The Electronic Structure of Tetraphosphorus- and Tetraarsenic-Trisulphides; Interpretation of their Photoelectron Spectra

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Ab initio SCF calculations of the X^1A_1 ground states of P_4S_3 and As_4S_3 are reported, together with configuration interaction studies of the $^2A_1$, $^2A_1$, $^2A_2$ and ^2E states of P_4S_3. A re-interpretation of the UV-photoelectron spectrum of the P_4S_3 molecule, and As_4S_3 by analogy, is presented and it is noted that Koopmans' theorem yields a very similar order and spacing between groups to the doublet states computed by configuration interaction.

Introduction

Recently we have reported *ab initio* SCF-MO calculations of P_4O_6 (1) [1], P_4O_{10}, S_2N_2 (2), S_4N_4 (3) [2], S_4N_2 (4) [3] and poly thiazyl $(SN)_x$ (5) [4] using a range of basis sets; for all except $(SN)_x$ we were interested in the interpretation of the rather complex UV-photoelectron spectra (UV-PES). We now extend the studies to P_4S_3 (6) and As_4S_3 (7) where conflicting assignments of the UV-PES have been given [5–7]. The envelopes of the photoelectron spectra for P_4S_3 and As_4S_3 are extremely similar in the upper valence shell region (9–15 eV) [6], and it seems probable that an assignment for P_4S_3 will also be applicable to As_4S_3. The previous assignments were based upon the scattered wave (XαSW) [5], extended Hückel (EH) [5] and Complete Neglect of Differential Overlap (CNDO) methods [5] and on intuitive arguments [6]. The need for *ab initio* studies had been noted [6].

In the present work the number of valence shell electrons made it necessary to use a relatively small basis set, if we were to be able to carry out configuration interaction studies similar to those used for S_4N_2 [3], and hence to avoid reliance upon the use of Koopmans' theorem ($IP_i = -E_i$, where E_i is the calculated orbital energy). The basis sets are thus equivalent to the ones used for P_4O_6, P_4O_{10} [1], $(SN)_x$ [4] and the smallest spd-basis used for S_4N_4 [2].

Methods

The gaussian bases were (10s6p1d) for P and S, (14s11p5d) for As and contracted to [4s2pld] for P/S and [5s3p1d] for As. An extra s-function $3s^1$(P/S) or

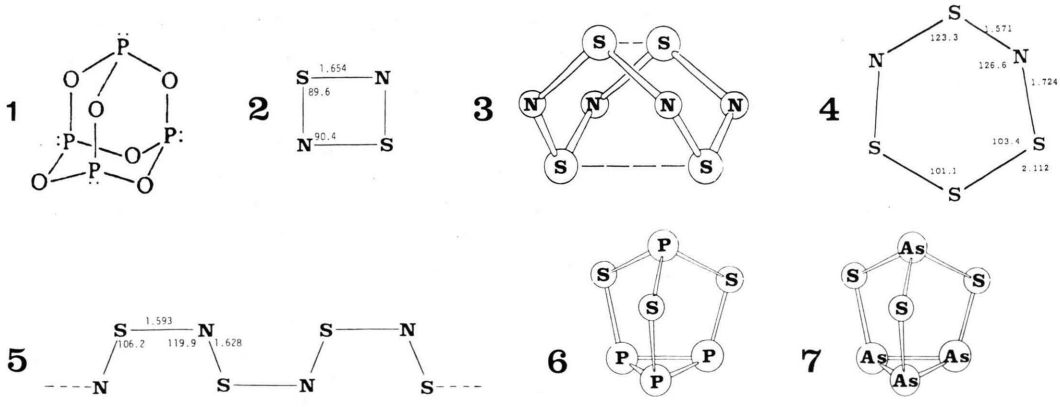

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Table 1. SCF Energies for P_4S_3 and As_4S_3.

Basis set	P_4S_3				As_4S_3	
	sp		spd		sp	
Total Energy	− 2550.3774		− 2551.2505		− 10119.3225	
Dipole moment (μ/D)	0.107		0.205		0.336	
Orbital energies (eV)	10.89	17e	9.60	17e	9.80	e
	11.94	$17a_1$	10.58	$17a_1$	10.65	a_1
	12.29	$3a_2$	10.71	$3a_2$	11.63	a_2
	12.63	16e	11.58	16e	11.69	e
	12.97	15e	12.05	15e	11.96	e
	13.30	$16a_1$	12.60	$16a_1$	12.95	a_1
	16.38	$15a_1$	15.04	14e	14.38	a_1
	16.42	14e	15.22	$15a_1$	14.39	e
	20.60	13e	19.11	13e	19.61	e
	21.21	$14a_1$	19.83	$14a_1$	20.57	a_1
	28.40	$13a_1$	25.49	$13a_1$	25.64	a_1
	28.60	12e	26.42	12e	26.62	e
	33.02	$12a_1$	29.69	$12a_1$	29.45	a_1

$4s^1$(As) was included to provide some extra variational flexibility. The d-type functions were used in the usual chemical set ($3d^5$), and do *not* carry an implicit extra s-type function that often occurs with gaussian functions (namely $3d_A$, where $A = x^2 + y^2 + z^2$). The principal energy and density based results from the single configuration calculations on P_4S_3 and As_4S_3 are shown in Tables 1 – 4.

For the CI study we were constrained by the CDC 7600 computer available core size (50 000 octal words), and the ability to restart incomplete jobs at fixed points within the program (ATMOL-SPLICE) [7] within a maximum job-time step (20 min); in practice this meant that the number of configurations used had to be selected from the maximum possible total (< 60 000) for each symmetry state by perturbation selection [8], and that the above limits led to a final configuraton number of < 10 000 and a maximum number of active electrons of 20.

Table 2. Atomic Populations for P_4S_3 and As_4S_3.

(a) SCF Single Configuration

Orbital Type	P Apical	P Basal	S	As Apical	As Basal	S
s	5.6085	5.6876	5.8035	8.2047	8.2266	5.9219
p	8.8664	9.0411	10.3154	14.7069	15.0456	10.3663
d	0.2412	0.1687	0.0783	9.6382	9.5897	0.0
Total	14.7161	14.9975	16.1971	32.5495	32.8619	16.2882
Net Charge	+ 0.2839	+ 0.1025	− 0.1971	+ 0.4505	+ 0.1381	− 0.2882

(b) Configuration Interaction P_4S_3

s	5.6059	5.6859	5.8030
p	8.8663	9.0957	10.3089
d	0.2472	0.1216	0.0743
Total	14.7194	14.9030	16.1905
Net Charge	+ 0.2806	+ 0.0970	− 0.1905

Table 3. Localised Orbitals for P_4S_3 and Hybridisation.

Orbital Atom	3 (P_A – S)		3 (P_B – S)		3LP_B		1 LP_A		3 (P_B – P_B)		6 LP_S	
	s	p	s	p	s	p	s	p	s	p	s	p
P	1.000	2.725	1.000	2.991	1.000	0.546	1.000	0.778	1.000	4.076	–	–
S	1.000	4.640	1.000	4.819	–	–	–	–	–	–	1.000	1.431

Table 4. Mulliken Analysis of Orbital from Valence Shell and those used in Configuration Interactions.

Symmetry	Basal Phosphorus	Apical Phosphorus	Sulphur
$12a_1$	27.2	20.8	52.0
12e	18.6	6.9	74.4
$13a_1$	66.3	17.5	16.2
$14a_1$	23.7	27.5	48.6
13e	59.8	8.8	31.4
$15a_1$	29.5	16.1	54.3
14e	27.6	15.6	56.7
$16a_1$	62.6	16.8	20.6
15e	44.1	0.7	55.2
16e	15.6	7.9	76.5
$3a_2$	5.7	0.0	94.2
$17a_1$	40.7	50.4	8.8
17e	73.6	3.6	23.0
$18a_1$	51.3 (z)	4.3	44.4 (z)
$4a_2$	92.7 (x, y)	0.0	7.3
18e	39.0	39.3 (y)	21.6
19e	72.0 (x, y, z)	12.5	15.5
$19a_1$	11.6	37.6 (z)	50.7 (x, y)
20e	46.8 (x, y, z)	13.5	39.7 (z)
$20a_1$	58.0 (xy)	19.5 (z^2)	22.5
$21a_1$	94.5 ($x^2 - y^2$)	3.6	1.8
21e	20.4	45.1 (xy, $x^2 - y^2$)	34.4
22e	71.0 (xz, yz)	7.0	22.0
23e	48.2 (z^2, $x^2 - y^2$)	21.4	30.4 (xy)
$22a_1$	54.4 (x^2)	1.7	43.8 (z^2)
$23a_1$	38.7 (xz)	50.0 (z^2)	11.4
$5a_2$	55.2 (xz)	0.0	44.7 (xz)

For the CI studies we need a simplified system of orbital numbering both for the occupied set, from which all double and single excitations are being made, and from the virtual set providing the replacement orbitals. We number the valence shell set $1a_1 \ldots$, 1e .. etc. upwards, from high to low binding energy (Table 5).

Series 1 Calculations. In the first phase of CI, the ground (X^1A_1) and first doublet states of each symmetry for P_4S_3 were computed using all single and double excitations from the 6 highest occupied orbitals (the "active" electrons) to the lowest 27 virtual orbitals. These single root functions containing the active electrons were used to show which configurations were of major importance for the multi-root (reference) calculations (Series 2), and which orbitals of the virtual set had negligible influence on the CI and hence could be safely omitted.

Series 2 Calculations. In order to calculate realistic values for three IP's of each symmetry, it was necessary to use triple root functions. The Koopmans' theorem order suggested that a fourth ^2E state could also lie in the observed UV-PES [6], but it was found impracticable to compute it in the present work. Thus we used 20 active electrons for the ground state and 19 electrons fro each doublet states. The orbitals for the root functions were those based upon the Koopmans' theorem order, except that 14e had been omitted although $15a_1$ was included, and are those shown in Table 5. The leading term in each case was that used for Series 1. In order to gain some insight into the variational flexibility available to the CI, we give Mulliken analyses for all the 32 orbitals used in the CI process (Table 4). These show a wide range of s, p, d-character.

Results and Discussion

a) The Ground States of P_4S_3 and As_4S_3

The only previous calculations are by semi-empirical methods for P_4S_3 by Head et al. [5]. The pres-

Table 5. Root-functions and Labelling Pattern used in the Configuration Interaction Study.

Orbital Labelling (SCF calculated order)								
Orbital	$15a_1$	14e	$16a_1$	15e	16e	$3a_2$	$17a_1$	17e
Label	1	–	2	3, 4	5, 6	7	8	9, 10
Obital	$18a_1$	$4a_2$	18e	19e	$19a_1$	20e	$20a_1$	$21a_1$
Label	11	12	13, 14	15, 16	17	18, 19	20	21
Orbital	21e	22e	23e	$22a_1$	$23a_1$	$5a_2$	24e	25e
Label	22, 23	24, 25	26, 27	28	29	30	31, 32	33, 34
Orbital	26e							
Label	35							
Root Functions								
X^1A_1	$1^2 - 10^2$			$^2A_2$	$1^2 - 6^2, 8^2 - 10^2, 7$			
$^2A_1$	$1^2 - 7^2, 9^2, 10^2, 8$			^2E	$1^2 - 9^2, 10$			
	$1^2, 3^2 - 10^2, 8$				$1^2 - 5^2, 7^2 - 10^2, 6$			
	$2^2 - 10^2, 1$				$1^2 - 3^2, 5^2 - 10^2, 4$			

ent single configuration results are closer to the extended Hückel [5], than to either XαSW or CNDO [5]; thus we find a higher positive charge on the apical P atom than on the basal P atom, with S atoms negative relative to all P atoms. A similar pattern emerges with As_4S_3, and the latter appears to be slightly more polar than P_4S_3 when equivalent basis sets are compared (sp- in both cases).

In the first CI study (Series 1) of the X^1A_1 state for P_4S_3, all single and double excitations for the 6 highest occupied orbitals (16e, 17e, 17a, and $3a_z$) to the lowest 24 virtual orbitals were tried. Perturbation selection at 50 μH [9] reduced the number of configurations to the final CI from 11 175 to 590 (Table 6); examination of the 50 leading terms in the CI showed that some of the virtuals had a negligible effect and thus could be omitted from the second series. It was clear that the most important virtual orbitals were rich in 3p character on both P and S, and that some of the orbitals rich in 3d were particularly low in effect.

Thus in Series 2, the orbitals 21e (largely $3d_{xy}$ on apical P) and 23e ($3d_{z^2}$ on basal P) were omitted from the virtual set, while the active set was increased from 12 electrons to 20 with all orbitals from $15a_1$ upwards being included except 14e; in fact the active set contains two other orbital pairs, 15e and 16e, of somewhat similar character to 14e, such that the CI process is unlikely to be restricted too much by the omission of 14e. A total of 10 149 configurations, reduced by energy selection as above to 1447, led to a ground state wave-function (Table 6) almost identical with that of Series 1, although a significant energy reduction (0.007 a.u., 200 kJ mol^{-1}) was obtained.

The leading term of the X^1A_1 ground state is dominated by the SCF wave-function (Table 6), with no eigenvectors for excited configurations reaching 5% of the total. In decreasing order of importance, the virtual orbitals appearing in the leading configurations were found to be $4a_2 > 19e > 18a_1 > 20e > 18 >$ others. In all the leading configurations, the inserted orbitals were of 3p rather than 3d character (Table 4). The most commonly replaced occupied orbitals were the highest occupied pair (HOMO, 17e) followed by $15a_1$; in the CI expansion, terms 2 and 3 correspond to the replacements (excitations) $17e^2 \rightarrow 4a_2^2$ rather than to the lowest unoccupied (LUMO) $17e^2 \rightarrow 18a_1^2$. Indeed this last process does not occur in the leading 50 terms of the expansion, although the replacement $15e^2 \rightarrow 18a_1^2$ is present. An explanation of these and other factors of the CI expansion can be seen from a study of the SCF orbital and CI natural orbital Mulliken analyses. Comparison of the two sets of data shows that the natural orbitals have a population on each basal phosphorus higher by 0.007e, and matched by a decrease on sulfur by the same amount; this arises from the overall shift $3p_s \rightarrow 3d_p$. The orbital $3a_2$, the only orbital of that symmetry in the SCF valence shell, is almost entirely localised on the S atoms, and is of tangential character. That is, it is tangential to the triangle of 3 S atoms obtained by viewing P_4S_3 down the C_{3v} symmetry z-axis; in contrast, $4a_2$ is of same form but almost entirely localised on the basal P atom triangle. The effect of the replacement $17e^2 \rightarrow 4a_2^2$ is thus two-fold: (i) a shift to higher proportion of 3pp/3dp character in the first available orbital of almost completely basal P atom character; (ii) an increase in flexibility in the a_2 orbital system leading to a ground state some $4a_2$ character. In contrast the LUMO, $18a_1$, is an almost even mixture of 3p orbitals on basal P and on S atoms, and the next orbitals higher in the virtual set of similar type are 20e; excitations involving these together with the two SCF occupied orbitals of this type ($15a_1 + 15e$) then leads to further re-distribution between S and basal P atoms. The same arguments apply with the next group of configurations, and thus overall the effect of the CI process is to refine the balance between S and the basal P atoms, with the apical P atom virtually uneffected.

b) 3d- Orbital Participation in P_4S_3 Bonding

The Mulliken analyses for the atomic composition in P_4S_3 show very little difference between the SCF single configuration and the Series 2 CI results (Table 2). The base is significantly closer to electrical neutrality than the apex but this is largely a result of attachment to only one sulfur atom rather than three at the apex; if we partition the final net charges into contributions in bonds [10], such that the total charge balances in the bond totals, then all six P bonds show polarisation $P^+–S^-$ where ± is ± 0.09 electrons, and very close to the $3d_S$ population. There does appear to be a significant difference between the 3d populations on apical relative to basal phosphorus, and the CI enhances the difference. Thus we find a higher 3dp population and lower 3p

Table 6. Configuration Interaction Studies on P_4S_3

State	Active Electrons	No. of Configurations			Eigen-vector	Leading Configurations Orbital Occupancy		Ionisation Potential	
		Total	Final Selection	Total Energy		Double	Single/ Mixed	Calculated	Observed
X^1A_1	12	11 175	590	− 2551.31383	0.976	5^2-10^2	−	−	−
					− 0.047	$5^2-9^2, 12^2$	−		
					− 0.047	$5^2-8^2, 10^2, 12^2$	−		
X^1A_1	20	10 149	1447	− 2551.37962	0.955	1^2-10^2	−	−	−
					− 0.041	$1^2-9^2, 12^2$	−		
					− 0.041	$1^2-8^2, 10^2, 12^2$			
1^2A_1	12	22 731	1619	− 2550.93803	0.965	$5^2-7^2, 9^2, 10^2$	8	10.23	9.57
1^2A_1	20	56 775	8300	− 2551.01789	0.925	$1^2-7^2, 9^2, 10^2$	8	9.84	9.57
					+ 0.077	$1^2, 3^2-10^2$	2		
					+ 0.060	$1^2-7^2, 9^2$	(10, 13), 8		
2^2A_1	20	56 775	8300	− 2550.94042	0.915	$1^2, 3^2-10^2$	2	11.95	11.72
					+ 0.102	2^2-10^2	1		
					− 0.081	$1^2-7^2, 9^2, 10^2$	8		
3^2A_1	20	56 775	8300	− 2550.85825	0.902	2^2-10^2	1	14.18	13.32
					− 0.127	$1^2, 3^2-10^2$	2		
					+ 0.085	$1^2, 2^2, 4^2-8^2, 10^2$	(9, 12), 3		
4^2A_1	12	22 731	1619	− 2550.69671	0.929	5^2-8^2	(9, 12), 10	16.79	
					+ 0.928	5^2-8^2	(10, 12), 9		
5^2A_1	12	22 731	1619	− 2550.67381	0.438	5^2-8^2	(10, 12), 9	17.42	
					− 0.433	5^2-8^2	(9, 12), 10		
					− 0.271	5^2-8^2	(9, 16), 10		
					− 0.273	5^2-8^2	(10, 16), 9		
1^2A_2	12	22 731	1890	− 2550.94999	0.956	$5^2, 6^2, 8^2-10^2$	7	9.90	9.57
1^2A_2	20	23 085	3479	− 2551.01766	0.932	$1^2-6^2, 8^2-10^2$	7	9.85	9.57
					+ 0.045	$1^2-6^2, 8^2, 10^2$	(9, 14), 7		
					+ 0.045	$1^2-6^2, 8^2, 9^2$	(10, 13), 7		
2^2A_2	12	22 731	1890	− 2550.69150	0.665	$5^2-8^2, 10^2$	12	16.93	
					− 0.665	5^2-9^2	12		
3^2A_2	12	22 731	1890	− 2440.68040	0.621	5^2-9^2	12	17.24	
					+ 0.621	$5^2-8^2, 10^2$	12		
1^2E	12	39 909	3065	− 2550.97734	0.965	5^2-9^2	10	9.16	9.01
1^2E	20	67 486	9316	− 2551.04830	0.938	1^2-9^2	10	9.02	9.01
					− 0.069	$1^2-6^2, 8^2, 9^2$	(7, 12), 10		
					+ 0.064	$1^2-7^2, 9^2$	(8, 11), 10		
2^2E	20	67 486	9316	− 2550.97611	0.934	$1^2-5^2, 8^2-10^2$	6	10.98	
					− 0.050	$1^2-6^2, 8^2, 10^2$	(9, 12), 7		
					− 0.050	$1^2-3^2. 5^2-10^2$	4		
3^2E	20	67 486	9316	− 2550.96415	0.928	$1^2-3^2, 5^2-10^2$	4	11.305	
					− 0.063	1^2-8^2	(9, 10), 12		
					+ 0.057	$1^2-3^2, 5^2-7^2,$ $9^2, 10^2$	(8, 11), 4		
4^2E	12	39 909	3065	− 2550.70094	1.02	5^2-8^2	(9, 11), 10	16.68	

population at the apex than the base. The reason for this difference is not clear but the difference in bond angles from approximately tetrahedral at the apex, to the heavily distorted arrangement in the triangular base would be expected to increase the level of 3p orbital bonding at the base as found. The 3d orbital difference can perhaps be seen as a reduction in donation into the $3d_S$ orbitals.

It has to be noted that only in the SCF orbitals 16e does the 3d population reach even 0.01e. The principal orbitals of the CI process (Table 4) show the spd character of the orbital nature, if one form is dominant; thus for example $18a_1$ is rich in $3p_z$ at both the basal P and the S atoms, and in this instance is P − S anti-bonding; several orbitals are however rich in 3d character (e.g. $20a_1$ and orbitals

above this in energy), and yet these were not utilised by the CI procedure to anything like the level of the 3p virtual orbitals. Hence in the ground state the 3d functions are purely variational in character; that is, they allow minor redistribution of the electrons into regions otherwise inaccesible to the atomic orbital basis, but the bonding would be largely unchanged in the absence of the 3d orbitals.

c) Localisation of the Wave-function

When the electronic wave-function was converted to a set of localised orbitals (Table 3) by the Foster-Boys [10, 11] technique, effectively all the density was converted into the conventional set of P – S/P – P bonds and lone pair (LP_P/LP_S) electrons; thus each S atom carried two and each P atom one lone pair orbital. There is a marked difference in character between the LP_S and LP_P electrons, the former being nearer to the classical sp^2 orbital; the LP_P are higher in (3s + 3s′) character than 3p character, and this is especially true of the basal P atoms. On the other hand, the P – S bonds are largely of 3p character, and this is especially true of the S atom contributions. The basal P – P bonds are dominated by 3p character, as expected from the equilateral triangle and associated small angle at the P atoms. Mulliken analyses (Table 4) of these orbitals show that $17a_1$ is effectively a lone pair orbital. It is this orbital in particular which provides the driving force for coordination, as previously discussed [5], rather than the basal phosphorus which although more negative lack an *individual* molecular orbital of localised LP_P character.

d) Ionised States by Configuration Interaction

As noted above we sought three ionised states for each of $^2A_1$ and ^2E symmetry, and one of $^2A_2$; since there is only one occupied A^2 orbital in the valence shell, the other states of $^2A_2$ must be of shake-up type and of less interest for the present work. The number of possible configurations was about 23 000 per root function (Table 5) and hence configuration selection was essential. This was done throughout, and the excitation energies given in Table 6 refer to energy differences between ground and ionised state at the same selection threshold energy (normally 50 μ Hartree).

In all of the seven states computed (3 + 3 + 1 for $^2A_1$, ^2E and $^2A_2$ respectively) the input root functions (Table 5) were dominant in the final CI expansion. Thus all of these states are well represented by a one-electron approach, and in fact the order of the SCF orbitals and their internal spacing, is rather well reproduced by the spd-basis set calculation, when compared with the CI doublet states. One outstanding omission was our inability to determine the position of 4^2E and whether it lay above or below 3^2A_1; Koopmans' theorem places these relatively close. Another interesting feature is that of all the ionised states computed (Table 6), by far the most common excitations other than thosed of the input reference configurations, is to configurations containing orbital 12 ($4a_2$); the same arguments as those put forward for the same phenomenon with the ground state apply.

Assignment of the Photoelectron Spectrum of P_4S_3

As has already been noted, the spectra of P_4S_3 and As_4S_3 are very similar and an assignment of one must approximate to an assignment for the other. In practice the two sets of orbital energies P_4S_3 and As_4S_3 and the CI study on P_4S_3 all lead to the same general order of symmetry states and of internal groupings. All can be directly compared with the experimental spectra.

For P_4S_3, the experimental spectrum (Fig. 1) shows a band between 9 and 10 eV consisting of two closely spaced peaks and a rather larger peak to higher binding energy. The three were assigned to two A_1 + one E state, of lone pair orbitals on sulphur and apical phosphorus, by Cannington and Whitfield [6], largely on the basis of analogy with PCl_3. In

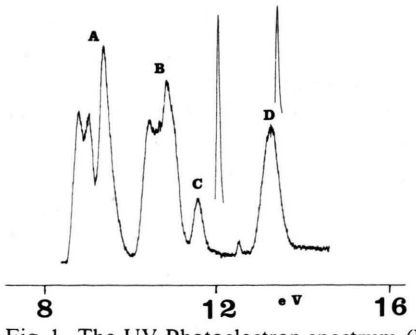

Fig. 1. The UV-Photoelectron spectrum (HeI) showing the principal grouping of ionisation potentials. Calibration lines from Xe are superimposed at 12.13 and 13.44 eV; Ar was also used in ad-mixture.

contrast, Head et al. [5] gave the assignment 17e, $3a_2$, $17a_1$ low to high binding energy, on the basis of an XαSW calculation and comparison with S_8 and other compounds. It is noted that the semi-empirical methods, EH and CNDO, do not even give the same order as the XαSW in this first group (A) of orbitals [5]. The present work finds 1^2A_2 and 1^2A_1 almost completely degenerate and at somewhat higher binding energy than 1^2E; we thus propose that the doublet at 9.05 and 9.25 eV represents Jahn-Teller splitting of 1^2E, with 1^2A_2 and 1^2A_1 under one band at 9.60 eV. On this basis the present order of states is effectively the same as that for XαSW [5] but the assignment ot IP's is different. Jahn-Teller effects have been considered previously for P_4S_3 in relation to the next main group of bands (B) where a very similar envelope occurs near 11 eV. Thus the close doublet at 10.70/10.88 eV has been assigned [5] to vacancies from 16e (2^2E) with 3^2E at 11.06 eV (unsplit) [5,6]; the present work supports these assignments. It is not possible to be certain with either groups A or B whether the Jahn-Teller splitting could be larger and consist of bands 1 to 3 and 2 to 3, namely 0.23 and 0.56 eV respectively; this would leave some difficulty in assigning $^2A_2$ and $^2A_1$; a smaller splitting as proposed above seems more probable and leads to 0.23 eV (1800 cm^{-1}) for band A, 0.15 eV (1200 cm^{-1}) for band B. The small band (C) at 11.7 eV is assigned to 2^2A_1, basically a vacancy from $16a_1$, as has been proposed earlier [5, 6], with the rather larger band at 13.3 eV as $3^2A_1 + 4^2E$. In the last case we are not able to give an order to the states, since we were not able to compute 4^2E precisely. The broadness of the band and its symmetrical structure do not lead to any clear conclusion, but it seems probable that some Jahn-Teller splitting may also occur here, with 3^2A_1 superimposed in the centre. Our spectrum (Figure 1) shows some asymmetry in this region, but this arises from superposition of $Xe^2P_{1/2}$ at 13.44 eV; the small peak at 12.6 eV is traces of water.

There is no calculated evidence of shake-up peaks in the binding energy region up to about 13 eV, but there does appear to be a group of such states involving 2^2A_2 and 4^2A_1 probably well before the present calculated values of 16.8 eV; since we have not used shake-up states as input root configurations, they are not fully participating in the CI process, and the present energies are only an upper limit. Given that our present value for 4^2E is almost equal to these shake-up states and that there is good reason to assign 4^2E to the IP at 13.3 eV, this suggests that the envelope from 13 eV onwards probably represents a series of complex phenomena.

In conclusion, the present calculations for P_4S_3 lead to a revised assignment of the first main group (A) of IP's and suggest that Jahn-Teller splitting may well be present in each of the states 1^2E to 3^2E. The presence of a $^2A_2$ state in the outer valence shell is confirmed, and its absence from discussion in [6] noted. The calculations show that configuration interaction studies can yield realistic energy values for ionised states even when a relatively small basis is used. The absence of incorporation of 3d functions is highly significant, for not only does it show that these functions are very unimportant in the bonding of P_4S_3, but it shows that the small basis set *ab initio* calculations do not follow one of the failings of the semi-empirical ones. Thus semi-empirical calculations, owing to very restricted variational freedom, frequently show much higher levels of 3d orbital participation than occurs with more refined calculations; examples of this are commonly found with compounds of P and S; in the present work the 3d character is already low at a single configuration level; it is slightly reduced by configuration interaction, where ample opportunites for 3d orbital enhancement of participation was available.

Finally, we note that the final order of states obtained is effectively the same as that given by Koopmans' theorem (the very small differences between 1^2A_2 and 1^2A_1 cannot be regarded as final). Thus as in our recent work with S_4N_2 [3] the performance of Koopmans' theorem (KT) is extremely satisfactory. It has become fashionable to criticise KT, in view of a number of known failures; it is important to avoid over-emphasis of the failings, and it remains true that for low binding energy states, KT probably provides a very reasonable interpretation when used with a good quality *ab initio* basis.

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