

202. Angular- and Energy-Dependence of Band Intensities in the Photoelectron Spectra of Phosphabenzene and Arsabenzene

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Summary. The He(II) photoelectron spectra of phosphabenzene **2** and arsabenzene **3** yield additional ionization energies in the region 17 to 20 eV. The relative intensity changes of the first three bands, compared to their relative intensities in the He(I) spectra, provide support for the previously proposed sequence of states $\tilde{X} = {}^2B_1$, $\tilde{A} = {}^2A_2$, $\tilde{B} = {}^2A_1$. This and the angular dependence of the photoelectron band intensities in the spectra of **2** and **3** is in excellent agreement with the theoretical predictions made by *von Niessen, Diercksen & Cederbaum* [9].

The intensities of photoelectron bands corresponding to transitions involving unpolarized photons and randomly oriented molecules depend on the angle θ between the directions of the incident photons and the ejected electrons according to [1]:

$$I(\theta) \propto 1 + (\beta/2) \left(\frac{3}{2} \sin^2 \theta - 1 \right). \quad (1)$$

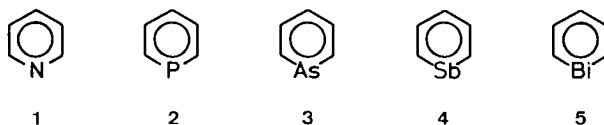
The parameter β is a function of the photon energy $h\nu$ and of the nature of the vacated orbital [2]. Although the orbital dependence of β is not yet completely understood, the empirical information accumulated by *Carlson et al.* [3] indicates that β increases with increasing atomic number for the outer orbitals of elements within a given group of the periodic table. Furthermore, the investigation of unsaturated hydrocarbons revealed that the π -bands are affected with higher β -values than the σ -bands [4]. Finally *Turner et al.* [5] have made use of angular intensity dependence measurements to discriminate between the π - and lone-pair-bands in the photoelectron spectra of pyridine, pyrimidine, pyridazine and pyrazine.

Another method used for distinguishing between orbitals extending mainly over second row atoms and those involving large contributions from outer atomic orbitals of higher-period heteroatoms consists in measuring the dependence of the photoelectron band intensity on the energy $h\nu$ of the exciting radiation. *Price et al.* have shown [6] that the latter tend to decrease much more than the former if $h\nu$ increases, e.g. if He(II) radiation (40.8 eV) is used instead of He(I) radiation (21.2 eV).

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Some time ago we presented the He(I) photoelectron spectra of the series of heterocyclic systems pyridine (**1**), phosphabenzene (**2**), arsabenzene (**3**) and stibabenzene (**4**) [7] and more recently of bismabenzene (**5**) [8] which terminates this series.



Using a simple, mainly empirical correlation technique, the following sequence of states has been derived for the radical cations 2^+ to 5^+ :

Band:	①	②	③	④	⑤
State:	$\tilde{X} = {}^2B_1$	$\tilde{A} = {}^2A_2$	$\tilde{B} = {}^2A_1$	$\tilde{C} = {}^2B_2$	$\tilde{D} = {}^2B_1$
Orb. Char.:	π, p	π	σ, n	σ	π

The orbital character (Orb. Char.) indicates the nature of the canonical orbital of the closed shell ground-state molecule from which the photoelectron has been removed to create the corresponding radical cation in the specified state. Thus the highest occupied orbital is of π -type with a large contribution of the hetero-atom p-atomic-orbital. The next lower orbital is again π with an additional node passing through the hetero-atom whereas the third is best described as a lone-pair σ -orbital.

In the photoelectron spectra of **2** to **4** the bands ② and ③ merge into a single broad band of double integrated intensity (*cf.* Fig. 1 and 2) and only in the spectrum of **5** are they resolved into two peaks [8]. Thus the sequence of the first and second excited states ($\tilde{A} = {}^2A_2, \tilde{B} = {}^2A_1$) given in [7] was mainly inspired guesswork.

In the meantime reliable calculations by an *ab-initio* many-body approximation, which include the effect of electron correlation and reorganization beyond the *Hartree-Fock* approximation, have been performed for **1** and **2** by *von Niessen, Diercksen & Cederbaum* [9], who have also given a complete review of previous calculations. The agreement between the experimentally observed band positions and the calculated ionization energies is almost perfect, both with respect of the absolute values and the relative spacings.

These theoretical results induced us to seek additional experimental data to gain information concerning the sequence of states in the radical cations of **2** and **3**, *i.e.* those members of the series available without too much synthetic expenditure. In Fig. 1 are shown the He(II) spectra of **2** and **3** and in Fig. 2 their He(I) spectra recorded with the photoelectrons collected at an angle of $\theta = 90^\circ$, and $\theta = 25^\circ$ with respect to the photon axis, respectively.

In the He(II) photoelectron spectrum of **2** one observes further bands; ⑩, which is partly obscured by the He^+ photoelectrons (from the $He(II)\beta$, 48.37 eV, shadow) with maximum at 16.8 ± 0.2 eV, and a double band (⑪, ⑫) at 18.5 ± 0.5 eV. These ionization energies agree nicely with the predicted $I_{v,10} = 17.3$ eV, $I_{v,11} = 19.2$ eV, $I_{v,12} = 20.2$ eV, calculated by the *Munich*-group [9].

A comparison of the He(I)-[7] and He(II)-photoelectron spectra (*cf.* Fig. 1) of **2** and **3** reveals that the intensity of band ① decreases with increasing excitation

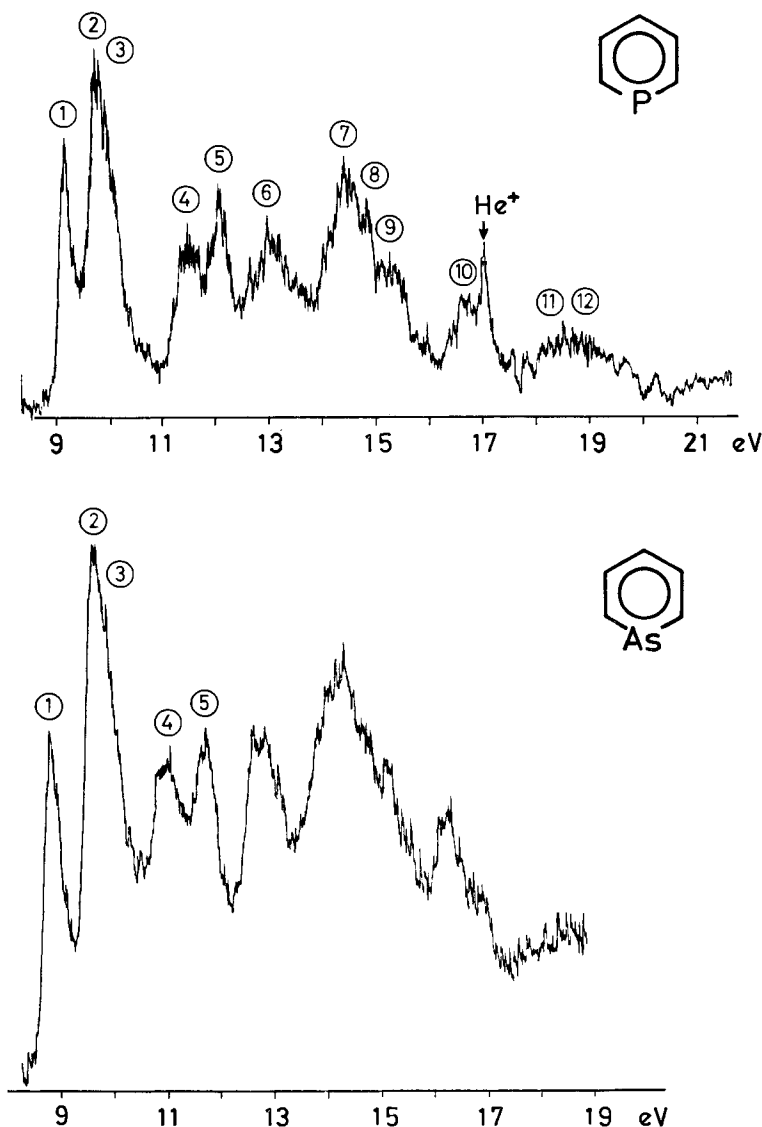


Fig. 1. He(II) excited photoelectron spectra of phosphabenzene and arsabenzene. Ordinate: counts/s (arbitrary scale), Abscissa: ionization energy (eV)

energy, relative to the combined intensities of the two components in the double feature ②, ③. According to previous experience [10] this has to be interpreted as being due to a large contribution from the phosphorus 3p-, or the arsenic 4p-atomic-orbital to the $b_1(\pi)$ orbital of **2** or **3**.

The sharp onset of the double band ②, ③ observable in the He(I) photoelectron spectra of **2** and **3** is retained in the He(II) spectra, whereas the higher energy component is noticeably lowered. This is particularly well presented in the spectrum of **3**.

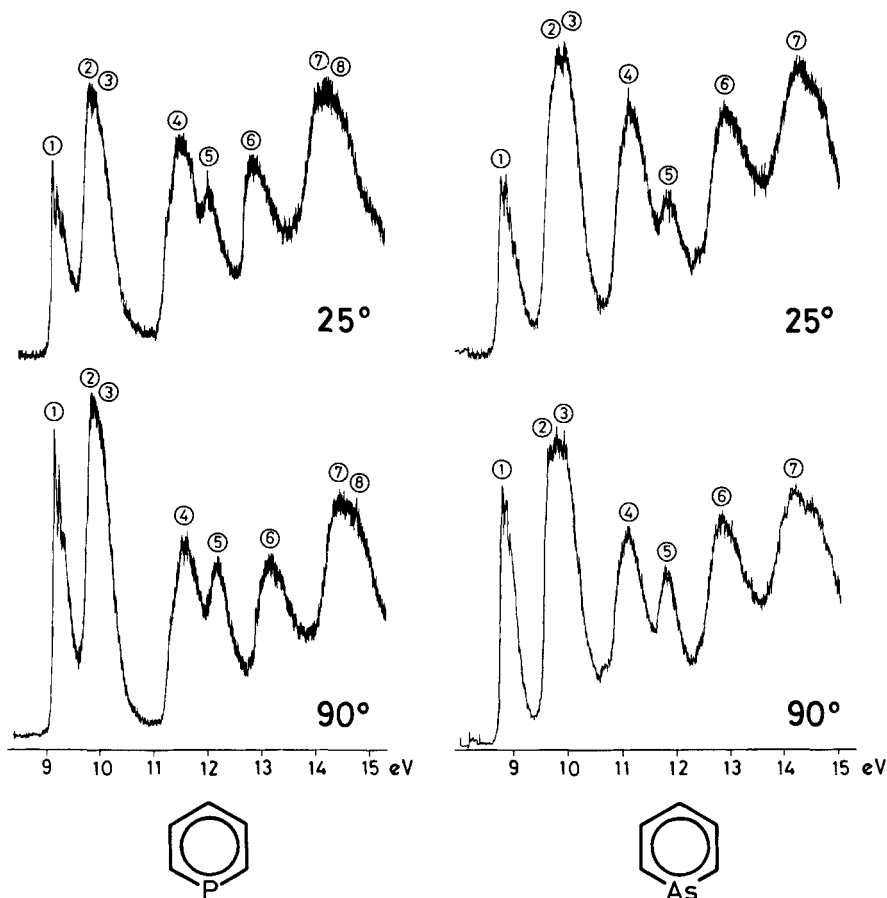


Fig. 2. He(I) excited photoelectron spectra of phosphabenzene and arsabenzene with photoelectrons collected at 25° and 90° with respect to the photon beam axis. Ordinate: counts/s (arbitrary scale), Abscissa: ionization energy (eV)

This result indicates that band ② has less P or As 'character' than band ③, and that it ought to be associated with the $a_2(\pi)$ orbital whereas band ③ with $a_1(\sigma, n)$, *i.e.* the 'lone-pair' orbital.

The interpretation of the angular-dependence of band intensities in the photoelectron spectra of **2** and **3** shown in Fig. 2 is hampered by the lack of information concerning the β -values appropriate for the outer orbitals of phosphorus and arsenic. It is presumably safe to assume that β must be rather large for their p-type orbitals but it is not obvious whether β for their s-type orbitals is smaller or larger than for carbon-2p-orbitals.

From formula (1) follows that the ratio of intensities observed under $\theta = 90^\circ$ and $\theta = 25^\circ$ is:

$$I(90^\circ)/I(25^\circ) = (1 + 0.25 \beta)/(1 - 0.37 \beta).$$

Therefore we conclude from the spectra shown in Fig. 2 that band ① is associated with a larger β -value than either band ② or band ③, both of which seem to exhibit

the same angular dependence judging from their intensity behaviour. This provides additional support for classifying band ① as a π -band, being associated with the ejection of an electron from a π -orbital with a large hetero-atom p-contribution, *i.e.* from $b_1(\pi)$. The lack of change in the *Franck-Condon* envelope of the double band ②, ③ indicates that the β -value for the P and As lone-pair orbital $a_1(\sigma, n)$ is close to that of the $a_2(\pi)$ orbital.

Finally, the intensity of band ⑤ clearly decreases relative to the intensities, of bands ④, ⑥ and ⑦, which keep their relative intensities, when the angle of observation is changed from $\theta = 90^\circ$ to $\theta = 25^\circ$. The higher β -value of band ⑤ can again be interpreted as being due to a larger contribution of phosphorus or arsenic p-orbitals to the molecular orbital from which the electron is removed. This would classify this orbital as a π -orbital, *i.e.* the $b_1(\pi)$.

All the conclusions derived above concerning the state sequence for the radical cations 2^+ are in perfect agreement with the theoretical predictions made by *von Niessen, Diercksen & Cederbaum* [9] and, gratifyingly with the assignment derived by an empirical correlation technique for 2^+ and 3^+ [7].

Experimental. – The He(II) excited photoelectron spectra were obtained as described [11]. Photoelectrons only close to 90° to the photon beam were, as usual, collected. The angular distribution dependence spectra were recorded on a modified *Perkin-Elmer* $\pi/2$ photoelectron spectrometer of the *Turner* design [12]. This incorporated two He(I) photon sources at 90° and 155° (*i.e.* equivalent to 25° ; *cf.* Fig. 2) with respect to the direction of collection of the photoelectrons. The spectra shown represent only the relative intensity changes for the two specified angles within each spectrum.

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