Anthracene and its Argon Complexes, Spectra and Lifetimes

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Fluorescence excitation spectra and fluorescence lifetimes at specific wavelengths are reported for anthracene and anthracene-argon complexes in a supersonic jet. At low argon pressures, complexes are observed with lifetimes and transition energies which are not dependent on the argon pressure.

At high pressures, the lifetimes reach a limiting value while the wavelength maximum continues to red shift within the pressure range observed. The possible relationship to solvent or matrix effects on a central ion are discussed.

The major use of supersonic jet spectroscopy has been the investigation of ultracold, isolated molecules [1–3]. Complexes formed between the molecule being studied and the carrier gas were often an unwanted nuisance. More recently, the complexes themselves have been the center of investigation [4–6] because of their potential for revealing facets of intermolecular interactions heretofore unstudiable. In a previous paper [7], we presented the results of such a study on anthracene fluorescence. In the present work, we look more closely at the effect of anthracene-argon complex formation on the spectra and lifetime of the various complexes, concerning ourselves almost exclusively with the possible relationship between the present results and the general area of matrix or solvent perturbations. At the lowest pressure there are no peaks observed to the red of the 0-0 band of the bare anthracene molecule. Increasing argon pressure causes the appearence of a number of peaks to the red of the 0-0. In general, the further red-shifted a peak in this region, the wider it is and the greater the number of argons in the complex, as evidenced by the dependence of the relative intensities on the argon pressure. The lifetime and transition energy of each peak is independent of argon pressure, and, although the absorption maximum shows a relatively smooth red shift with pressure, the lifetimes show no such smooth trend.

At higher pressure the peaks are so broad that they are no longer observable as individual peaks but, rather, appear as one broad, almost structureless peak. Excitation spectra at different argon pressures are shown in Figure 1. The spectral range covers 65 to 115 A to the red of the electronic origin at 3610.6 A. The wavelength shift to the red continues with increasing pressure, but the lifetimes at the maximum reach a limiting value. The lifetimes are recorded in Table 1. The implications of the present work with regards to any theory of matrix or solvent effects on a central molecule are significant. At lower argon pressures presumably, the complexes formed are dominated by argons having direct bonding to the central anthracene

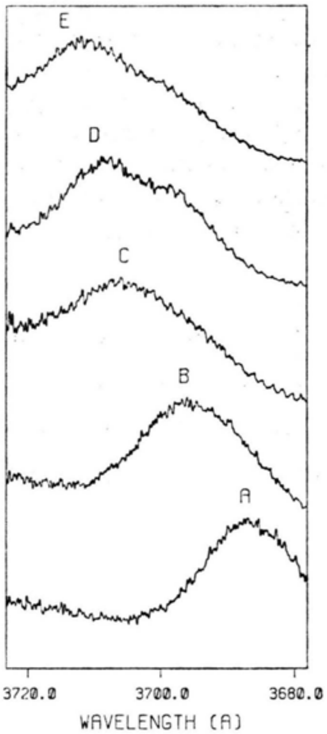

Fig. 1. Spectra of Anthracene-Argon Complexes at *A* 1.5, *B* 2.0, *C* 2.5, *D* 3.0 and *E* 3.5 atm of Ar carrier gas. Excitation bandwidth is 0.3 cm^{-1}.

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Table 1. Lifetimes of Anthracene and Anthracene-Argon Compleces in a hypersonic jet.

Peak	Ar Pressure [atm]	Lifetime [nsec]
0–0	0.2	25.4
	0.5	24.7
	0.7	24.5
A	1.5	14.0
B	2.0	11.4
C	2.5	9.8
D	3.0	10.0
E	3.5	10.0

0–0 lifetime of Jortner et al. is 16.3 nsec (private communication).

molecule. The wavelength maximum shifts fairly smoothly to the red, but the peaks themselves are not equally spaced. The fact that the peaks are not equally spaced means that the shifts are not determined by two-body interactions, which would result in evenly spaced peaks such as have been observed in some systems [5], but that three-body, or more, interactions must also be considered. This unequal spacing seems to be a common feature for noble gas complexes with aromatic molecules [4]. Also, the lifetimes are not a smooth function of complex formation. The relative ability or inability of a theory to reproduce these considerable lifetime fluctuations will be a severe test of its completeness and accuracy.

At high pressure, we see a limit in the lifetime but not in the wavelength shift. Since the low pressure region spectra and their dependence on pressure indicate a large number of different complexes are observed, the high pressure region must represent anthracene-argon complexes with so many argons attached that the outer ones cannot possibly be in direct contact with the anthracene but are more likely equivalent to outer solvation shells. Such a high degree of complex formation seems to be a common property for these systems [6]. Thus, any effects seen here can be correlated to the long-range effect of outer solvation shells. If this is indeed true, it means that long-range interactions are important only for wavelength effects, while short-range interactions affect both lifetimes and transition energies. Just where the cut-off takes place cannot, unfortunately, be determined by our results, since more information on the composition and the structure of most of the species studied is needed. If the effects seen here are general and not just a quirk of the system studied, they indicate an interesting potential for both experimental and theoretical work in this area. The ability to form and study specific complex species, plus the apparent distinction between wavelength and lifetime changes resulting from the surrounding molecules could provide more accurate and more detailed information which would greatly increase our understanding of this difficult area.

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