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Photoionization of Naphthalene

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Studies of the photoionization of aromatic hydrocarbons in the vapour phase play an important role in obtaining the direct information on the highly-excited states of these molecules. These results can also be used in the estimation of the exciton states in the molecular aggregates.

Recently, several articles concerning the ionization phenomena of naphthalene have been published. Various experimental values of the ionization potential have been obtained by an electron-impact method, by the spectroscopic method, and by photoelectron spectroscopy.[1-5] During the last decade, the theory of the ionization has also been improved.[6-9]

In this paper, we wish to report the ionization potentials of some aromatic hydrocarbons involving naphthalene and to compare the photoionization efficiency curve of naphthalene with the photoelectron spectrum obtained by Turner, and Dewar and Worley.[4,5]

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Experimental

The photoionization efficiency curve obtained in this study was made by the method developed by Watanabe.[10] The experimental arrangements and the procedure were nearly the same as those described in Kitagawa's article.[3]

The apparatus employed consisted of a Seya-Namioka-type, 0.5-m vacuum ultraviolet monochromator. A spectral resolution of about 2 Å was obtained with the two slits set about 100 μ in width. The high-voltage discharge of hydrogen was used as the light source.

The photoionization cell was made of Pyrex glass, and LiF windows were attached. Non-magnetic stainless-steel electrodes were set in a cylindrical form 2 mm apart from each other.

The applied voltage of 10 V was sufficient to collect the electrons produced. The collected ionization current was measured on a Cary 31 vibrating-reed electrometer.

All the photoionization-yield measurements were made with a static pressure and at room temperature.

The naphthalene used was a zone-refined material; it was subjected to over 50 passes of the zone heater. Durene, acenaphthene, and indene were purified according to the usual procedures.

The ionization efficiency, Y, was obtained from the equation:

$$Y = \frac{Ki}{I - I_0} \qquad (1)$$

where K is an apparatus constant, i is the photocurrent, I is the intensity of the incident light, and I_0 is the intensity of the transmitted light through the gaseous specimen.

Results and Discussion

The photoionization efficiency of naphthalene is plotted as a function of the energy in electron volts in Fig. 1. The wavelength scale is also given. The lowest adiabatic ionization energy is denoted by I.P. The photoelectron spectrum of naphthalene is also shown in Fig. 1.[4]

In the region observed, the products caused by photolysis are considered to be small in amount. Therefore the ionization yield is mainly that of the naphthalene cation, $C_{10}H_8^+$.[11]

The photocurrent rapidly increased as the photon energy increased. Various structures exist in the ionization efficiency curve. In the first, this curve is a gradually varying-step function of the energy. The threshold is the first step: it corresponds to the first ionization potential, 8.12 eV. This value agrees well with that obtained by Watanabe *et al.*[2] The literature values of the ionization potential of naphthalene are summarized in Table 1.

In the region below the threshold energy, the yield exponentially increases forward the threshold energy. This exponential rise can be explained by the population of thermally-activated molecules in the ground state.

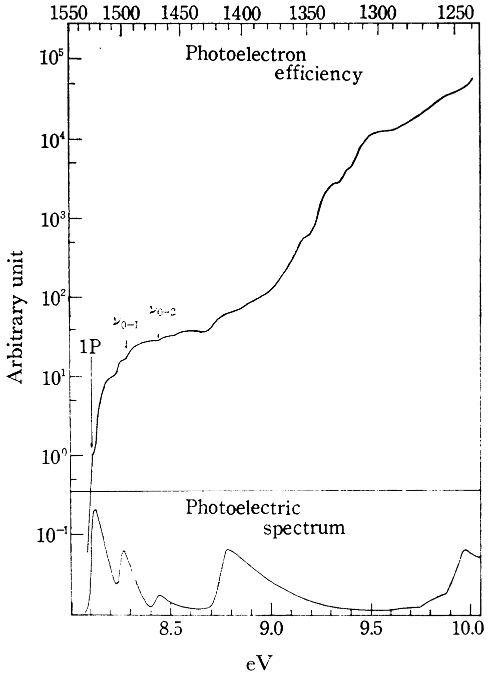

Fig. 1. Photoionization efficiency curve and photoelectron spectrum of naphthalene.*
* cited from Ref. 4.

Table 1. First ionization potential of naphthalene

Experimental	This work	8.12 eV
	Photoionization[2]	8.12
	The convergence limit of Rydberg series[3]	8.13
	Electron impact[1]	8.26
Theoretical	*Ab initio*[8]	9.20 eV
	Modified Koopman's theorem[6]	8.61
	Half-electron method[7]	8.30

In the first ionization region, three vibrational structures were observed. They were located at 1506, 1497, and 1466 Å. The origin of the first band is unknown. The second and the third bands correspond very well to the vibronic bands in the photoelectron spectrum.[4] Accordingly, these are interpreted as 0-1 and 0-2 bands. The vibrational spacings are around 0.17_5 eV.

The ratio of the contributions of the 0-0, 0-1, and 0-2 bands to the ionization yield is approximately 5 : 3 : 1. This trend is comparable to that of the integrated strengths of the vibrational structures in the photoelectron spectrum.

The ionization potential value, 8.26 eV, is that obtained by the electron-impact method.[1] It

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was considered to be the vertical ionization potential. However, the strongest vibronic transition to the first ionization state is the 0-0 band, as is shown in Fig. 1. From this point of view, the vertical ionization potential should coincide with the adiabatic one; that is, the vertical ionization also takes place without any change in the molecular geometry. The observed difference in the measured ionization potentials, 0.14 eV, should be attributed not to the Franck-Condon factors, but to the experimental difficulties latent in the electron impact.

The higher ionization potentials have been reported to be located at 8.79, 9.96, and 10.90 eV.[5]

The electronic binding energies have also been calculated by the MINDO method in the energy range covering all the valence orbitals.[5] However, if we assume that the reorganization energy of an ion is the same in all the states, the higher ionization potentials can be estimated by means of the π-electron approximation by applying a constant correction. 1.15 was subtracted from the binding energies cited in the article of Baird and Dewar.[12] The results are entered in Table 2.

Table 2. Higher Ionization potentials of naphthalene

Experimental*	Theoretical	From the efficiency curve
8.11 eV	8.12 eV	8.12 eV
8.79	8.92	8.6—8.9
9.96	9.96	>9.6
10.90	10.89	
12.26	12.48	

* cited from Ref. 5.

When a radiation shorter than 1430 Å was used, there was a marked enhancement of the yield, mainly due to the second ionization by the resemblance to the photoelectron spectrum.

However, in the region concerned, the structure could not be observed distinctly. These phenomena are perhaps caused by the overlapping of possible vibrational modes. The Franck-Condon envelopes are smoothed. Consequently, the total ionization yield may become apparently continuous, or at least diffuse. These broad peaks, as well as the sub-step at 1506 Å, do not reflect on the photoelectron spectrum. In view of this the significance of such experiments is clear.

The efficiency curve shows a gradual rise again in the region shorter than 1250 Å; this is interpreted as the beginning of the third ionization region.

The approximate values of the ionization potentials estimated from the efficiency curve are also listed in Table 2. However, the exact potentials can not be obtained in this manner, since the efficiency in the higher-energy regions is closely related to the change in the molecular geometry and to such other effects as autoionization and predissociation.[13]

In spite of this, the spectral efficiency is well correlated with the photoelectron spectrum, as has been mentioned above. Further measurements in the higher-energy region are desirable: we are also preparing an apparatus for photoelectron spectroscopy.

In order to analyse the amount of the ionization yield, it is necessary to calculate the photoionization probability. Some theoretical formalisms have been reported using the hydrogenic continuum-wave function.[14,15] The probability of each ionization state depends on the wavelength of the exciting light, so no detailed analysis can be made between the efficiency curve and the photoelectron spectrum.

The behaviour of the experimental ionization cross-section is quite similar to the efficiency curve. The cross section in the first ionization region is of the order of 10^{-19} cm^2. It seems rather a reasonable value, judging from the calculated value of benzene, 10^{-19}—10^{-18} cm^2.[16]

We also measured the first ionization potentials of three compounds, durence, acenaphthene, and indene; they are 8.03±0.02, 7.66±0.03, and 8.08±0.02 eV respectively.

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