

**INTERNATIONAL CENTRE FOR
THEORETICAL PHYSICS**

**LAMP
SERIES REPORT**
(Laser, Atomic and Molecular Physics)

**PHOTOELECTRON SPECTROSCOPY VIA ELECTRONIC
SPECTROSCOPY OF MOLECULAR IONS**

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Zahid H. Khan*
International Centre for Theoretical Physics, Trieste, Italy.

ABSTRACT

In this work, a new aspect of the correlation between optical and photoelectron spectra is discussed on the basis of which the first ionization potentials of condensed-ring aromatics can be estimated from certain features in the electronic spectra of their positive ions. Furthermore, it is noticed that the first IP's are very sensitive to molecular size as the latter's inclusion in the regression formulas improves the results considerably. Once the first ionization potential for a molecule is determined, its higher IP's may be computed if the lower-energy electronic bands for its cation are known. This procedure is especially useful for such systems whose uv photoelectron spectra are unknown.

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Preface

The ICTP-LAMP internal reports consist of manuscripts relevant to seminars and discussions held at ICTP in the field of Laser, Atomic and Molecular Physics (LAMP).

These reports aim at informing LAMP researchers on the activity carried out at ICTP in their field of interest, with the specific purpose of stimulating scientific contacts and collaboration of physicists from Third World Countries.

* Permanent address: Department of Physics, Jamia Millia Islamia (Central University), New Delhi-110025, India.

1. INTRODUCTION

The advent of ultraviolet photoelectron spectroscopy in the early 1960's brought a great revolution in our understanding of the spectra and structure of molecules. It was welcomed by the spectroscopist community with great enthusiasm as it provided an experimental tool to look into and to verify the existence of molecular orbitals, which till then had merely been a theoretical concept. In words of W.C. Price [1], "Chemists can see the orbital structure of even fairly large molecules and no longer have to rely on the predictions of the theoreticians."

Yet another great advantage of the photoelectron (PE) spectroscopy was realized more than a decade later by Zahradnik et al. [2,3] who for the first time suggested the use of PE spectroscopy as a source of electronic spectral data for radical cations of conjugated aromatic systems. This suggestion was based on the fact that the energy difference between the first and (n+1)-th electron energy peaks corresponds to the difference in the energies of the ground state of the cation and its n-th excited doublet state. A further contribution to this work was made by Shida and co-workers [4] who studied the correspondence between the results obtained from optical and PE spectra of a large number of aromatics. It might, however, be mentioned that there are some differences between the two types of spectra. First, the electronic absorption measurements are usually made in solutions and rigid glasses, whereas photoelectron spectra are measured in the gas phase. Secondly, electronic absorption spectra are often complicated by the presence of neutral species, formation of dimers and solvent shifts. Fortunately, the PE spectroscopy is free from such shortcomings. In spite of these differences, the PE spectroscopy of neutral molecules provides valuable information about the electronic states of their positive ions.

To study further the usefulness of the PE spectroscopy in understanding the optical spectra of condensed-ring

aromatic positive ions, we have, during the past few years, carried out a detailed and systematic study of this problem [5-7]. From these studies, it emerges out that except for slight matrix shifts, the electronic energies of the cations inferred from the PE spectra of the neutral molecules are in close agreement with the observed low-energy electronic absorption bands of the positive ions.

Here we present yet another and an entirely new aspect of the correlation where it is shown that from the spectral features of optical absorption bands in radical cations of condensed-ring aromatics, it is possible to extract useful information about the vertical ionization potentials of the parent molecules and hence about their photoelectron spectra. For this, we start first with a brief introduction of electronic transitions in molecular ions followed by a description of the main features of photoelectron spectroscopy. Finally, we discuss the relations that lead to the prediction of the first ionization potentials (IP's) of molecules.

2. ELECTRONIC SPECTRA OF MOLECULAR IONS

Various experimental techniques are now available for the preparation of radical ions of organic molecules. In our laboratory, we have produced aromatic hydrocarbon monocationic ions by ultraviolet irradiation of the parent molecules doped in boric acid glass at room temperature. The optical absorption spectra of the ionic species were measured on a spectrophotometer. For the identification of the electronic bands, guidance is needed from theoretical calculations, a brief introduction of which is given in the following.

An alternant hydrocarbon, in its ground state, has an even number of π electrons. On ionization, the molecule is transformed to its ion with the ejection of a photoelectron:



If the unpaired electron is in the ground state, the system can be described by a single configuration wave function (Slater determinant):

$${}^2\Psi_0 = | \varphi_1^\alpha \varphi_1^\beta \dots \varphi_i^\alpha \varphi_i^\beta \dots \varphi_m^\alpha | \quad (2)$$

where φ_i^α 's and φ_i^β 's are spin orbitals.

For the construction of the excited state wave functions, we consider only one-electron excitations. The various types of excited state doublet configurations may be classified according to the scheme in Fig. 1 [8]:

- I : $i \rightarrow m$,
- A : $m \rightarrow m+1$,
- B : $m, i \rightarrow k$.

Here i represents doubly-occupied molecular orbitals, m is the singly-occupied MO, and $(m+1)$ and k correspond to the vacant orbitals. In the light of this, the excited doublet configurations for the ion can be written as

$${}^2\Psi_I = | \varphi_1^\alpha \varphi_1^\beta \dots \varphi_i^\alpha \varphi_m^\beta \dots \varphi_m^\alpha |; \quad (3)$$

$${}^2\Psi_A = | \varphi_1^\alpha \varphi_1^\beta \dots \varphi_i^\alpha \varphi_{m+1}^\beta \dots \varphi_{m+1}^\alpha |; \quad (4)$$

$${}^2\Psi_{B1} = | \varphi_1^\alpha \varphi_1^\beta \dots \varphi_i^\alpha \varphi_i^\beta \dots \varphi_k^\alpha |;$$

$${}^2\Psi_{B2} = \frac{1}{\sqrt{2}} \{ - | \varphi_1^\alpha \varphi_1^\beta \dots \varphi_i^\alpha \varphi_k^\beta \dots \varphi_m^\alpha | + | \varphi_1^\alpha \varphi_1^\beta \dots \varphi_i^\alpha \varphi_k^\beta \dots \varphi_m^\alpha | \};$$

$${}^2\Psi_{B3} = \frac{1}{\sqrt{6}} \{ 2 | \varphi_1^\alpha \varphi_1^\beta \dots \varphi_i^\alpha \varphi_k^\alpha \dots \varphi_m^\beta | + | \varphi_1^\alpha \varphi_1^\beta \dots \varphi_k^\alpha \varphi_i^\beta \dots \varphi_m^\alpha | - | \varphi_1^\alpha \varphi_1^\beta \dots \varphi_i^\alpha \varphi_k^\beta \dots \varphi_m^\alpha | \}. \quad (5)$$

At a first glance, it appears that the configurations of types A and B characterize the parent molecules and only the I type configurations are characteristic of the ion. But in reality, the situation is not so straightforward. Due to configuration mixing, the electronic states do not remain pure anymore and are, in fact, mixtures of various doublet configurations. For the calculation of electronic transition

energies and intensities of radical cations, open-shell SCF-MO calculations with limited configuration interaction (CI) have been carried out which help in the assignment of the individual cation bands. Electronic absorption spectra for some ionic species together with the assignment of their electronic bands are given in the following section.

3. SALIENT FEATURES OF PHOTOELECTRON SPECTROSCOPY

Photoelectron spectroscopy is a modern development of early experiments on the photoelectric effect. It was realized that radiations of sufficiently short wavelengths can ionize atoms and molecules. Furthermore, it was established that the kinetic energy of the photoelectrons depends only upon the wavelength of the incident photons and not on their intensity. According to the Einstein's photoelectric equation, the kinetic energy, K.E., of the ejected photoelectron is essentially the difference of the the energy of the incident photon, $h\nu$, and the ionization potential, I , of the target,

$$\text{K.E.} = h\nu - I \quad (6)$$

In reality, the Einstein's equation is only an approximate one, both for atoms as well as for molecules. For instance, on interaction of a photon with molecules, molecular ions may be formed with vibrational or rotational excitation energy.

When radiation interacts with an ensemble of molecules, electrons may be ejected from a variety of molecular orbitals for which the binding energies are less than the energy of the incident photon. The probability of ionization will, however, differ from orbital to orbital. The net effect of photoionizing a large number of molecules by a photon of energy $h\nu$ is that some will lose an electron from one orbital and some from other particular orbital and so on. "Bundles" of electrons are therefore emitted, each electron originating from a different individual molecule and each bunch having a different energy according to the

modified Einstein's equation,

$$E_n = h\nu - I_n, \quad (7)$$

where E_n represents the energy of the different bundles ($n = 1, 2, 3, \dots$) and I_n represents the IP's for an electron in the first (outermost), second (next outermost) orbital etc.

In a photoelectron spectrometer, an intense beam of monochromatic uv light (He I, 58.4 nm) ionizes the molecules in the ionization chamber. The ejected photoelectrons are separated according to their kinetic energies in an electron energy analyser and detected. Thus a photoelectron spectrum is a record of the number of electrons detected at each energy, and in the spectrum a peak is found at each energy, $h\nu - I_n$, corresponding to the binding energy (ionization potential), I_n , of an electron in the system (Fig. 2).

Figure 3 shows the correlation between the photoelectron spectrum of a molecule and the electronic spectrum of its positive ion. According to this, the energy difference between the first and (n+1)-th peaks in a photoelectron spectrum correspond to the transition energy of a radical cation from its ground doublet state to the n-th excited doublet state, i.e.,

$$E_{i,n} = IP_{n+1} - IP_1; \quad (n \geq 1), \quad (8)$$

where $E_{i,n}$ is the energy for the n-th electronic transition and IP_n 's are the n-th electron energy peaks. To compare the results obtained from optical and PE spectra, we have sketched in Fig. 4 the PE spectrum of pyrene and the electronic absorption spectrum of its radical cation. A similar spectral diagram for perylene is displayed in Fig. 5. The closeness of the energies of I-type optical bands obtained from the two different techniques clearly demonstrates the usefulness of Eq. 8 and hence that of the PE spectroscopy as a source of spectral data for radical cations.

4. ELECTRONIC SPECTROSCOPY OF RADICAL CATIONS AS A PREDICTOR OF IONIZATION POTENTIALS OF PARENT MOLECULES

Apart from the above correlation between the photoelectron spectrum of a molecule and the electronic spectrum of its positive ion, there is yet another interesting relation which predicts the first ionization potentials (IP_1 's) of condensed-ring aromatic hydrocarbons from the energies of the optical A bands for their cations. In order to derive such a relation, we consider the simple theoretical model as depicted in Fig. 6 where the two highest bonding and the two lowest antibonding orbitals are labeled as i, m, m+1 and k, respectively. Using the Koopmans' approximation [9], according to which the negative of the SCF orbital energies give the ionization potentials,

$$IP_i = -\epsilon_i^{SCF}, \quad (9)$$

the first ionization potential can be expressed as,

$$IP_1 = -\epsilon_m. \quad (10)$$

It has already been demonstrated by Brogli and Heilbronner [10] that the use of Hückel orbitals instead of SCF orbitals in the above equation is equally valid. Let us now assume that in the first approximation, the molecular energy levels remain unaltered after the molecule gets ionized. In the light of this picture, the following correlation between IP_1 and E_A is expected [11]:

$$IP_1 = -\alpha + 1/2 E_A. \quad (11)$$

In the above equation, if we treat α and $1/2$ as empirical parameters a and b, respectively, then Eq. (11) can be rewritten in a more general form,

$$IP_1 = a + b E_A. \quad (12)$$

This leads to a regression problem which can be solved by standard least-squares techniques.

Fitting the experimental data for the optical A bands and the vertical first IP's for 36 aromatic hydrocarbons to Eq. (12) results in the following regression:

$$IP_1 = 5.32 + 0.79 E_A, \quad (13)$$

$$SE (IP_1) = 0.18 \text{ eV.}$$

This is depicted in Fig. 7. The above regression is very interesting for the following reasons: (i) the regression comprises different varieties of aromatics, and (ii) in hydrocarbons having a degenerate ionic ground state, there is a first-order configuration interaction which might influence the energy levels considerably. There is, however, an appreciable shift in the slope of the above regression from the value of $1/2$ expected from the simple Hückel model. This can be explained on the basis of an increase in the coefficient if the model includes electron interaction and configuration interaction explicitly.

Although the results obtained from above regression is satisfactory, its rather large standard deviation (0.18 eV) is still disturbing. From the scatter of points around the regression line in Fig. 7 it appears that the results could be improved if some sort of structural effects are incorporated in the regression formula. To examine this problem in further detail, separate regressions were obtained for the different series of hydrocarbons which improved the results considerably. Our next attempt was therefore to consider "size effect" and more specifically to include in the regression one more parameter, viz., the number of benzene rings, N . A three-parameters fit of the data with the same data points leads to the regressions,

$$IP_1 = 5.48 + 0.55 E_A + 2.20 / N, \quad (14)$$

$$SE (IP_1) = 0.11 \text{ eV ;}$$

and

$$IP_1 = 4.94 + 0.55 E_A + 2.20 / N^{1/2}, \quad (15)$$

$$SE (IP_1) = 0.09 \text{ eV.}$$

These regression curves are plotted in Figs. 8 and 9, respectively, and the first IP's thus calculated are collected in Table 1.

Once the first ionization potential of a molecule is found using the above procedure, its higher ionization

potentials can also be estimated if the energies of I type electronic bands of its radical cation are known. This can be achieved from the relation,

$$IP_{n+1} = IP_1 + E_{I,n}, \quad (n \geq 1). \quad (16)$$

The usefulness of this approach is demonstrated in Fig. 10 for the case of 1,2,5,6-Dibenzanthracene where the calculated IP's of 7.26, 8.32, 8.90, 9.05, 9.89 and 10.51 eV are in close agreement with the observed values of 7.38, 8.43, 9.00, 9.23, 9.98 and 10.73 eV, respectively. It must, however, be noted that the reliability of this empirical approach depends upon the accuracy of the estimated first IP's and the correct identification of the I type electronic bands in the cation spectra.

5. CONCLUSION

This work sheds a new light on the correlation between optical and photoelectron spectroscopies and demonstrates as to how the optical spectra of molecular ions could be used to its good advantage to estimate the first ionization potentials and, in some cases, even the higher IP's of parent molecules. For this, a set of novel correlations between the first IP's of polycyclic aromatics and the optical A bands of their cations are proposed. It is further noticed that the results are considerably improved if size effect is also incorporated in the formulas which shows that the molecular size plays a significant role in the estimation of first IP's.

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TABLE - 1

Calculated Values of First IP's of Condensed-Ring Aromatics from Energies of Optical A Bands of Their Cations (All energies are in eV).

Hydrocarbon	E_A^{obs}	IP_1^{obs}	IP_1^{cal} (a)	IP_1^{cal} (b)	IP_1^{cal} (c)
Naphthalene	3.24	8.15	7.89	8.35	8.29
Anthracene	2.00	7.41	6.91	7.31	7.32
Phenanthrene	2.90	7.86	7.62	7.80	7.81
Tetracene	1.61	6.97	6.60	6.91	6.94
Chrysene	2.59	7.59	7.37	7.45	7.47
1.2-Benzanthracene	2.18	7.41	7.05	7.22	7.25
3.4-Benzphenanthrene	2.79	7.60	7.53	7.56	7.58
Triphenylene	3.03	7.88	7.72	7.69	7.71
1.2,7.8-Dibenzo-chrysene	2.55	7.20	7.34	7.24	7.25
1.2,3.4-Dibenzanthracene	2.66	7.39	7.43	7.38	7.39
1.2,5.6-Dibenzanthracene	2.42	7.38	7.24	7.24	7.26
1.2,7.8-Dibenzanthracene	2.57	7.40	7.36	7.33	7.34
3.4,8.9-Dibenzo-tetraphene	2.27	7.19	7.12	7.09	7.09
Naphtho-(2'.3':6.7)-pentaphene	2.66	7.35	7.43	7.25	7.24
Perylene	2.29	6.97	7.13	7.17	7.19
2.3-Benzoperylene	2.19	6.92	7.06	7.05	7.05
2.3,8.9-Dibenzo-perylene	2.15	6.86	7.03	6.97	6.96
2.3,10.11-Dibenzo-perylene	2.13	6.85	7.01	6.96	6.95
1.12-Benzoperylene	2.40	7.15	7.22	7.16	7.16
1.12-Benzo-naphtho-(2'.3':2.3)perylene	2.26	7.04	7.11	6.99	6.97

1.12,4.5-Dibenzo- perylene	2.22	6.99	7.08	7.01	7.00
1.12-o-phenylene- perylene	2.31	6.96	7.15	7.06	7.05
Coronene	2.65	7.29	7.42	7.24	7.23
1.12-Benzocoronene	2.47	7.08	7.28	7.11	7.08
Naphtho-(2'.3':1.2)- coronene	2.19	6.88	7.06	6.92	6.88
Pyrene	2.75	7.41	7.50	7.54	7.56
1.2-Benzopyrene	2.87	7.41	7.60	7.49	7.51
3.4-Benzopyrene	2.24	7.10	7.10	7.15	7.16
1.2,4.5-Dibenzo- pyrene	2.25	7.11	7.11	7.08	7.08
1.2,3.4-Dibenzo- pyrene	2.20	7.07	7.07	7.05	7.05
3.4,8.9-Dibenzo- pyrene	1.88	6.82	6.81	6.88	6.88
1.2,3.4,6.7,9.10- Tetrabenzopyrene	2.17	6.95	7.04	7.03	7.04
1.2,4.5,8.9-Tri- benzopyrene	2.17	6.99	7.04	6.98	6.97
1.2,3.4,9.10-Tri- benzopyrene	2.17	6.96	7.04	6.98	6.97
3.4,9.10-Dibenzo- naphtho-(2'.3':1.2)- pyrene	2.12	6.94	7.00	6.92	6.89
pyreno-(1'.2':1.2)- pyrene	2.03	6.90	6.93	6.87	6.84
Standard Error (IP ₁) ₁			0.18	0.11	0.09

(a) Calculated from: $IP_1 = 5.32 + 0.79 E_A$.

(b) Calculated from: $IP_1 = 5.48 + 0.55 E_A + 2.20/N$.

(c) Calculated from: $IP_1 = 4.94 + 0.55 E_A + 2.22/N^{1/2}$.

CAPTIONS FOR FIGURES

Fig. 1. Classification of one-electron excitations in open-shell systems.

Fig. 2. Photoelectron peaks as observed at the energies of $h\nu - I_n$ in a photoelectron spectrum.

Fig. 3. A picture showing the correlation between the photoelectron spectrum of a molecule (M) and the electronic spectrum of its positive ion (M⁺).

Fig. 4. Comparison between the photoelectron spectrum (PES) of pyrene molecule and the electronic spectrum (ES) of its radical cation.

Fig. 5. Comparison between the photoelectron spectrum (PES) of perylene molecule and the electronic spectrum (ES) of its radical cation.

Fig. 6. A molecular orbital diagram showing the correlation between the first ionization potential (IP₁) of a molecule (M) and the energy of the A type transition for its positive ion (M⁺).

Fig. 7. A regression curve obtained from a two-parameters fit of observed IP₁'s and E_A's.

Fig. 8. A plot of observed first IP's over calculated IP's obtained from a least squares fit of observed E_A's and the number of benzene rings, N.

Fig. 9. A plot of observed first IP's over calculated IP's obtained from a least squares fit of observed E_A's and N^{1/2}.

Fig. 10. Calculated ionization potentials of 1.2,5.6-Dibenzanthracene estimated from the electronic spectrum of its cation and their comparison with the photoelectron peaks of the neutral molecule.

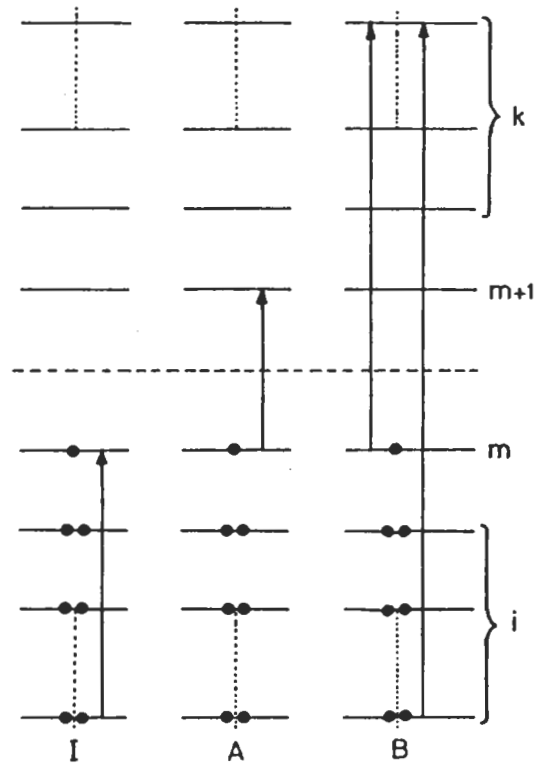


Fig.1

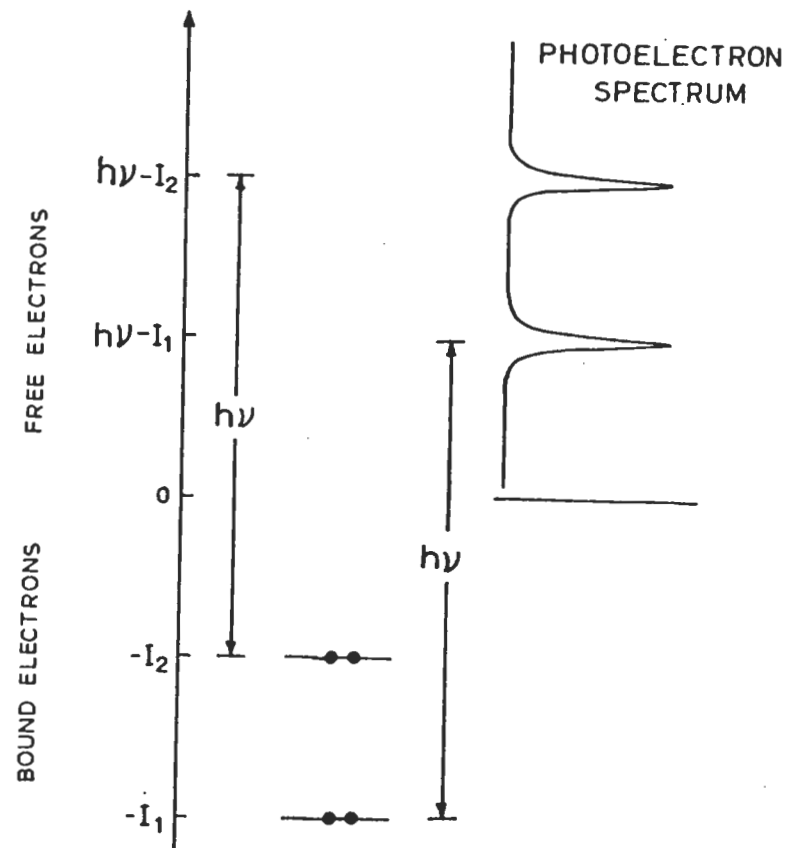


Fig.2

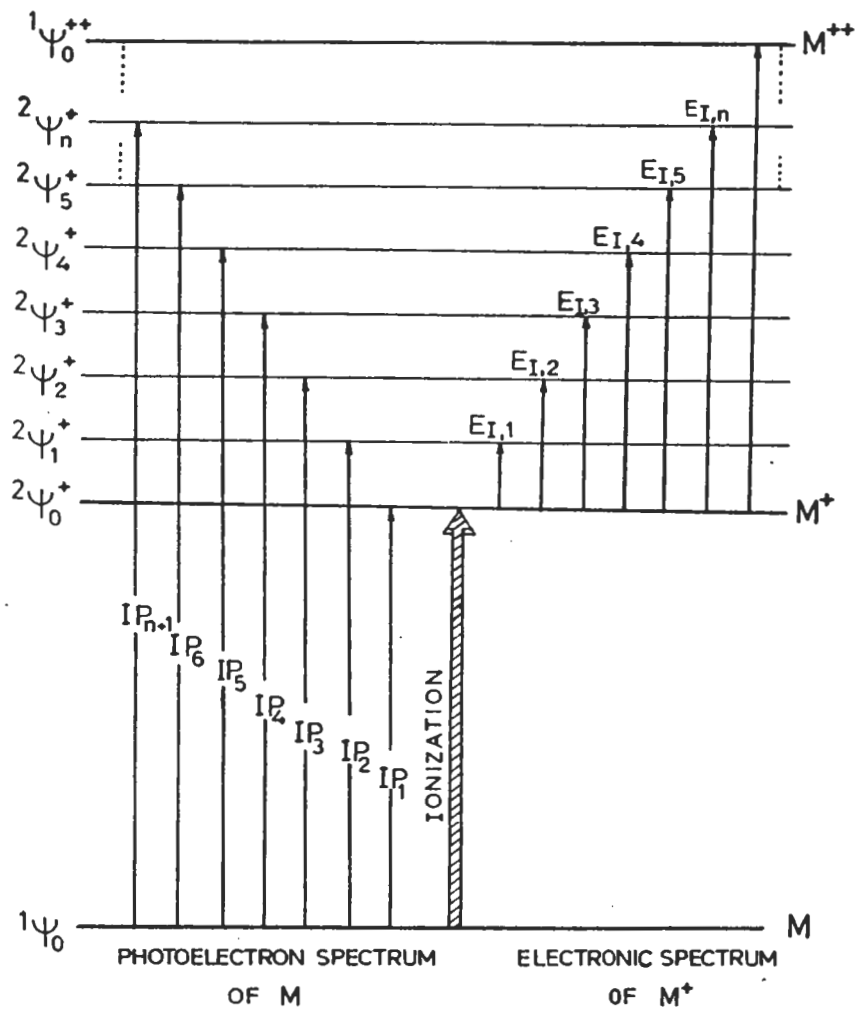


Fig.3

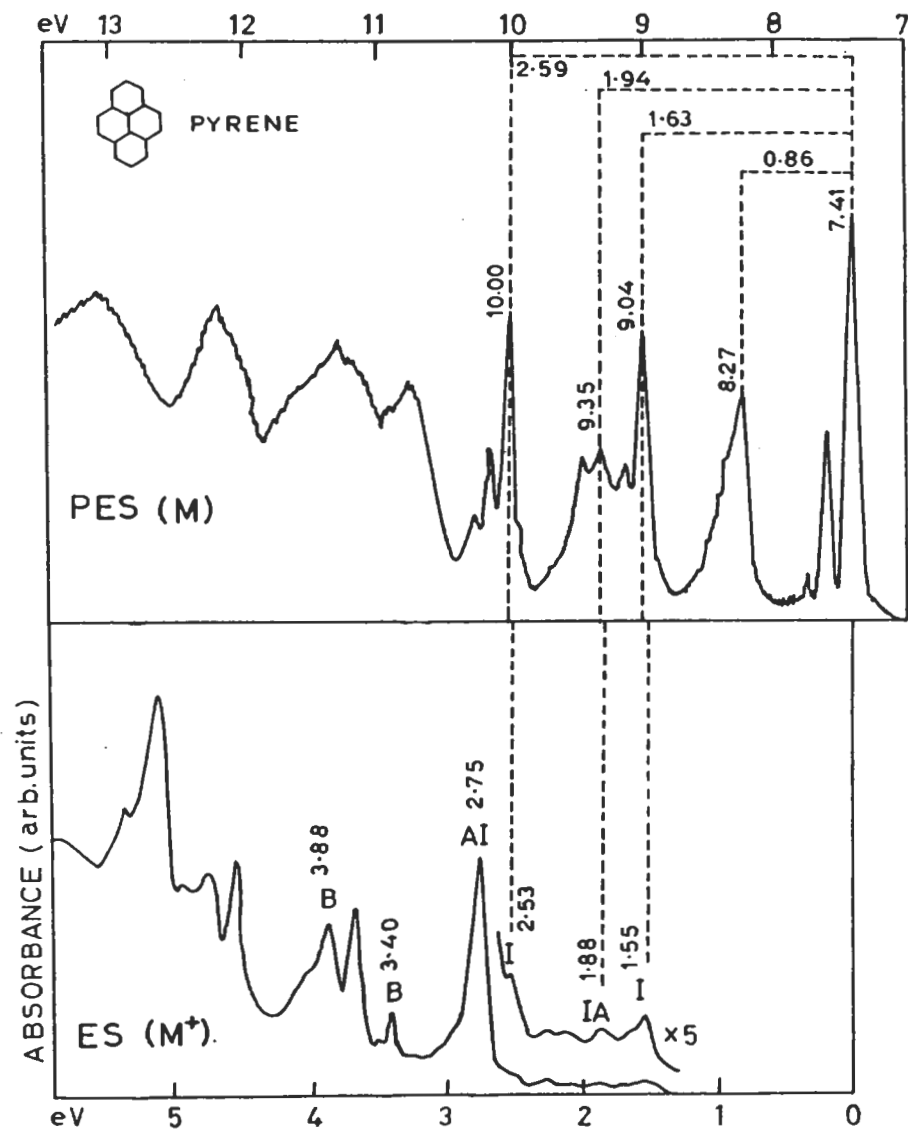


Fig.4

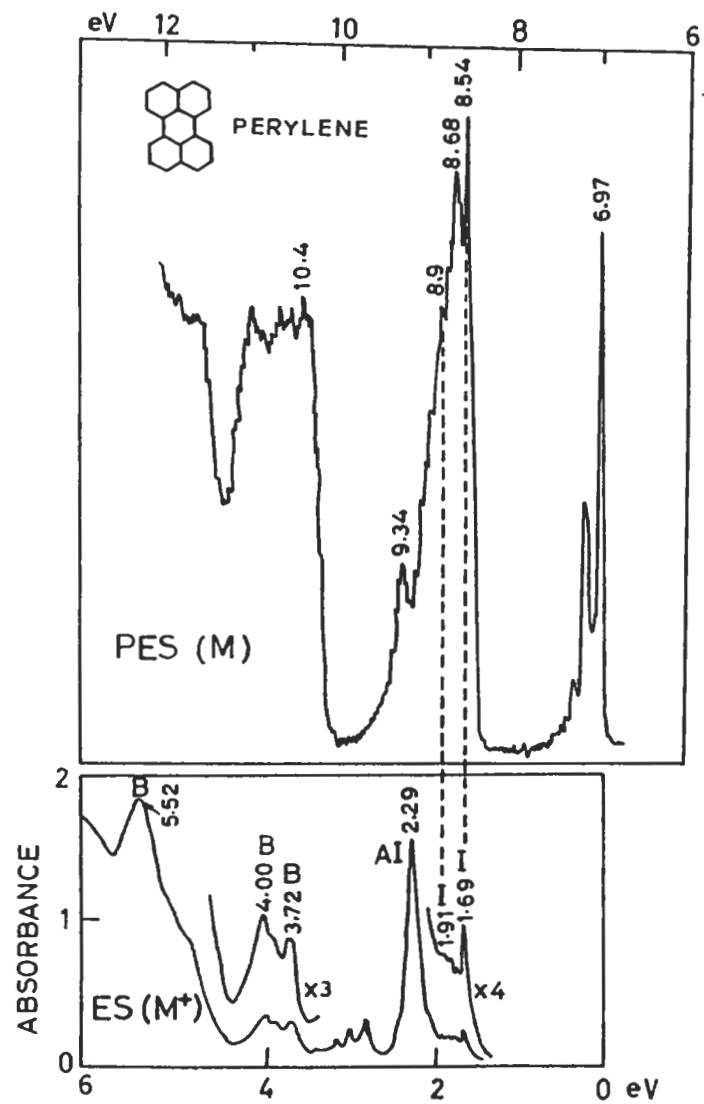


Fig.5

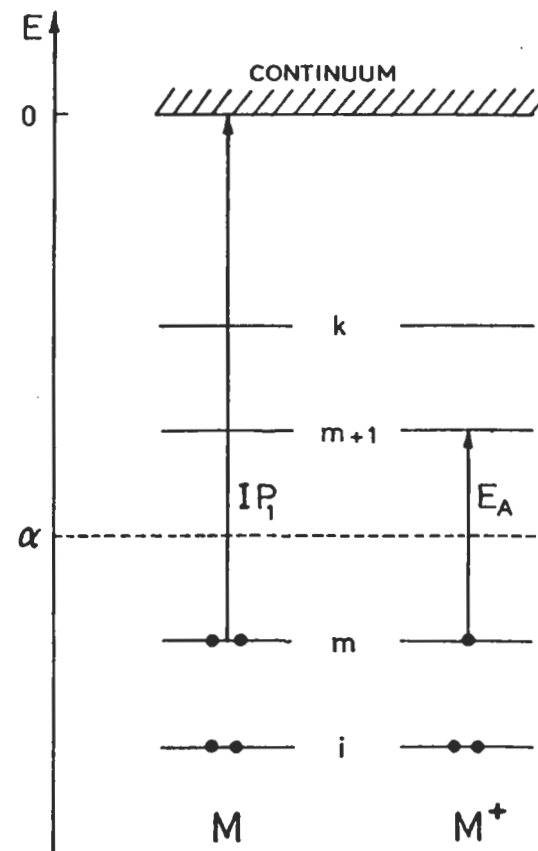


Fig.6

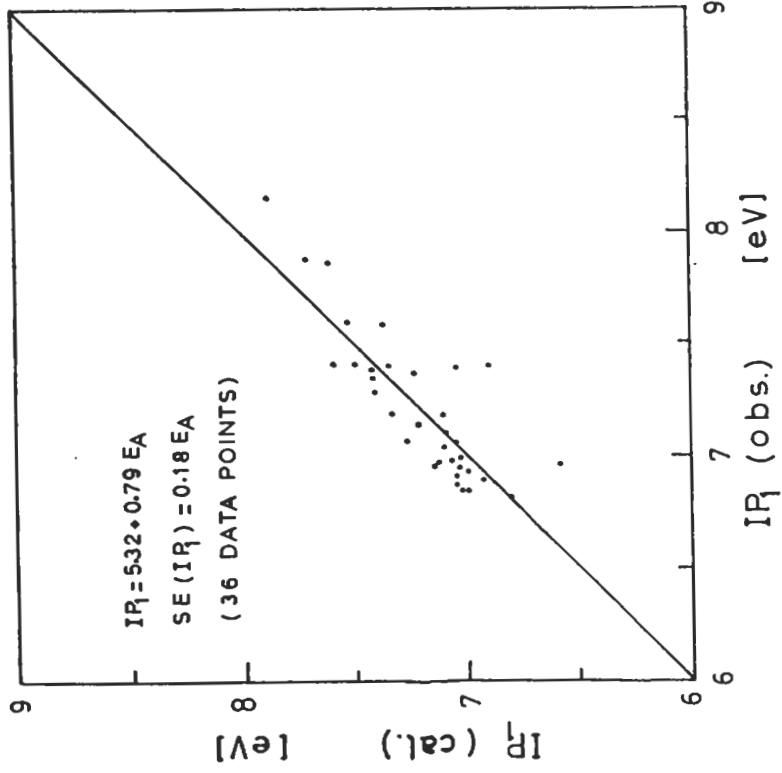


Fig.7

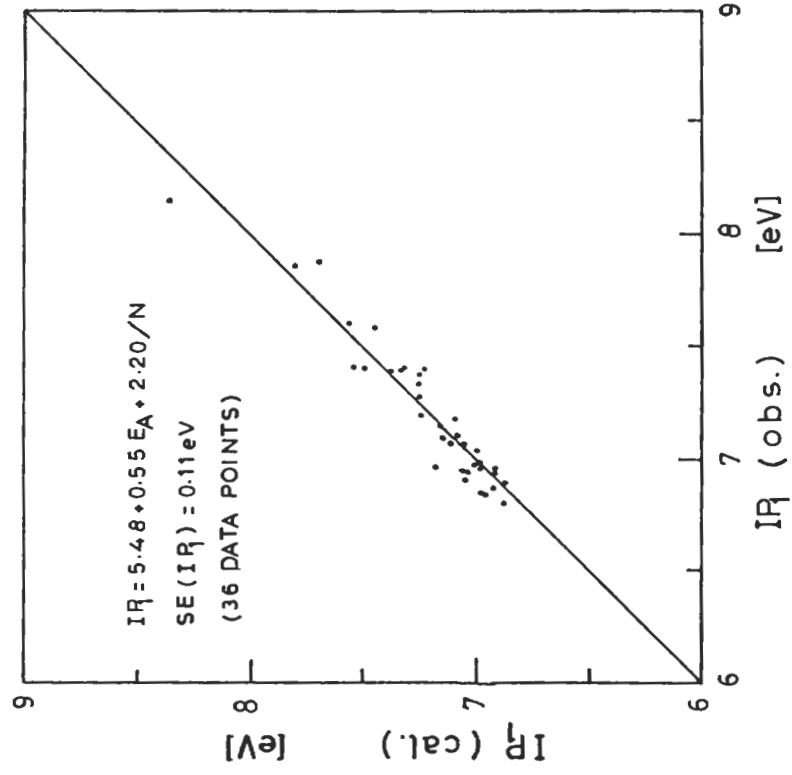


Fig.8

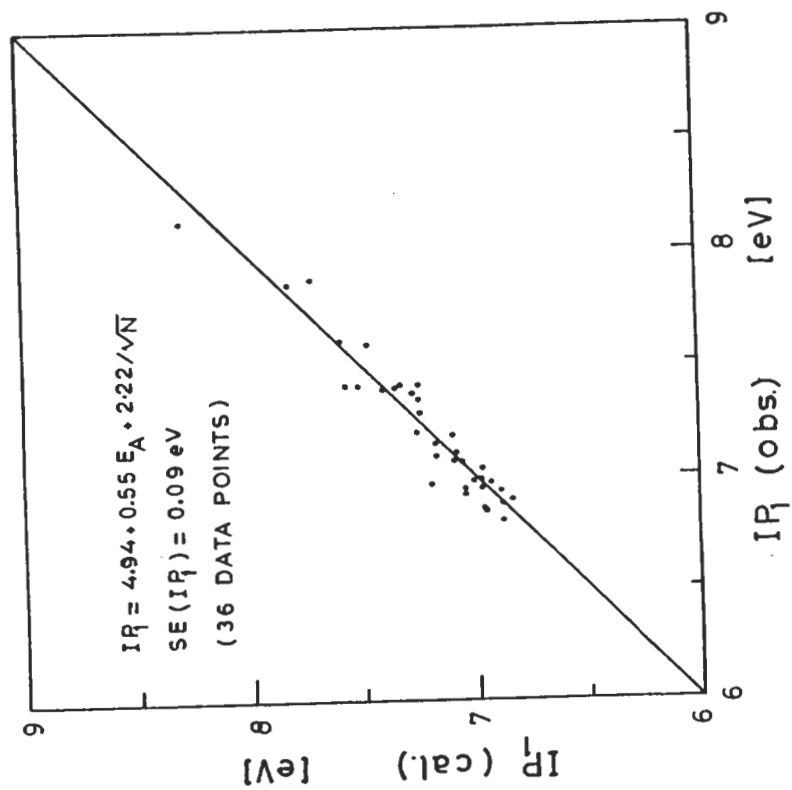


Fig.9

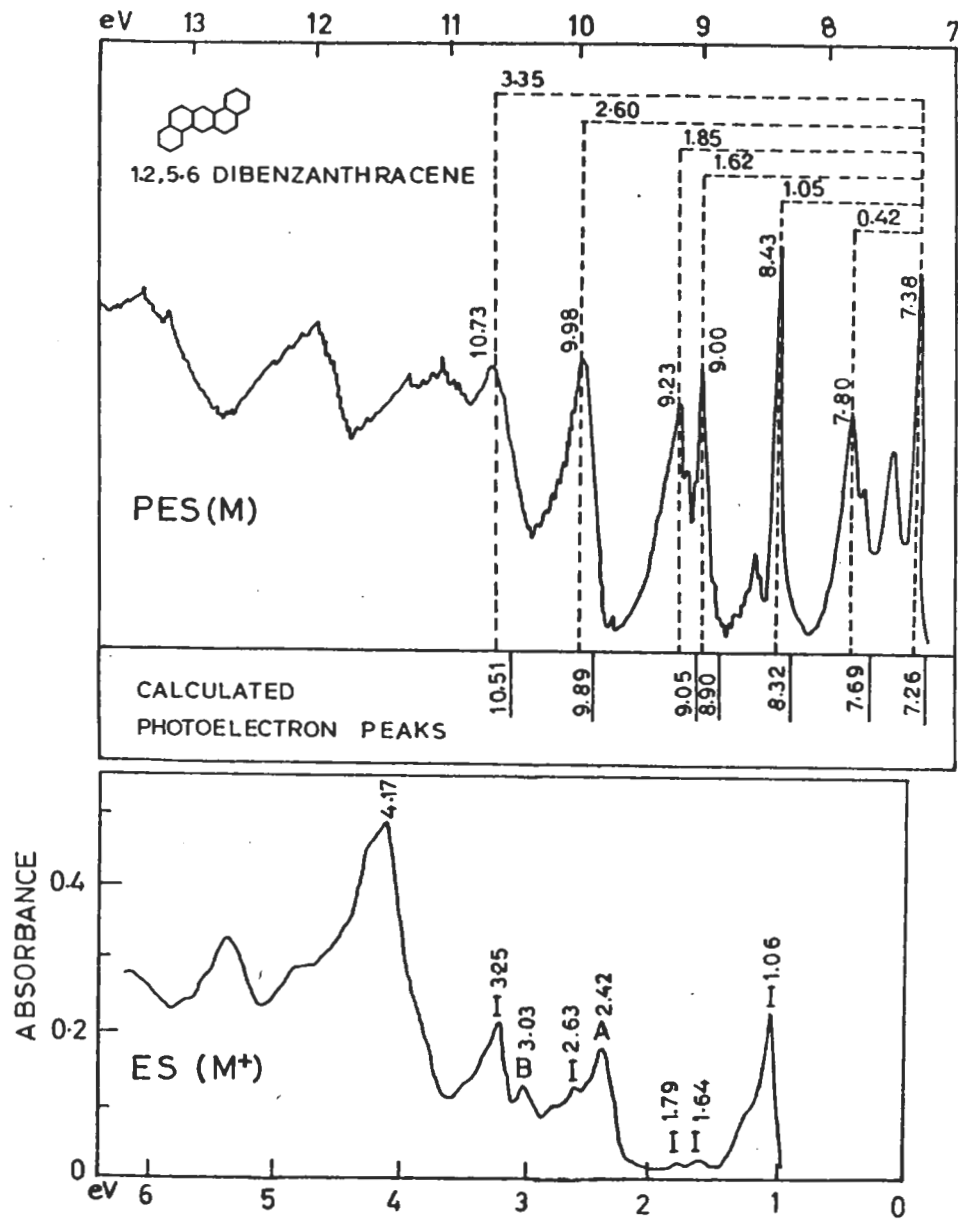


Fig.10