Inorganica Chimica Acta, 53 (1981) L101–L102
© Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Photoelectron Spectra of Group V Compounds*, As_4 and As_2

SUSANNE EBEL, HEINDIRK TOM DIECK,
HORST WALTHER

Institut für Anorganische und Angewandte Chemie der Universität Hamburg, Martin-Luther-King-Platz 6, D-2000 Hamburg 13, F.R.G.

and J. KRIZEK

Leybold Heraeus GmbH, Postfach 510760, D-500 Cologne 51, F.R.G.

Received September 12, 1980

Earlier studies of the UV PE spectra of analogous group V compounds (*e.g.*, R_3E, E = N → Sb [1]) have shown that the PE spectroscopic peculiarities within such a series follow a trend which is predominantly governed by the elemental properties of the central atom E. Therefore it seemed of great interest to us to investigate the group V elements themselves. So far PE spectra of N_2 [2], P_2 [3], PN [4], Bi_2/Bi [5], and P_4 [6] have been published. To further fill in the gap between phosphorus and bismuth we studied arsenic with a new type of PES heated inlet construction where temperatures up to 1500 °C could be attained by electron bombardment heating of the pyrolysis tube.** On heating both, sample reservoir and pyrolysis zone, up to 450–500 °C the He I PE spectrum of subliming As_4 could be gained (Fig. 1a). Subsequent pyrolysis by successively increasing the temperature up to at least 1300 °C (Fig. 1b) yielded the PE spectrum of the equilibrium mixture of As_2 and As_4.

The dissociation $As_4 \rightarrow As_2$ proceeds *via* the D_{2d} transition state, a process which was shown to be symmetry-allowed [7]. The interconversion of the involved MO models $2 \times D_{\infty h} \rightarrow D_{2d} \rightarrow T_d$ will be discussed in conjunction with the PE data of antimony [8].

The PE spectra of As_4 and As_2 are easily assigned on the basis of the expected energy splitting pattern produced by their underlying molecular symmetries T_d and $D_{\infty h}$, respectively, and by comparison with the known experimental ionization energies of N_2, P_2, Bi_2 (Fig. 2) and P_4 (Fig. 1a).

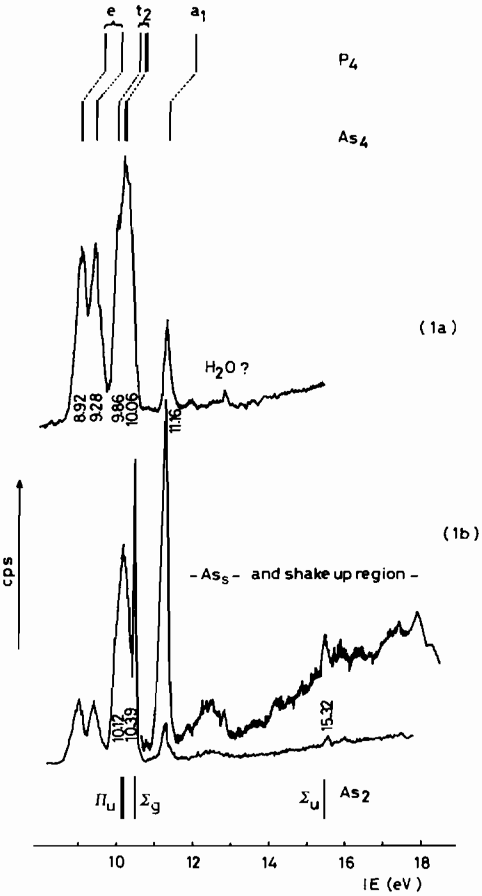

Fig. 1. Gas phase He I PE spectra of (a) As_4, correlated with vertical IP's of P_4, and (b) the As_2/As_4 equilibrium mixture at 1300 °C. Numerical IPs (vertical) for As_4 and As_2 are included.

The π_u-band of As_2 and the low energy a_1-band of As_4, both show vibrational fine structure which could not yet be properly resolved (resolution = *ca.* 25 meV at 1300 °C).

The presented assignment for the IPs of As_4 and As_2 is in excellent agreement with those of their lighter congeners P_4 and P_2, provided the sequence ($e \rightarrow t_2 \rightarrow a_1$) [6a]is correct for both E_4 tetrahedra. The low energy IPs of the diatomics E_2 shown in Fig. 2 reflect strongly the trend of the respective pVSIPs of the atoms. The characteristic feature of this energy correlation $N_2 \rightarrow Bi_2$ is not so much the large spin orbit splitting observed for Bi_2 as the crossing of e/e- and a_1/a_1-correlation lines between N_2 and P_2 MOs, causing a differing assignment on going from N_2 to P_2. This interchange between e- and a_1-energies can be mainly attributed to the decrease in atomic interactions which is obviously steep between N_2 and P_2, but only slight between P_2 and the heavier analogs. It is the actual reason for differing MO sequences and

---

*Part VII; for Part VI see S. Ebel, H. tom Dieck and R. Demuth, *Z. Naturforsch.*, *31b*, 1472 (1976).

**The design by Dr. J. Krizek will be published elsewhere. The construction is based on the commercial valve lock VLH 10 (Leybold Heraeus, Cologne) in conjunction with the heatable sample rod SRT 10 equipped with a sublimation chamber (T up to 500 °C). The volatilized sample is pyrolyzed on passing a tungsten wire wrapped molybdenum tube which can be heated up to *ca.* 1500 °C.

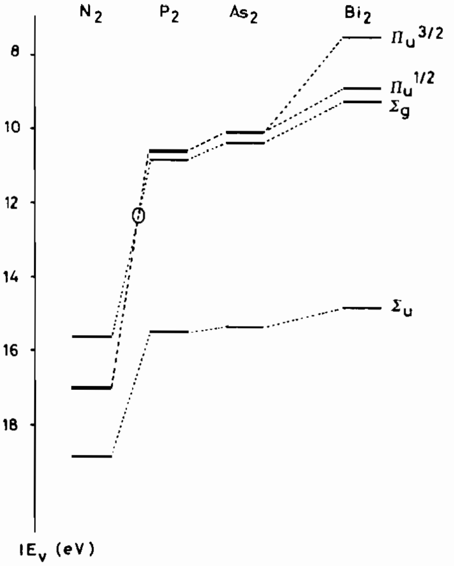

Fig. 2. Correlation of the experimental vertical IP's of the series E_2 ($N_2 \rightarrow Bi_2$, excluding Sb_2). The interchange of e- and a_1-correlation lines is marked.

hence differing PE band patterns for analogous phosphorus and nitrogen compounds and is observed wherever comparable second and third row compounds are involved (*cf.* R_nEH_{3-n}, E = N ↔ P, As, Sb) [8].

The PE spectra of As_2, P_2 as well as those of As_4, P_4 suggest comparable bonding and bond strengths for the diatomics and the tetrahedra, respectively, revealing thus another example for this general feature between analogous phosphorus and arsenic compounds.

References

1 S. Elbel, H. Bergmann and W. Ensslin, *J. Chem. Soc. Faraday II, 70,* 555 (1974).
2 D. W. Turner, C. Baker, A. D. Baker and C. R. Brundle, 'Molecular Photoelectron Spectoscopy—A Handbook of He 584 Å Spectra', Wiley–Interscience, 1970.
3 D. K. Bulgin, J. M. Dyke and A. Morris, *J. Chem. Soc. Faraday II, 72,* 2225 (1976).
4 D. K. Bulgin, J. M. Dyke and A. Morris, *J. Chem. Soc. Faraday II, 73,* 983 (1977); M. Wu and T. P. Fehlner, *Chem Phys. Lett., 36,* 114 (1975).
5 S. Süzer, S.-T. Lee and D. A. Shirley, *J. Chem. Phys. 65,* 412 (1976).
6a C. R. Brundle, N. A. Kuebler, M. B. Robin and H. Basch, *Inorg. Chem., 11,* 20 (1972).
6b S. Evans, P. J. Joachim, A. F. Orchard and D. W. Turner, *Int. J. Mass Spectrom. Ion Phys., 9,* 41 (1972).
7 R. Osman, P. Coffey and J. R. van Wazer, *Inorg. Chem., 15,* 287 (1976).
8 S. Elbel, H. tom Dieck and H. Walther, to be published.