Assignment of the UV-Photoelectron Spectrum of Tetrasulfur Tetranitride

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Ab initio configuration interaction calculations of the ground and doublet states of S_4N_4 show changes in the order of states relative to a large basis set Koopmans' Theorem order. Consequential changes in the assignment of the UV-photoelectron spectrum are reported.

Introduction

Recently we reported [1] an assignment of the UV-photoelectron spectrum of tetrasulfur tetranitride, S_4N_4 (**1**) based upon (i) consideration of changes in the spectral profile when the radiation was changed from He(I) to He(II), (ii) variations in SCF orbital energy as a function of basis set from a minimal *ab initio* basis up to a better than double zeta sp-basis which included mid-bond functions. The presence of 7 IP's in the range 9–14 eV made the spectral assignment complex, and that assignment differed from earlier ones [2] based upon a smaller basis set, CNDO-S [2] or Xα [3] calculations.

Recently we have carried out *ab initio* configuration interaction studies on S_4N_2 (**2**) [4, 5], P_4S_3 (**3**) [6] and P_4S_4 (**4**) [7], with various sizes of the basis set, and now extend these to S_4N_4 using the largest possible CI basis, and one comparable with that for S_4N_2 [4]. The starting basis set was the "better than double zeta" basis of [1], but excluding the mid-bond functions; this was necessary owing to the large scale of the Cl and restrictions on computing facilities; the direct comparison is with the double zeta calculation of energy -1807.14078 a. u. in Tables 1–3 of Ref. [1]. In summary, no $3d_S$ functions were incorporated, as discussed below.

Computational Methods

The earlier [1] S(12s9p) and N(9s5p) bases of Dunning [8] and Veillard [9] were contracted to S[7s4p] (not [7s2p] as in Ref. [10]) and N[4s2p], a total of 116 Gaussian type orbitals (GTO's). In the CI study a perturbation selection procedure was employed, [11], in which the contribution of a configuration is estimated, rejected if below a certain level, here 5×10^{-6} Hartree, and a correction applied to the final energy. Excitation (ionisation) energies are then based upon energy differences between the ground and doublet state after correction, at the same level of selection. In practice the energy loss corrections are relatively constant, so that these do not alter the order of states. It was important to carry out the CI on at least one state of each symmetry in the D_{2d} point group for S_4N_4; also the earlier ionisation cross-section differences for HeI and HeII, had suggested ionisation from orbital $8a_1$ (a S lone pair, S_{LP}) was the IP at 13.7 eV. Hence we took all single and double replacements from the valence shell from the highest occupied orbital ($8b_2$ in this basis [1]) down to $8a_1$, but excluding $9e$ (for reasons described below); thus there were 19 active electrons. The valence shell virtual orbitals up to $13b_2$ were included, a total of 28 virtual orbitals in Aufbau order (Table 1). In the case of $^2A_1$, $^2B_2$, and ^2E states multi-reference configurations were used with all occupied active orbitals included; in the case of ^2E the triple reference set containing a shake up satellite was employed, since preliminary calculations suggested that this state was low-lying. The list of root configurations is also shown in Table 1. The computations were performed on a Cray-1 computer using the ATMOL-SPLICE system [11] of programs, and the largest CI (118318 configurations) took approximately 1 h of CPU.

Results

(a) Comparison of the Excitation Energies by CI and SCF Calculations

For the ground X^1A_1 state three levels of CI threshold (100, 50 and 25 micro Hartree) all led to

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Table 1. Active orbitals and sequence numbering with corresponding root-functions.

Active Orbitals

Sequence Number	1	2, 3	4, 5	6	7	8	9	10
Symmetry	$8\,a_1$	$10\,e$	$11\,e$	$7\,b_2$	$4\,b_1$	$9\,a_1$	$3\,a_2$	$8\,b_2$
Sequence Number	11, 12	13	14	15, 16	17	18, 19	20	21, 22
Symmetry	$12\,e$	$5\,b_1$	$10\,a_1$	$13\,e$	$9\,b_2$	$14\,e$	$4\,a_2$	$15\,e$
Sequence Number	23	24	25	26, 27	28	29, 30	31	32
Symmetry	$10\,b_2$	$11\,a_1$	$11\,b_2$	$16\,e$	$12\,a_1$	$17\,e$	$5\,a_2$	$6\,b_1$
Sequence Number	33	34, 35	36	37	38			
Symmetry	$13\,a_1$	$18\,e$	$12\,b_2$	$14\,a_1$	$13\,b_2$			

Root Functions

State	Orbital occupancy	Configurations (total)
X^1A_1	1^2-10^2	17193
$^2A_1$	$\left\{\begin{matrix}1^2-7^2, 9^2, 10^2, 8^1\\ 2^2-10^2, 1^1\end{matrix}\right\}$	68258
$^2B_2$	$\left\{\begin{matrix}1^2-5^2, 7^2-10^2, 6^1\\ 1^2-9^2, 10^1\end{matrix}\right\}$	68258
$^2A_2$	$1^2-8^2, 10^2, 9^1$	38103
$^2B_1$	$1^2-6^2, 8^2-10^2, 7^1$	38103
^2E	$\left\{\begin{matrix}1^2-4^2, 6^2-10^2, 5^1\\ 1^2, 3^2, 4^2-10^2, 2^1\\ 1^2-9^2, 12^1\end{matrix}\right\}$	118318

virtually the same final energy, after incorporation of the energy loss, and the leading configurations were the same (Table 2 gives the results for one level, 50 μH). The excitation energies for all the doublet states obtained, at this same selection level, show that at least one shake-up state (3^2E) occurs by 14.3 eV; thus since the first IP is calculated about 1.1 eV to too high energy, this suggests shake-up probably occurs by about 12 ~ 13 eV experimentally In our previous study of S_4N_2 [4] we found evidence of shake-up as soon as 12 eV. The large number of lone-pair orbitals (LP_N and LP_S) together with the low-lying first virtual orbital (13e) are generally responsible; in the present case of 3^2E this is basically ionisation and shake-up $8\,b_2^2 \rightarrow 13\,e^*$ ie from a LP_N combination to the lowest virtual orbital (LUMO). There are several electronic spectral absorptions for S_4N_4 in the range 2.7−6.0 eV [12]; the lower ones together with a first IP of 9.36 eV are consistent with this conclusion.

With the exception of the above, all of the doublet states (Table 2) are well represented by the one-electron approximation, ie the configuration representing ionisation from a particular orbital is dominant in the final CI vector. As a consequence of this, the changes of density at the atoms do not differ markedly (Table 3) from those obtained in the SCF Mulliken analysis [1]. The 1^2E state is unusual (for the lowest state of a particular symmetry) in having a relatively high level of contamination by a single shake-up state (Table 2); this led to the incorporation of the latter as a root function (Table 1); the effect on 1^2E is however relatively low in terms of excitation energy (the 2-root calculation gave 12.90 eV, while the 3-root gave 12.73 eV). In view of the computational expense of this process (76976 and 11838 configurations respectively), it was not repeated for the other states.

Generally the CI leads to a shift of state relative to the SCF orbital energy of about 0.2−0.8 eV, increasing in this range with progressive increase with binding energy, and both 1^2B_1 and 1^2E being affected more than the other states. However, Koopmans' Theorem ($IP_i = -\varepsilon_i$ where ε is the SCF orbital energy) is not obeyed in the present order of doublet states; the change in Koopmans' order $3\,a_2 < 8\,b_2$ between the sp- and (sp + midbond) calculations [1] is confirmed by the CI calculations; the marked shift in position of 1^2B_1 which now occurs to lower (binding) energy than 1^2A_1 is not

Table 2. Total energy (a. u.) and excitation energy (eV) of states for S_4N_4.

State	Energy		Principal configurations	
	Total	Excitation	Coefficient	Root function
X^1A_1	−1807.37417	–	0.938	1^2-10^2
			−0.054	$1^2-7^2, 9^2-11^2$
			−0.053	$1^2-7^2, 9^2$, (11, 8) (12, 10)
1^2A_1	−1806.96914	11.02	0.923	$1^2-7^2, 9^2, 10^2$, 8
			−0.063	$1^2, 2^2, 4^2-7^2, 9^2, 10^2$, (12, 3) 8
			+0.063	$1^2, 3-7^2, 9^2, 10^2$, (11, 2) 8
2^2A_1	−1806.72565	17.65	0.873	2^2-10^2, 1
			−0.141	$1^2-4^2, 6^2, 7^2, 9^2, 10^2$, (5, 8) 12
			−0.077	$1^2-3^2, 5^2-7^2, 9^2, 10^2$, (4, 8) 11
3^2A_1	−1806.6477[a]	–[a]	0.365[a]	$1^2-4^2, 6^2, 7^2, 9^2, 10^2$, (5, 8) 12
			−0.362[a]	$1^2-3^2, 5^2-7^2, 9^2, 10^2$, (4, 8) 11
			−0.196	$1^2-4^2, 6^2-9^2$, (5, 11) 10
1^2B_2	−1806.98647	10.55	0.920	1^2-9^2, 10
			+0.085	$1^2-5^2, 7^2-10^2$, 6
			−0.054	$1^2-4^2, 6^2-8^2, 10^2$, (12, 9) 5
2^2B_2	−1806.91704	12.44	0.907	$1^2-5^2, 7^2-10^2$, 6
			−0.085	1^2-9^2, 10
			−0.065	$1^2, 2^2, 4^2, 5^2, 7^2-10^2$, (12, 3) 6
3^2B_2	−1806.66247[a]	–[a]	0.305[a]	$1^2-3^2, 5^2-9^2$, (11, 10) 4
			−0.300[a]	$1^2-4^2, 6^2-9^2$, (12, 10) 5
			+0.290	$1^2-4^2, 6^2-9^2$, (5, 12) 10
1^2A_2	−1806.98875	10.49	0.922	$1^2-8^2, 10^2$, 9
			−0.063	$1^2-4^2, 6^2-8^2, 10^2$, (5, 9) 12
			−0.053	$1^2-3^2, 5^2-9^2$, (11, 10) 4
1^2B_1	−1806.96993	11.00	0.918	$1^2-6^2, 8^2-10^2$, 7
			−0.076	$1^2, 2^2, 4^2-6^2, 8^2-10^2$, (7, 3) 12
			−0.064	$1^2, 2^2, 4^2-6^2, 8^2-10^2$, (12, 3) 7
1^2E	−1806.90629	12.73	0.889	$1^2-4^2, 6^2-10^2$, 5
			0.151	1^2-9^2, 12
			−0.112	1^2-8^2, (9, 12) 10
2^2E	−1806.85825	14.04	0.896	$1^2, 3^2-10^2$, 2
			+0.120	$1^2-6^2, 8^2, 9^2$, (12, 10) 7
			−0.096	$1^2-6^2, 9^2, 10^2$, (11, 8) 7
3^2E	−1806.84800	14.32	0.862	1^2-9^2, 12
			−0.180	$1^2-8^2, 10^2$, 12
			+0.125	$1^2-3^2, 5^2-10^2$, 4

[a] Since the final configurations shown were not input as reference configurations, not all single and double configurations arising from these configurations were performed. Hence the total energy is too positive and the IP (excitation energy) is too large.

apparent in the two SCF calculations, where no relative shifts of the 3rd to 5th orbitals occur on addition of the mid-bond functions.

(b) Assignment of the UV-Photoelectron Spectrum

The numerical agreement with respect to the UV-PES [1] is comparatively poor, and the internal spacing of states does not lead to any immediate conclusions concerning the most probable assignment. It is clear that the numerical agreement with experiment in the corresponding calculations for S_4N_2 (**2**) is much better; since the sp-basis was the same in both cases, the most obvious explanation is that $3d_S$ functions, incorporated in the latter but not in S_4N_4 have some effect. The reason for the non-inclusion here is (a) the very large number of integrals generated; for S_4N_2 some 7 × 2400 ft of magnetic tape were filled at 1600 BPI: for S_4N_4 a marked increase was expected, and possibly this would be beyond the user limits imposed, and (b) there would be a corresponding large increase in the

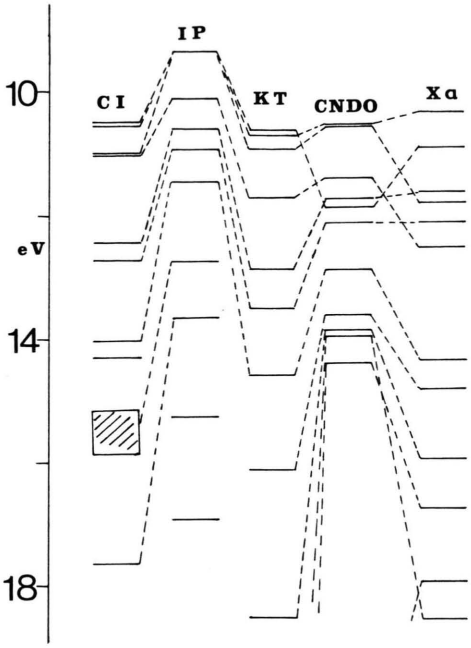

Fig. 1. Comparison of CI results and Koopmans' Theorem with the IP's for S_4N_4.

scale of the CI both in size and time. Thus the present restrictions were a necessary, but undesirable restriction. This is not to imply that the $3d_S$ orbitals are vital to the bonding, for in the case of S_4N_2, the 3d orbital population is always low [1, 13] and the CI in fact does not enhance this level. Indeed for P_4S_4 and P_4S_3 [6, 7], the CI actually decreases the 3d orbital participation, in what are much smaller basis set calculations.

In our previous assignment [1] for S_4N_4, we allocated 3 states to the first IP, corresponding to vacancies from $3a_2$, $8b_2$ and $9a_1$; open-shell calculations of the IP's with largest basis sets (ie including the mid-bond functions) yielded IP's ($= E_{MOL} - E_{ION}$) 10.22 ($^2B_2$), 10.39 ($^2A_2$) and 10.84 ($^2A_1$) suggesting that the 3 states were relatively close. Unfortunately we were unable to converge the other obvious state ($^2B_1$). Thereafter the states were assigned to spectrum in 1:1 correspondence down to 13.66 eV ($8a_1$); as mentioned above there is experimental evidence to support this last IP assignment on the basis of cross-section differences under HeI/HeII irradiation changes. The present CI results (Table 2) suggest that the primary difference in grouping and order relative to the Koopman's Theorem [1] results lies in the first group of IP's, with 1^2B_1 being lower in (binding) energy than previously suspected. Thus of the alternatives that present themselves for the IP's at 9.36 and 10.11 eV (the latter is basically a small peak), we favour the 3:1 rather than 2:2 ratio on a cross-section basis comparison with the probable ^2E state to slightly higher energy; hence we suggest that the present CI may be correct in shifting 1^2B_1 to markedly lower binding energy relative to Koopmans' Theorem, but that the shift is perhaps not yet enough. Thus rather than the earlier 3:1 assignment [1] we favour the same ratio, but consisting of $(1^2A_2 + 1^2B_2 + 1^2B_1):(1^2A_1)$; this leaves the remaining group to higher binding energy down to 2^2A_1 unchanged (Figure 1).

It is appropriate to mention that the present CI results, whilst bearing some relationship to the (sp + mid-bond) SCF orbital energies, do not have much in common with either the CNDO-S [2] or Xα-calculations [3]. Thus both these yield a highest occupied orbital of b_2 symmetry, and marked differences in the groupings and order from these down to $7a_1$ of the valence shell (n. b. in both [2] and [3] the orbitals are numbered from the valence shell only; hence $7a_1$ of the present work is $2a_1$ in [2, 3]). Although the CNDO-S density of states envelope bears some relationship to the experimental envelope it (i) wrongly assigns the IP's for 1^2A_1 and 1^2A_2, and (ii) leads to wrong relative intensities for the IP's at 9.36/10.11 eV and at 10.92/11.44 eV. A further serious aspect is the fact that the parametrization of the CNDO-S method for S/N compounds was explicitly based upon the interpretation of the UV-PES of S_4N_4 [2]. Hence the application of the method using these parameters to interpret the UV-absorption spectrum of S_4N_4 [2] seems in doubt. This will be considered in a future paper.

Conclusions

The CI studies of the present paper suggest a slightly modified assignment of the 3:1 ratio of IP's at 9.36 and 10.11 eV previously given [1]; a large orbital basis containing $3d_S$ may well be necessary to confirm this, but at the present time this seems prohibitive in computational expense. Thereafter the assignments do appear to agree with the Koopmans' Theorem order down to the IP at 13.66 eV;

however, there are clearly shake-up states before this energy, and some breakdown of the one-electron orbital picture can be anticipated from that point. There seems little relationship between the CNDO-S [2] and Xα order of states and that currently proposed.

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