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The Orbital Electronic Structure of the As_4O_6 Molecule by Photoelectron Spectroscopy

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The one-electron structure of the valence shell of the As_4O_6 molecule has been studied by means of He(I) photoelectron spectroscopy. Commercial samples were purified by vacuum sublimation and introduced at 270 °C to a Vacuum Generators UVG 3 instrument. The recorded spectrum is displayed in the figure, the photoionisation data for the As_4O_6 molecule along with the proposed assignments are given below:

PE band	vertical IP (eV)*	assignment	EHMO calcn.	population
A	10.01	t_2	10.9	>80% As
	10.27			
	(10.4_5)			
A′	(11.2)	a_1	12.4	
B	11.47	e, t_2	13.66; 13.68	60–95% O
C	12.42	t_2	13.74	
D	13.84	t_2	14.3	
	(14.0_6)			
E	15.62	t_2, a_1	14.6; 15.1	
F	(18.2)**	t_2	17.9	*ca.* 60% As

*± 0.05 eV, values in parentheses relate to shoulders.
**see text.

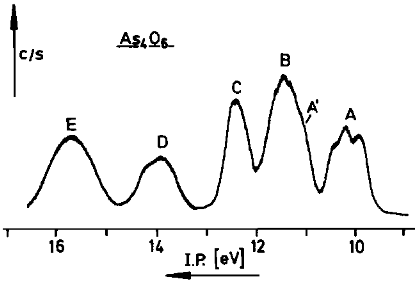

Figure. The He(I) photoelectron spectrum of As_4O_6.

The assignments of the different signals in the PE spectrum to particular states of the molecular ion – or, *via* Koopmans' theorem, to distinct molecular orbitals of As_4O_6 – is entirely straightforward and in good accord with the results of an Extended Hückel calculation. Input data for the EHMO program [1] were interatomic distances as determined by electron diffraction (T_d symmetry, d(AsO) = 180 pm) [2], single Slater orbital exponents from Clementi and Raimondi [3] and the diagonal matrix elements (H_{ii}) as the valence state ionization potentials from the tabulation given by Ballhausen and Gray [4].

The off-diagonal elements of the effective Hamiltonian were estimated by $H_{ij} = -0.5\ KS_{ij}(H_{ii} + H_{jj})$, with K set equal to 1.75. Although such calculations lack quantum mechanical rigor, they do tend to yield fair accounts of the valence shell electronic structure. The last occupied one-electron-MO turns out to have t_2 symmetry and is predominantly composed from arsenic 4p functions. In fact, the first signal in the experimental PE spectrum (designated as A in the figure) shows clearly to be split into three maxima. Spin–orbit coupling splits the ionic $^2T_2$ state in T_d molecular symmetry into $E_{5/2}$ and $G_{3/2}$ components, where the latter state is still degenerate and susceptible to the Jahn–Teller distortion *via* e and t_2 vibrational modes of the As_4O_6 cage. ΔE due to spin–orbit coupling only is *ca.* 0.3 eV from the experimental spectrum. Completely made from As 4p functions the splitting of this signal should be $1.5\ \zeta_{As} = 0.33$ eV [5], not far away from the experimental result and thus in accord with the population derived from the computation.

Excluding the low energy shoulder A′ at 11.2 eV, the following signals B–E are mainly due to ionization of levels with predominantly oxygen character. Although the agreement between calculated and observed data is rather poor, the relative ordering of levels seems to be correct and the experimental band shapes indicate an increasing participation in the bonding which is also in line with the computational trends. The simple EHMO procedure, however, presumably underestimates the non-bonding character of the e and t_2 levels belonging to bands B and C, which are probably further destabilized by interelectronic repulsion.

Band D shows a pronounced splitting into ^2E and ^2A Jahn–Teller components of the ionic $^2T_2$ state. Again in line with the computation, multiplet fine structure is unlikely to be resolved here since these levels strongly involve oxide functions and a splitting far less than 0.1 eV is then expected. Finally we assign band F at 18.2 eV to the strongly bonding t_2 orbital mainly on energetic grounds. This signal could only be detected in a largely increasing background and exhibits rather broad features without superimposed structures. Thus the accuracy of this IP has to be regarded as less than the other readings.

Acknowledgments

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