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High-resolution Photoelectron Spectroscopy of Naphthacene Polycrystal by Means of Helium 21.22 eV Resonance Line

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The photoelectron spectrum of naphthacene polycrystal was obtained with a high-resolution photoelectron spectrometer using a helium 21.22 eV light source, and the vibrational fine structures were examined. The resolution, 21 meV FWHM for the argon $P_{3/2}$ peak, became much better than that obtained by means of a retarding-potential-type electron analyzer. Broad peaks with no distinct intramolecular vibrational structure were observed, and the origin of the peak width was discussed.

Recent progress in the molecular photoelectron spectroscopy of the polycyclic aromatic hydrocarbons[1–3] has made possible a direct comparison between the photoelectron spectra of these compounds in the gaseous and solid states. From the comparison, it has been made clear that the ionization in the solid state reflects that of one molecule very well.[4,5] Until the present time, however, almost all solid-state photoelectron spectroscopic studies of these compounds[6] have been carried out by rather low-resolution retarding-potential-type electron-energy analyzers, and the precise examination of the fine structures associated with the electronic transitions was very difficult.

Considering the narrow electronic valence-band width of the molecular crystals, one might expect to find the well-seperated intramolecular vibrational levels of the ionic states by means of photoelectron spectroscopy.

Recently Kiyono *et al.*[7] studied the energy states of naphthacene polycrystal with a high-resolution photoelectron spectrometer. They suggested the existence of some intramolecular vibrational structures, but the weak intensity of the signal prevented them from drawing any definite conclusion. On the other hand, some mechanisms have been proposed which lead to the broadening of the peaks. Zagrubskii and Vilesov[8] pointed out the possibility of a Franck-Condon quantum-mechanical spread. Further, Silinsh[9] and Sworakowski[10] suggested the dispersion of the ionization potential by the lattice vibrations in the neutral state.

In this paper, we wish to report our findings regarding the high-resolution photoelectron spectrum of naphthacene polycrystal obtained using the helium 21.22 eV line.

Experimental

The photoelectron spectrometer was an electrostatic 127° co-axial cylindrical-type one which has already been reported.[11] The ionization chamber of the instrument, however, was modified for the solid sample. Naphthacene was evaporated on a copper substrate and was inserted into the ionization chamber. The resolution of the electron spectrometer was 21 meV FWHM for the argon $P_{3/2}$ peak, but it was about one-third of this FWHM value at the first ionization peak of naphthacene, since the kinetic energy of the photoelectron was scanned by the voltage between the two deflector electrodes. The contact potential difference between the sample and the deflector electrodes was hard to estimate, so in calculating the ionization potentials it was assumed to be zero.

Results and Discussion

In Figs. 1a and 2a, the full and expanded spectra of the lower ionization potential region of naphthacene polycrystal are shown. In Figs. 1b and 2b, the molecular photoelectron spectra of the corresponding regions[1] are shown for comparison. In Table 1, the numerical values of the ionization potentials for the region of Fig. 2a are listed, along with the gaseous-state values and also other photoemission results.

Figures 1a and 2a show that the resolution is much better than that of the previous retarding potential method.[5] For example, the peaks at 8.77 and 10.72 eV appeared as shoulders in the retarding potential study. The position of the small shoulder at 8.3 eV was a little less reproducible than the other peaks, so the numerical value in Table 1 is given as 0.1 eV. A comparison with the other photoemission works in Table 1 shows that the agreement is very good; this finding suggests that the contact potential difference,

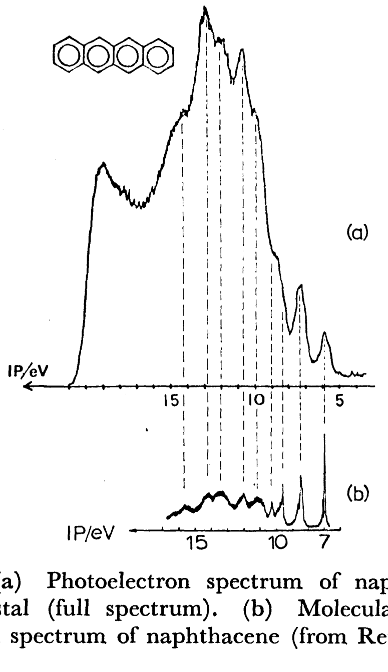


Fig. 1. (a) Photoelectron spectrum of naphthacene polycrystal (full spectrum). (b) Molecular photoelectron spectrum of naphthacene (from Ref. 1).

TABLE 1. IONIZATION POTENTIALS OF THE PEAKS IN FIG. 2

	Gas1),a)		This work a)		Seki *et al.*5),a)		Kiyono *et al.*7),a)		Hirooka *et al.*4),b)	
	IP	ΔIP	IP	ΔIP	IP	ΔIP	IP	ΔIP	IP	ΔIP
A	7.01	0.0	5.83	0.0	5.9	0.0	5.75	0.0	5.83	0.0
B	8.41 (8.6)	1.41 (1.5_9)	7.31	1.48	7.3	1.4	7.27	1.52	7.28	1.45
C	9.56	2.55	(8.3)	2.5					8.29	2.46
D	(9.7)	(2.6_9)	8.77	2.94	8.7	2.8	8.64	2.89	8.70	2.87

a) $h\nu = 21.22$ eV b) The average values obtained by several photon energies ($h\nu \leq 10.78$ eV).

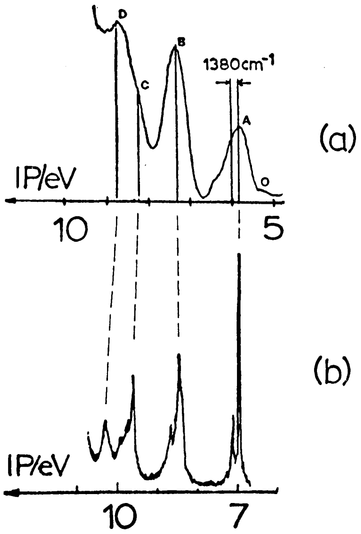


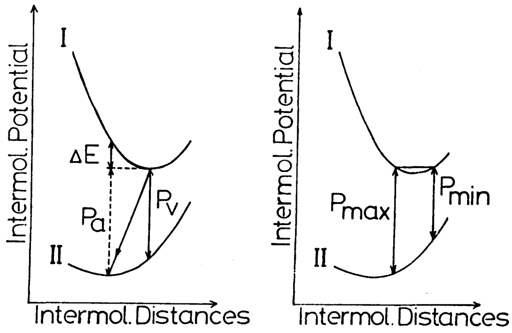
Fig. 2. (a) Expanded photoelectron spectrum of the lower ionization potential region of naphthacene polycrystal. (b) Molecular photoelectron spectrum of the region corresponding to (a) (from Ref. 1).

ignored in this work, is really very near to zero.

The work in the gaseous state shows1) that the first ionization peak contains only one electronic transition, so it is appropriate for the examination of fine structures. As is shown in Fig. 2b, there is an intramolecular vibrational structure of 1380 cm^{-1} (0.17 eV) in the gas spectrum, but, at least at this stage of resolution, there is no distinct corresponding structure in the first ionization peak in the solid state and the peak width (the overall FWHM of this band is 0.64 eV) is much larger than that of the gas spectrum (*cf.* Fig. 2a).

The fact that the 0–0 transition is very strong in the gaseous state suggests that no large deformation of the molecule occurs upon ionization; therefore, it is difficult to ascribe the large peak width in the solid state to intramolecular vibrations.

Some other mechanisms which lead to the broadening of the peaks have been proposed. If these effects are large enough, and if every intramolecular vibrational level is accompanied by them, the disappearance of the fine structures may be explained. Considering the interaction of the ion as a point charge with the nearest four molecules, Zagrubskii and Vilesov8) estimated the Franck-Condon quantum-mechanical spread due to the local lattice deformation for anthracene and obtained a value of 0.35 eV for the difference between the adiabatic and vertical transitions (*cf.* Fig. 3a, where this difference is $P_a - P_v$). However, they took the value for the total ion-dipole and dipole-dipole interactions and neglected the energy for the lattice deformation itself (ΔE in Fig. 3a). After correction for this, the value for anthracene is only 0.08 eV. We made similar calculations for naphthacene with a mean molecular polarizability of 32.4 Å^3 12) and with a force constant of 100 cm^{-1} for the lattice deformation; we thus obtained a value of 0.17 eV. With this value, and considering the roughness of the approximation, we are not able to decide at this stage whether this mechanism can explain the large peak width or not.



(a) (b)

Fig. 3. Two mechanisms for the broadening of the peaks. On ionization, potential curve of the neutral state (curve I) changes to that of the ionized state (curve II) due to the polarization effect.
(a) Franck-Condon quantum-mechanical spread.
(b) Polarization energy dispersion due to the lattice vibrations in the neutral state.

Further, Silinsh9) and Sworakowski10) suggested a dispersion of the polarization energy due to the lattice vibrations in the neutral state (P_{max} to P_{max} in Fig. 3b). The FWHM expected for this mechanism amounts to about 0.3 eV (assuming $\sigma = 0.1$ eV for the gaussian distribution). It seems certain that this mechanism plays some role in the broadening of the peaks.

In both mechanisms, the first peak is expected to correspond to the vertical ionization from the equilibrium position for the lattice vibrations. The fact that the ionization energies estimated for this process (5.81 eV by Sworakowski10) and 5.83 eV by Batley *et al.*13)) agree well with the value for the first peak confirms this idea.

Other possible mechanisms contributing to the peak width are as follows: (1) a variation in the ionization potential between the bulk and the surface;14) (2) an energy loss of the photoelectrons on the way to the surface15) as a result of the excitations of the intramolecular vibrations of the other neutral molecules (an energy loss due to the phonons is less likely because of their small energy quantum), and (3) the lifetime broadening of the photoelectrons.[16] To determine the degrees of contribution from these factors, however, further comprehensive studies, including the improvement of the resolution, will be necessary.

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