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The Photoionization of Molecular and Crystalline Anthracene

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The photoionization efficiency curve of gaseous anthracene was examined by comparing it with the photoemission yield curve of solid anthracene. The direct ionization processes were found to dominate the two curves primarily. Some σ-valence orbitals of this compound were associated with considerably low ionization potentials. The cube law for the photoemission yield near the threshold was also established.

A considerable amount of effort has been devoted during the last decade to elucidate the ionization mechanism and the related valence-band structure of the organic crystal. The photoionization in the gas phase is an important phenomenon which provides a key to the electronic structure of the molecule; the solid-state ionization potential is, correspondingly, an important parameter governing the behavior of molecules in the solid state. Because of our great interest in the electronic behavior of polycyclic aromatics, anthracene and related molecules have recently been chosen for photoionization studies in the gas and solid phases.[1-11] In order to advance further the understanding of the molecular and solid-state photoionization, we attempted to measure the photoionization efficiency curve of molecular anthracene. In this article, we would like to examine the spectral response of the photoionization efficiency for this compound, and correlate the structure of the curve with that of the photoemission yield curve previously published.

Experimental

The photoionization efficiency (PIE) for the anthracene molecule was obtained as follows. The continuous flow of the anthracene vapor between the two electrodes was irradiated with a vacuum ultraviolet light. A 0.5 m vacuum monochromator was used under the same conditions as in Refs. 9 and 10. The light source was a hydrogen discharge tube. The photocurrent collected with the plate electrodes was arithmetically divided by the incident-light intensity. The spectral distribution thus defined is supposedly similar to that of the photoionization cross section,[12] since the vapor pressure employed was considerably lower than the saturated vapor pressure at room temperature. The synthetic anthracene was further purified and then used.

Results and Discussion

The PIE curve of the gaseous anthracene is shown in Fig. 1. The ionization efficiency increases gradually 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 of a photon energy. The various sharp bands characteristic of the PIE curve are not present. The possible autoionization peaks seem to be effectively suppressed for this compound. The smoothness of the curve can be phenomenally ascribed to the large molecular dimension of anthracene, since the PIE curves of simpler molecules generally display a more complex dependence on the photon energy.[13-18]

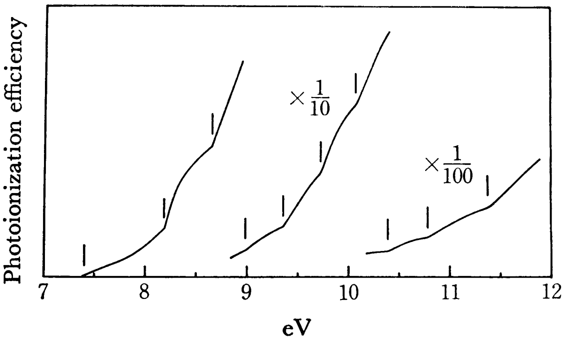

Fig. 1. Photoionization efficiency curve of the molecular anthracene. (Breaks are indicated by lines.)

This effect strongly suggests that, as for anthracene, most photoelectrons are emitted through the direct ionization processes. As long as the possibility of the autoionization processes can be ruled out, the breaks in the curve should correspond to the minimum energies needed to excite the ground-state molecule to the excited-state molecular cations. Every spacing between the adjacent two breaks is obviously too large to be explained in terms of vibrational levels. In other words, these breaks express the adiabatic ionization potentials associated with the lower-lying valence bands in the anthracene molecule.

The structure of the PIE curve is straightforwardly identified by comparing it with the external photoemission data on the crystalline anthracene. In 1963, Vilesov *et al.* carried out a photoemission study of the anthracene crystal and determined the valence-band structure from the kinetic energy distribution curves (EDC) of photoelectrons.[7] Furthermore, Kochi *et al.* observed the existence of several distinct breaks in the photoemission yield (PEY) curve.[10] The PEY curve itself is also a monotonously-varying function of the photon energy. The locations of the breaks in both phases are all listed in Table 1. The values in parentheses are given relative to the first ionization potential or to the threshold energy.

First of all, it is noteworthy that the breaks in the PIE curve are well reproduced in the PEY curve. The breaks in the PIE curve almost coincide with those in the PEY curve, if the threshold of the former curve is appropriately shifted to that of the latter one. The energy differences between the corresponding breaks

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TABLE 1. IONIZATION POTENTIALS OF ANTHRACENE (eV)

PIE[a]	PEY[b]	POL[c]	EDC[d]	PES[e]	TYPE[f]
7.40(0.00)	5.65(0.00)	1.75	0.0	7.40(0.00)	π
8.19(0.79)	6.40(0.75)	1.79	—	—	σ
8.65(1.25)	6.93(1.28)	1.72	1.2	8.52(1.12)	π
8.98(1.58)	7.18(1.53)	1.80	—	—	σ
9.35(1.95)	7.61(1.96)	1.74	1.8	9.16(1.76)	π
9.72(2.32)	7.83(2.18)	1.89	—	—	σ
10.07(2.67)	8.48(2.83)	1.59	2.6	10.13(2.73)	π
10.39(2.99)	—	—	—	10.21(2.81)	π
10.78(3.38)	—	1.7	3.4	10.7 (3.3)	σ
11.37(3.97)[g]	—	—	—	11.3 (3.9)	σ

a) From breaks in the photoionization efficiency curve. b) Ref. 10; from breaks in the photoemission yield curve. c) Polarization energy as defined by the difference between PIE and PEY. d) Ref. 7; from the kinetic energy distribution curves of photoelectrons. e) Ref. 2; from the photoelectron spectrum. f) The type of the valence orbital concerned. g) Note that this value was erroneously typewritten in Ref. 6.

are also listed in Table 1.

According to Lyons,[19] the ionization potential of the molecular crystal, I_c, is related to the gaseous ionization potential of the component molecule, I_g, by:

$$I_c = I_g - P, \tag{1}$$

where P is the positive polarization energy of the crystal. This equation implies that the energy of the crystalline state can be described in terms of the molecular properties and the electrostatic polarization energy. This equation has often been applied to the explanation of the photoemission threshold energy of the molecular crystal.

However, the present results show that the energy difference between the corresponding breaks, which is considered the pertinent polarization energy, is almost preserved among the higher ionization potentials of the crystal. The polarization energy related to the first ionization potential is 1.75 eV. The energies for the first five ionization potentials are substantially the same. This means that the polarization energy is almost independent of the orbital symmetry of the molecular ion formed in the crystal. Several authors have calculated the polarization energy for the anthracene crystal.[20,21] The experimental polarization energy is, however, situated at the upper limit of the theoretical values (1.63 and 1.38 eV,[20] and 1.52 eV[21]). The accordance of the structures in the two curves gives further support to the first-mentioned aspect that both the PIE and PEY curves are primarily determined by the direct ionization processes, though different autoionization processes are possible for the different phases.[22–25]

Next, let us classify the breaks in the two curves. The assignment of the π-ionization potentials of anthracene has been completely established on the basis of recent molecular orbital calculations,[2–4] since these calculations are quite consistent with each other. These π-ionization potentials have all been identified by photoelectron (PE) spectroscopy.[2–4] Accordingly, breaks which correspond to such π-ionization potentials can readily be ascribed to the π-valence orbitals. However, additional breaks are also present in the PIE curve. They have no counterparts in the PE spectrum, the lower part of which comprises only photoelectrons ejected from π-valence orbitals. These breaks were necessarily attributed to the σ-valence orbitals, now that the locations of all the π-valence orbitals have been established with little doubt.

Here, it should be noted that the lowest σ-ionization potential of anthracene is as low as 8.19 eV. If one remembers the fact that the ionization potentials of n-alkanes converge to about 10 eV,[26] this value seems to be too small. The counterpart of the 8.19 eV break in the PIE curve is nevertheless found at 6.40 eV in the PEY curve. This break is found noticeably in the PEY curve obtained by Lyons and Morris.[27] Marchetti and Kearns also observed a PEY curve with a similar structure.[28] Such a common feature of the PEY curve appears to favor our interpretation of the 8.19 eV break in the PIE curve.

Why are these breaks undetected in the PE spectrum? The reason is presumably that such transitions induce appreciable ionization cross sections only when the photon energy does not much exceed the corresponding minimum ionization energies. This explanation is just the same one as Momigny and Lorquet presented for the photoionization of benzene.[29] Dewar *et al.* also suggested that there might be some missing bands, especially some bands related to the σ-valence orbitals, in the PE spectra of aromatic hydrocarbons.

The EDC curves of the solid species generally resemble the PE spectrum of the molecule.[7,10] Exceptionally, some trace of the 8.19 eV break is found, though it is not pronounced, in the EDC curves observed by Vilesov *et al.*[7] A shoulder is present between the first two peaks ascribed to the π-valence orbitals in some EDC curves. This is the most direct evidence for the presence of the valence orbital associated with it. The other σ-electron bands are substantially dissipated except for the higher-energy ones. Such an aspect of the σ-ionization potentials can be traced in Fig. 1, where the second step, beginning at 8.19 eV, is somewhat rounder, suggesting an abrupt decrease in the partial ionization cross section of the second transition with an increase in photon energies.

With the EDC data, we can estimate further the polarization energy of the crystal. The first σ-ionization potential which was clearly detected in the EDC curve of anthracene is located 3.4 eV above the first π-ionization potential.[7] On the other hand, the corresponding break in the PIE curve is found at 10.78 eV. Accordingly, the polarization energy concerned amounts to about 1.7—1.8 eV. This is almost the same value as that determined for lower ionization potentials. For the present, there is little evidence for the rearrangement of the molecule in the crystal, the occurrence of which was suggested in the carbon suboxide crystal.[31]

The above-mentioned results can be used to examine the threshold law for the photoemission from the organic solid. In general, the quantum efficiency of the photoemission near the threshold is very low and does not show any abrupt change.[8–10] Therefore, it is quite difficult to determine the accurate photoemission threshold energy. This is in marked contrast to the distinct threshold behavior of the gaseous photoionization.12)

However, the onsets of the transitions related to the higher ionization potentials are often easily distinguished as breaks in the PEY curve.8,10) Supposing that the polarization energy is preserved among the first and higher ionization potentials, these breaks can be employed as a secondary standard in determining the actual threshold energy for the photoemission from the crystal. If the higher ionization potentials of the crystal could be identified by comparing the breaks in the PEY curve with those in the PIE curve, the threshold energy of the PEY curve would be the first ionization potential of the gaseous species minus the polarization energy associated with the higher ionization potentials. As has been mentioned above, the experimental threshold energy for the anthracene crystal satisfies these requirements, and so it can be regarded as the actual ionization potential of the crystal.

This fact verifies that the cube law for the photoemission threshold is valid for an organic crystal such as anthracene.9,10) According to this law, the experimental threshold energy of anthracene (5.65 eV) can almost be reproduced by the extrapolated value of 5.68 eV.10) This implies that the quantum efficiency of the photoemission near the threshold, $Y(h\nu)$, is adequately expressed as:

$$Y(h\nu) \propto (h\nu - E_{\text{th}})^3, \qquad (2)$$

where E_{th} signifies the extrapolated threshold energy.

On the other hand, the threshold energy derived by Marchetti and Kearns (5.85—5.95 eV) seems to be somewhat larger,28) probably because they did not take into account the discrete valence band structure and the related vibrational structure of the crystal in constructing their threshold law. Another power law was presented by Sworakowski.32) According to his square-root law, the threshold energy must be 6.25 eV for the anthracene crystal. However, this law apparently retains the spectral behavior of the gaseous photoionization, since the photoionization efficiency of the gaseous molecule is approximately proportional to the square root of the energy difference between the threshold and the applied photon.17,18) This aspect of the law is in contradiction to his theory, in which the escape probability and so on are also taken into consideration.32) This is probably due to his density-of-state function which is not fit for the polycyclic aromatics.

In conclusion, the agreement between the structures of the PIE and PEY curves confirms the predominant direct ionization processes and the parallel valence-band structures in both phases. The parallel valence-band structures appear to characterize the organic molecular crystal and indicate that the whole valence-band structure of the solid is expressed in terms of molecular ionization potentials and a single polarization energy, as is suggested by Eq. (1). In this connection, the cube law for the photoemission threshold was established. It is noteworthy that the measurement of the PIE curve complements the PE spectroscopy well. A comparative study of these phenomena would be very helpful to a deeper understanding of the ionization mechanism in both gas and solid phases.

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