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IONIZATION POTENTIALS OF ANTHRACENE

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From the observation of the breaks of the photoionization efficiency curve (PIE) of molecular anthracene in the vacuum ultraviolet wavelength region, the higher ionization potentials could be estimated.

In comparison with the photoelectron spectroscopical data, we could better assign the breaks of PIE to the σ-orbitals of the molecule.

The detailed structure of the valence and conduction bands in anthracene has been of considerable interest to the investigators of the organic molecular crystals. Recently, Clark _et al._ and Eland independently determined the orbital energies of anthracene and related compounds by the photoelectron (PE) spectroscopic method.[1,2] The observed π-orbital energies were well correlated with the energies predicted by the molecular orbital theories. In order to further advance the study of the electronic structure of anthracene, we observed the photoionization efficiency (PIE) curve for the molecular anthracene.

Figure 1 shows the spectral distribution of the PIE for this molecule in the gas phase. The experimental

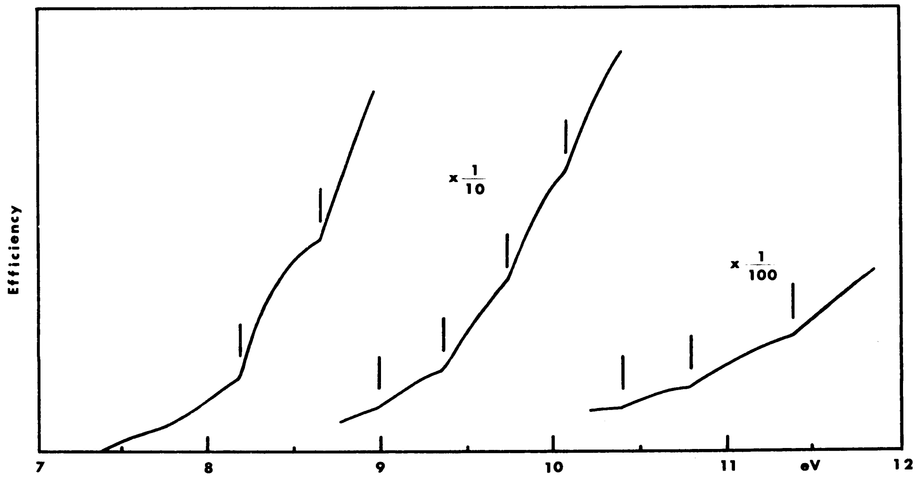

Figure 1. Photoionization Efficiency Curve of Anthracene
(Breaks are indicated by lines.)

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procedure was almost the same as that adopted by Watanabe.3) The ionization efficiency gradually increases with an increase in the exciting photon energy, exhibiting several distinct breaks, i. e., inflection points, in the observed energy region. The curve is composed of a series of smoothed step functions. Various autoionization peaks characteristic of the PIE curve seem to be effectively suppressed. This just exemplifies the idealized curve for the molecular photoionization only due to the direct ionization process. Therefore, we can expect to obtain the higher ionization potentials from the breaks in the PIE curve, as Potakov and Yuzhakova successfully tried for pyrroles.4)

Table 1 shows the locations of the breaks in comparison with the PE bands observed by Clark et al.1) Most breaks are in good agreement with the PE data, though the former ones might be somewhat affected by the difference between the adiabatic and vertical ionization potentials concerned.

Table 1. Ionization Potentials of Anthracene

PIE curve	PE spectrum
7.40 (eV)	7.40 (eV)
8.19	-
8.65	8.52
8.98	9.16
9.35	-
9.72	-
10.07	10.13
10.39	10.21
10.78	10.7
11.73	11.3

However, it must be noticed that some bands corresponding to breaks are missing in the PE spectrum. For example, there is a clear break at 8.19 eV between two π-ionization potentials of 7.40 and 8.65 eV. This cannot be attributed to the excitation of the vibrations of the molecular ions, since the energy interval is too large for this explanation to be valid.

On the other hand, Lyons and Morris detected the steep rise around 6.40 eV in the external photoemission yield curve for the crystalline anthracene.5) This break is situated about 0.75 eV above the first ionization potential of the crystal, 5.65 eV. In our case, the difference in energy between the threshold and the first break is 0.79 eV. Both differences are almost the same, though the physical phases are quite different between them. This kind of coincidence could not safely explained in terms of autoionization. We can also find a trace of this band, as a shoulder, in the kinetic energy distribution curves of photoelectrons from the crystalline anthracene.6)

Now that the whole structure of the π-electron system has been solved consistently for this compound, it seems that we had better assign such breaks to the removal of a σ-electron from anthracene. That is, the first σ-ionization potential of anthracene is 8.19 eV, which is by 3.29 eV lower than that of benzene.7) Dewar et al. also suggested that there would be some missing bands, especially, some bands related to the σ-valence orbitals, in the PE spectra of aromatic hydrocarbons.8)

Why do such bands disappear in the PE spectra? The reason for this is that such bands are somewhat resonant. In other words, these bands have appreciable ionization cross sections, when the energy of the exciting light does not much exceed the ionization potentials. This explanation is just the same one as Momigny and Lorquet presented for benzene.$^{9)}$ Indeed, such a tendency can be read from Fig. 1, where the second step is much rounder, suggesting the abrupt decrease in the partial ionization cross section of the second band at increasing photon energies.

Recent theoretical calculations of the ionization cross sections also indicate that, when the 584 A radiation is used to ionize the molecules, the PE bands due to the σ-orbitals are considerably weaker as compared with those due to the π-orbitals for several compounds.$^{10)}$

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