

THE TEMPERATURE DEPENDENCE OF THE FLUORESCENCE DECAY OF AZULENE DERIVATIVES

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Summary

The decay times of the S_2 fluorescence of azulene and five derivatives were determined using the single-photon counting method. Whereas the lifetimes are only slightly altered by the nature of the solvent they are definitely temperature dependent. Furthermore, the variation in fluorescence lifetime with temperature is also strongly influenced by the positions of substituents. Our results show that the calculation of fluorescence lifetimes in azulene compounds using quantum yields and integrated absorption spectra is not very reliable; this is caused by the varying ratios between the allowed component and the vibronically induced component of the oscillator strength.

1. Introduction

The anomalous fluorescence from the second excited singlet state of azulene and many of its derivatives has been extensively investigated with respect to the spectral properties. However, not much information is available concerning the kinetic behaviour of the S_2 state. Murata *et al.* [1] have measured the quantum yield ϕ of the $S_2 \rightarrow S_0$ fluorescence of azulene and several derivatives, and have calculated the radiative lifetimes τ_0 of the S_2 state using the Strickler-Berg equation [2]. The fluorescence lifetime (900 ps), calculated using the relation $\tau = \tau_0\phi$, differs from the value of 1.4 ns obtained from a direct measurement at room temperature [3] by a factor of 1.5. This correction factor was taken to be the same for all the compounds investigated. Apart from the uncertainty introduced into the data by this assumption, a further point to be considered is that, because the work was performed at room temperature, substituent rotation and similar effects could increase the rates of radiationless transitions to varying degrees depending on the type of substituent present. This therefore precludes the determination of the "real" deactivation rates of the "frozen" molecule which are required for fitting to theoretical models.

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The lifetime of the $S_2 \rightarrow S_0$ fluorescence has been directly measured by Knight and Selinger [4] on azulene and azulene- d_8 , and by Eber *et al.* [5] on azulene and several of its derivatives. In both studies the measurements were performed at room temperature and at 77 K.

Knight and Selinger [4] found an increase of 12% (for the lifetime measured at 77 K relative to that at room temperature in the fluorescence lifetime of azulene and of 28% in that of azulene- d_8 when methylcyclohexane was used as solvent. In contrast, Eber *et al.* [5] used ethanol solutions and did not find any dependence of the lifetimes on temperature. Since a $\pi\pi^*$ state is involved in all the molecules considered, it is unlikely that this result can be explained on the basis of solvent effects.

The single-photon counting technique with nanosecond lamps was used in both these previous studies. Since the observed lifetimes were related to the width of the exciting light pulse, their actual values had to be determined by a convolution and fitting method and by a deconvolution method respectively.

We decided to reinvestigate this problem using a single-photon counting apparatus with a mode-locked argon ion laser as the excitation source. This had a pulse width of 250 ps and the high repetition rate enabled us to achieve sufficient time resolution to study precisely the small temperature effects obtained in the previous work [4].

Our results confirm the dependence of the lifetimes on temperature. Furthermore, we find that the temperature dependence varies strongly with the positions of the substituents. The changes in the lifetimes and of the fluorescence spectra due to solvent type are very small and do not noticeably modify the kinetic behaviour of the S_2 state. We conclude that lifetime measurements in frozen solutions are necessary to elucidate the "real" rate constants of the radiationless processes in the azulene system.

2. Experimental

The fluorescence lifetime apparatus and the deconvolution method have been described previously [6]. A mode-locked argon ion laser (Coherent Radiation model 52) emitting a train of 250 ps pulses separated by 8.71 ns was used as the excitation source. The laser line of 5145 Å was frequency doubled by an ammonium dihydrogen phosphate crystal placed in a Coherent Radiation 440 UV generator. In the temperature range 77 - 298 K, the samples were contained in thin sealed quartz tubes degassed by repeated freeze-thaw cycles and placed in an Oxford DN 704 cryostat the temperature of which could be stabilized. An Oxford CF 100 continuous flow cryostat was used in the range 7 - 110 K.

No decomposition occurred under the excitation conditions used; this was verified by recording fluorescence spectra before and after the lifetime measurements. The decay curves were measured at several vibronic bands with a spectral resolution of 2 - 10 Å. They were identical, within the experi-

mental error of ± 50 ps, in all cases. The average values, taken from at least five decay deconvolutions, are believed to be correct to within ± 30 ps.

Emission spectra were recorded on a home-built computer-controlled luminescence spectrometer using the photon counting technique described in ref. 7. The samples and cryostats were the same as those employed for the lifetime measurements. Absorption spectra were obtained using a Beckman Acta V spectrometer.

Azulene, guaiazulene (Fluka, puriss) and azulene- d_8 (Merck, 98 atom % D) were purchased commercially and were purified by sublimation. 1,3-Dichloroazulene and 1,3-dibromoazulene were synthesized according to the method of Anderson *et al.* [8] and were purified respectively by sublimation and by chromatography on alumina. 5,6-Dichloroazulene [9] was supplied by Dr. D. Leaver, Edinburgh, and was purified by chromatography on alumina. The purity of the products was checked using high pressure liquid chromatography. The solvents 3-methylpentane and ethanol were purified using standard procedures.

3. Results and discussion

3.1. Spectra

The absorption and fluorescence spectra of 1,3-dibromoazulene, 1,3-dichloroazulene and 5,6-dichloroazulene are shown in Figs. 1 and 2. The absorption spectra of 1,3-dichloroazulene (Fig. 1(b)) and guaiazulene are very similar to the absorption spectra recorded by Murata *et al.* [1] in cyclohexane. Our room temperature fluorescence spectra also agree closely with those given in ref. 1.

For all the derivatives investigated, the absorption spectrum of the $S_1 \leftarrow S_0$ transition is very similar to the absorption spectrum of the parent azulene. In all cases a bathochromic shift is observed as a consequence of substitution. The vibrational structure, although somewhat blurred, always remains the same.

However, the spectrum of the $S_2 \leftarrow S_0$ transition is altered; the degree to which this occurs depends on the positions of the substituents but is almost independent of the nature of the substituents. Substitution at the 1-position, *i.e.* on the five-membered ring, leads to an increase in the intensity of the 0-0 band. The absorption spectra of guaiazulene, 1,3-dibromoazulene (Fig. 1(a)) and 1,3-dichloroazulene (Fig. 1(b)) are almost identical in the region of the $S_2 \leftarrow S_0$ transition.

The $S_2 \rightarrow S_0$ fluorescence spectra similarities parallel those observed in the absorption spectra, although there is no mirror symmetry relationship between the shapes of the absorption and emission bands. The spectra of 5,6-dichloroazulene (Figs. 1(c) and 2(c)) are dominated by the vibronic band (1580 cm^{-1} in emission) which is a prominent feature of the spectra of all azulene compounds. The almost indistinguishable fluorescence spectra of guaiazulene, 1,3-dibromoazulene and 1,3-dichloroazulene again

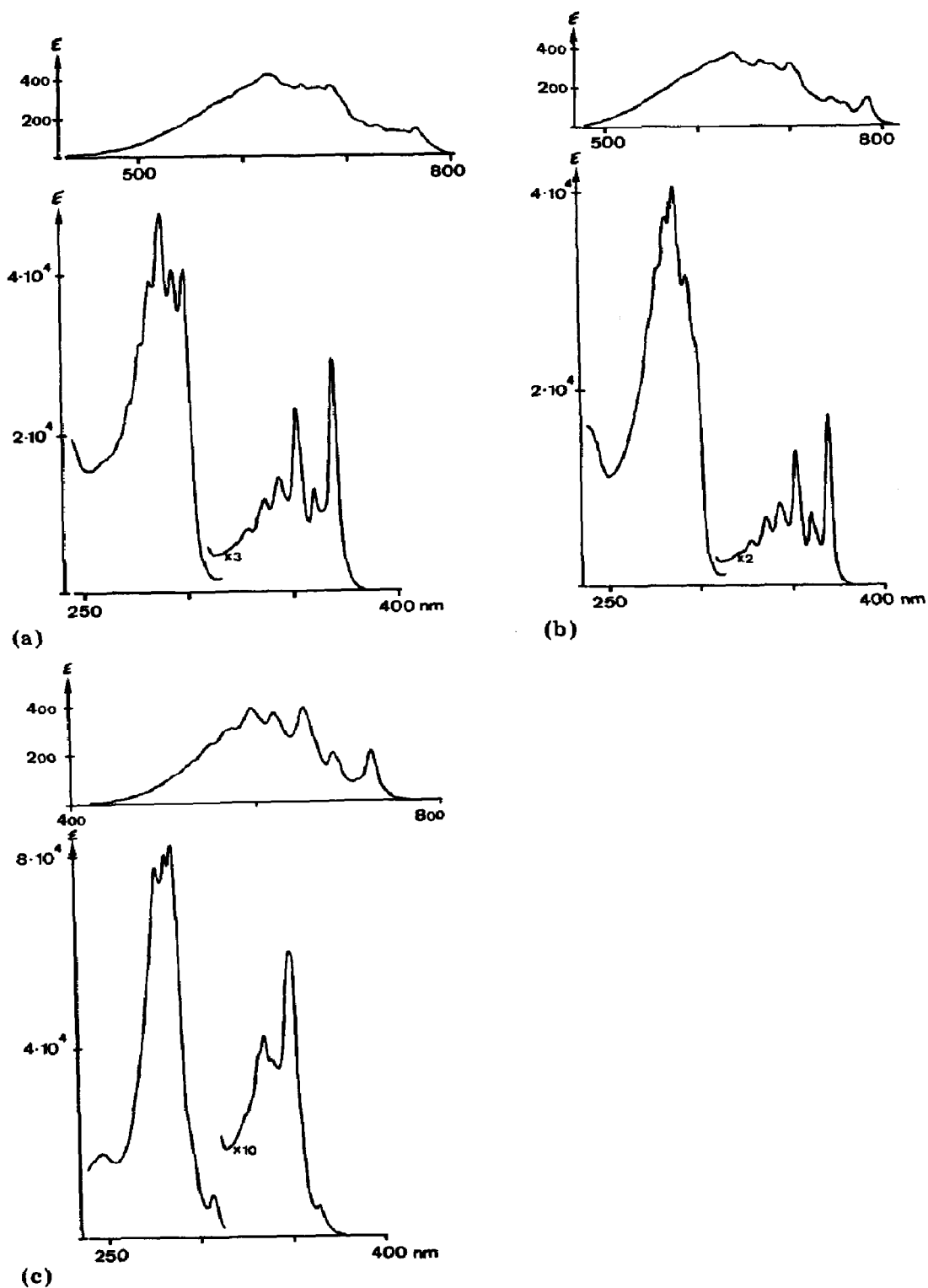
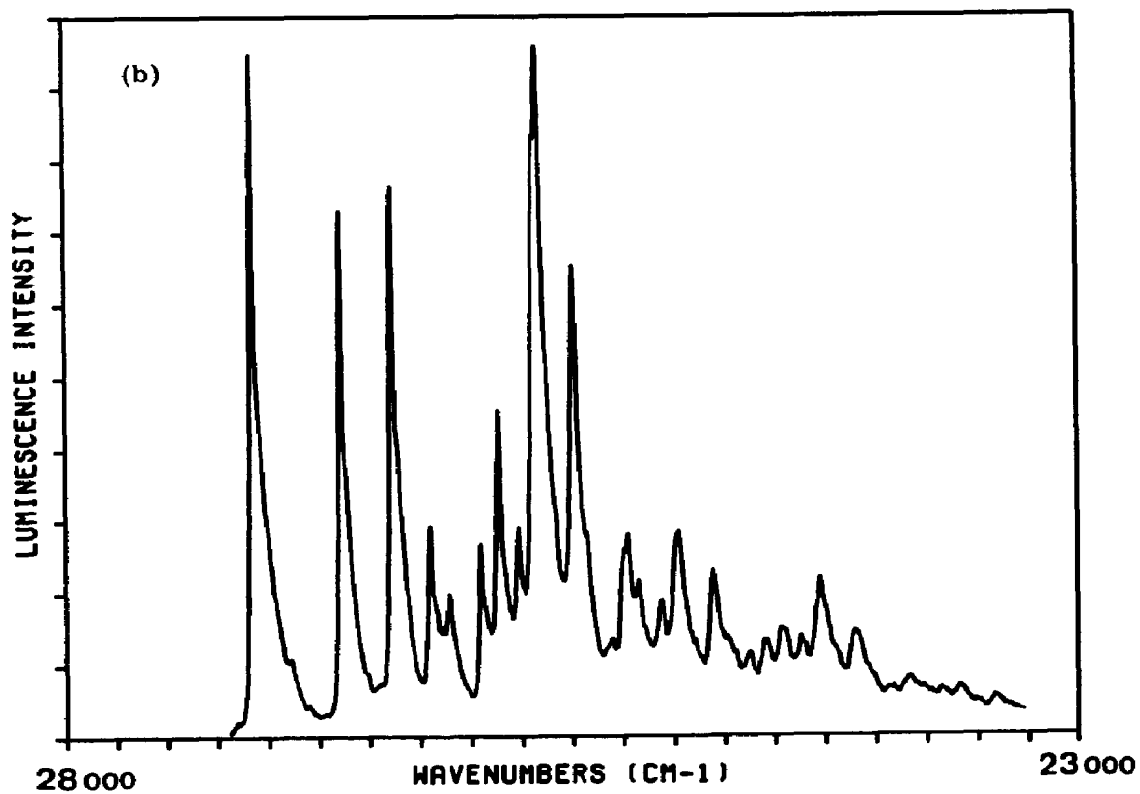
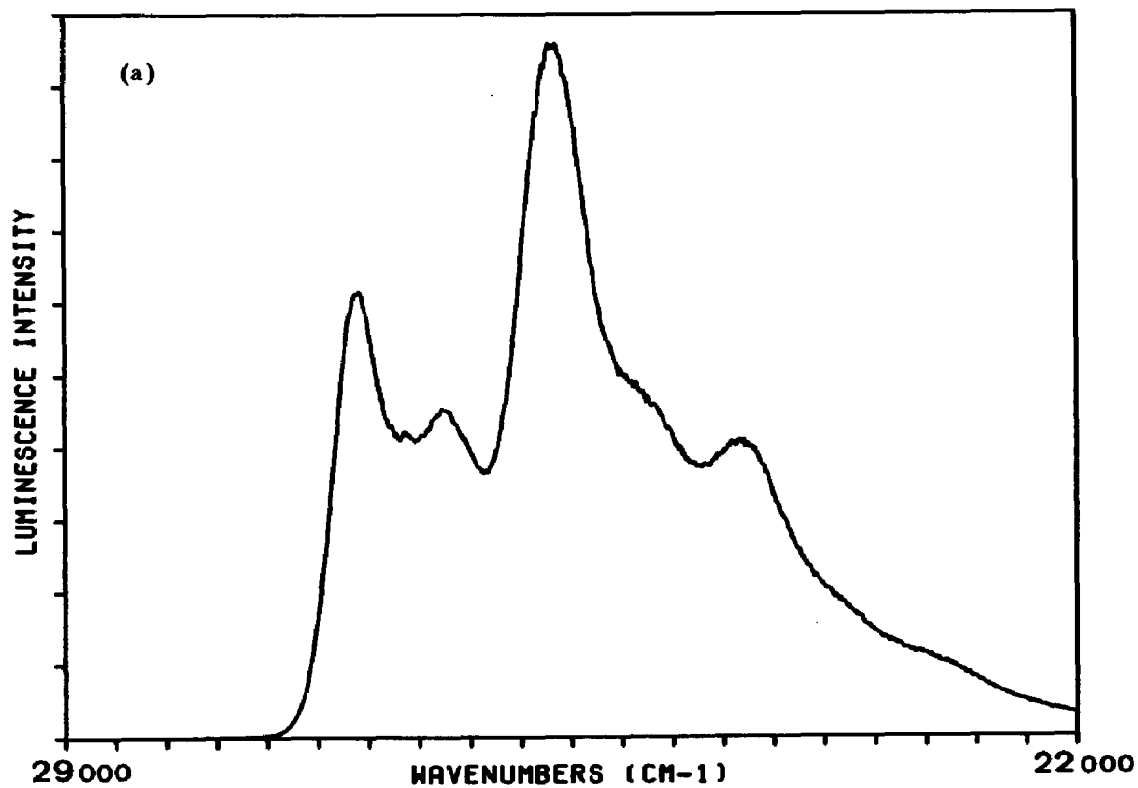


Fig. 1. Absorption spectra in 3-methylpentane at room temperature: (a) 1,3-dibromoazulene; (b) 1,3-dichloroazulene; (c) 5,6-dichloroazulene.



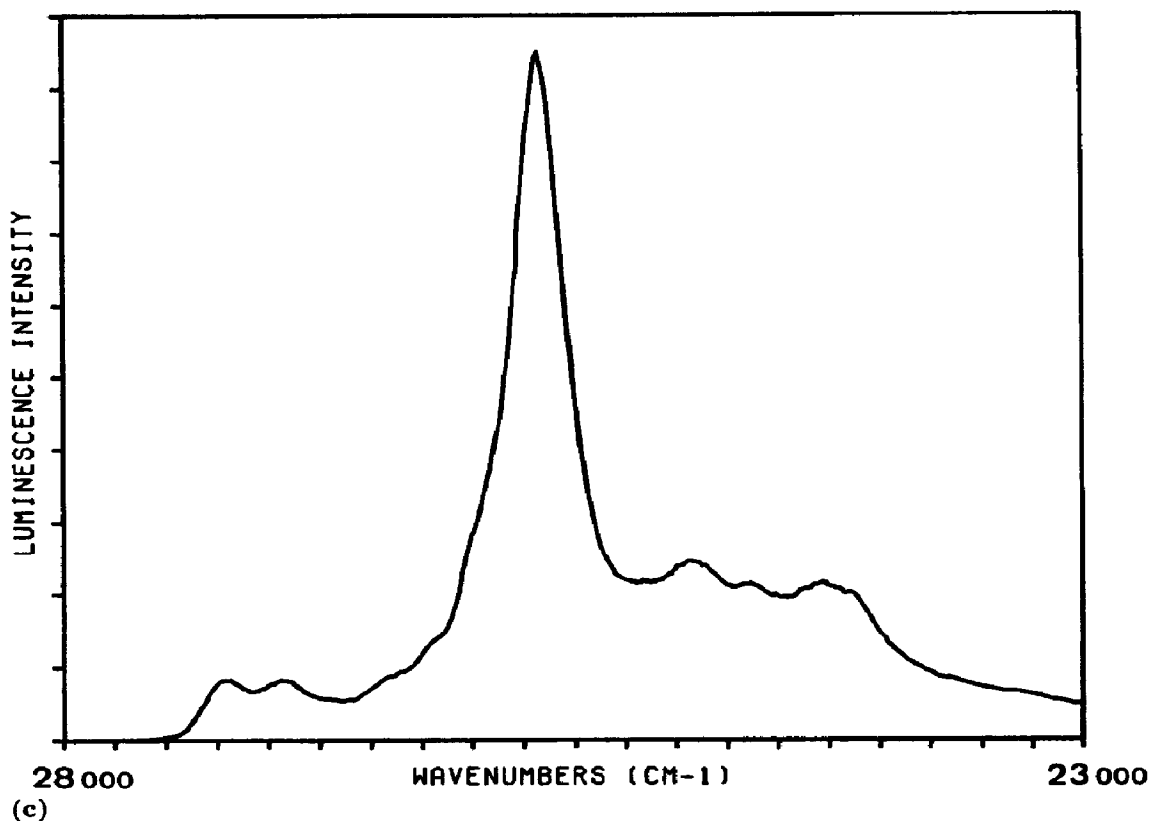


Fig. 2. $S_2 \rightarrow S_0$ fluorescence spectra: (a) 1,3-dibromoazulene in ethanol at 77 K; (b) 1,3-dichloroazulene in 3-methylpentane at 7 K; (c) 5,6-dichloroazulene in 3-methylpentane at 77 K.

differ from the emission spectrum of azulene by an enhanced intensity of the 0-0 band. The low resolution spectra recorded at 77 K (*e.g.* Fig. 2(a)) hide a rich vibrational structure that becomes apparent using high resolution measurement conditions at low temperatures. A typical highly resolved fluorescence spectrum, recorded at 7 K with spectral bandwidths of the excitation and emission beams of 10 cm^{-1} , is shown in Fig. 2(b).

3.2. Fluorescence lifetimes

For all six compounds studied the decay of the $S_2 \rightarrow S_0$ fluorescence exhibits single exponential behaviour. Figure 3 shows a typical fluorescence decay curve. It also shows the excitation pulse obtained from Rayleigh-scattered light together with the computer evaluation. The lifetime values are summarized in Table 1, together with the results from previous studies.

The decay times of all the compounds are almost independent of the nature of the solvent, even though the polarities of ethanol and 3-methylpentane are significantly different. Thus, in both of these frozen matrices the interaction between solute and solvent is weak. The weakness of the

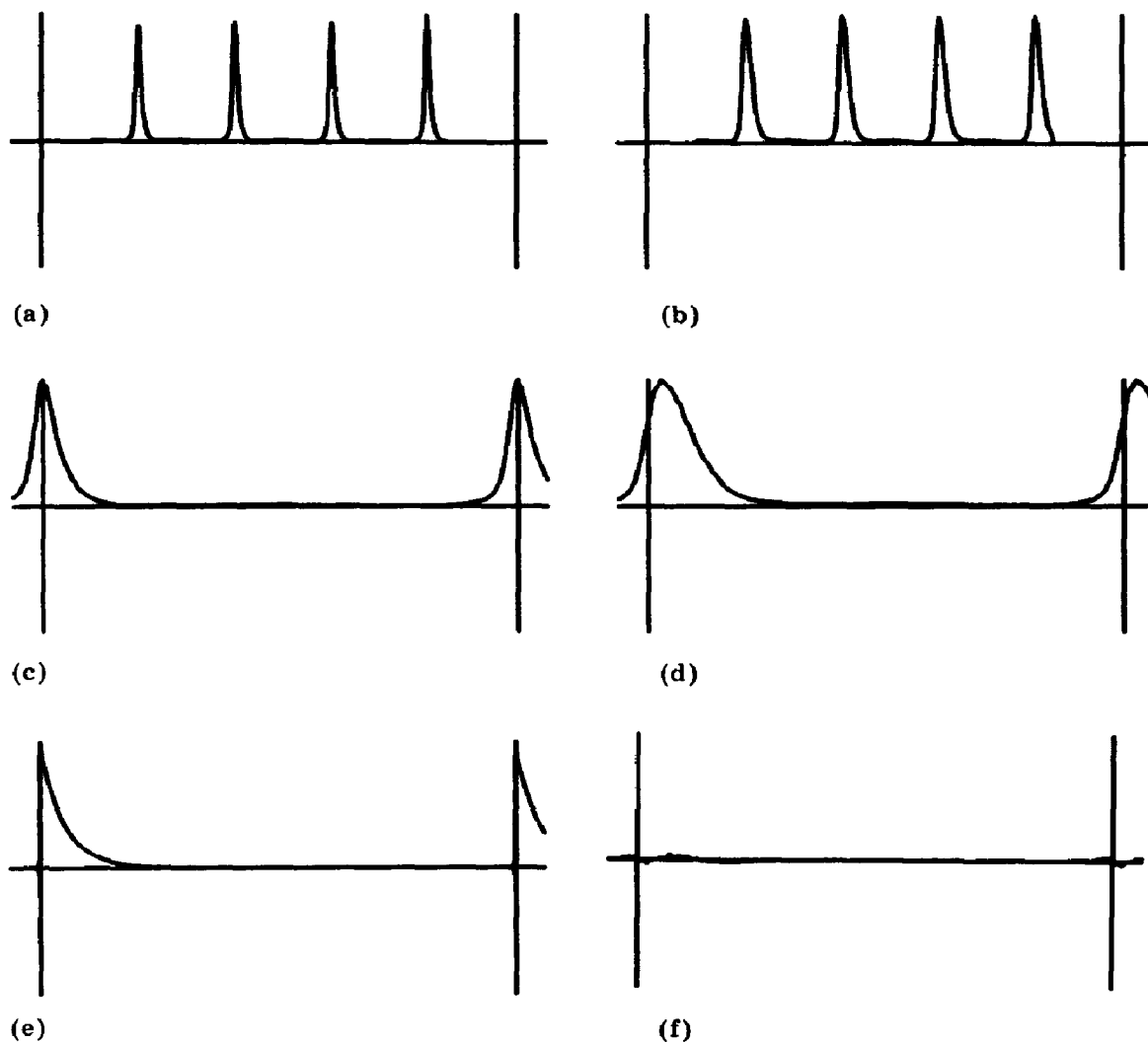


Fig. 3. The fluorescence decay of guaiazulene in 3-methylpentane at 77 K: (a) excitation pulse at 2573 Å; (b) experimental fluorescence decay curve (1024 data points); (c), (d) Figs. 3(a) and 3(b) mapped onto the standard pulse interval; (e) single exponential decay curve; (f) deviation from single exponential behaviour. The lifetime obtained from these data is 0.44 ns.

interaction is also manifested in the fluorescence spectra; these spectra are well structured in both solvents and are indistinguishable except for small shifts of the S_2 state energies.

It is noteworthy that the calculated lifetime of 1,3-dichloroazulene reported by Murata *et al.* [1] exceeds our measured value by 60%. This discrepancy seems too large to be attributable to quantum yield measurement errors and a more likely cause is the largely vibronically induced nature of the $S_2 \rightarrow S_0$ transition. Strickler and Berg [2] state that the calculation of radiative lifetimes is expected to be less accurate for weak

TABLE 1

Lifetimes of the S_2 state of azulene and some derivatives

Substance	Solvent	Temperature (K)	τ_2 (ns)	Literature values of τ (ns)
Azulene	3-Methylpentane	298	1.30	1.63 ^a [4], 1.4 ^b [3]
		77	1.63	1.82 ^a [4]
	Ethanol	298	1.28	1.65 [5]
		77	1.69	
Azulene-d ₈	3-Methylpentane	298	1.99	2.08 ^a [4]
		77	2.55	2.67 ^a [4]
	Ethanol	298	1.72	
		77	2.60	
Guaiazulene	3-Methylpentane	298	0.395	0.50 ^b [1]
		77	0.45	
	Ethanol	298	0.34	2.0 [5]
		77	0.60	
1,3-Dichloroazulene	3-Methylpentane	298	1.01	1.61 ^b [1]
		77	1.18	
	Ethanol	298	0.89	0.80 [5]
		77	1.05	
1,3-Dibromoazulene	3-Methylpentane	298	0.270	
		77	0.340	
	Ethanol	298	0.300	0.34 [5]
		77	0.360	
5,6-Dichloroazulene	3-Methylpentane	298	0.160	
		77	1.08	
	Ethanol	298	≈0.15	
		77	1.19	

^aIn methylcyclohexane.^bIn cyclohexane.

transitions. This point is exemplified in the case of azulene where the calculated lifetime differs from the measured lifetime by a factor of 1.5 (see Section 1). This correction factor must be related to the amount of vibronically induced intensity compared with the allowed transition intensity. Lacey *et al.* [10] have estimated that Herzberg-Teller vibronic coupling to S_4 is responsible for about two-thirds of the intensity of the $S_2 \leftarrow S_0$ transition. The ratio will be strongly dependent on the S_2 - S_4 energy gap, on the vibronic coupling strength and on the active vibrations.

In order to undertake a detailed study of these effects, similar to that of Lacey *et al.* [10], highly resolved absorption spectra are needed. For the purpose of our present discussion, however, only a qualitative consideration will be attempted. Thus the room temperature absorption spectra shown in Figs. 1(b) and 1(c) serve to illustrate this point. The ratio of the intensity

of the 0-0 band to that of the strongly active vibronic band at about 1300 cm^{-1} gives a good indication of the ratio of the allowed transition moment to the vibronically induced transition moment. Even within the group of simple derivatives investigated, this ratio varies over a wide range. 5,6-Dichloroazulene shows spectral features very similar to those of azulene, although with a somewhat larger degree of vibronic intensity which is probably caused by a smaller S_2 - S_4 gap. However, because the 1,3-substituted derivatives exhibit a higher percentage of allowed character in the $S_2 \leftarrow S_0$ transition, they require a smaller correction to the Strickler-Berg formula.

It would appear, therefore, that application of a constant correction factor to the lifetimes calculated from the relation $\tau = \tau_0\phi$ is not justified. The inherent uncertainty in the calculated lifetimes of vibronically induced transitions requires direct lifetime measurements to be made in order that quantitative discussions of the radiationless processes originating from the S_2 state of azulene and its derivatives can be undertaken.

Our results clearly confirm the dependence of the lifetimes on temperature as observed by Knight and Selinger [4]. Figure 4 shows the behaviour of the fluorescence lifetime of 5,6-dichloroazulene as a function of temperature. In liquid solution the lifetime increases gradually with decreasing temperature. Below the glass point of the solvent and down to 7 K, the fluorescence lifetime is independent of temperature. At 77 K, in

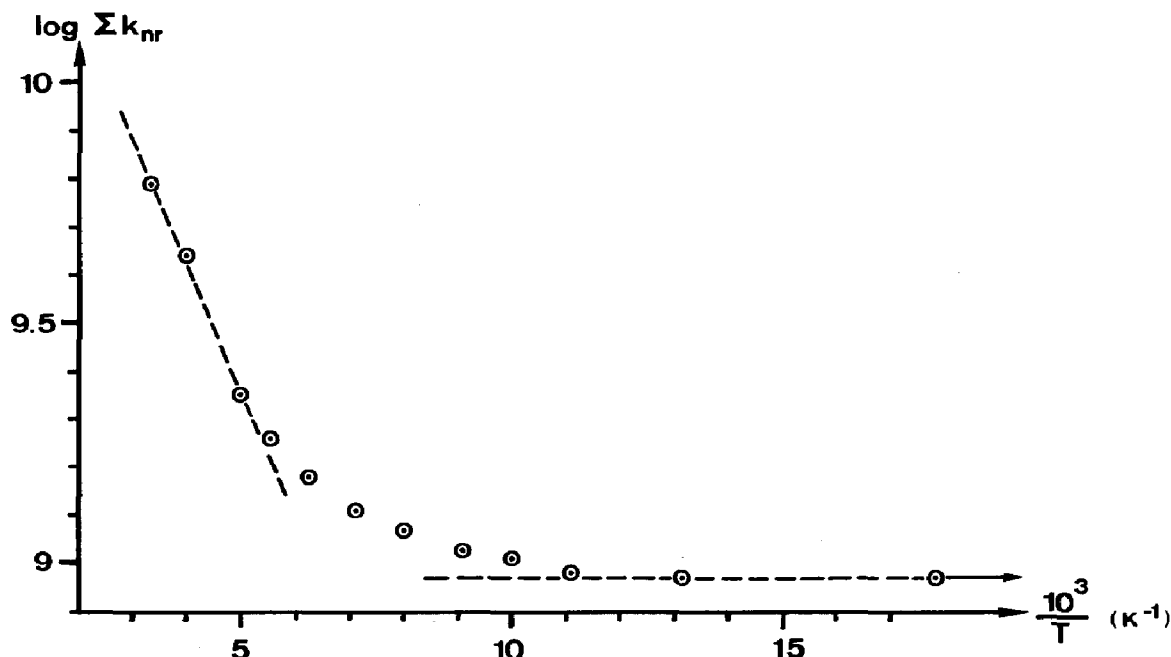


Fig. 4. The temperature dependence of the radiationless deactivation of the S_2 state of 5,6-dichloroazulene in 3-methylpentane. ($\Sigma k_{nr} = \tau^{-1} - k_f$.)

these weakly interacting surroundings, the kinetic behaviour of the S_2 state of these molecules, summarized in Table 1, is a good approximation to that of the isolated frozen molecule case.

In most of the compounds studied the lifetime increase on lowering the temperature from 298 to 77 K lies within the range 10 - 50%. We believe that this is caused by a gradual relaxation of constraints on solute molecular motion as the temperature is increased. Therefore we adopt the explanation put forward by Hung and Henry [11] to account for the small increase in the non-radiative decay rate of anthracene triplets in polymethyl methacrylate.

The much larger temperature effect on the fluorescence lifetime of 5,6-dichloroazulene is accompanied by a corresponding behaviour of the fluorescence quantum yield. This must be attributed to a temperature dependence of the sum of the radiationless rate constants. The data show an Arrhenius-type behaviour:

$$k_{nr}(T) = k_0 + k_1 \exp(-\Delta E/kT)$$

This behaviour is best fitted by the following parameters:

$$k_0 = 9.2 \times 10^8 \text{ s}^{-1}$$

$$k_1 = 4.7 \times 10^{10} \text{ s}^{-1}$$

$$\Delta E = 430 \text{ cm}^{-1}$$

One possible explanation involves a temperature-activated intersystem crossing to a triplet state, the energy of which is slightly above that of S_2 . This implies a very fast intersystem crossing rate from $S_{2,v}$ to T_n , which would not be expected on the basis of weakly perturbing chlorine substituents alone. The absorption spectrum and the fluorescence spectra of both the $S_2 \rightarrow S_0$ and the $S_2 \rightarrow S_1$ transitions are practically identical to those of the parent compound [12], and are independent of temperature apart from some line narrowing. This indicates that the S_2 state is hardly perturbed by the chlorine substitution on positions 5 and 6.

Alternatively, the increased rate of internal conversion may be due to an increased mobility, resulting from a decreasing solvent viscosity. The temperature dependence of the fluorescence lifetime of this compound may be only a manifestation of the "loose bolt" effect, although there is no mobile substituent attached to the chromophore. The Arrhenius-type behaviour of the additional decay channel then simply parallels the temperature dependence of the solvent viscosity.

The temperature dependence of the radiationless relaxation observed in 5,6-dichloroazulene thus basically relies on the same mechanism as that observed for the other five derivatives investigated. This implies, however, that a much larger amplitude of solute molecular motion is achieved in 5,6-dichloroazulene compared with those obtained with the other compounds. An alternative is that the coupling of the geometry distortion to the radiationless process is much more efficient. We believe it is reasonable to

assume a potentially larger mobility of the seven-membered ring compared with that of the five-membered ring. Thus, while substituents in the 1-, 2-, and 3-positions on the five-membered ring are held rather rigidly in-plane, the larger size of the seven-membered ring facilitates out-of-plane motions of its substituents.

Hence the vibrational amplitudes of the chlorine motions in 5,6-dichloroazulene are expected to be substantially larger than those in the isomeric 1,3-dichloroazulene. This leads to a decrease of the S_2 lifetime with increasing temperature which is dependent on the potential mobility of the substituent. However, further experiments with azulene derivatives substituted at the seven-membered ring are needed in order to reinforce this hypothesis.

In summary, the single-photon counting technique with a mode-locked argon laser as the excitation source allows a precise determination of fluorescence lifetimes in azulene systems over the temperature range studied. As well as yielding information on position-dependent temperature effects on radiationless transitions, measurements of this kind disclose the real photophysical parameters of the frozen azulene chromophore. The results may lead to the identification of the relevant decay processes and serve to test quantitatively the energy gap law, *i.e.* whether it is a function of the S_2-S_1 gap as reported by Murata *et al.* [1], or whether it is a function of the S_2-S_0 gap as suggested by Hirata and Lim [13]. These experimental correlations, which will be discussed elsewhere [14], are supported by the fact that all the compounds studied show a clearly identifiable $S_2 \rightarrow S_1$ fluorescence [12], very similar to that reported recently by Gillispie and Lim [15] for azulene. The correlations are also supported by the observation of structured emissions which allow the energy gaps involved to be precisely determined.

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