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Van der Waals Complexes of 2-Chloro-, 2-Methyl-, and 1,3-Dimethylazulene with Rare Gases: Microscopic Solvent Shifts, Structures, and Binding Energies

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The $S_2-S_0(^1L_a)$ fluorescence excitation and emission spectra of the van der Waals complexes of three azulene (Az) derivatives, 2-chloroazulene (ClAz), 2-methylazulene (MAz), and 1,3−dimethylazulene (DMAz), with the rare gases, Ar, Kr, and Xe, have been measured under jet-cooled conditions. The microscopic solvent shifts, $\delta\bar{\nu}$, of the origin bands in the S_0-S_2 spectra associated with complexation of the chromophores with one and two rare gas atoms increase with increasing polarizability of the adatom(s), consistent with the dominance of dispersion in the binding. Although there are substantial variations in the relative values of $\delta\bar{\nu}$ among the Az derivatives examined, all of the $\delta\bar{\nu}$ values are relatively small and are similar to those of the $^1L_b(S_0-S_1)$ transitions in the rare gas complexes of naphthalene and its methyl-substituted derivatives. The theory of microscopic solvent shifts of Jortner *et al.* has been used to analyze the solvent shift data. Comparisons of the sources of the oscillator strengths and van der Waals binding interactions in the azulene− and naphthalene−rare gas systems are revealing and suggest that the variations in $\delta\bar{\nu}$ with substitution pattern are primarily electronic in their origin and arise from variations in excited state configuration interactions, the magnitude of which depend on the S_2-S_n energy spacings. These spacings can be varied by placing substituents either along the long axis (2-position) or parallel to the short axis(1,3-positions) so that they selectively perturb, respectively, the long axis polarized and the short axis polarized transitions. The structures and binding energies of the complexes of these derivatives have also been modeled using Lennard-Jones type calculations and have been compared with those of Az itself. The observed progressions in the low-frequency intermolecular vibrations in each case are assigned to that excited state bending mode which is parallel to the long axis of the chromophore, in agreement with model calculations using one-dimensional Morse and Taylor's series potential functions.

Introduction

Azulene is the first-discovered and best-known organic compound exhibiting relatively intense anomalous fluorescence ($S_2 \rightarrow S_0$) from a higher excited electronic state in violation of what became known as Kasha's Rule in the early days of photophysics.[1] Recent experiments supplemented by high-level theoretical calculations have been instrumental in building a detailed understanding of the spectroscopy and excited state dynamics of azulene,[2−12] so the origins of this fluorescence anomaly are now well understood. Fluorescence quantum yields of a few percent are observed because the rate of S_2's radiative decay is enhanced by coupling with still higher electronic states whereas its competing radiationless decay processes, both intersystem crossing and internal conversion, are unusually slow. Weak spin−orbit coupling with the triplet manifold inhibits intersystem crossing from low-lying vibrational states of S_2 in all but heavy-atom-substituted derivatives. The slow rate of internal conversion is associated with the nonalternant structure of azulene which results in S_2-S_1 and S_1-S_0 electronic energy gaps that are large and comparable in magnitude. Unlike S_1, which undergoes rapid internal conversion to S_0 because of S_1-S_0 conical intersection, S_2 apparently does not intersect the S_1 surface and conforms to the weak coupling case of radiationless transition theory. The rate of S_2-S_1 internal conversion is thus strongly Franck−Condon inhibited, as expected when the S_2-S_1 gap is large. Azulene's alternant isomer, naphthalene, on the other hand, has more conventional electronic state spacings and is "well behaved".[13,14]

Using this background, our previous investigations of the effects of solvents and substituents on the nonradiative relaxation rates of the excited states of azulene in bulk condensed media have shown that the S_2 and S_1 decay rates depend primarily on the magnitudes of the S_2-S_1 and S_1-S_0 energy gaps, respectively, in accordance with the energy gap law, but are otherwise independent of the nature of the solvents or substituents (excluding heavy atoms).[2,3,15] We are now investigating the nature of these solute−solvent interactions at the molecular level, and our initial results indicate certain parallels between the condensed and gas phases.

In a recent publication we showed that the relatively small shifts in the energies of the $S_0-S_2(^1L_a)$ transitions of azulene produced by complexation with the rare gases are comparable to those observed for the $S_0-S_1(^1L_b)$ transitions of naphthalene and its rare gas complexes.[10] In naphthalene the ^1L_b transition is of modest intensity (oscillator strength $f = 0.003$) and can be described in terms of the out-of-phase superposition of two zero-order one-electron excitations, a situation which results in extensive cancellations of the effects of excited-state intermolecular dispersive interactions.[17] As a result, the solvent shifts measured for the ^1L_b transitions in the naphthalene•rare gas complexes are considerably smaller than those associated with the ^1L_a excitations of other alternant aromatic molecules. Previous work has shown that the ^1L_a excitation (S_0-S_2) in azulene correlates, in at least some respects, with the ^1L_b excitation of naphthalene. It thus seems reasonable to ask if the small spectral shifts measured in the S_0-S_2 spectra of

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azulene•rare gas complexes might also be due to such cancellation effects.[10]

It is well-known that the electron distributions and energies of the ^1L_a and ^1L_b states of the polycyclic aromatic hydrocarbons are sensitive to the nature and position of their substituents.[18] For example, substitution at the 2- and 3-positions in naphthalene stabilizes the ^1L_b state more than the ^1L_a state and increases the separation between them. On the other hand, substitutions at the 1,2- or 1,4-positions stabilize ^1L_a more than ^1L_b, resulting in a narrowing of the spacing between the two states and a greater interaction between them. Recently Leutwyler *et al.*[19,20] reported that 2,3-dimethylnaphthalene•Ar has a spectral shift of only -4.4 cm^{-1}, whereas the shifts for 1,2-dimethylnaphthalene•Ar and naphthalene•Ar are $+11.5$ and $+14$ cm^{-1}, respectively, but did not comment on their magnitude. It therefore seems reasonable to ask if the differences in these solvent shifts have their origins in changes in the extent of $^1L_a-{}^1L_b$ mixing or if they have some other explanation. Since a similar pattern is evident in the $S_0-S_2(^1L_a)$ transitions of azulene and its derivatives,[10] it also seems reasonable to ask if there is a parallel with that observed for the $S_0-S_1(^1L_b)$ transitions in the naphthalene system.

In this paper we examine this important parallelism in the spectroscopic behavior of azulene and naphthalene by examining the jet-cooled spectra of three azulene derivatives, 2-chloroazulene, 2-methylazulene, and 1,3-dimethylazulene, and their van der Waals complexes with the rare gases Ar, Kr, and Xe. We compare their microscopic spectral shifts with those of azulene itself and with some simple naphthalene derivatives.

Experimental Section

The S_2-S_0 fluorescence excitation and dispersed emission spectra were obtained using a pulsed supersonic free-jet expansion and laser excitation. The details of the experimental apparatus and techniques employed have been described in detail elsewhere.[22,23] Briefly, the vapor from a heated solid sample of the three azulene derivatives was entrained in a stream of ultrapure He backing gas. Typical operating conditions were $P(\mathrm{He}) = 1-3$ bar, $T(\mathrm{inlet}) = 40-60$ °C, repetition rate $= 20$ Hz, and nozzle diameter $= 0.5$ mm. The van der Waals complexes were synthesized by premixing desired partial pressures of the rare gas with He in a 10 dm^3 cylinder, seeding the vapor of the chromophore into the flowing rare gas mixture and expanding the lot into a high vacuum chamber evacuated by an 8 in. diffusion pump. Partial pressures of the He, added rare gas, and solid were adjusted to obtain signals with acceptable signal to noise ratio in spectra which were sufficiently cold to suppress hot bands of the bare chromophore.

Excitation was effected by a XeCl excimer-pumped dye laser operating on BBQ or BPBD or TMQ dyes which intercepted the expansion 5−10 mm downstream from the nozzle. When excitation spectra were measured, spatially filtered, undispersed emission was observed through a Schott WG 335 cutoff filter using a cooled RCA C31034 photomultiplier coupled to a boxcar averager (Stanford Research Systems). Dispersed emission spectra were obtained by collecting the emission with a 4 in. diameter *f*:1 quartz lens and focusing it onto the entrance slit of a Heath-MacPherson EUE-700 series scanning monochromator equipped with a stepping motor. The signal from the photomultiplier (Hamamatsu R943-02) was further amplified by a preamplifier and was processed by the boxcar averager to improve signal to noise.

2-Chloroazulene was synthesized by the method of Garst *et al.*[24] 2-Methylazulene and 1,3-dimethylazulene were custom synthesized for us by Drs. Irvine and Majewski of the author's department, using a modification of a previously published method.[25] Ultrahigh purity helium (Matheson) and high-purity Ar, Kr, and Xe (Matheson) were used as received.

TABLE 1: Spacings between the S_2 and S_1, S_3, and S_4 Electronic States of Az, ClAz, MAz, and DMAz in Cyclohexane[a]

	Az	ClAz	MAz	DMAz
$\Delta E(S_2-S_1)/10^3$	14.01	12.59	13.08	14.29
$\Delta E(S_2-S_3)/10^3$	5.52	5.18	5.18	5.40
$\Delta E(S_2-S_4)/10^3$	7.31	7.21	7.46	8.04

[a] From the absorption spectra in cyclohexane, in cm^{-1}.

Results and Discussion

(i) Spectra of the Bare Molecules and Their 1:1 Complexes with Rare Gases. The S_1 and S_3 states of Az are of $^1B_1$ symmetry (non-Mulliken convention for the C_{2v} point group) and the S_0-S_1 and S_0-S_3 transitions are of the $^1L_b(\alpha)$ and ^1B_b types, respectively, with polarizations which are parallel to the short axis of the molecule. The S_0, S_2, and S_4 states are of $^1A_1$ symmetry and the S_0-S_2 and S_0-S_4 transitions are of the $^1L_a(p)$ and ^1B_a types, respectively, and long axis polarized. The S_2-S_n spacings can be changed without altering the structural symmetry of the molecule (considering only the heavy atom skeleton) either by introducing single substituents along the long axis at the 2- or 6-positions or by disubstituting at structurally-equivalent positions of the long axis, e.g. at the 1- and 3-positions. Table 1 summarizes the available information for the transitions S_0-S_n, $n = 1-4$, of the four compounds chosen for study, obtained from their absorption spectra in solution and from literature sources.[26]

In a recent paper we presented vibrational analyses of the jet-cooled S_2-S_0 laser-induced fluorescence excitation and dispersed fluorescence spectra of azulene and three of its derivatives, ClAz, MAz, and DMAz.[27] The excitation spectra of the four compounds exhibit markedly different intensities and vibrational structures, and we suggested that this was attributable to relatively small changes in the spacings between S_2 and those nearby electronic states to which it is coupled. Such couplings are known to determine the observed relative intensities of bands in the absorption spectra of azulene, and particularly affect the S_2-S_0 fluorescence excitation spectra because they control both the radiative and radiationless decay rates of the initially excited vibronic states.

The spacing between S_2 and S_1 was thought to be particularly important in determining the *differences* in the *overall* intensities of the excitation spectra of azulene and its three derivatives because S_2-S_1 radiationless relaxation dominates the decay of S_2; its rate is approximately inversely proportional to the exponential of the S_2-S_1 spacing (the energy gap law[21]). Substitution at the 2-position in Az (MAz, ClAz) reduces the S_2-S_1 spacing, accelerates the S_2-S_1 nonradiative relaxation rate, and results in S_2-S_0 excitation spectra which are very weak. On the other hand, substitution at the 1,3-positions (DMAZ) produces a relatively larger S_2-S_1 spacing, so that the excitation spectrum has an overall intensity comparable to that of the parent Az chromophore. Thus, qualitatively, the Az chromophore behaves similarly both under isolated conditions in the jet and in bulk media. This is consistent with the fact that nonradiative relaxation is the main mode of deactivation in both media and exhibits a rate that is controlled by the magnitude of the S_2-S_1 energy gap.[2,3,27]

The interesting differences in the numbers and relative intensities of bands of different vibrational symmetry in the S_2-S_0 spectra of the three Az derivatives are also associated with

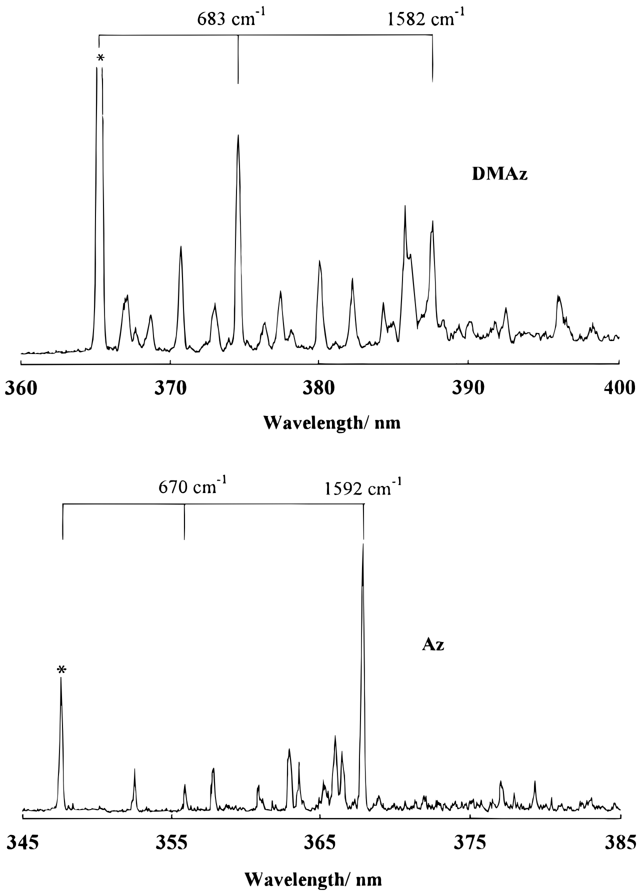

Figure 1. Dispersed S_2-S_0 emission spectrum of DMAz (top) obtained by exciting the jet-cooled compound in its origin band (marked with an asterisk). The emission spectrum of azulene itself (bottom), excited under similar conditions, is shown for comparison.

differences in the coupling of S_2 with other electronic states and vary as the energy spacings between these states change with substitution pattern. The vapor-phase absorption spectra of the derivatives have not been measured, but their spectra in cyclohexane are similar to that of azulene itself in condensed media. The S_2-S_0 absorptions of the derivatives all have similar oscillator strengths and exhibit three or four broad features whose relative intensities and spacings are slightly different for the four compounds. The most noticeable difference in this respect is in the spacing between the two broad vibrational features of lowest energy: 1330 cm^{-1} in DMAz *vs* a range of 1040−1080 cm^{-1} for the other three compounds.

The dispersed emission spectra obtained by exciting these compounds in prominent bands in their excitation spectra under jet-cooled conditions are more revealing. A detailed spectrum of DMAz obtained by exciting in its origin band is presented in Figure 1, and the corresponding spectrum of azulene itself, obtained under similar conditions, is shown for comparison. The strongest bands in the spectra of Az, ClAz, and MAz excited in their origin bands all lie 1550−1600 cm^{-1} to the red of the origin "resonance" emission. In ClAz and MAz this band completely dominates the emission spectrum, whereas in Az itself other weaker bands at 404, 670, 828, 1064, 1221, 1270 1394, 1454, and 1488 cm^{-1} are also distinct, in agreement with Lawrance and Knight.[11] Similar features are attached to the 1−1 bands in those SVL-excited spectra in which one quantum of vibrational energy is deposited in the upper state. The SVL emission spectra of DMAz are quite different, however, with a band at 1582 cm^{-1} having only modest intensity and the strongest feature lying 683 cm^{-1} to the red of the origin or 1−1 bands.

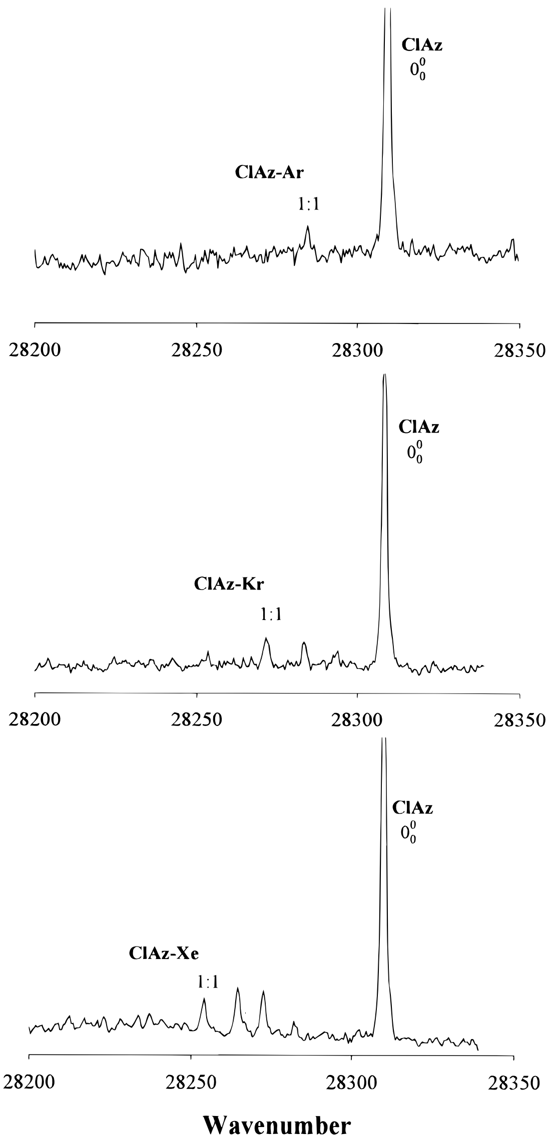

Figure 2. S_2-S_0 fluorescence excitation spectra of the Ar, Kr, and Xe complexes with ClAz in a supersonic expansion. The origin bands of the bare molecule and the 1:1 complexes are marked.

Lawrance and Knight[11] have argued that bands in the emission spectra at *ca.* 1050 and 1580 cm^{-1} are the signatures of S_2-S_4 vibronic coupling, whereas that at *ca.* 670 cm^{-1} is characteristic of S_2 itself. If this model is correct, the emission spectra suggest that S_2-S_4 vibronic coupling is responsible for most of the oscillator strength in the S_2-S_0 spectra of Az, ClAz, and MAz, whereas the S_2 state of DMAz contains much less S_4 character. Thus the emission spectra appear to be in qualitative accord with the model of Lawrance and Knight, since the S_2-S_4 electronic energy spacing is largest in DMAz and is about the same in Az, ClAz, and MAz, based on their absorption spectra in cyclohexane. However, the S_2-S_4 spacing in DMAz is only *ca.* 730 cm^{-1} larger than that of Az itself (based on comparisons of the absorption spectra of the two compounds in cyclohexane). Even using the extended coupling model of Lawrance and Knight,[11] this larger energy gap is not large enough to account for the very big difference in the observed spectra. On the other hand, coupling between S_2 and S_1 is also significantly weaker in DMAz due to its larger S_2-S_1 spacing, and the spectrum suggests that if coupling to still higher singlet states, S_n ($n > 4$), is important, such couplings may also be weaker in DMAz than in the other three compounds. We shall return to this point later.

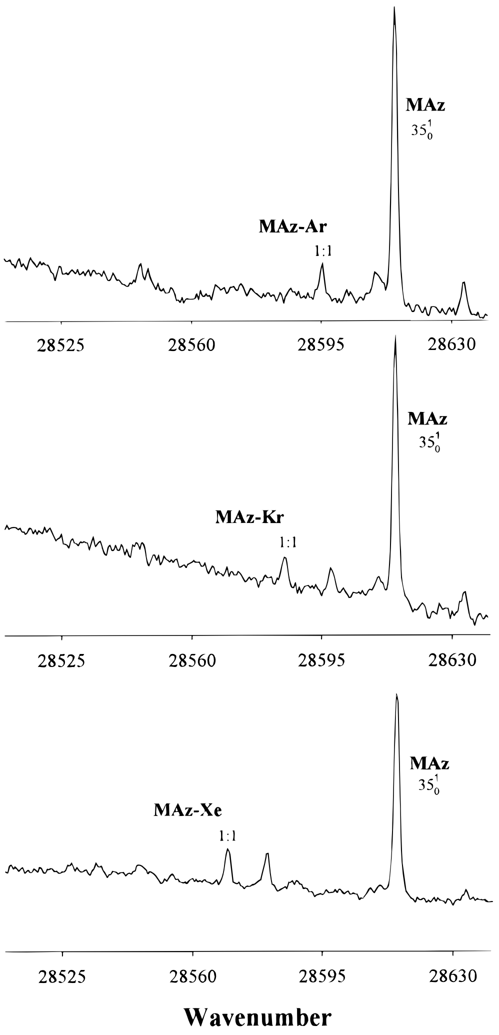

Figure 3. $S_2{-}S_0$ fluorescence excitation spectra of the Ar, Kr, and Xe complexes with MAz in a supersonic expansion. The 35^1_0 bands of the bare molecule and of the 1:1 complexes are marked (see text).

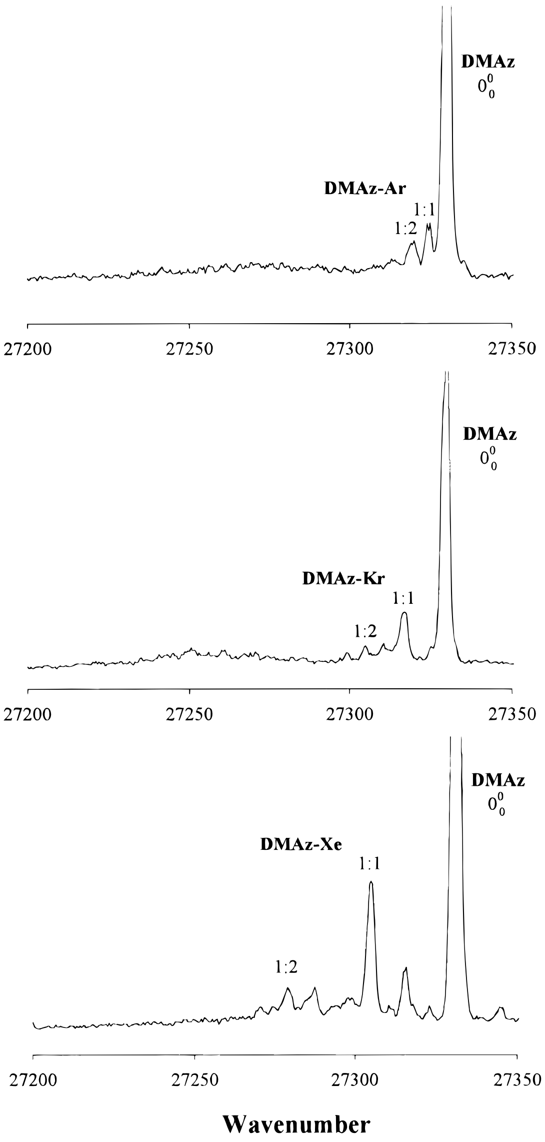

Figure 4. $S_2{-}S_0$ fluorescence excitation spectra of the Ar, Kr, and Xe complexes with DMAz in a supersonic expansion. The origin bands of the bare molecule and the 1:1 and 2:1 complexes are marked.

The jet-cooled $S_2{-}S_0$ fluorescence excitation spectra of ClAz•RG, MAz•RG, and DMAz•RG (where RG = Ar, Kr, Xe), obtained by observing spectrally unresolved emission to the red of the strongest band of the bare molecule, are shown in Figures 2, 3, and 4. For the ClAz•RG and DMAz•RG complexes, these spectra were measured by exciting in the region near the $S_2{-}S_0$ origin of the bare molecule. However, in MAz the origin band is extremely weak and the spectral shift was therefore measured relative to the stronger 35^1_0 transition, which lies 355 cm^{-1} to the blue of the origin.[27] By analogy with the spectra of the rare gas complexes of azulene[10] and many other systems,[16,17,28,29] the additional weak bands lying immediately to the red of strong features found in the spectra of the bare molecule are assigned to the origin and progressions in one or more excited state van der Waals vibrations of the 1:1 complex. For each group of such red-shifted bands, the one of relatively high intensity furthest displaced from the corresponding feature in the bare molecule is taken as the origin of the 1:1 complex. The remaining weak features in each group lying to the blue of this origin are assigned to transitions terminating in one or more quanta of its excited state intermolecular van der Waals modes. The spectra of the 1:2 complexes, which lie further to the red of 1:1 origins, are too weak for detailed analysis except for DMAz in which, like Az,[10] the magnitude of the spectral shift of the origin is a factor of almost exactly 2 larger than that of the 1:1 complex. The microscopic solvents shifts, $\delta\bar{\nu} = \bar{\nu}$(bare) $- \bar{\nu}$(complex), of the origin bands of the 1:1 and 1:2 complexes of Az, ClAz, MAz, and DMAz are collected in Table 2.

Excitation in the origin bands of the 1:1 complexes of DMAz with Ar, Kr and Xe produced emission which was sufficiently intense to resolve spectroscopically. The emission spectra, obtained at ca. 3 Å resolution, are shown in Figure 5. Due to weak signal intensities similar spectra could not be obtained with the ClAz and MAz chromophores. The emission spectra of Az•RG and DMAz•RG are identical in each case to those of the bare molecule except for being offset to the red by $\delta\bar{\nu}$. Such spectra are typical of van der Waals complexes in which the adduct introduces low-frequency vibrations which are only weakly coupled to the much higher frequency vibrations of the chromophore. The emission spectra in Figure 5 suggest that the van der Waals complexes of the rare gases with DMAz in its S_2 state are not qualitatively different from those of the rare gases with both the S_2 state of Az itself[10] and the S_1 states of many other aromatic molecules.[16,17,28,29]

(ii) Structures and Binding Energies of the Complexes. The structures and binding energies of the 1:1 and 1:2 ClAz•RG, MAz•RG, and DMAz•RG complexes in their ground electronic states were calculated using Lennard-Jones 6−12 potential functions in a manner described in detail in previous publica-

TABLE 2: Shifts, $\delta\bar{\nu}$, of the S_2-S_0 Origin Bands of Az, ClAz, MAz, and DMAz Complexed with Rare Gases[a]

R	1:1	1:2
	Az−Rare Gases	
Ar	−19.0	−40.0
Kr	−29.0	−61.5
Xe	−45.5	−97.5
	ClAz−Rare Gases	
Ar	−24.5	
Kr	−37.0	
Xe	−55.5	
	MAz−Rare Gases	
Ar	−19.5	
Kr	−30.0	
Xe	−45.5	
	DMAz−Rare Gases	
Ar	−6.5	−12.0
Kr	−13.0	−27.0
Xe	−27.0	−53.0

[a] Shifts, $\delta\bar{\nu}$, are in cm^{-1}, relative to the origins in the bare molecule (35^1_0 in MAz). Uncertainties are $\pm0.5\ cm^{-1}$.

tions.[10,32] In these calculations, the structures of the bare chromophores were obtained by *ab initio* methods and were fixed at their optimum geometries.[27] The binding energy was then calculated as a function of the position(s) of the adatom(s) on the molecule's surface(s). The coordinates and binding energies of the most stable complexes are given in Table 3. (The previously calculated values for Az·RG are also included in Table 3 to facilitate comparison.)

The results of these calculations show that the interaction of the first adatom with the chromophore produces a potential well with a single minimum residing over the seven-membered ring. In each derivative, the position of the adatom shifts slightly toward the five-membered ring, consistent with the additional dispersive stabilization provided by the substituent(s). The values of *z* (perpendicular distance from the adatom nucleus to the nuclear plane of the chromophore) in each case are comparable to those in other similar complexes and are exactly the same as those of the rare gas complexes of Az itself. These results suggest that simple substitutions in the five-membered ring of the Az chromophore do not alter the geometry of the complex to a significant extent and add weight to the conclusion that electronic effects must be primarily responsible for the variations in the microscopic spectral shifts of the rare gas complexes of azulene's derivatives.

With the first rare gas atom frozen in its minimum energy geometry, the calculations reveal that the second adatom in the most stable 1:2 complex is located in a position which is structurally equivalent to that of the first on the other surface of the molecule, in agreement with the additivity of the observed spectral shifts. Similar additivities in red shift have been observed in Az and many other systems and have been explained on a similar basis. The total binding energy is only slightly greater than twice the binding energy in the 1:1 complexes, indicating that the transannular interaction in the (1|1) 1:2 complexes is small.

As previously observed in the excitation spectra of the rare gas complexes of Az, low-frequency, mildly anharmonic progressions of between 10 and 13 cm^{-1} are attached to the origins in the excitation spectra of the 1:1 complexes of Kr and Xe with ClAz and MAz, and of the 1:1 complex of Xe with DMAz (see Figures 2, 3, and 4). On the basis of arguments made for Az, these transitions are assigned to single quantum transitions in the "*x*" (long axis) bending mode. This is in complete accord with the nature of the S_0-S_2 transitions in these chromophores which are expected to be polarized parallel to the *x* axis, as in azulene itself. Franck−Condon activity is expected in this mode because of the change in the magnitude (and probably the direction) of the permanent dipole moment along this axis.

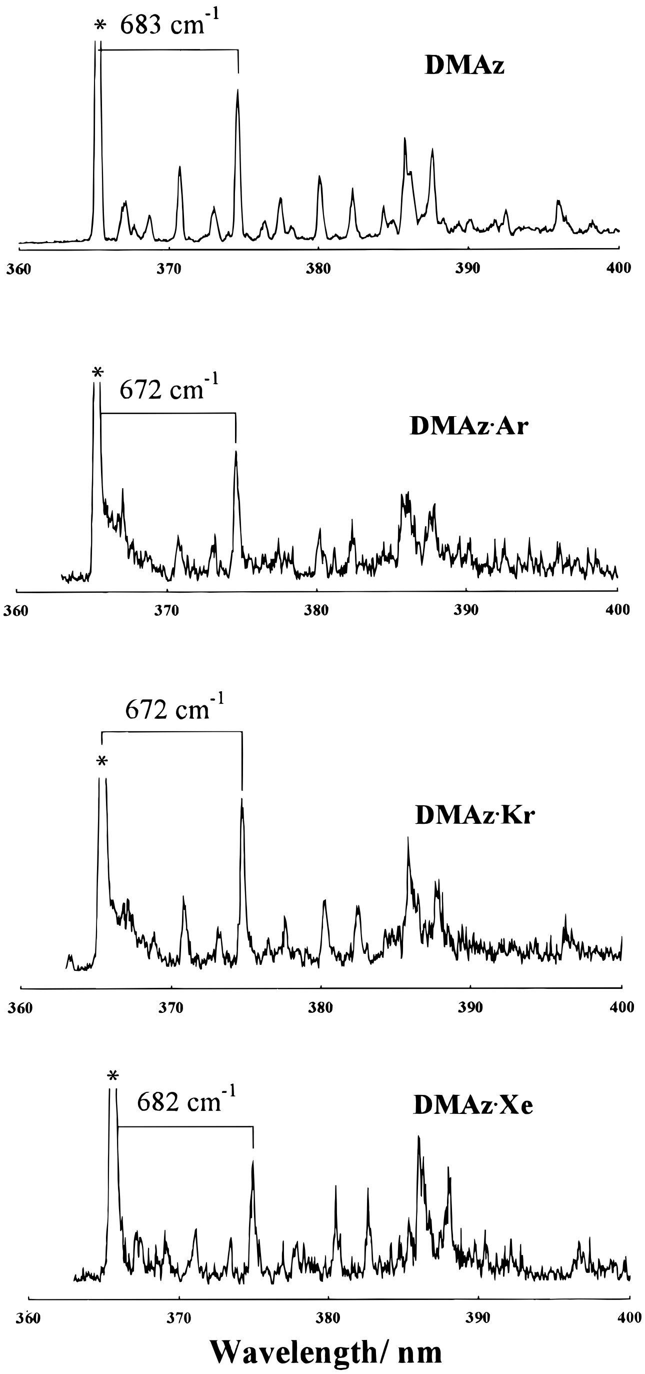

Figure 5. Dispersed S_2-S_0 emission spectra of DMAz and its 1:1 complexes with Ar, Kr, and Xe, obtained by exciting the jet-cooled species in their origin bands (marked with asterisks).

These assignments were confirmed by calculating all three intermolecular vibrational frequencies of the ground states of the 1:1 complexes using one-dimensional Morse and Taylor's series expansion functions, as described in detail previously.[10] The data for the three azulene derivatives are presented in Table 3 along with those of Az for comparison. The frequencies of the three van der Waals vibrations are found to be very similar in all four compounds. As might be expected, substitution at sites remote from the adatom has no significant effect. As was the case with Az, the excitation spectra of these derivatives do

TABLE 3: Binding Energies[a] and Structural Coordinates[b] for the Complexes of Az, ClAz, MAz, and DMAz with One, R_1, and Two, R_2, Rare Gas Atoms[c]

	R_1				R_2			
R	*x*	*y*	*z*	energy	*x*	*y*	*z*	energy
				Az−Rare Gases				
Ar	0.65	0.00	3.30	−567	0.65	0.00	−3.30	−574
Kr	0.65	0.00	3.44	−683	0.65	0.00	−3.44	−692
Xe	0.54	0.00	3.62	−844	0.54	0.00	−3.62	−859
				ClAz−Rare Gases				
Ar	0.62	0.00	3.30	−564	0.62	0.00	−3.30	−571
Kr	0.60	0.00	3.44	−692	0.60	0.00	−3.44	−703
Xe	0.54	0.00	3.57	−909	0.54	0.00	−3.57	−930
				MAz−Rare Gases				
Ar	0.58	0.00	3.30	−574	0.58	0.00	−3.30	−580
Kr	0.53	0.00	3.44	−705	0.53	0.00	−3.44	−716
Xe	0.46	0.00	3.57	−929	0.46	0.00	−3.57	−950
				DMAz−Rare Gases				
Ar	0.51	0.00	3.30	−604	0.51	0.00	−3.30	−611
Kr	0.42	0.00	3.44	−749	0.42	0.00	−3.44	−758
Xe	0.30	0.00	3.57	−993	0.30	0.00	−3.57	−1011

[a] Binding energies are in cm^{-1}. [b] Dimensions are in Å measured from the center of mass of bare azulene. [c] The 1:2 complex of (1|1) structure (see text).

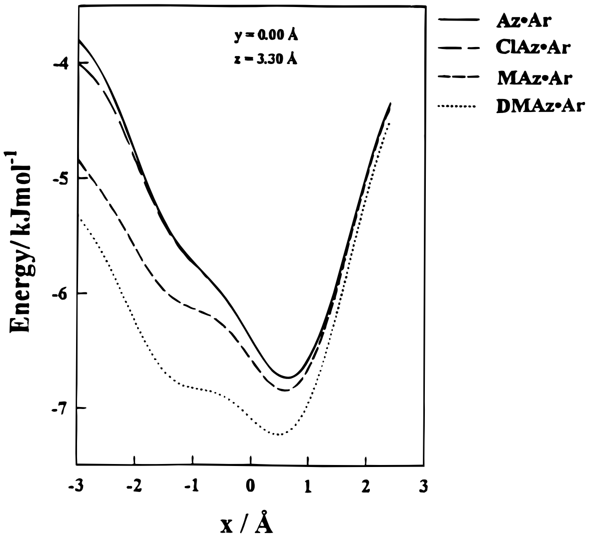

Figure 6. Potential energies of the 1:1 complexes of Az, ClAz, MAz, and DMAz with Ar along the long (*x*) axis of the chromophore calculated using the sum of Lennard-Jones atom−atom potentials (see text). The Ar atom is held at its equilibrium van der Waals distance of 3.30 Å. The origin of the coordinate system in all four molecules is the center of mass of the bare azulene chromophore.

not contain observable transitions in the out-of-plane stretching (z) mode. Finally, significant anharmonicity is observed in the van der Waals bending progressions of the 1:1 Xe complexes. This observation is consistent with the shapes of the potential functions in the xz plane, which have minima over the seven-membered ring but which, in the series ClAz, MAz, and DMAz, become more severely anharmonic in the direction of the five-membered ring, as shown in Figure 6.

(iii) Microscopic Solvent Shifts. We now turn to the interesting problem of understanding why the microscopic spectral shifts of these complexes are so small and how they are affected by changes in the spacings between S_2 and the other excited singlet states of Az and its derivatives. The measured microscopic solvation shifts in Table 2 reveal a number of interesting features. First, the values of $\delta\bar{\nu}$ for the 1:1 complexes increase with increasing polarizability of the adatoms (Figure 7), as expected when dispersive forces dominate binding.

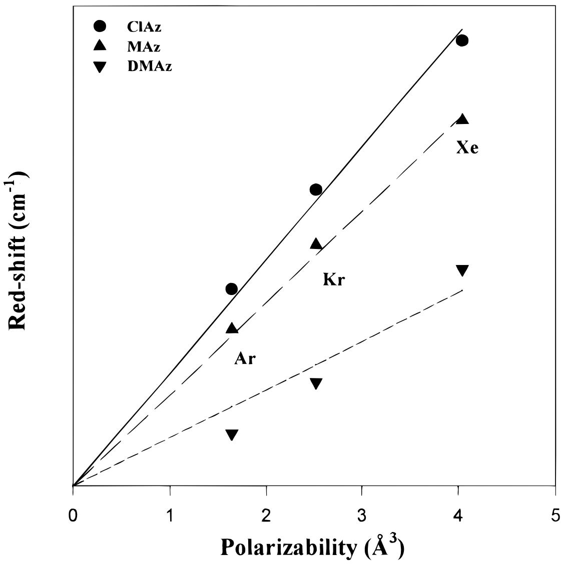

Figure 7. Microscopic solvent shifts for the 1:1 complexes of ClAz, MAz, and DMAz with Ar, Kr, and Xe as a function of the volume polarizability of the rare gas atoms. The straight lines are best-fit regressions from the origin but have no physical significance.

Second, except for DMAz (*vide infra*), the observed spectral shifts for the $S_0-S_1(^1L_a)$ transitions are similar in magnitude to those of the corresponding Az•RG complexes[10] but are a factor of 2−3 smaller than those associated with the ^1L_a transitions of alternant aromatic hydrocarbons of about the same size.[16,17] The spectral shifts for the ^1L_a transitions in Az and its derivatives are, however, comparable in magnitude to those observed for the $^1L_b(S_0-S_1)$ transitions in the rare gas complexes of naphthalene and its derivatives.[19,20,31] Third, among the Az derivatives studied here, the observed spectral shifts in the DMAz•RG complexes are significantly smaller, by a factor of 2−3, than those of Az•RG, ClAz•RG, and MAz•RG.

Azulene has a small dipole moment in both the S_0 and S_2 states, and the dipole−induced dipole contribution to $\delta\bar{\nu}$ can be crudely assessed, using the point dipole approximation via

$$\delta\bar{\nu}_{\mathrm{D-ID}} = -{}^1/_2\alpha_{\mathrm{R}}(R_{\mathrm{M\cdot R}})^{-6}[|\mu_2|^2 - |\mu_0|^2] \qquad (1)$$

where α_R and $R_{M\cdot R}$ are the polarizability of the rare gas atom and its distance from the plane of the chromophore and the $|\mu_i|$ are the dipole moments of the chromophore in the relevant states.[30] Using $\mu_0 = 0.79$ D and $\mu_2 = -0.35$ D, and previously established values of α_R and $R_{M\cdot R}$,[10] the contributions of dipole−induced dipole interactions to $\delta\bar{\nu}$ are found to be *ca.* +2.3, 1.9, and 1.6 cm^{-1} for Xe, Kr, and Ar, respectively. The dipole moments of the azulene derivatives used in the present study are not known. However, they cannot be greatly different in magnitude from those of azulene itself and thus inductive effects are not likely to be responsible for either the small values of $\delta\bar{\nu}$ or the differences in $\delta\bar{\nu}$ among the derivatives.

Jortner and co-workers have recently developed a semi-empirical theory which can be used, with scaling, to predict the microscopic spectral shifts in the S_0-S_1 spectra of nonpolar, alternant hydrocarbon−rare gas heteroclusters.[16,17] The predicted dispersive spectral shift, $\delta\bar{\nu}$, produced by complexing 1 to *n* rare gas atoms R to an aromatic chromophore M is given by the sum of the dispersive $M-R_n$ pairwise interactions

$$\delta\bar{\nu} = -\eta\sum_{i=1}^{n}\delta E_i \qquad (2)$$

where η (<1) is a single empirical scaling factor chosen to obtain the best fit between calculation and experiment and $\delta\bar{\nu}$ is taken to be >0 for a red shift. The contribution of each pairwise interaction to the shift is given by

$$\delta E_i = \sum_{J\neq 1}\sum_{P>0}\frac{|H'_{10,JP}|^2}{E_1-(E_J+F_P)} - \sum_{J>0}\sum_{P>0}\frac{|H'_{00,JP}|^2}{-(E_J+F_P)} \quad (3)$$

where

$$H'_{00,JP} = \langle \mathrm{M_0R_0}|H'|\mathrm{M}_J\mathrm{R}_P\rangle \quad (4a)$$

$$H'_{10,JP} = \langle \mathrm{M_1R_0}|H'|\mathrm{M}_J\mathrm{R}_P\rangle \quad (4b)$$

The zero-order electronic states of M are $|\mathrm{M}_J\rangle$ ($J = 0, 1, 2, ...$) and the ground state, $|\mathrm{M}_0\rangle$, is given an energy $E_0 = 0$, whereas the electronic states of the atom are $|\mathrm{R}_P\rangle$ ($P = 0, 1, 2, ...$) and its energies are F_P of which $F_0 = 0$.

The extension of this theory to polar, nonalternant aromatic hydrocarbons is straightforward and involves the inclusion of additional inductive contributions to the spectral shift.[16] The magnitudes of these additional contributions to the shift, when scaled, are small for azulene and those of its derivatives chosen for study here. We therefore proceed by considering only dispersion in the following analysis.

The intermolecular electrostatic interactions, H', are evaluated conventionally and the electronic states of M are described terms of Slater determinants involving W Hückel molecular orbitals, ϕ_W. The one- and two-electron transitions originating in the ground state of M are expressed as described by Murrell.[14] For naphthalene in order of increasing energy (M = N; in the order $^1\mathrm{L_b}(\alpha)$, $^1\mathrm{L_a}(\mathrm{p})$, $^1\mathrm{B_b}$, and $^1\mathrm{B_a}$), they are

$$|\mathrm{N}_1\rangle = (1/\sqrt{2})[(\phi_{W/2} \rightarrow \phi_{W/2+2}) - (\phi_{W/2-1} \rightarrow \phi_{W/2+1})] \quad (5a)$$

$$|\mathrm{N}_2\rangle = (\phi_{W/2} \rightarrow \phi_{W/2+1}) \quad (5b)$$

$$|\mathrm{N}_3\rangle = (1/\sqrt{2})[(\phi_{W/2} \rightarrow \phi_{W/2+2}) + (\phi_{W/2-1} \rightarrow \phi_{W/2+1})] \quad (5c)$$

$$|\mathrm{N}_4\rangle = (\phi_{W/2-1} \rightarrow \phi_{W/2+2}) \quad (5d)$$

where $W/2$ is HOMO, $W/2 + 1$ is LUMO, etc. Finally, the pairwise dispersive spectral shift is expressed in the form

$$\delta E_i = \alpha e^2 \bar{F}_{\mathrm{IP}} \sum_{\beta=1}^{N}\sum_{\gamma=1}^{N} K_{\beta\gamma} G^{\mathrm{R}}_{\beta\gamma} \quad (6)$$

where α is the static polarizability of the rare gas atom, $\bar{F}_{\mathrm{IP}}$ is the rare gas ionization potential, and $K_{\beta\gamma}$ and $G_{\beta\gamma}$ are electronic and geometric terms respectively summed over β π-orbitals of M and γ atomic orbitals of R.[16,17]

Two kinds of alternant hydrocarbons were examined by Jortner *et al.*; those such as anthracene, tetracene, and pentacene which have $\mathrm{S_0-S_1}$ transitions of the $^1\mathrm{L_a}$ type, and others such as naphthalene, phenanthrene, and pyrene which have $\mathrm{S_0-S_1}$ transitions of the $^1\mathrm{L_b}$ type. The latter group exhibit very low oscillator strengths because, within the framework of Hückel theory, they arise from the out-of-phase superposition of two zero-order one-electron excitations, as described in eq 5a. Jortner and co-workers showed (i) that the contribution to the dispersive stabilization of $\mathrm{S_1}$ from the lowest four states, $|\mathrm{N}_J\rangle$ ($J = 0-3$), is particularly small due to extensive cancellations which appear among terms describing contributions to $\mathrm{S_1}$'s intermolecular interactions in such molecules, and (ii) that $\mathrm{S_1}$ is stabilized primarily through contributions from higher states, $|\mathrm{N}_J\rangle$ ($J > 3$). On the other hand, $\mathrm{S_0}$ is stabilized by dispersive contibutions to binding through interactions with the $J = 0-3$ states and the $J > 3$ state which are comparable in magnitude. In addition, the contribution of vibronic $^1\mathrm{L_a}-{}^1\mathrm{L_b}$ coupling to the spectral shift was shown to be rather small (*ca.* 3% of the total), despite the fact that about 90% of the oscillator strength of the $\mathrm{S_0-S_1}$ transition arises from this source. Thus, Jortner and co-workers predicted that the microscopic $\mathrm{S_0-S_1}$ spectra shifts of rare-gas clusters of alternant aromatic molecules exhibiting $^1\mathrm{L_b}$ transitions should be 2−4 times smaller than those with $^1\mathrm{L_a}$ transitions in which such cancellation effects do not occur. With appropriate scaling, the predicted spectral shifts of naphthalene−rare gas clusters are in good agreement with experimental observation.[17]

Azulene presents a rather different situation, since it does not possess the pairing properties of Hückel orbitals in alternant molecules. Following the model of Jortner *et al.* and again using the one- and two-electron descriptions of Murrell, one can express the four lowest energy electronic transitions in azulene (M = A; in the order $^1\mathrm{L_b}$, $^1\mathrm{L_a}$, $^1\mathrm{B_a}$, and $^1\mathrm{B_b}$) as

$$|\mathrm{A}_1\rangle = (\phi_{\mathrm{W}/2} \rightarrow \phi_{\mathrm{W}/2+1}) \quad (7a)$$

$$|\mathrm{A}_2\rangle = (1/\sqrt{2})[(\phi_{\mathrm{W}/2-1} \rightarrow \phi_{\mathrm{W}/2+1}) + (\phi_{\mathrm{W}/2} \rightarrow \phi_{\mathrm{W}/2+2})] \quad (7b)$$

$$|\mathrm{A}_3\rangle = (\phi_{\mathrm{W}/2-1} \rightarrow \phi_{\mathrm{W}/2+2}) \quad (7c)$$

$$|\mathrm{A}_4\rangle = (1/\sqrt{2})[(\phi_{\mathrm{W}/2-1} \rightarrow \phi_{\mathrm{W}/2+1}) - (\phi_{\mathrm{W}/2} \rightarrow \phi_{\mathrm{W}/2+2})] \quad (7d)$$

Unlike naphthalene, in Az the $\mathrm{S_0-S_1}$ transition is best descibed as an electric−dipole allowed HOMO−LUMO one-electron transition, eq 7a, which has a low oscillator strength because HOMO and LUMO reside on different atoms and their overlap is small. (This also accounts for the small $\mathrm{S_1-T_1}$ splitting in Az.) On the other hand, the $\mathrm{S_0-S_2}$ transition is of the $^1\mathrm{L_a}$ type and may be considered to arise from the *in-phase* superposition of two zero-order one-electron excitations, eq 7b. Nevertheless, the intrinsic oscillator strengths of these one-electron transitions are both relatively small because the separation of charge associated with them is small. Thus, the $\mathrm{S_0-S_2}$ absorption system acquires most of its intensity by vibronic coupling of $\mathrm{S_2}$ with $\mathrm{S_4}$ (major) and with $\mathrm{S_1}$ and $\mathrm{S_3}$ (minor). The former is mediated by at least six of the $\mathrm{a_1}$ vibrational modes,[11] whereas the latter are promoted by $\mathrm{b_1}$ modes.[27]

The influence of $\mathrm{S_2-S_4}$ vibronic coupling on the spectral shifts of *vibronically-induced bands* in $\mathrm{S_0-S_2}$ can be estimated using an extension of the theory[17] in which the contributions of the coupled states are scaled by the ratios of the oscillator strengths for the $\mathrm{S_0-S_2}$ and $\mathrm{S_0-S_4}$ transitions, $|B|^2 = f_{02}/f_{04}$, *viz.*

$$\delta\bar{\nu}' = (1-|B|^2)\delta\bar{\nu}(A_2) + |B|^2\delta\bar{\nu}(A_4) \quad (8)$$

where $\delta\bar{\nu}(A_2)$ and $\delta\bar{\nu}(A_4)$ are the spectral shifts of the electronic origins of the $\mathrm{S_0-S_2}$ and $\mathrm{S_0-S_4}$ transitions respectively. For azulene, $|B|^2 \approx 0.1$ and if $\delta\bar{\nu}(A_2)/\delta\bar{\nu}(A_4) < 1/3$, then $\delta\bar{\nu}'$ will be no more than 20% larger than that of the "pure" transition, a modest effect. Similar values are expected for the derivatives. Thus vibronic coupling is not expected to make a striking difference to the magnitude of the shift. Measuring the spectral shift for MAz with respect to a vibronic band of $\mathrm{a_1}$ symmetry

TABLE 4: Wavenumbers of the Fundamental van der Waals Vibrations in 1:1 Complexes of Az, ClAz, MAz, and DMAz with the Rare Gases Calculated Using Morse and Taylor's Series Potentials

	vibrational frequencies						
	Morse^a			Taylor's series^a			
R	x	y	z	x	y	z	$\bar{\nu}_{obs}{}^a$
			Az−Rare Gases				
Ar	18.5 (0.15)	14.9 (0.10)	49.8 (1.10)	15.8 (0.11)	16.4 (0.19)	51.6 (1.7)	not observed
Kr	14.9 (0.08)	12.0 (0.05)	44.3 (0.69)	12.7 (0.05)	12.9 (0.11)	42.6 (1.2)	16.5
Xe	13.2 (0.05)	10.9 (0.03)	43.1 (0.52)	10.0 (0.08)	11.6 (0.09)	39.9 (1.3)	15.5 (1.0)
			ClAz−Rare Gases				
Ar	17.3 (0.13)	14.7 (0.09)	47.7 (1.01)	13.8 (0.15)	15.9 (0.19)	50.4 (1.72)	not observed
Kr	13.5 (0.07)	11.4 (0.05)	40.5 (0.60)	10.9 (0.13)	12.5 (0.11)	43.6 (0.93)	12.0
Xe	12.7 (0.04)	10.9 (0.03)	38.3 (0.40)	10.1 (0.08)	11.6 (0.08)	41.5 (0.70)	10.5 (1.0)
			MAz−Rare Gases				
Ar	18.1 (0.14)	15.0 (0.10)	48.6 (1.03)	13.8 (0.26)	15.0 (0.10)	51.5 (1.81)	not observed
Kr	14.1 (0.07)	12.0 (0.05)	40.8 (0.59)	10.7 (0.16)	12.7 (0.07)	43.1 (1.03)	12.5
Xe	13.1 (0.05)	11.3 (0.03)	39.9 (0.43)	9.85 (0.14)	11.9 (0.08)	42.1 (0.72)	10.0 (1.7)
			DMAz−Rare Gases				
Ar	15.4 (0.10)	14.2 (0.08)	49.1 (1.00)	12.6 (0.39)	15.4 (0.21)	51.8 (1.64)	not observed
Kr	13.4 (0.06)	11.1 (0.04)	43.5 (0.63)	9.1 (0.31)	12.0 (0.12)	42.7 (1.15)	not observed
Xe	12.7 (0.04)	10.3 (0.03)	42.0 (0.45)	8.8 (0.19)	11.0 (0.09)	40.6 (0.82)	11.0 (2.0)

[a] The wavenumber of the fundamental vibration is followed by the anharmonicity in parentheses.

(35^1_0) will also make no qualitative difference in the overall analysis of the effects of substitution.

We thus proceed to examine the similarities and differences between the S_2 state of Az and the S_1 state of its alternant isomer, naphthalene, by considering the microscopic spectral shifts of their simply-substituted derivatives. We begin by considering if a simple three-state (S_0, S_1, and S_2) model is adequate. The ^1L_b transition in naphthalene is largely vibronically induced with $^1L_b-{}^1L_a$ interstate mixing contributing about 90% of the overall intensity of the system. Since the $^1L_b-{}^1L_a$ mixing coefficients are a function of the spacing between the two electronic states and the density of vibrational states, the extent of interstate mixing in naphthalene's derivatives is expected to depend on the nature and position of its substituents. Recently, Leutwyler *et al.*[19,20] investigated the jet-cooled fluorescence excitation spectra of the rare gas complexes of two naphthalene derivatives, 1,2-dimethylnaphthalene (1,2-DMN) and 2,3-dimethylnaphthalene (2,3-DMN), and reported their spectral shifts without comment (−4.4 and 11.5 cm^{-1} for 2,3-DMN·Ar and 1,2-DMN·Ar, respectively *vs.* 14 cm^{-1} for N·Ar itself). Because these two derivatives have similar densities of states, the extent of their $^1L_b-{}^1L_a$ mixing will be determined primarily by the magnitude of their S_1-S_2 energy spacings. In 2,3-DMN, $^1L_a-{}^1L_b$ interstate mixing is diminished since substitution is symmetric about the long axis and the ^1L_b state will be stabilized more than ^1L_a state, creating a larger S_1-S_2 energy gap than in naphthalene itself. The lower excited state will contain more ^1L_b character, and the cancellation effects among terms describing its intermolecular interactions are expected to be more pronounced. As a result, a smaller spectral shift is expected for the rare gas complexes of 2,3-DMN than for those of unsubstituted naphthalene. On the other hand, 1,2-DMN has a smaller S_1-S_2 gap and cancellation effects similar to those of naphthalene itself are expected. Thus the experimental measurements of the microscopic solvent shifts by Leutwyler *et al.* appear to be qualitatively correlated with the extent of $^1L_a-{}^1L_b$ interstate mixing in a three state (S_0, S_1, S_2) coupling scheme. Note, however, such a correlation is only consistent with the model of Jortner *et al.* if changes in the contributions to $\delta\bar{\nu}$ from higher states are about the same for naphthalene and the derivatives under consideration.

Similar substituent-dependent spectral shifts in the azulene−rare gas system are clearly evident from the data presented in Table 2. ClAz·RG and MAz·RG have values of $\delta\bar{\nu}$ which are similar to or slightly larger than those observed in Az·RG, whereas in DMAz·RG the observed spectral shift is considerably smaller. Substitution of azulene at its 2-position, as in ClAz and MAz, will stabilize both the S_0 and S_2 states (S_0-S_2, ^1L_a, is long axis polarized), whereas the S_1 state will be less perturbed (S_0-S_1, ^1L_b, is short axis polarized). So, analogous to 1,2-DMN, the reduced gap between the S_2 and S_1 states in ClAz and MAz should result in an S_2 state having greater $^1L_a-{}^1L_b$ mixed character. On the other hand, when the substitution pattern is perpendicular to the C_2 symmetry axis, as in DMAz, the $S_1(^1L_b)$ state will be preferentially stabilized, resulting in a larger $^1L_a-{}^1L_b$ separation. In this case the ^1L_a state would acquire substantially less ^1L_b character. On the basis of this limited analysis, then, the spectral shifts of the S_0-S_2 transitions in the azulene system and the S_0-S_1 transitions in the naphthalene system would appear to have a common origin. However, this is not the entire picture because the S_2-S_n ($n > 2$) electronic energy spacings also differ among the various azulene derivatives, as shown in Table 1. The S_2-S_3 spacings are not very different among the azulene derivatives, but the S_2-S_4 do differ significantly, being rather larger in DMAz than in Az, ClAz, and MAz.

The parallel between the S_0-S_1 transition, which is of the ^1L_b type, in naphthalene and the S_0-S_2 transition, which is of the ^1L_a type, in azulene is mainly due to the fact that the transition in each case is due to a nominal superposition of two zero-order one-electron excitations. However, in naphthalene it is an out-of-phase superposition, whereas in Az a transition from S_0 to a pure S_2 state would involve an in-phase superposition.[13,14] The oscillator strength of the transition to a pure S_2 state is rather small, however, and most of the oscillator strength in the transition which is actually observed arises from vibronic coupling with S_4. However, the S_0-S_4 transition involves the same sort of out-of-phase superposition of one-electron transitions as is seen in the S_0-S_1 transitions of naphthalene and its derivatives. Thus, within the framework of the theory due to Jortner *et al.* the microscopic solvent shifts of the S_0-S_2 origin bands of the rare gas van der Waals complexes of azulene result from cancellations of intermolecular interaction terms, just as with the naphthalene S_0-S_1 system. Since the geometries of these van der Waals complexes are nearly the same (see the earlier discussion of their structures), the variations in the microscopic solvent shift must be primarily due to electronic effects. The nature and position of the substituents change the spacings between the electronic states and modify the character of the S_2 state, which in turn determines the magnitude of the microscopic solvent shift. Such effects should also be reflected in the dynamics of S_2 state decay of these Az derivatives and their van der Waals complexes. These studies are underway in our laboratories.

Conclusions

The $S_2-S_0(^1L_a)$ fluorescence excitation and emission spectra of the van der Waals complexes of three azulene (Az) derivatives, 2-chloroazulene (ClAz), 2-methylazulene (MAz), and 1,3-dimethylazulene (DMAz), with the rare gases, Ar, Kr, and Xe, have been measured under jet-cooled conditions. The microscopic solvent shifts, $\delta\bar{\nu}$, of the origin bands in the S_0-S_2 spectra increase with the increasing polarizability of the adatom(s), consistent with the dominance of dispersion in the binding. Although there are substantial variations in the relative values of $\delta\bar{\nu}$ among the Az derivatives examined, all of the $\delta\bar{\nu}$ values are relatively small and are similar to those of the $^1L_b(S_0-S_1)$ transitions in naphthalene and its derivatives. The theory of microscopic solvent shifts of Jortner *et al*. has been used to analyze the solvent shift data. Within the framework of this theory, the small solvent shifts associated with both the S_0-S_1 transition in naphthalene and the S_0-S_2 transition in azulene can be traced to nominal out-of-phase superpositions of two zero-order one-electron excitations which lead to cancellations of terms describing the intermolecular interactions in the complexes. However, whereas in naphthalene it is a straightforward out-of-phase superposition in S_1, in azulene it is associated with S_2-S_4 configuration interaction by which the S_0-S_2 transition obtains the majority of its oscillator strength. Comparisons of the azulene−rare gas and naphthalene−rare gas systems have proved revealing and suggest that variations in $\delta\bar{\nu}$ with substitution pattern are primarily electronic in their origin and arise from differences in the strengths of configuration interactions in the excited state which are related to the S_2-S_n energy spacings. These energy spacings have been varied by placing substituents either along the long axis (2-position) or parallel to the short axis (1,3-positions) so that they selectively perturb either those transitions which are long axis polarized (^1L_b, ^1B_b), or those which are short axis polarized (^1L_a, ^1B_a).

The structures and binding energies of the complexes of these derivatives, obtained using Lennard-Jones type calculations, are similar to those of Az itself. The observed progressions in the low-frequency intermolecular vibrations in each case have been assigned to that excited state bending mode which lies in the direction of the change in the dipole moment, i.e., parallel to the long axis of the chromophore. Model calculations using one-dimensional Morse and Taylor's series potential functions support this assignment.

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