

## ON THE ELECTRONIC RELAXATION PROCESSES OF CARBONYL COMPOUNDS OF AZULENE IN SOLUTION

G. EBER, S. SCHNEIDER and F. DOERR

*Institut für Physikalische und Theoretische Chemie der Technischen Universität München, Arcisstrasse 21, D 8 München 2 (F.R.G.)*

(Received October 1, 1976; in revised form January 7, 1977)

### Summary

Lifetimes and quantum yields were determined as a function of temperature for two carbonyl compounds which show dual fluorescence emission as a result of alteration of their energy gaps. It was found that in both compounds the lifetime of the  $S_1$  state is raised into the nanosecond range and the lifetime of the  $S_2$  state is lowered into the picosecond range.

---

### 1. Introduction

In a preceding paper [1] it was shown that by proper substitution one can change the fluorescence emission behaviour of azulene (which exhibits a dominant  $S_2 \rightarrow S_0$  fluorescence) such that either dual fluorescence ( $S_2 \rightarrow S_0$  and  $S_1 \rightarrow S_0$  fluorescence) or dominant  $S_1 \rightarrow S_0$  fluorescence only is observed. Whilst the intensity of the  $S_2 \rightarrow S_0$  emission was shown to be fairly independent of temperature, a logarithmic dependence on temperature was found for the  $S_1 \rightarrow S_0$  fluorescence intensity. The activation energy which was derived from an Arrhenius-type plot was approximately  $60 \text{ cm}^{-1}$  and this could be interpreted as being due to the barrier to internal rotation of the substituents.

To gain further insight into the temperature dependence of radiationless processes, the fluorescence quantum yields and lifetimes of two derivatives of azulene (Fig. 1) have been measured. The major difference between these derivatives is that compound 2 possesses no group that is capable of executing any internal rotation.

### 2. Experimental

Compound 1 was extracted from 5 kg of fresh mushrooms (*Lactarius deliciosus* L.) and it was purified as described in ref. 2; compound 2 was prepared according to refs. 3 and 4.

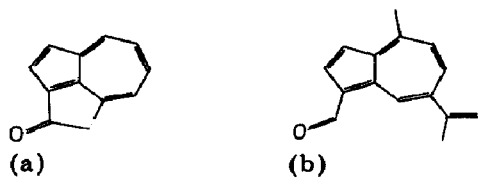


Fig. 1. The azulene derivatives investigated: (a) compound 1 4-methyl-7-isopropenylazulene-1-carboxaldehyde; (b) compound 2 1,2-dihydrocyclopent[c,d]azulene-2-one.

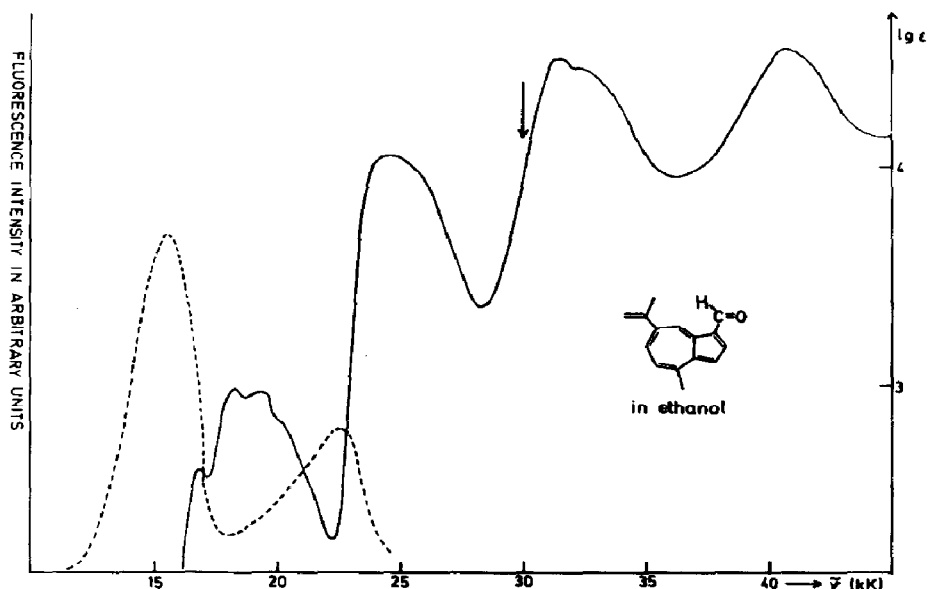


Fig. 2. Absorption and fluorescence emission spectra of compound 1: — absorption; ---- fluorescence emission,  $10^{-3}$  M in EtOH at 77 K,  $\nu_{\text{ex}} = 30$  kK.

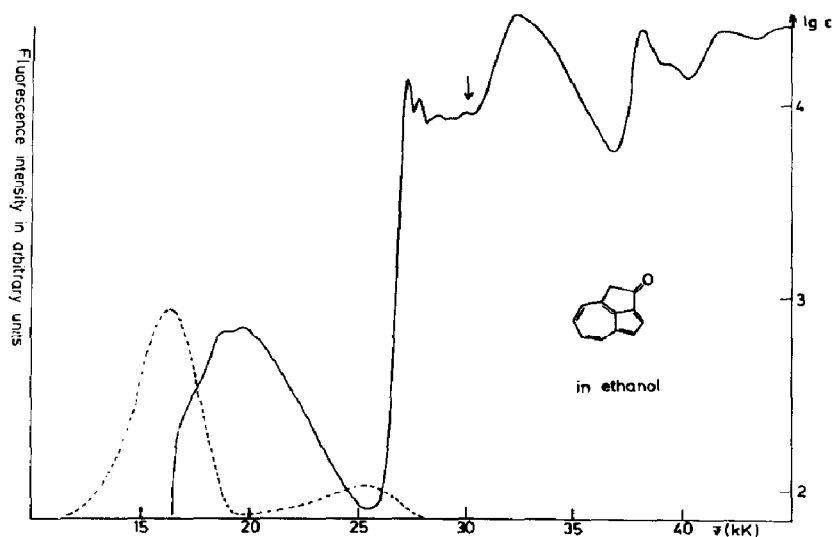


Fig. 3. Absorption and fluorescence emission spectra of compound 2: — absorption; ---- fluorescence emission,  $10^{-3}$  M in EtOH at 77 K,  $\nu_{\text{ex}} = 30$  kK.

Fluorescence emission and excitation spectra were recorded by means of a fluorimeter described earlier [1]. Quantum efficiency measurements were performed following the procedure given by Parker and Rees [5], using Rhodamin B as a reference ( $\phi_F = 0.97$  [6]). The degree of polarization was determined by an apparatus described in ref. 7.

For lifetime measurements the single-photon timing technique was applied. The light from an Ortec model 9362 nanosecond flashlamp was imaged on the sample after passing through a Zeiss M4QIII monochromator. Thereby, either of the two strong lines of the  $N_2$  spectrum (at  $28\,000\text{ cm}^{-1}$  and  $29\,600\text{ cm}^{-1}$ ) could be chosen for the excitation. Stray light that overlapped the fluorescence emission was filtered out by a Schott OG 550 filter; sampling times were as long as 18 h.

The deconvolution of the observed fluorescence decay curves was done on a TR 440 computer, employing both a Laplace transformation [8] and the method of momenta [9].

The quantum mechanical model calculations were performed in the well-known  $\pi$  electron approximation after Pariser, Parr and Pople (PPP). Since only general features were looked for, we did not vary the parameters in order to achieve an optimum agreement between the calculated and experimental values but we used without any modification a set of parameters developed earlier [10]. The calculated bond orders  $P_{\mu\nu}$  and charge densities  $q_\mu$  displayed in Fig. 5, as well as the dipole moments  $\mu$  mentioned in Table 2, refer to the contribution of the  $\pi$  electrons only.

### 3. Results and discussion

The absorption spectrum of the parent compound azulene is characterised by a weak first band ( $\epsilon_{\text{max}} = 300$ ) which is separated from the intense higher transitions by a wide and deep valley. The position of the absorption bands is fairly independent of the nature of the solvent, *i.e.* no solvatochromic shift is observed (Table 1).

The absorption spectra (Figs. 2 - 4) at 77 K of the compounds 1 and 2 are distinguished by a smaller energy gap between the  $S_1$  and  $S_2$  excited states. (This is important for our later discussions.) In both cases the transition to the  $S_1$  state shows a hypsochromic shift and the transition to the  $S_2$  state shows a bathochromic shift with respect to azulene. The magnitudes of these shifts are dependent on the polarity of the solvent used, as can be seen by inspection of Table 1 or by a comparison of Figs. 3 and 4. An explanation for this behaviour can be found in the fact that in the electronic ground states both compounds possess very large dipole moments which, on excitation, are reduced in magnitude and are rotated with respect to the  $x$  axis (see Table 1). The calculated charge distribution (Fig. 5(c)) shows that the enlargement of the ground state dipole moment stems mainly from the contribution of the carbonyl group.

The absorption spectra of compound 2 closely resemble in their overall structure the spectrum of azulene; the absorption spectrum of compound 1,

TABLE 1

Spectroscopic data of azulene and the derivatives 1 and 2

State	Calculated					$E(\text{experimental})$ (kK)	
	$E$ (kK)	$f$	$\alpha$ ( $^\circ$ )	$\mu$ (D)	$\beta$ ( $^\circ$ )	in EtOH	in 3-MeC <sub>5</sub> H <sub>11</sub>
<i>Azulene</i>							
S <sub>0</sub>				3.4	0		
S <sub>1</sub>	16.0	0.028	90	2.3	180	14.3	14.4
S <sub>2</sub>	25.8	0.006	0	2.9	180	28.3	28.4
S <sub>3</sub>	34.3	0.100	90			33.8	33.8
<i>Compound 1</i>							
S <sub>0</sub>				8.1	25.5		
S <sub>1</sub>	18.4	0.055	63	2.9	51	16.8	15.7
S <sub>2</sub>	24.8	0.277	-5	4.4	28	24.2	24.5
S <sub>3</sub>	31.3	0.522	155			31.2	31.5
<i>Compound 2</i>							
S <sub>0</sub>				8.7	15		
S <sub>1</sub>	18.7	0.032	101	2.3	46	16.9	16.0
S <sub>2</sub>	26.7	0.050	20	3.1	49	27.3	27.6
S <sub>3</sub>	33.7	0.38	45			32.0	32.5

The parameters in the model calculation were chosen as in ref. 15;  $\alpha$  and  $\beta$  denote the angles between the  $x$  axis and the transition and stationary dipole moments, respectively.

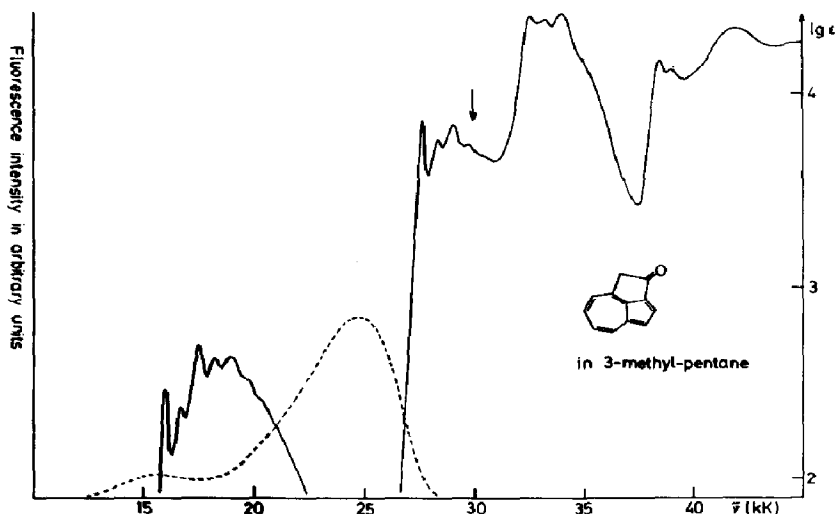


Fig. 4. Absorption and fluorescence emission spectra of compound 2: — absorption; ---- fluorescence emission,  $10^{-3}$  M in 3-methylpentane at 77 K,  $\nu_{\text{ex}} = 30$  kK.

however, is dominated in the range  $\nu \geq 22$  kK by well-separated broad bands which, even at low temperature, do not show any vibronic structure. The striking difference in the shape of the  $S_0 \rightarrow S_2$  band is predicted by the results of the model calculations in the PPP approximation (Table 1). It is well known that these calculations are in general not very good for azulene.

According to them, the oscillatory strengths of the  $S_0 \rightarrow S_1$  and the  $S_0 \rightarrow S_3$  transitions are similar for all three compounds. The oscillatory strength for the  $S_0 \rightarrow S_2$  transition, however, differs by a factor of about 50 if one compares compound 1 with azulene. This means vibronically induced contributions, which play a major role in the case of azulene [11, 12], cannot be detected in the absorption spectra, although they are certainly present because of the large changes in  $\pi$  bond order (Figs. 5(a) and 5(b)).

In ethanolic solution both derivatives exhibit dual fluorescence emission (Figs. 2 and 3) when excited into the second or higher excited singlet states. Whilst the intensity of the  $S_2 \rightarrow S_0$  fluorescence is found to be essentially independent of the temperature, there is a rapid increase in the intensity of the  $S_1 \rightarrow S_0$  fluorescence when the sample temperature is lowered to 77 K. If 3-methylpentane is used as the solvent, the  $S_1 \rightarrow S_0$  fluorescence of compound 2 is extremely weak (Fig. 4). Therefore, all data reported below refer to ethanol as the solvent. In Fig. 6 the quantum efficiencies (*i.e.* the number of emitted photons divided by the number of absorbed photons) of the  $S_1 \rightarrow S_0$  fluorescence are displayed as functions of both the temperature  $T$  ( $77 \leq T \leq 300$  K) and the excitation wavelength ( $\tilde{\nu}_{\text{ex}} = 20$  kK and 30 kK). The radiative rates  $k_r(S_1 \rightarrow S_0)$  and  $k_r(S_2 \rightarrow S_0)$ , calculated via the simplified Strickler-Berg equation [13], are also listed in Table 2, where

$$k_r = 2.88 \times 10^{-9} n^2 (\tilde{\nu}_f^3 / \tilde{\nu}_a) \int \epsilon \, d\tilde{\nu}$$

Making use of the experimentally determined values of the quantum yields  $\phi_F(S_2 \rightarrow S_0)$  and  $\phi_F(S_1 \rightarrow S_0)$ , it is possible to derive estimates for the lifetimes  $\tau(S_1)$  and  $\tau(S_2)$  of the excited states  $S_1$  and  $S_2$ ; these are also included in Table 2.

By definition, the ratio of the quantum efficiencies

$$\frac{\phi'_F(S_1 \rightarrow S_0, \text{excitation into } S_1)}{\phi'_F(S_1 \rightarrow S_0, \text{excitation into } S_2)}$$

is equal to the quantum yield of internal conversion  $\phi_{\text{IC}}(S_2 \rightarrow S_1)$ . Since this ratio is found to be unity within experimental error (Fig. 6), we have to assume that internal conversion is the dominant relaxation process in the deactivation of the second excited singlet state in spite of the large energy

TABLE 2

Quantum yields and lifetime data

State	$\phi_F(S_n \rightarrow S_0) \times 10^{-5}$		$k_r(S_n)(s^{-1})$ (Strickler-Berg)	$\tau(S_n)$ at 77 K (ns)	$\tau(S_1)$ (exp.) at 77 K (ns)
	at 77 K	at 300 K			
<i>Compound 1</i>					
$S_1$	50	6	$4.4 \times 10^6$	0.11	$1.4 \pm 0.2$
$S_2$	9.1	7.2	$8.9 \times 10^7$	$1.0 \times 10^{-3}$	
<i>Compound 2</i>					
$S_1$	70	8.5	$6.7 \times 10^6$	0.10	$1.2 \pm 0.2$
$S_2$	7.7	5.8	$2.6 \times 10^7$	$3.4 \times 10^{-3}$	

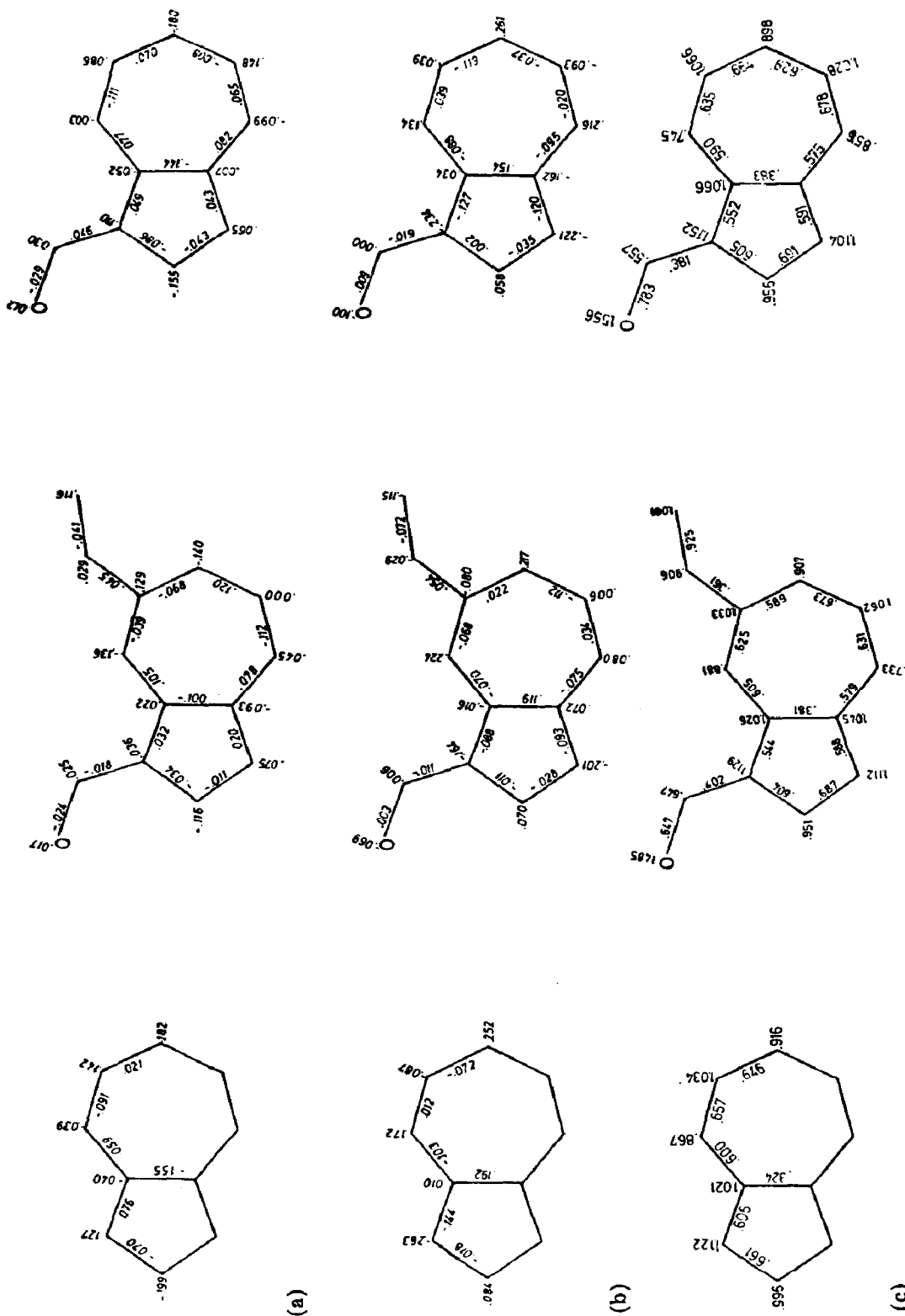


Fig. 5. Differences in bond order and charge density: (a)  $P_{\mu}(S_2) - P_{\mu}(S_1)$  and  $q_{\mu}(S_2) - q_{\mu}(S_1)$  respectively, and (b)  $P_{\mu}(S_1) - P_{\mu}(S_0)$  and  $q_{\mu}(S_1) - q_{\mu}(S_0)$ , respectively; (c) calculated charge densities and  $\pi$  bond orders in the electronic ground state.

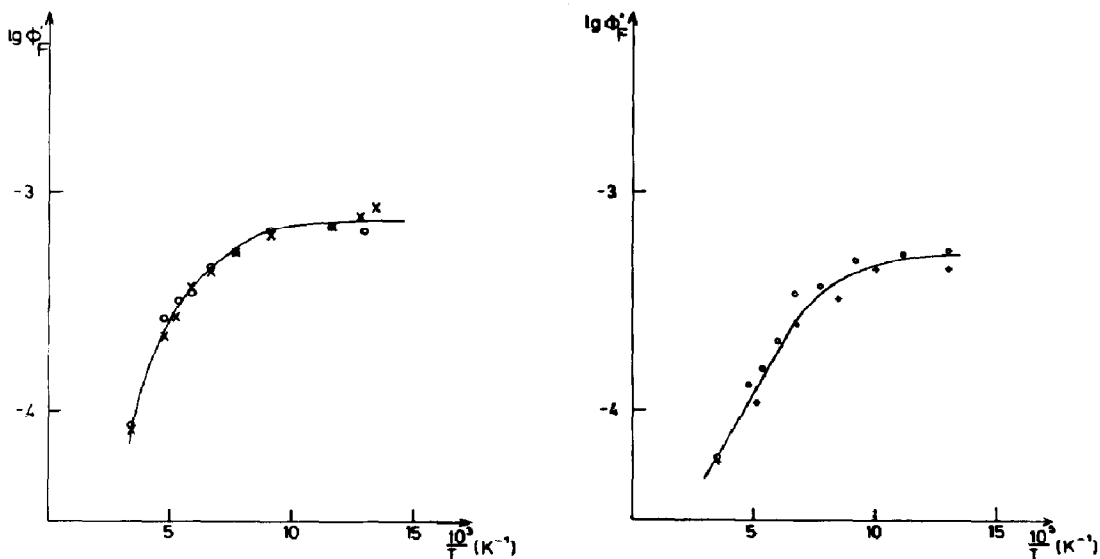


Fig. 6. Temperature dependence of the  $S_1 \rightarrow S_0$  fluorescence efficiency ( $\circ \bar{\nu}_{\text{ex}} = 20 \text{ kK}$ ;  $\times \bar{\nu}_{\text{ex}} = 30 \text{ kK}$ ) (a) for compound 1 and (b) for compound 2 (solvent EtOH).

gap ( $\Delta E(S_2-S_1) \geq 7400 \text{ cm}^{-1}$ ). Furthermore, this ratio is essentially independent of temperature, a fact which implies that the rate constant for internal conversion  $k_{\text{IC}}(S_2 \rightarrow S_1)$  is almost independent of temperature.

The estimates given in Table 2 place the lifetimes of the  $S_2$  state in the range 1 - 10 ps, *i.e.* they are about two orders of magnitude shorter than that in the parent compound azulene. As a consequence, the fluorescence emission  $S_2 \rightarrow S_0$  should be anisotropic if the sample is excited with polarized light, even when the measurement is performed at room temperature (in a liquid solution). Assuming a volume  $V$  of  $1.4 \times 10^{-22} \text{ cm}^3$  for a molecule of compound 2 and its solvent shell, one calculates in the Debye approximation [4] an orientational relaxation time  $\tau_D (= V\eta/kT)$  of 40 ps. The experimental value for the degree of polarization  $P = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$  [7] is  $0.38 \pm 0.1$  for compound 2 in ethanol at 300 K ( $\bar{\nu}_{\text{ex}} = 30 \text{ kK}$ ,  $\bar{\nu}_{\text{obs}} = 25 \text{ kK}$ ) which is smaller than the limiting value of 0.5. The observed reduction is most likely caused by vibronic coupling to higher states, since it does not change when the sample temperature is lowered to the condition of a rigid solution. However, lowering the temperature from 300 K to 77 K increases the quantum yield of the  $S_1 \rightarrow S_0$  fluorescence by a factor of approximately 10. Since the radiationless processes are the dominant deactivation processes, the temperature dependence of the fluorescence intensity should be determined by the temperature dependence of the rates of internal conversion  $k_{\text{IC}}(S_1 \rightarrow S_0)$  and/or intersystem crossing  $k_{\text{ISC}}(S_1 \rightarrow T)$ . If the estimates for  $\tau(S_1)$  (Table 2), which make use of the Strickler-Berg relationship, were right, it would be fair to assume that the contribution of inter-

system crossing is negligible (as in the case of the parent azulene) and that the observed temperature dependence is due to that of the internal conversion process  $S_1 \rightarrow S_0$ . The fluorescence decay curves, however, lead to values of 1.4 and 1.2 ns for compounds 1 and 2 respectively, when the deconvolution is performed under the assumption that internal conversion  $S_2 \rightarrow S_1$  takes place on a picosecond time scale. Since the latter assumption seems reasonable in view of the experimental evidence given above, a definite association of the temperature dependence with either radiationless process cannot be made until further experimental evidence is available.

Unfortunately, we were not able to measure the fluorescence lifetime of either compound at 300 K in order to make a clear-cut statement about the temperature dependence of both the radiative and the non-radiative decay channels. Since we can exclude fluorescence quenching by oxygen, the observed variation in the quantum yield  $\phi_F(S_1 \rightarrow S_0) = \phi'_F(S_1 \rightarrow S_0)$  must be due to the temperature dependence of the intramolecular relaxation processes. Because the onset temperature is approximately the same in both compounds and coincides with the softening point of the solvent matrix, one is forced to assume that the solvent cage strongly influences the deactivation rates.

#### 4. Conclusion

One of the still open questions concerning the fluorescence behaviour of azulene is why the internal conversion rates  $k_{IC}(S_2 \rightarrow S_1)$  and  $k_{IC}(S_1 \rightarrow S_0)$  differ by more than three orders of magnitude despite the fact that the corresponding energy gaps are the same. It has already been pointed out by Small and Kusserow [12] that large differences in the electronic matrix element may be one part of the explanation; different changes in geometry (Fig. 1) causing different Franck-Condon factors may be the other part. The results reported here also indicate this. For the  $S_1$  state, a change in the lifetime by about three orders of magnitude (for azulene  $\tau(S_1) \leq 1$  ps [15]) is concomitant with an increase in the energy gap of about  $1500 \text{ cm}^{-1}$ . In the  $S_2$  state a decrease in the energy gap by more than twice as much is again accompanied by a factor of about 1000 for the shortening of the lifetime.

#### Acknowledgments

The authors thank the Deutsche Forschungsgemeinschaft for financial support and the Bayerische Akademie der Wissenschaften for computer time.



## References

- 1 G. Eber, F. Grüneis, S. Schneider and F. Dörr, *Chem. Phys. Lett.*, 29 (1974) 397.
- 2 H. Willstaedt, *Ber. Dtsch. Chem. Ges.*, 68 (1935) 333.
- 3 K. Hafner and H. Weldes, *Liebigs Ann. Chemie*, 606 (1957) 90.
- 4 K. Hafner, H. P. Meinhardt and W. Richarz, *Angew. Chem.*, 235 (1974).
- 5 C. A. Parker and W. T. Rees, *Analyst (London)*, 85 (1960) 587.
- 6 J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley-Interscience, New York, 1970.
- 7 J. Friedrich, F. Metz and F. Dörr, *Mol. Phys.*, 30 (1975) 289.
- 8 A. Heiss, F. Dörr and J. Kühn, *Ber. Bunsenges. Phys. Chem.*, 79 (1975) 294.
- 9 S. S. Brody, *Rev. Sci. Instrum.*, 28 (1957) 1021.
- 10 F. Dörr, G. Hohlneicher and S. Schneider, *Ber. Bunsenges. Phys. Chem.*, 70 (1966) 803.
- 11 A. L. Lacey, E. F. McCoy and I. G. Ross, *Chem. Phys. Lett.*, 21 (1973) 233.
- 12 G. J. Small and S. Kusserow, *J. Chem. Phys.*, 60 (1974) 1558.
- 13 S. J. Strickler and R. A. Berg, *J. Chem. Phys.*, 37 (1962) 814.
- 14 P. Debye, *Polare Molekeln*, Verlag S. Hirzel, Leipzig, 1929.
- 15 P. Wirth, S. Schneider and F. Dörr, *Chem. Phys. Lett.*, 42 (1976) 482.