimes of the $S_1 \rightarrow S_0$ fluorescences at 77 K[a]

Compound	Solvent	S_1 energy (cm^{-1})	τ_1 (ps)
I	Ethanol	17 600	400 ± 40
	n-Hexane	16 800	≤150
II	Ethanol	17 200	200 ± 50
	n-Hexane	16 000	<150
III	Ethanol	16 600	<150

[a]Excitation at 5145 A; sample concentrations, 5×10^{-4} - 10^{-3} M.

— the quantum yield is smaller than 10^{-3} in all cases — precludes the attainment of the lower decay time limit of about 50 ps. Furthermore it is important (see Section 3.3) to ensure that the decay is characterized by a single exponential decay only. This definitely holds true for compounds I and II in ethanol, but is almost impossible to state with certainty in the other three cases where the decay time is comparable with or smaller than half the excitation pulse width. For this study, therefore, a practical lower limit of about 150 ps must be placed on the decay times that can be obtained with sufficient accuracy.

Dual emission is observed following excitation into a higher electronic state by means of the frequency-doubled 2573 Å laser line. The lifetime of the S_2 state is very short in all three compounds; for the $S_2 \rightarrow S_0$ fluorescence the response curves deviate very little from the 250 ps excitation pulse shape, not allowing a meaningful deconvolution. Concomitantly, the decay curves of the $S_1 \rightarrow S_0$ fluorescences following UV excitation are almost identical with the decay curves obtained with 5145 Å excitation into the S_1 states. For instance the $S_1 \rightarrow S_0$ fluorescence decay time determined following UV excitation of compound I in ethanol is 430 ± 40 ps. Because the difference between this value and the directly measured lifetime of S_1 (400 ± 40 ps) is smaller than the experimental error, we can only conclude that the internal conversion $S_2 \rightsquigarrow S_1$ takes place on a time scale which is smaller than our present experimental time resolution of 50 ps at best, in agreement with the direct evidence from the rapid decay of the S_2 fluorescence.

3.3. The lowest triplet state

We did not find any spectral evidence for the occurrence of the phosphorescence emission $T_1 \rightarrow S_0$ on scanning to the photomultiplier sensitivity limit at about 880 nm. We believe it is very unlikely that the energy of the T_1 state of these compounds is smaller still, since the singlet—triplet splitting is quite small in the parent compound azulene. The sensitizer quenching experiments of Kröning [13] and of Herkstroeter [14] place the T_1 state of azulene at 13 530 cm^{-1} and at 13 700 cm^{-1} respectively. Since the S_1 state is negligibly perturbed by the carbonyl substituents, the associated triplet state T_1 is also likely to remain an azulenoid state, possibly undergoing a similar hypsochromic shift.

If the singlet—triplet splitting is very small in these compounds, most of the phosphorescence emission could be hidden underneath the $S_1 \rightarrow S_0$ fluorescence. In our fluorescence lifetime apparatus the sample is excited at a rate of about 100 MHz, given by the mode-locking frequency of the argon ion laser. Every electronic state with a lifetime of more than about 30 ns will therefore build up to an almost stationary concentration. In order to detect a weak constant background on its own, the time interval during which the excitation pulse has to be blanked out amounts to about 2 ns, leading to a collecting efficiency for phosphorescence photons of 80%. Fluorescence and phosphorescence photons of the same energy are collected indiscriminately in the standard experiment and therefore an admixture of phosphorescence and fluorescence would show up in the temporal decay curves in the shape of a constant baseline. It is evident from the example of actual experimental data shown in Fig. 5(b) that this is not observed; the emission decay monitored in the region of the two main peaks (further to the red the photomultiplier sensitivity drops rapidly) is clearly of the single exponential type, proving that the emission consists solely of fluorescence.

If, however, the triplet state T_1 is located at an energy lower than about 15 000 cm^{-1}, structured features due to phosphorescence emission

might be superimposed on the fluorescence that is tailing off smoothly in the spectral region beyond 670 nm. This is not observed. Accordingly, whatever the energy of T_1 may be, we can confidently place an upper limit of 3.5×10^{-5} on the phosphorescence quantum yield; this is based on the value (7×10^{-4}) of the quantum yield of the $S_1 \rightarrow S_0$ fluorescence of compound II determined by Eber et al. [10].

4. Discussion

As an independent check, estimates for the lifetimes of the excited states can be obtained by means of the relation $\tau = \tau^\circ \phi$. For compound II in ethanol at 77 K this is achieved by making use of the experimentally determined values of the quantum yields of the emissions $S_1 \rightarrow S_0$ ($\phi_1 = 7 \times 10^{-4}$) and $S_2 \rightarrow S_0$ ($\phi_2 = 7.7 \times 10^{-5}$) [10] and the radiative lifetimes calculated using the Strickler–Berg equation ($\tau_1^\circ = 150$ ns and $\tau_2^\circ = 38$ ns). We arrive at the estimates $\tau_1 \approx 105$ ps and $\tau_2 \approx 3$ ps. Taking into account the limited accuracy of the Strickler–Berg equation for weak transitions as well as the experimental errors, the agreement with the directly measured lifetime values ($\tau_1 = 200$ ps and $\tau_2 < 50$ ps) is wholly satisfactory.

On exciting into the S_2 state with a nanosecond nitrogen flashlamp, Eber et al. [10] have obtained a value of 1.2 ± 0.2 ns for the decay time of the $S_1 \rightarrow S_0$ fluorescence of compound II in ethanol at 77 K and a value of 1.4 ± 0.2 ns for an aldehyde compound similar to compound I. They have also observed polarization anisotropy of the $S_2 \rightarrow S_0$ fluorescence in liquid solution at room temperature and have concluded that the lifetime of the S_2 state must be smaller than the orientational relaxation time of 40 ps. Furthermore, the quantum yield of internal conversion $S_2 \leadsto S_1$ has been found to be unity. Therefore the decay of the S_2 state has been interpreted as being characterized by a rapid dominant internal conversion to S_1. This in turn has allowed the fluorescence decay times to be equated with the lifetimes of the S_1 state.

Our results agree with those of the earlier study with respect to the kinetic behaviour of the S_2 state of carbonyl derivatives of azulene. Such high speed internal conversions across the S_2-S_1 energy gaps involved are also predicted by extrapolating the data reported by Murata et al. [1], who have noted a close correlation between the rates of internal conversion $S_2 \leadsto S_1$ and the energy gap for a large number of azulene derivatives. The S_1 lifetime values we obtained are, however, significantly smaller than those reported by Eber et al. [10], probably because of the improvement in resolution capability that can be attained using mode-locked laser excitation compared with conventional nanosecond sources. Concomitantly, their conclusion that the change in the lifetime with a change in the energy gap is much larger (more than twice as great) for S_1 than for S_2 is refuted by our results. We will return to this point later.

It is remarkable that the carbonyl substituent in all cases does not give rise to the introduction of a low-lying $n\pi^*$ state into the electronic energy

level structure of the azulene moiety. The observation of an emission clearly attributable to the azulene-like electronic state designated S_2, as well as the lack of additional absorption bands between S_1 and S_2, shows that the lowest $^1n\pi^*$ singlet state possesses an energy larger than that of the $\pi\pi^*$-type S_2 state. The associated triplet $^3n\pi^*$, however, could have an energy comparable with that of S_2, thereby causing efficient intersystem crossing by means of the favourable $^1\pi\pi^*-^3n\pi^*$ coupling. The quantum yield data of Eber et al. [10] indicate that this is not effected.

Since the singlet–triplet splitting is very small for $n\pi^*$ states, the energy of $^3n\pi^*$ will certainly be significantly larger than the energy of S_1, and so the $^3n\pi^*$ state will not interfere with the deactivation of S_1 either. We can therefore omit the $n\pi^*$ states from a discussion of the deactivation of the two lowest excited singlet states of these carbonyl compounds.

There remains to discuss the relative importance of the various decay mechanisms originating from the S_1 states of the compounds under study. It is evident from the fact that the quantum yields are smaller than 10^{-3} that the rate k_f of spontaneous emission does not make a significant contribution to

$$\tau_1^{-1} = k_f(S_1 \rightarrow S_0) + k_{IC}(S_1 \rightsquigarrow S_0) + k_{ISC}(S_1 \rightsquigarrow T_1)$$

Internal conversion (IC) and intersystem crossing (ISC) cannot be separated unambiguously without additional experimental information. Unfortunately T_1 is just as elusive in these derivatives as in the parent compound azulene.

Inspection of the data listed in Table 1 suggests that the lifetimes of S_1 might be governed by the energy gap S_1-S_0. Such an energy gap dependence of the deactivation rate would of necessity imply that intersystem crossing plays only a minor role in the deactivation. Both the intensity and the Franck–Condon structure of the transition $S_1 \leftarrow S_0$ are not noticeably altered by the addition of the carbonyl group. The geometry changes associated with this transition are thus the same as those occurring in azulene, the carbonyl group not being involved in the active modes. If the same applies to the intersystem crossing process $S_1 \rightsquigarrow T_1$ we can discuss the decay mechanisms of the S_1 states of the carbonyl compounds as if they were of purely azulene-like $\pi\pi^*$ aromatic hydrocarbon character. Now, since intersystem crossing $S_1 \rightsquigarrow T_1$ makes a negligible contribution in azulene and since the rate constant k_{ISC} is very likely of the order of 10^6 - 10^8 s^{-1}, similar to those of other aromatic hydrocarbons, we would not expect it to be very important in these carbonyl compounds either.

The lack of phosphorescence supports this hypothesis. Again presuming typical aromatic hydrocarbon behaviour in spite of the carbonyl substituent, we estimate the ratio of phosphorescence to intersystem crossing $T_1 \rightsquigarrow S_0$ to be about 10^{-3} across a T_1-S_0 energy gap of 13 500 cm^{-1}, based on Siebrand's [15] comprehensive collection of data on intersystem crossing. If neither $n\pi^*-\pi\pi^*$ coupling occurs nor an efficient promoting mode is supplied by the substituent, this figure provides a lower limit since T_1 is likely to have an energy higher than 13 500 cm^{-1}. The experimental

upper limit for the phosphorescence yield of 3.5×10^{-5} thus allows us to propose that intersystem crossing $S_1 \leadsto T_1$ can be neglected as a decay channel of S_1, its yield being less than 0.03.

Therefore the lifetimes of S_1 listed directly yield the rate constants of internal conversion $S_1 \leadsto S_0$. Spectral data, especially the vibronic structure in absorption, provide strong evidence that the geometry changes accompanying both the transitions $S_2 \leftarrow S_0$ and $S_1 \leftarrow S_0$ remain invariant towards substitution in these molecules. Among the molecular variables that are of importance in the theories of radiationless transitions, only the energy gap seems to be altered, thereby giving the possibility of investigating the energy gap dependence of the internal conversion $S_1 \leadsto S_0$ in a series of closely related compounds.

In conjunction with the most recent value (1.9 ps [7]) for the S_1 lifetime of azulene across an energy gap of $14\,300$ cm^{-1}, our data yield a tentative value for the energy gap dependence of the internal conversion rate: $k_{IC}(S_1 \leadsto S_0)$ changes by one order of magnitude with respect to a change in the energy gap of 1435 cm^{-1}. This does not differ dramatically from the corresponding value for the $S_2 \leadsto S_1$ internal conversion. From the slope of the regression line fitting the data of Murata *et al.* [1] we find that $k_{IC}(S_2 \leadsto S_1)$ changes by one order of magnitude with respect to a change in the energy gap of 1800 cm^{-1}.

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