Picosecond dynamics of the S2 excited state of azulene and its van der Waals complexes with Ar and Xe

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Picosecond dynamics of the S_2 excited state of azulene and its van der Waals complexes with Ar and Xe

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Abstract

The dynamics of the second excited singlet (S_2) states of jet-cooled azulene (Az) and its van der Waals complexes with one and two atoms of Ar and Xe have been investigated. Quantum interference effects due to restricted intramolecular vibrational redistribution in azulene have been reinterpreted. Lifetime shortening in the 1:1 and 1:2 complexes with Xe is attributed to an enhancement of the rate of S_2–T_1 intersystem crossing by the external heavy atom effect. Excitation of the complexes to states with $E_{vib} > E_b$ produces energy-resolved fluorescence decays which exhibit sequential intramolecular vibrational redistribution–vibrational predissociation.

1. Introduction

Studies of the spectroscopy and dynamics of van der Waals (vdW) complexes of aromatic chromophores with rare gases and small molecules have provided valuable insights into the effects of solvation on the excited state properties of large molecules (see Ref. [1] for a review). Such complexes are characterized by binding energies on the order of a few hundred cm^{-1}, so that one-quantum excitation of even relatively low-frequency modes of the chromophore can result in a flow of vibrational energy to the low-frequency vdW modes of the complex (intramolecular vibrational energy redistribution, IVR),

followed by elimination of one or more rare gas atoms by the process of vibrational predissociation (VP) [2,3]. The direct measurement of the excited state dynamics of these complexes has been the subject of many recent experiments and supporting theoretical developments [3–7]. Vibrational quantum beats which result from the preparation of a coherent superposition of a small number of molecular eigenstates (restricted IVR) have been observed in several polyatomic molecules and in some of their van der Waals complexes [8], and provide a real-time view of the process of vibrational coupling and VP [1,9]. Such studies require, however, that the spectroscopy of the bare chromophore be well established in order to correctly assign the vibronic states produced on excitation and the product states resulting from predissociation.

Azulene, the chromophore of choice in the present study, has been the subject of long-standing spectroscopic and photophysical interest, in part be-

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cause its second excited singlet state has a lifetime, τ, in the 1–5 ns range, and it fluoresces relatively strongly ($\phi_f(S_2-S_0) \approx 0.04$ [10,11]). Demmer, Hager, Leach and Wallace (DHLW [8]) have previously examined the picosecond dynamics of the S_2 state of jet-cooled azulene, and have reported the observation of vibrational quantum interference effects in its spectrally resolved fluorescence decays on exciting to the $0^0 + 1315$ cm^{-1} level [8]. However, the interpretation of DHLW was based, in part, on ground state vibrational assignments of azulene which are now known to be incorrect. The implications of reassigning some of the lower state termini of the fluorescence which results from excitation to the $0^0 + 1315$ cm^{-1} level are reviewed here in light of our recent spectroscopic analysis of the dispersed S_2-S_0 emission spectra of azulene and related compounds [12].

We have recently examined the S_2-S_0 spectroscopy of the rare gas complexes of azulene [13]. The effects on the dynamics of the S_2 state of azulene produced by complexation with one or two atoms of Ar and Xe are examined in the present study.

2. Experimental

The dispersed emission spectra and fluorescence decay curves of jet-cooled azulene and its complexes with Ar and Xe were obtained using a picosecond pulsed laser and time-correlated single-photon counting system described in detail elsewhere [14,15]. Briefly, the excitation source was a cw mode-locked Nd:YAG laser (Spectra Physics, 3460), which synchronously pumped a cavity-dumped dye laser (Spectra Physics, Models 344 and 375B). The dye laser, operating on dcm, was cavity-dumped at a 4 MHz repetition rate, had output pulses with a temporal width of < 8 ps, a spectral bandwidth of ≈ 5 cm^{-1}, and an output power > 100 mW between 640 and 680 nm. The dye laser fundamental was frequency doubled by focusing it into a 10 mm thick LiIO$_3$ crystal with a 10 cm focal length lens, producing up to 10 mW of power in the ultraviolet. The UV beam was collimated prior to entering the expansion chamber, and was focussed to a 50 μm spot in front of the nozzle.

The expansion chamber consisted of a rectangular box evacuated by a high-capacity vapor booster pump. A continuous free-jet expansion was produced by seeding the vapor of the chromophore into a high-pressure of ultrahigh-purity He. In these experiments the He pressure was typically ≈ 20 psia, and the mixture was expanded through a heated ($\approx 80°C$) nozzle fitted with a 100 μm orifice. The laser beam crossed the expansion 1–2 mm downstream from the nozzle.

The resulting fluorescence was collected at right angles with a quartz doublet and focused onto the entrance slit of a 0.35 m monochromator (McPherson, 270). A Hamamatsu R1527 photomultiplier tube was used to obtain the dispersed emission spectra, and a Hamamatsu R2809U-02 microchannel plate photomultiplier was used to obtain the time-resolved fluorescence decay curves. The time-correlated single photon counting instrumentation and methods employed have been described in detail elsewhere [14]. Instrument response functions, typically 100 ps full width at half-maximum, were obtained by opening the expansion chamber to air and collecting the resulting Rayleigh scatter. Fluorescence decays were analyzed by convoluting a synthetic decay function with the measured instrument response function. The parameters of the synthetic decay function were adjusted until the best fit with the observed decay, as judged by the distribution of weighted residuals, was obtained. Single exponential lifetimes were reproducible to better than 5% in repeated experiments, and contain an estimated absolute error of no more than ±0.2 ns.

Azulene (Aldrich 99%) was used as received. Ultrahigh-purity He (99.999%) and high-purity Ar and Xe (99.995%) were obtained from Matheson and were also used as received.

3. Results and discussion

3.1. Picosecond dynamics of the S_2 excited state of azulene

Initially, the fluorescence lifetimes of azulene were determined by observing undispersed emission from all of the low and intermediate energy vibrational levels accessible by excitation in bands of the

S_2–S_0 spectrum having acceptable oscillator strength. Certain of these lifetimes, all of which exhibit single exponential decays, are given in Table 1 together with their S_2 vibrational assignments. The data are in good agreement with those of Woudenberg et al. [11] for the same excitation energies. Excitation to some states produced fluorescence which was sufficiently intense to permit the measurement of the temporal decay profiles of several bands in the dispersed fluorescence spectra. Single exponential fluorescence decays were observed for all except the $0^0 + 1315$ cm^{-1} excitation band which showed modulated fluorescence decay curves (i.e. quantum beats), in agreement with the previous results of DHLW [8].

In agreement with the previous work of DHLW [8], we observe two beat patterns, differing only in their modulation depth and relative phase, when monitoring the emission of individual bands in the fluorescence spectrum produced by exciting at 30072 cm^{-1} (origin $+ 1315$ cm^{-1}). Several strong bands (e.g. that at 3702 Å, which terminates at $E_{vib} = 3068 = (1457 + 1579)$ cm^{-1} in the ground state) exhibit fluorescence decays with a single modulation frequency of 2.75 ± 0.02 GHz. Fluorescence decays of bands which terminate in $E_{vib} = 1536$ cm^{-1} or $E_{vib} = 3113 = (1536 + 1579)$ cm^{-1} in the ground state have the same modulation frequency, but are 180° out-of-phase with respect to the beating observed for all other bands. DHLW assigned a $+ 1$ phase to the

beats which have a maximum at $t = 0$ (as determined by the instrument response profile), while those which are 180° out-of-phase were assigned to a $- 1$ phase and are referred to as 'phase-shifted'. Emission bands exhibiting a $+ 1$ phase arise from 'unredistributed' fluorescence, while those displaying a $- 1$ phase can be assigned to emission from states populated by IVR ('redistributed fluorescence'). The unredistributed fluorescence arises from optically active vibrational modes in S_2 which are directly accessible from $v = 0$ in the ground electronic state. The redistributed fluorescence, however, arises from $\Delta v = 0$ transitions among optically inactive or weakly active modes in S_2 which are populated via IVR. Only one beat frequency, corresponding to coupling of two of the coherent superposition of states prepared by the laser, is observed and the temporal evolution of the system thus corresponds to a case of 'restricted' IVR.

DHLW assigned the fluorescence bands with a $+ 1$ phase modulation to transitions terminating only in a_1 ground state levels, and assigned the two bands displaying a $- 1$ phase modulation to transitions terminating in $\nu_{27}''(b_1) = 1536$ cm^{-1} and a $\nu_{27}''(b_1)$ combination in the ground state. They therefore concluded that the dark upper state involved in IVR was 27^1, of b_1 character, implying the existence of an a_1–b_1 mode mixing mechanism. However, more recent work on the vibrational spectroscopy of azulene reveals that there are two errors in these assignments. First, DHLW based their ground state vibrational assignments on the jet-cooled spectra of Fujii et al. [16] and the IR spectra of Chao and Khanna [17] who, among other things, incorrectly assigned the 1536 cm^{-1} vibration to a b_1 mode. Second, DHLW assigned the $+ 1$ phase modulation of emission monitored at $- 1489$ cm^{-1} to a transition terminating in $\nu_7''(a_1)$ instead of $\nu_{28}''(b_1)$. We have recently concluded a detailed re-examination of the S_2–S_0 spectra of azulene and several of its simple derivatives [26], and have concluded that the 1536 cm^{-1} vibration is ν_7'', a very weakly active a_1 mode, in agreement with the recent work of Bree et al. [18] and Cable and Albrecht [19]. We have also reassigned several other vibrations so that the entire set of ground state vibrational wavenumbers is now consistent with recent measurements and calculations [20,21]. As a result, we are now able to provide

Table 1

Undispersed fluorescence lifetimes of some vibrational levels of the S_2 state of azulene

Displacement from 0^0 (cm^{-1})[a]	τ_f (ns)[b]	Assignment
0	3.56	0^0
237	3.35	39^1 (b_1)
370	3.25	17^1 (a_1)
608	2.77	39^1 (b_1) + 17^1 (a_1)
658	3.28	16^1 (a_1)
912	3.10	13^1 (a_1)
975[c]	2.60	12^1 (a_1)
989[c]	2.60	11^1 (a_1)
1145[c]	2.60	
1299[c]	2.60	
1315[c]	2.60	
1642[c]	2.00	

[a] The origin is 28752 cm^{-1}. The assignments are taken from Ref. [12].

[b] The absolute uncertainty in these values is ± 0.2 ns.

[c] These assignments are uncertain.

further information about the coupling mechanism which leads to IVR in azulene's S_2 state.

Table 2 presents the original results of DHLW [8], including the frequencies, the phases of the beats in the fluorescence decays of the various emission bands excited at $0^0_0 + 1315$ cm^{-1}, the assignments made by them, and the new assignments based on our previous publication [12] and the present analysis. With these new assignments in hand, one notes that emission excited at $+1315$ cm^{-1} having a $+1$ phase modulation may terminate in both a_1 and b_1 levels of the ground state, and that transitions having a -1 phase terminate in $\nu_7''(a_1)$ and its combination with $\nu_6''(a_1)$. Because redistributed fluorescence is only observed for vibrations in which $\Delta v > 0$ are absent (or very weak), and because only one modulation frequency is observed, the one upper state mode populated by IVR must be 7^1. Mode 7 is of a_1 character, but carries only a tiny fraction of the oscillator strength of the S_2–S_0 transition, and qualifies as an optically inactive mode solely because of its unfavorable Franck–Condon factors for $\Delta v > 0$ transitions. Because the majority of the oscillator strength of the S_2–S_0 transition is carried by other a_1 modes, acquired by first order $S_2(^1A_1)$–$S_4(^1A_1)$ vibronic coupling [21], the restricted IVR leading to redistributed fluorescence can therefore be associated

with mode mixing within the a_1 manifold. Finally, the observation of a b_1 terminus among the unredistributed fluorescence bands suggests that $S_2(^1A_1)$–$S_3(^1B_1)$ vibronic coupling also contributes significantly to the upper state populated by excitation at $+1315$ cm^{-1}, and that the vibrational scrambling observed in the S_2–S_0 spectrum may therefore be more complex than suggested by Lawrance and Knight [21].

3.2. Picosecond dynamics of the S_2 states of azulene · Ar and azulene · Xe

Allowing for differences in resolution, the dispersed emission spectra (cf. Refs. [12,13]) resulting from excitation in the S_2–S_0 origin bands of Az · Ar$_1$ and Az · Xe$_1$ are identical to those of azulene itself except that they are offset to the red by the measured shifts in the corresponding excitation spectra [12,13]. Thus, the van der Waals complexes of azulene are similar to those of many other polyatomic organic substrates, in that the three low-frequency (van der Waals) vibrations introduced by complexing each adatom are only weakly coupled to the higher frequency, optically active vibrations of the chromophore.

The temporal profiles of the undispersed fluorescence obtained from the zero point and other selected S_2 levels of the 1:1 and 1:2 complexes of Ar and Xe with Az were measured by exciting in the strongest bands of the corresponding S_2–S_0 excitation spectra. (Due to weak signal intensities, only the time-resolved emission of the zero point levels could be measured for Az · Ar$_2$ and Az · Xe$_2$.) When the excitation energies are such that the resulting vibrational energy is less than the binding energy of the complex ($E_{vib} < E_b$, vide infra), these temporal profiles are all well represented by single exponential decay functions convoluted with the measured instrument response function. No measurable risetime is found. These lifetime data are compiled in Table 3 and are compared to the undispersed fluorescence lifetimes of bare Az excited to the same levels. In all cases, the measured lifetime decreases upon complexation with one atom of Ar or Xe (although the changes for Ar are not statistically significant) and decreases further upon adding a second adatom, for

Table 2
Energy and time-resolved modulated fluorescence decay data for bare azulene excited to the $0^0 + 1315$ cm^{-1} level, the original assignments of DHLW, and the revised assignments

Displacement from 0_0 (cm^{-1})	DHLW [a] assignment	Phase [a]	New assignments [b]
0	–	$+1$	
676	$16_1 (a_1)$	$+1$	
816	$15_1 (a_1)$	–	
894	$14_1 (a_1)$	–	
1405	$9_1 (a_1)$	$+1$	
1447	$8_1 (a_1)$	–	
1489	$7_1 (a_1)$	$+1$	$28_1 (b_1)$
1538	$27_1 (b_1)$	-1	$7_1 (a_1)$
2979	$9_1 6_1 (a_1)$	–	
3016	$8_1 6_1 (a_1)$	–	
3068	$7_1 6_1 (a_1)$	$+1$	$28_1 6_1 (b_1)$?
3113	$27_1 6_1 (b_1)$	-1	$7_1 6_1 (a_1)$

[a] Taken from Ref. [8]. The assignments are based on the work of Fujii et al. [16] and Chao and Khanna [17].
[b] These assignments are based on the work discussed in Ref. [12].

Table 3
Undispersed fluorescence lifetimes of azulene, azulene·Xe and azulene·Ar excited to selected S_2 vibrational states

Displacement from 0^0 (cm^{-1})	τ_f (ns) [a]	Assignment
azulene [b]		
0	3.56	0^0
370	3.25	17^1 (a_1)
658	3.28	16^1 (a_1)
azulene–Ar [c] 1:1		
0	3.49	
370	3.24	
658	3.13	
azulene–Ar [c] 1:2		
0	3.37	
azulene–Xe [d] 1:1		
0	2.82	
370	3.09	
658	2.84	
azulene–Xe [d] 1:2		
0	2.54	

[a] The absolute uncertainty in these values is ±0.2 ns.
[b] Origin at 28752 cm^{-1}.
[c] Origin at 28733 cm^{-1}.
[d] Origin at 28707 cm^{-1}.

the same excited state vibrational energy, including $E_{\mathrm{vib}} = 0$.

There are two possible explanations for the fact that the measured lifetimes decrease as one and then two atoms are complexed to the chromophore, and that Xe causes a larger decrease than Ar. Both involve the effect of complexation on the rates of radiationless decay of the S_2 state. Consider first S_2–S_1 radiationless relaxation (internal conversion, IC), which accounts for the vast majority of S_2 decay events in bare azulene at low E_{vib} ($\phi_f = 0.04$ [10,11]). The rate of S_2–S_1 internal conversion is known to be sensitive to the S_2–S_1 energy gap which, in turn, is affected by solvent [10]. The S_2–S_1 energy gap decreases with increasing solvent–solute interaction energy in the bulk, and there is every reason to believe that the same holds true for microscopic solvation in small van der Waals complexes. Thus Xe, with the larger polarizability, will cause a greater decrease in the S_2–S_1 energy gap than Ar, and two atoms will have greater effect than one. However, radiationless transition theory predicts that if the system is in the statistical limit, then the rate

should increase exponentially with decreasing energy gap, in accordance with the energy gap law [22]. The microscopic solvent shifts are small and additive, so the changes in the S_2–S_1 energy gap and the changes in the rates should double when the second rare gas atom is complexed. However, the effect of adding one or two Ar atoms is negligible compared with one or two Xe atoms, despite the fact that their microscopic solvent shifts of Ar and Xe only differ by about a factor of two. Moreover, given the slope of the energy gap law correlation for Az in solution ($\Delta k_{\mathrm{IC}}/\Delta E = 5 \times 10^5$ s^{-1} cm at this energy [10]), the decrease in the S_2–S_1 energy gap induced by two rare gas atoms is almost certainly too small to account for the substantial increases in the radiationless transition rates observed in Az·Xe$_1$ and Az·Xe$_2$.

The alternative explanation for the effects observed in the azulene–rare gas system involves an enhancement of the rate of intersystem crossing (ISC) by complexation. Amirav et al. have observed an external heavy atom effect in the van der Waals complexes of tetracene, in which the probability of S_1–T_1 ISC increases in the rare gas series from Ar to Xe [6]. The effects of Ar and Xe on the lifetimes of the S_2 states of azulene and its 1:1 and 1:2 van der Waals complexes at $E_{\mathrm{vib}} < E_b$ can also be interpreted in terms of an external heavy atom effect.

The qualitative effect of increased triplet yield and decreased S_2 lifetime when azulene is examined in a Xe matrix has been known for several decades. Previous work in our laboratory on substituted azulenes in bulk solution [10] has shown that spin–orbit coupling between the S_2 state and the triplet manifold is enhanced by intramolecular heavy atom effects. T_1 is the most likely final electronic state since spin–orbit coupling between S_2 and T_2 is expected to be very much weaker on orbital symmetry grounds [23]. (Strong spin–orbit coupling between S_2 and T_3 also is possible if T_3 lies below S_2, but the location of T_3 is not known.) An external heavy atom effect on the lifetime of S_2 is observed when azulene is dissolved in several heavy atom-containing bulk solvents [10,24] or is trapped in Ar or Xe matrices [25], and results in an enhancement of the S_2–T_1 intersystem crossing process.

The heavy atom effect is generally understood to be associated with a contribution of the 'solvent' to the spin–orbit coupling term in the Hamiltonian of

the system, the magnitude of which increases rapidly with increasing atomic number of the solvent atom(s) [26,27]. Standard perturbation treatments [28] predict that the change in ISC rate of a given aromatic hydrocarbon due to the heavy atom effect, $\Delta\text{Rate}(X)$, should scale as $\zeta^2(X)$, the square of the spin–orbit coupling constant of a perturbing heavy atom, X, placed a fixed distance from the chromophore's surface. If this distance were the same in all three 1:1 rare gas complexes studied here, one would predict:

$$\Delta\text{Rate}(\text{Xe}):\Delta\text{Rate}(\text{Kr}):\Delta\text{Rate}(\text{Ar})$$

$$= \zeta^2(\text{Xe}):\zeta^2(\text{Kr}):\zeta^2(\text{Ar}) = 56:14:1. \qquad (1)$$

(Values of the spin–orbit coupling constants are taken from McGlynn et al. [28].)

However, the equilibrium van der Waals distances in rare gas–aromatic hydrocarbon complexes actually increase in the Ar–Xe series, so the rate-enhancing effect of complexing one rare gas atom should scale by a factor somewhat smaller than ζ^2. Quantitative measurements on benzene show that its rate of S_1–T_1 ISC is a factor of 10–100 faster in Xe than in Ar matrices at 4 K [26]. In addition, the lifetime of the S_1 state of tetracene is decreased by factors of 4.5 and > 10 on adding one Kr and one Xe atom, respectively, compared with one Ar atom in its vdW complexes [6]. Both observations are in order-of-magnitude agreement with the expectation that the ratios of the changes in the rates of intersystem crossing should scale by factors somewhat smaller than the ratios of the values of ζ^2 for the rare gas atoms.

In the present work when azulene and its complexes are excited to their zero-point levels, the addition of one Ar atom has no statistically significant effect ($\Delta\tau(1) = 0.07$ ns). However, one Xe atom decreases the lifetime by 21% ($\Delta\tau(1) = 0.74 \pm 0.2$ ns), whereas addition of two Ar atoms decreases the lifetime by 5% ($\Delta\tau(2) = 0.19 \pm 0.2$ ns), compared with the bare molecule, and two Xe atoms decrease the lifetime by 29% ($\Delta\tau(2) = 1.02 \pm 0.2$ ns). The minimal effect of Ar is compatible with expectations based on an external heavy atom effect model, but the small effect of Xe on the S_2 decay rates of azulene compared with those found for the S_1 states of tetracene (in its vdW complexes [6]) and of benzene and other aromatic hydrocarbons (in con-

densed media [26]) requires explanation. In the S_1 states of tetracene and benzene the dominant radiationless decay process is S_1–T_1 ISC [28], whereas in the S_2 state of azulene radiationless decay is almost exclusively internal conversion (most likely S_2–S_1 [10,11], but possibly S_2–S_0 at higher E_{vib} [29]). Thus, the heavy atom effect will directly enhance the major excited state relaxation process in tetracene and benzene, but will only affect a minor process in azulene. Nevertheless the relative changes in the decay rates of azulene induced by one or two Ar or Xe atoms can still be treated quantitatively in terms of an external heavy atom effect.

If the external heavy atom effect involves mixing of the singlet and triplet manifolds of the chromophore via a mechanism involving neutral excitations of the heavy atom, then the addition of a second atom to the chromophore would be expected [6] to have almost the same effect as that of the first-complexed atom in a geometrically equivalent position, i.e. $\Delta\tau(2):\Delta\tau(1) = 2:1$. On the other hand, if mixing is via charge transfer states involving specific pair interactions, then the addition of the first atom is expected to produce the largest effect. The latter mechanism appears to prevail in tetracene–rare gas complexes, whereas both spin–orbit coupling mechanisms may be operative in pentacene–Kr_n [6]. In the present system, if only the zero-point lifetimes are compared, the data for Ar ($\Delta\tau(2)/\Delta\tau(1) = 2.7$) have no statistical significance, and for Xe $\Delta\tau(2)/\Delta\tau(1) = 1.4$. However, if the entire data set (Table 3) is used and lifetimes of states with the same vibrational energy content are compared, the average effect of adding one Xe atom is $\Delta\tau(1) = 0.44$ ns, yielding $\Delta\tau(2)/\Delta\tau(1) = 2.3$, a value which is, within experimental error, equal to the value of 2 expected for the neutral excitation mixing mechanism.

The azulene complexes described above provide an illuminating contrast with the more thoroughly investigated rare gas complexes of 9,10-dichloroanthracene in which the excited state lifetime *increases* slightly with the number and polarizability of the adatoms [7,30,31], and is sensitive to the geometric arrangement of the solvent atoms around the chromophore. However, the S_1 state in the 9,10-dichloroanthracene system decays exclusively by radiative means (the S_1–S_0 fluorescence quantum yield

is close to unity in the bare molecule and its rare gas complexes), and its lifetimes are modified only by interactions between the multicenter transition monopoles of the chromophore and the transition dipoles of the rare gas atoms [7]. The yield of triplets is negligible, and the rate of radiationless decay and the excited state lifetimes are therefore unaffected by the presence of heavy atoms.

3.3. IVR and vibrational predissociation in the S_2 states of azulene · Ar and azulene · Xe

The excitation of bare azulene to its $0^0 + 1315$ cm^{-1} level produces quantum interference effects in its time-resolved fluorescence decays [8]. It was therefore of interest to examine the complexes of azulene at the same E_{vib}. The dispersed emission spectrum of Az · Xe$_1$ excited in the $0^0 + 1315$ cm^{-1} level of the complex is shown in Fig. 1 and is compared with that of bare Az excited to the same vibrational energy. At 1315 cm^{-1} the initial vibrational energy content is well above the binding energy of the excited complex ($E_b \approx 1000$ cm^{-1}, vide infra), and it is therefore expected that excitation will be followed by dissociation which is (in this case, vide infra) faster than the lifetime of the excited chromophore. By comparing the spectrum of Fig. 1 with the dispersed emission spectrum resulting from excitation in the Az · Xe$_1$ S_2–S_0 origin [13], it may be seen that the strong bands in the spectrum resulting from excitation to the $0^0 + 1315$ cm^{-1} level in the complex are not offset to the red by the differential microsolvation energy. The majority of the emission is therefore produced from bare excited Az.

Time-resolved fluorescence profiles were obtained by exciting the Az · Xe$_1$ complex at $0^0 + 1315$ cm^{-1} and monitoring the emission in several of the strong bands. The time-resolved profile measured at 3708 Å (26969 cm^{-1}) is shown in Fig. 2. The quantum beats which are observed in bare azulene at this wavelength are missing when the bare molecule is monitored following excitation of the complex to the same E_{vib}. All of the measured time-profiles can be well described by a two-component emission function convoluted with the measured instrument response. The minor, short-lived component of the emission grows in at the same rate as the excitation pulse and decays exponentially with a time constant
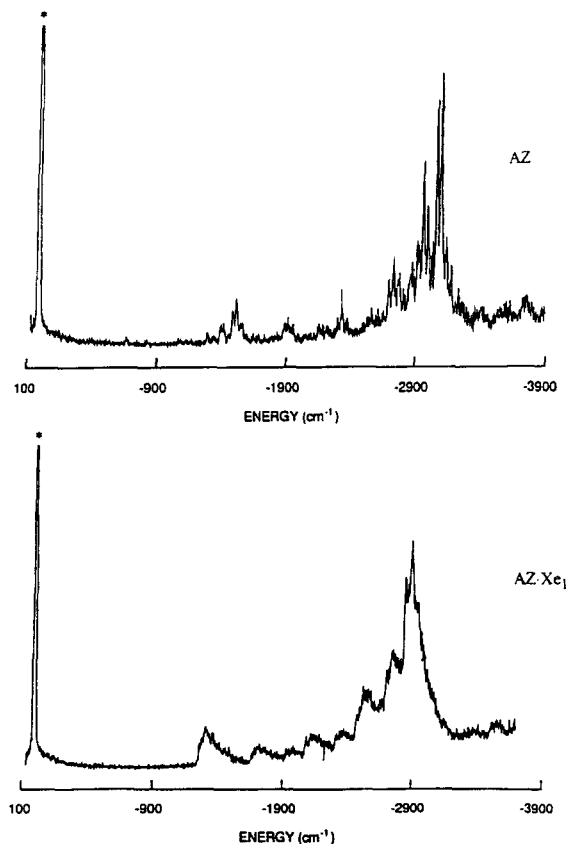

Fig. 1. Dispersed fluorescence spectra following excitation to the $0^0 + 1315$ cm^{-1} levels in the S_2 states of Az and Az·Xe$_1$. The fluorescence bands in resonance with the laser excitation are marked with asterisks. The spectral resolution is 2 Å.

$\tau_1 = 1/\Gamma_1$, and the major, longer-lived component has a rise time equal to $1/\Gamma_1$ and an exponential decay time $\tau_2 = 1/\Gamma_2$. The unconvoluted fluorescence decay profile of the short-lived component is thus described by

$$I_1(t) = a_1\{\exp(-\Gamma_1 t)\}, \qquad (2)$$

whereas the fluorescence profile of the major component is described by the function

$$I_2(t) = a_2\{-\exp(-\Gamma_1 t) + \exp(-\Gamma_2 t)\}. \qquad (3)$$

The total emission is given by

$$I_T(t) = I_1(t) + I_2(t). \qquad (4)$$

Convolution of the instrument response function with Eq. (4) was continued iteratively using trial values of the adjustable parameters in Eqs. (2) and (3) until the
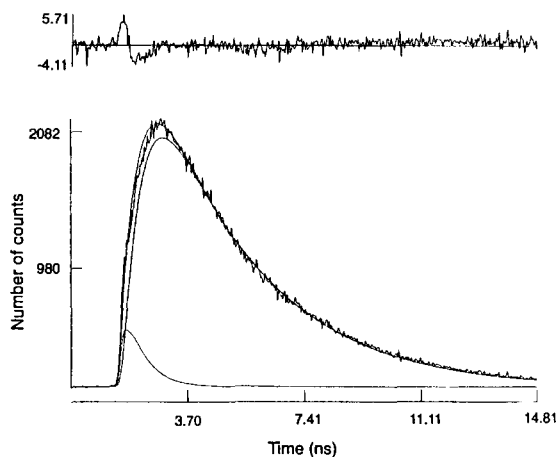
Fig. 2. Time-resolved fluorescence profile obtained by exciting $Az \cdot Xe_1$ to the $0^0 + 1315$ cm^{-1} level of the S_2 state. The detection wavelength is 3708 Å. The best fit of the measured profile to a synthetic rise and decay function is found for a rise time of 0.60 ± 0.02 ns and a decay of 3.1 ± 0.2 ns. $\chi_r^2 = 2.50$. The distribution of weighted residuals for the fit is shown above the decay curve.

synthetic function produced the best fit to the total measured time-resolved normalized fluorescence profiles. For the profile of Fig. 2, the best fit is obtained with $\tau_1 = 1/\Gamma_1 = 0.60 \pm 0.02$ ns, $\tau_2 = 1/\Gamma_2 = 3.1 \pm 0.2$ ns, and $a_1/a_2 = 0.05$ (cf. Fig. 2). This value of a_1/a_2 is consistent with the fact that the dispersed fluorescence spectrum consists largely of emission from bare azulene. (Note, however, that larger values of a_1/a_2 are expected for transitions with more favorable ratios of Franck–Condon factors, and are found when the temporal profiles of other emission bands are measured [32].)

Resolved emission could not be obtained for excitation of the $0^0 + 1315$ cm^{-1} level of the Az · Ar$_1$ complex due to interference with the nearby $0^0 + 1299$ cm^{-1} band of the bare molecule. However, a clean emission spectrum for Az · Ar$_1$ was obtained by exciting the complex at the $0^0 + 1145$ cm^{-1} level. This spectrum is displayed in Fig. 3 along with the emission spectrum of bare Az excited to the same vibrational energy. The time-resolved fluorescence profile for this complex, obtained by monitoring at 3708 Å, is shown in Fig. 4. As with Az · Xe$_1$, the spectrum shows that the majority of the emission terminates in the ground state levels of bare Az. The time-resolved fluorescence shows a rise time $\tau_1 =$

0.75 ± 0.02 ns, a decay time $\tau_2 = 3.0 \pm 0.2$ ns, and a value of $a_1/a_2 = 0.13$.

The temporal evolution of the excited species following excitation of the Az · Ar$_1$ and Az · Xe$_1$ complexes to their $0^0 + 1145$ and $0^0 + 1315$ cm^{-1} levels, respectively, can be described by a model in which intramolecular vibrational redistribution involving energy transfer from the optically active modes in the chromophore to the vdW modes of the complex precedes dissociation [2,3]. We first note that, at these excitation energies, $E_{vib} > E_b$ in both complexes. The binding energy in the excited state can be roughly estimated by adding the observed red-shift to the calculated ground state binding energy. Using our previously calculated ground state
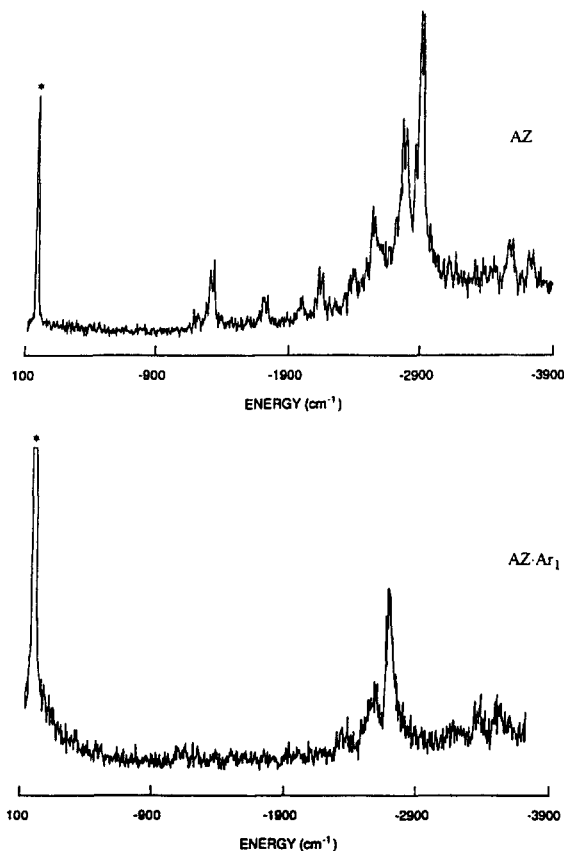

Fig. 3. Dispersed fluorescence spectra obtained by exciting to the $0^0 + 1145$ cm^{-1} levels in the S_2 states of Az and Az · Ar$_1$. The fluorescence bands in resonance with the laser excitation are marked with asterisks.
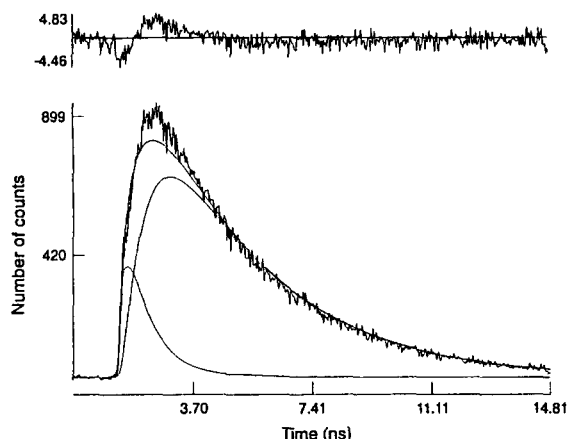
Fig. 4. Time-resolved fluorescence obtained by exciting the Az·Ar$_1$ complex to the $0^0 + 1145$ cm^{-1} level of its S$_2$ state. The detection wavelength is 3708 Å. The best fit of the measured profile to a synthetic rise and decay function is found for a rise time of 0.75 ± 0.02 ns and a decay of 3.0 ± 0.20 ns. The distribution of weighted residuals for the fit is shown above the decay curve.

binding energies [13], the binding energies of the rare gas atoms in the S$_2$ states of Az·Ar$_1$ and Az·Xe$_1$ should therefore be ≈ 586 and 889 cm^{-1}, respectively. However, based on observations in other systems [33], the binding energies calculated using various models (including the Lennard-Jones 6-12 model used by us [13]) are often about 15% smaller than those obtained by accurate experimental measurement. Therefore, the true binding energies of the rare gas atoms in the S$_2$ states of Az·Ar$_1$ and Az·Xe$_1$ are expected to be about 700 and 1000 cm^{-1}, respectively. Thus Az·Ar$_1$ exhibits a single exponential undispersed fluorescence decay following excitation to its $0^0 + 658$ cm^{-1} level, typical of a stable complex in the excited state, but excitation of the Az·Ar$_1$ and Az·Xe$_1$ complexes to their $0^0 + 1145$ and $0^0 + 1315$ cm^{-1} levels, respectively, results in fluorescence from systems in which, initially, $E_{vib} > E_b$.

We therefore assign the short-lived emission to the vibronically excited complex, which contributes only a small fraction of the total emission because it dissociates, following IVR, on a subnanosecond timescale. The source of the major, long-lived component of the emission is the bare excited molecule which is produced with a vibrational energy equal to

the difference between E_{vib} and $(E_b + E_{trans})$. The values of τ_2 (≈ 3 ns) obtained for both the Az·Ar$_1$ and Az·Xe$_1$ complexes is typical of the decay times of electronically excited bare azulene containing up to a few hundred wavenumbers of vibrational energy (cf. Table 1 and Ref. [11]).

In this analysis, the rise time of the emission of bare Az is assumed to be identical to the decay time of the complex. An attempt was made to observe the time-resolved fluorescence profile of Az·Xe directly by exciting at $0^0 + 1315$ cm^{-1} and monitoring the emission at 3710 Å. At this wavelength, 45 cm^{-1} to the red of the strong emission band of bare Az at 3708 Å (Fig. 1), emission which is red-shifted by the microscopic solvent shift produced by one Xe atom should be observed [13]. The emission at this wavelength was too weak to obtain a statistically meaningful temporal profile, but was observed to decay much faster than that of bare Az. Despite our inability to quantify the rate of decay of the excited complex directly, it is reasonable to interpret these observations in terms of a simple model in which Az·Xe is excited to a vibrational level in S$_2$ which lies above the dissociation threshold of the complex and which decays by sequential IVR and vibrational predissociation, leaving the bare excited molecule in a state which is depleted in energy by the sum of E_b and the translational energy of the separating species.

After excitation the vibrational energy, which is initially localized in optically active modes of the chromophore, is redistributed to the optically inactive 'bath' modes of the chromophore and the vdW modes of the complex. At vibrational energies of the complex where the coupled modes constitute an effective continuum, the rate of the redistribution step which excites the vdW modes is given by the Golden Rule expression [34]:

$$\Gamma = 2\pi\hbar^{-1}\Sigma\langle i|V|f\rangle^2\rho(E_f). \tag{5}$$

In Eq. (5), i is the initially prepared level containing one or more quanta in an optically active mode of the chromophore which is coupled to the manifold of final levels, f, in which the vdW modes are excited, and $\rho(E_f)$ is the density of final vibrational states. V is the nuclear kinetic energy operator which couples the chromophore and vdW vibrations. For planar

molecules like azulene, in which the vdW partner is situated above the plane, perturbation treatments predict that the out-of-plane vibrations of the chromophore will couple most effectively to the vdW vibrations [5]. Preferential coupling such as this should, in principle, result in measurable complexation-induced shifts in the frequencies of those out-of-plane vibrations that are most strongly coupled. Unfortunately, spectral complexity in many of the regions probed in these systems precludes such an observation, and the only transitions which are strong enough to produce observable spectrally and temporally resolved fluorescence populate a_1 upper state vibrations.

In terms of the above model, the rise times of emission from the bare chromophore in the time-resolved fluorescence profiles of the $Az \cdot Ar_1$ and $Az \cdot Xe_1$ systems, 0.75 ± 0.02 and 0.60 ± 0.02 ns, respectively, may be taken as the times required for the slowest step in the overall dissociation process. The slow step could be either IVR or VP, but the observation of emission mainly from the bare chromophore with lifetimes characteristic of an energy-depleted species, suggests that IVR, i.e. the transfer of some energy from the chromophore to the low-frequency vdW modes, is the slow step in these cases. Assuming this is correct, then complexes which pass the initial IVR bottleneck must subsequently undergo complete, rapid vibrational energy randomization and (if the total vibrational energy is greater than the binding energy) dissociation. The rates of VP are a function of $\rho(E_f)$ and $(E_{vib} - E_b)$ and can be calculated using RRKM theory [1,7]. Rates faster than the rise times of the fluorescence of bare azulene observed here are consistent with such calculations on other vdW molecules containing one rare gas atom [15].

The absence of beats in the fluorescence decay of the azulene–rare gas complexes might suggest that coupling between the vdW modes and the optically active chromophore modes is stronger than the coupling between the optically active vibrations and the optically inactive vibrations which participate in IVR in the bare molecule. If this is the case, the increased density of states produced by complexation would cause the molecule to move out of the regime in which restricted IVR occurs, toward the dissipative, statistical limit [9] and would eliminate observable

quantum interference. However, it is much more difficult to identify the cause of the disappearance of beating than it is to interpret the retention of beat-modulated resonance fluorescence [35] in vdW molecules excited above E_b.

Acknowledgements

References

[1] S. Sun and E.R. Bernstein, J. Phys. Chem. 100 (1996) 13348.

[2] D.H. Semmes, J.S. Baskin and A.H. Zewail, J. Chem. Phys. 92 (1990) 3359.

[3] M.R. Nimlos, M.A. Young, E.R. Bernstein and D.F. Kelley, J. Chem. Phys. 91 (1989) 5268.

[4] D.F. Kelley and E.R. Bernstein, J. Phys. Chem. 90 (1986) 5164.

[5] P.M. Weber and S.A. Rice, J. Chem. Phys. 88 (1988) 6120.

[6] A. Amirav, U. Even and J. Jortner, Chem. Phys. Lett. 67 (1979) 9.

[7] E. Shalev, N. Ben-Horin and J. Jortner, J. Chem. Phys. 94 (1991) 7757.

[8] D.R. Demmer, J.W. Hager, G.W. Leach and S.C. Wallace, Chem. Phys. Lett. 136 (1987) 329, and references therein.

[9] P.M. Felker and A.H. Zewail, Phys. Rev. Lett. 53 (1984) 501.

[10] B.D. Wagner, D. Tittelbach-Helmrich and R.P. Steer, J. Phys. Chem. 96 (1992) 7904.

[11] T.M. Woudenberg, S.K. Kulkarni and J.E. Kenny, J. Chem. Phys. 89 (1988) 2789.

[12] O.K. Abou-Zied, H.K. Sinha and R.P. Steer, J. Mol. Spectrosc., in press.

[13] O.K. Abou-Zied, H.K. Sinha and R.P. Steer, J. Phys. Chem. 100 (1996) 4375.

[14] D.R. Demmer, G.W. Leach, E.A. Outhouse, J.W. Hager and S.C. Wallace, J. Phys. Chem. 94 (1990) 582.

[15] E.A. Outhouse, G.R. Bickel, D.R. Demmer and S.C. Wallace, J. Chem. Phys. 95 (1991) 6261.

[16] M. Fujii, T. Ebata, N. Mikami and M. Ito, Chem. Phys. 77 (1983) 191.

[17] R.S. Chao and R.K. Khanna, Spectrochim. Acta 33A (1977) 53.

[18] A. Bree, A.J. Pal and C. Talliani, Spectrochim. Acta 46A (1990) 1767.
[19] J.R. Cable and A.C. Albrecht, J. Chem. Phys. 84 (1986) 1969.
[20] F. Negri and M.Z. Zgierski, J. Chem. Phys. 99 (1993) 4318, and references therein.
[21] W.D. Lawrance and A.E.W. Knight, J. Phys. Chem. 94 (1990) 1249.
[22] R. Englman and J. Jortner, Mol. Phys. 18 (1970) 145.
[23] M.S. El-Sayed, J. Chem. Phys. 38 (1963) 2834.
[24] G. Eber, S. Schneider and F. Dörr, Chem. Phys. Lett. 52 (1977) 59.
[25] G.W. Robinson and R.P. Frosch, J. Chem. Phys. 38 (1963) 1187.
[26] G.W. Robinson, J. Mol. Spectrosc. 6 (1961) 58.
[27] M. Kasha, J. Chem. Phys. 20 (1952) 71.
[28] S.P. McGlynn, T. Azumi and M. Kinoshita, Molecular spectroscopy of the triplet state (Prentice-Hall, Englewood Ciffs, NJ, 1969) p. 183 ff.
[29] Y. Hirata and E.C. Lim, J. Chem. Phys. 69 (1978) 3292.
[30] A. Penner, A. Amirav, J. Jortner and A. Nitzan, J. Chem. Phys. 93 (1990) 147.
[31] E. Shalev and J. Jortner, Chem. Phys. Lett. 178 (1991) 31.
[32] O.K. Abou-Zied and R.P. Steer, unpublished results.
[33] J. Boesiger and S.L. Leutwyler, Chem. Phys. Lett. 126 (1986) 238.
[34] S. Mukamel and J. Jortner, in: The excited state, Vol. III, ed. E.C. Lim (Academic Press, New York, 1977) p. 57.
[35] A.J. Kaziska and M.R. Topp, Chem. Phys. Lett. 180 (1991) 423.