The Ground and Ionised States of S_2N_2; *Ab initio* Configuration Interaction Studies of the UV-Photoelectron Spectrum

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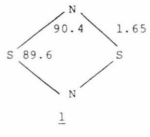
Ab initio CI calculations using a large spd-basis with polarisation functions have been obtained for the ground state of S_2N_2 and for many doublet state radical cations of each symmetry. All valence shell electrons were considered in the CI, leading to markedly lower energies than previous work. All doublet states down to about 20 eV have probably been found – this leads to a more general description of the UV-photoelectron spectrum, but the principal IP's are still assigned according to our previous work. Some deficiencies in the Green's Function/Tam Dancoff Method have been noted. The principal groups of shake-up states seem to agree with weak structure in the observed spectrum.

Introduction

The small cyclic molecule S_2N_2 is very nearly square and planar (**1**) and has attracted a considerable interest both because of its non-classical structure – a resonance hybrid based on (**2**) (for a bibliography see [1]) and because it is a precursor to the conducting polymer $(SN)_x$ (**3**) (for a bibliography see [2]); the latter consists of chains formed by polymerisation *down the stack* of S_2N_2 molecules, i.e. perpendicular to the local molecular planes [2], and hence is a π-electron process at some stage in the transformation.



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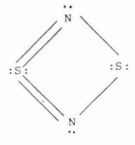

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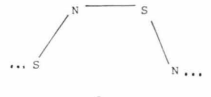

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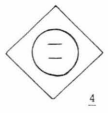
The S_2N_2 molecule is π-isoelectronic with the cyclobuta-1,3-diene dianion (**4**) in the valence shell; the latter is a pseudoaromatic species [3a] on the basis of the Hückel $(4n+2)\,\pi$-electron rule, with D_{4h} symmetry, and has been identified [3b]. The alternating S/N atoms of S_2N_2 mean that the degenerate e′ and e″ levels of D_{4h} are broken (D_{2h}).



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The present paper is concerned with a more detailed interpretation of the UV-photoelectron spectrum (UV-PES) and uses our previous work as a starting point [1]. There has been a Green's Function/Tam Dancroff (GF/TD) study [4] in the interval; that paper is valuable in drawing attention to the break-down of the one-particle approach beyond about 14 eV, but used a strangely unbalanced spd-basis set as discussed below, and was already markedly poorer in energy than our previous work [1]. With respect to the UV-PES the GF/TD study [4] did not give a good quantitative account of the available spectral information. Indeed, while none of the three sets of data in [4] is particularly convincing, the best fit is obtained with their poorest calculation.

Methods

(a) *The SCF basis.* The starting point was the 102-basis function SCF calculation of [1], energy -903.8599 a.u. (1 a.u. = 27.21 eV = 2626 kJ mol^{-1}), which uses a S(12s9p) and N(9s5p) basis contracted to S[7s4p] and N[4s2p], augmented by $3d_S$, $3d_N$, mid-bond (sp) and centre (sp) functions.

(b) *The CI Method.* The restriction on number of input reference configurations, which was necessary in our previous work on S_8 [5], S_4N_2 [6, 7] and S_4N_4 [8], through use of the SPLICE program, has been lifted through use of the MRD-CI program [9]. The latter does not produce the large temporary files which cause difficulty in SPLICE, and also is considerably more efficient in speed. The full val-

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Table 1. Active set of CI orbitals and corresponding SCF sequence numbers.

Symmetry type	SCF sequence numbers	
	Occupied set	Virtual set
$1a_g - 11a_g$	13, 16, 19	28, 33, 35, 37, 40, 49, 54, 56
$1b_{1u} - 5b_{1u}$ (π)	18	24, 29, 41, 45
$1b_{3u} - 7b_{3u}$	14, 21	25, 34, 38, 50, 53
$1b_{2g} - 3b_{2g}$ (π)	22	39, 47
$1b_{2u} - 8b_{2u}$	15, 20	26, 30, 36, 42, 48, 52
$1b_{3g} - 3b_{3g}$ (π)	23	31, 46
$1b_{1g} - 6b_{1g}$	17	27, 32, 44, 51, 55
$1a_u$	–	43

ence shell (22 electrons for the ground state) was input into the CI, and all double and quadruple excitations into a set of 33 virtual orbitals were performed. The virtual orbitals were the lowest group from the SCF wavefunction in Aufbau order. These are divided into the 8 representations of D_{2h} symmetry and re-sequenced for simplicity as shown in Table 1. At least 4 roots of each symmetry were sought, and this required an *ad hoc* search for the relevant input reference configurations, after allowance for the Koopmans' states. Thus the CI was performed in several stages.

(c) *The Ground State CI.* After use of the single reference (SCF) configuration, the first 3 terms of the CI expansion were used in a triple reference calculation. Table 2 shows these configurations, while the principal energy results are in Table 3.

(d) *The Cationic States.* In the first phase of CI, the reference states were from the SCF wave-function by removal of one-electron from each occupied orbital (Koopman's type states). These doublet states without the incorporation of shake-up are shown in the first entries of each state in Table 3,

Table 2. Multi-reference functions used in the CI studies.

State	Sequence No.	Change from ground state SCF occupancy	
		Doubly occupied	Singly occupied
^1A_g	1	Nil	–
	2	$-1b_{2g}^2 + 2b_{1u}^2$	–
	3	$-1b_{3g}^2 + 2b_{1u}^2$	–
^2A_g	1		$3a_g$
	2		$2a_g$
	3		$1a_g$
	4		$2b_{1u}, 2b_{3u}, 1b_{2g}$
	5		$2b_{1u}, 2b_{2u}, 1b_{3g}$
$^2B_{1u}$	1		$1b_{1u}$
	2	$-1b_{2g}^2$	$2b_{1u}$
	3	$-2b_{3u}^2$	$2b_{1u}$
	4	$-1b_{2g}^2$	$2b_{1u}$
	5	$-2b_{2u}^2$	$2b_{1u}$
	6	$-3a_g^2$	$2b_{1u}$
$^2B_{3u}$	1		$2b_{3u}$
	2		$1b_{3u}$
	3	$-1b_{2g}^2 + 2b_{1u}^2$	$2b_{3u}$
	4	$-1b_{3g}^2 + 2b_{1u}^2$	$2b_{3u}$
	5		$1b_{1u}, 2b_{1u}, 2b_{3u}$
	6		$3a_g, 2b_{1u}, 1b_{2g}$
$^2B_{3g}$	1		$1b_{3g}$
	2	$-1b_{2g}^2 + 2b_{1u}^2$	$1b_{3g}$
	3	$-3a_g^2 + 2b_{1u}^2$	$4a_g, 1b_{2g}, 1b_{3g}$
	4		$2b_{1u}, 1b_{2g}, 1b_{3g}$
	5		$2b_{2u}, 3b_{3u}, 1b_{2g}$
	6		$2b_{1u}, 4b_{1u}, 1b_{3g}$
	7		$2b_{3u}, 4b_{3u}, 1b_{3g}$
	8		$4b_{3u}, 1b_{2g}, 2b_{2u}$

Table 2. (continued)

State	Sequence No.	Change from ground state SCF occupancy	
		Doubly occupied	Singly occupied
$^2B_{1g}$	1		$1b_{1g}$
	2	$-1b_{2g}^2 + 2b_{1u}^2$	$1b_{1g}$
	3	$-3a_g^2 + 2b_{1u}^2$	$4a_g, 1b_{2g}, 1b_{3g}$
	4		$2b_{1u}, 1b_{2g}, 2b_{2u}$
	5		$2b_{1u}, 2b_{3u}, 1b_{3g}$
	6	$-1b_{3g} + 2b_{1u}^2$	$1b_{1u}, 2b_{3a}, 1b_{3g}$
$^2B_{2g}$	1		$1b_{2g}$
	2	$-1b_{3g}^2 + 2b_{1u}^2$	$1b_{2g}$
	3		$1b_{1u}, 2b_{1u}, 1b_{2g}$
	4	$-1b_{1u}^2 + 2b_{1u}^2$	$1b_{2g}$
	5		$2b_{3u}, 3b_{3u}, 1b_{2g}$
$^2B_{2u}$	1		$2b_{2u}$
	2		$1b_{2u}$
	3	$-1b_{2g}^2 + 2b_{1u}^2$	$2b_{2u}$
	4	$-1b_{3g}^2 + 2b_{1u}^2$	$2b_{2u}$
	5		$1b_{1u}, 2b_{1u}, 2b_{2u}$
	6		$2b_{3u}, 3b_{3u}, 2b_{2u}$
	7		$2b_{3u}, 4b_{3u}, 2b_{2u}$
^2A_u	1		$2b_{1u}, 1b_{2g}, 1b_{3g}$
	2		$2b_{3u}, 1b_{2g}, 2b_{1g}$
	3		$2b_{3u}, 1b_{2g}, 3b_{1g}$
	4		$2b_{3u}, 1b_{2g}, 4b_{1g}$
	5		$3a_g, 2b_{1u}, 1b_{1g}$
	6		$2b_{2u}, 1b_{3g}, 2b_{1g}$
	7		$3b_{2u}, 1b_{3g}, 1b_{1g}$
	8		$3b_{3u}, 1b_{2g}, 1b_{1g}$
	9		$4a_g, 1b_{1u}, 1b_{1g}$

Table 3. Final CI energies of states and excitation energies (eV)

State	No. of ref. conf. (CI ser.)	Full CI energy	Leading vector (C_7^2)	Config. function	Excitation energy
X^1A_g	1 (I)	−904.33036	0.8558	1	–
	3 (III)	−904.34145	0.8565	1	–
			0.0101	2	
			0.0033	3	
^2A_g	3 (I)	(1) −903.79400	0.7987	1	14.95
		(2) −903.69716	0.7823	2	17.59
	4 (II)	(1) −903.82479	0.6883	1	14.06
		(2) −903.77893	0.7852	4	15.31
		(3) −903.74842	0.3384	2	16.14
			+0.4286	5	
		(4) −903.71157	0.6682	5	17.14
			+0.1266	2	
	7 (III)	(1) −903.82705	0.6796	1	14.00
			+0.1407	4	
		(2) −903.79377	0.7848	4	14.901
		(3) −903.74691	0.3056	2	16.176
			+0.4522	5	
		(4) −903.71234	0.5049	4	14.117
			0.0982	5	
		(5) −903.71157	0.6682	5	17.144
		(6) −903.66799	0.3053	2	18.326
			+0.4251	5	
$^2B_{1u}$	1 (I)	(1) −903.78900	0.8001	1	14.79
	6 (III)	(1) −903.82270	0.2610	2	13.814
			+0.4459	1	
		(2) −903.75330	0.4352	2	15.702
		(3) −903.74615	0.7289	3	15.900
		(4) −903.67790	0.1188	2	17.813
			+0.3130	4	
			+0.3303	1	
		(5) −903.65369	0.7755	5	18.413
$^2B_{3u}$	2 (I)	(1) −903.94088	0.8392	1	10.66
	6 (II)	(1) −903.96027	0.8143	1	10.07
		(2) −903.66935	0.3724	5	18.05
			+0.3959	6	
		(3) −903.66564	0.4962	4	18.15
			+0.2513	5	
	7 (III)	(1) −903.95904	0.8153	1	10.163
		(2) −903.71817	0.7316	7	15.901
		(3) −903.71567	0.2730	4	16.785
			+0.2909	5	
			+0.1518	3	
		(4) −903.63922	0.3142	7	18.866
			+0.2458	6	
			+0.1497	4	
		(5) −903.62000	0.3870	6	19.389
			+0.3204	5	
			+0.1324	4	
$^2B_{3g}$	1 (I)	(1) −903.96113	0.8424	1	
	9 (III)	(1) −903.96612	0.8340	1	9.970
		(2) −903.79601	0.8094	3	14.599
		(3) −903.77907	0.8109	3	15.060
		(4) −903.72261	0.8061	5	16.597
		(5) −903.70381	0.8100	5	17.108
		(6) −903.67183	0.5226	2	17.998
			+0.2844	4	
$^2B_{1g}$	1 (I)	(1) −903.71692	0.8324	1	
	4 (II)	(1) −903.76377	0.4577	1	
			+0.3832	4	
		(2) −903.73210	0.3075	1	
			+0.5384	4	
	8 (III)	(1) −903.82049	0.8546	5	13.933
		(2) −903.7444	0.4256	1	16.004
			+0.2333	5	
			+0.1778	4	
		(3) −903.74388	0.5115	5	16.018
			+0.2507	4	
		(4) −903.66887	0.7841	3	18.059
^2A_u	9 (III)	(1) −903.84520	0.8384	1	13.261
		(2) −903.77088	0.7752	1	15.283
		(3) −903.63056	0.6792		19.101
$^2B_{2g}$	1 (I)	(1) −903.96724	0.8422	1	9.89
	3 (II)	(1) −903.96906	0.8315	1	9.89
		(2) −903.65802	0.5768	2	18.35
			+0.2346	3	
	8 (III)	(1) −903.97176	0.8306	1	9.817
		(2) −903.74959	0.7579	5	15.862
		(3) −903.72774	0.7529	5	16.457
		(4) −903.65028	0.4365	2	18.565
			+0.3614	3	
		(5) −903.56944	0.5668	3	20.764
			+0.1493	2	
$^2B_{2u}$	2 (I)	(1) −903.88780	0.8440	1	
		(5) −903.6352	0.3720	2	
	7 (III)	(1) −903.89515	0.8274	1	11.901
		(2) −903.69232	0.7768	6	17.420
		(3) −903.64844	0.7893	6	17.644
		(4) −903.63019	0.3741	5	19.111
			+0.2356	3	

and in Column CI-I of Figure 1. The second and third phases (CI-II, CI-III) then incorporated multi-reference sets of shake-up states in each representation, such that no state was omitted whose contribution to the density function was > 0.01 e; this led to up to 10 reference functions, as in Table 2. The total number of configurations generated was often up to 100000 but configuration selection and extrapolation by MRD-CI put a maximum of 10000 on any final CI.

Results and Discussion

(a) *The Ground State of S_2N_2.* The energy lowering by the CI is quite large (0.48 a.u.); the low starting SCF energy using 102 basis functions,

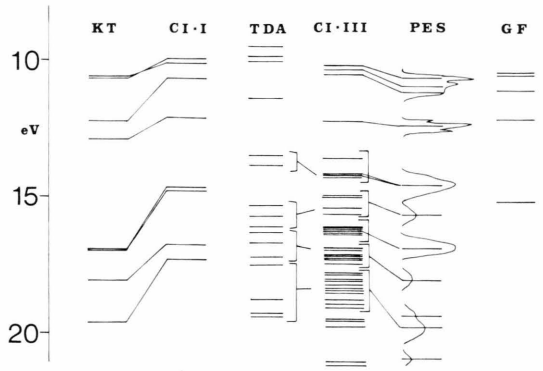

Fig. 1. Comparison of IP's by different methods.

which itself was already close to two CI energies for S_2N_2 [10, 11], is markedly lower than any previous work, as is shown by the following (CI energy/basis functions): − 903.91387/74 [10], − 904.02444/60 [11]. In fact the CI in [10] has only a marginal effect upon the ground state energy (0.172 a.u.) owing to the rather restricted nature of the CI (16 virtual orbitals), whereas the CEPA-CI lowering of the SCF energy [11] is closer (0.400 a.u.) to the present work. It seems probable that the present energy must be close to the Hartree-Fock limit for a valence shell only CI, although a further significant lowering might well occur if the core electrons were included.

It was previously shown [1] that the $3d_S/3d_N$ orbital population was low at the SCF single-configuration level (0.1348/0.0200 e); this was also true of the "centre" functions, while rather more was apparent at the "mid-bond" functions. The single reference CI showed the SCF wave-function to be extremely dominant (85.6%), and this was unchanged by the 3 reference calculation. The two 'replacement' configurations of the latter correspond to the processes $1b_{2g}^2 \rightarrow 2b_{1u}^2$, $1b_{3g}^2 \rightarrow 2b_{1u}^2$; both are $\pi^2 \rightarrow (\pi^*)^2$ (LUMO), and the $1b_{2g}/1b_{3g}$ orbitals are the (now non-degenerate) pair of e″ in D_{4h}; unlike e″ however, $1b_{2g}$ and $1b_{3g}$ are localised on a single element (N and S respectively). Thus the CI process appears to find the π-system more in need of refinement than the σ-system, a result explicable in terms of the single member of each π-representation in the occupied set. The reason for the *importance of the LUMO* ($2b_{1u}$) is that like $1b_{1u}$ it consists of *both* S and N atom density and thus allows repartition of S/N density from $1b_{2g}$ (N) and $1b_{3g}$ (S). The situation for S_2N_2 is thus extremely unusual; of the 3π occupied orbitals *only the most highly bound* ($1b_{1u}$) is S-N π-bonding at the SCF level; both the remainder are so heavily localised, that they are effectively cross-ring bonding as a result of the nodal positions. The $3d_{S/N}$ orbitals do allow a small amount of S-N bonding in $1b_{2g}/1b_{3g}$, and it is conceivable that this might have been high. The present results, like the earlier ones [1] show this is not the case. The major importance of the LUMO has been noted previously [4], but not discussed; this same orbital is vital to the CI studies on the ions.

The Cationic States of S_2N_2-CI Results

In the first phase, each of the orbitals of Rep(i) where $i = 1$ to 8 were input as singly occupied reference functions (Table 1); thus ^2Ag had 3 reference functions corresponding to $1a_g^{-1}$ to $3a_g^{-1}$ etc. It was not expected that each of these configurations would be a leading term in the CI of the states, although this would occur with the outer valence if Koopmans' Theorem (orbital energy (i) = $\varepsilon_i = -$ IP$_i$) was valid (cf. [4]). The results (Table 3, Fig. 2) show that all the Koopmans' states, except those $1a_g^{-1}$, $1b_{2u}^{-1}$ and $1b_{3u}^{-1}$, were in fact possible doublet states of S_2N_2 with the reference configuration as leading term. However, the smaller terms in these states indicated the necessity for, and nature of, the shake-up states for additional reference configurations, and this proceeded through stages CI-II and CI-III (Table 3, Fig. 2), by which time the number of

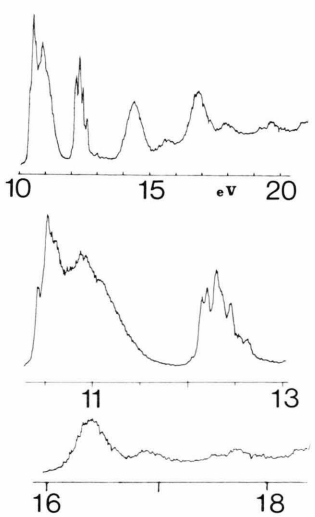

Fig. 2. He(I) Photoelectron spectrum of S_2N_2.

reference functions seemed to be saturated, and little movement of the doublet states was to be expected. It is worth noting that MRD-CI, as presently constructed, does not automatically produce the lowest ***n*** roots, but the lowest ***n***-roots in which a reference configuration is present in significant amount; thus, if (say) the set of reference configurations are numbered A–E, this may lead to roots 1, 2, 3, 6, 14 where reference configurations D and E are rich in roots 6 and 14 respectively; it does not automatically lead to roots 4 and 5. Thus an element of trial and error is involved at this stage.

Study of the set of reference configurations *necessary to produce* the first few roots of each symmetry (Table 2) shows for all states, except $^2B_{1u}$ and ^2A_u, that double replacements of $1b_{2g}$ and $1b_{3g}$ (π-orbitals) by $2b_{1u}$ (π^*, LUMO) are the most common, although the replacement of $3a_g^2$ by $2b_{1u}^2$ also occurs. The $^2B_{1u}$ states ($^2\pi$) are more simple, since when shake-up is included in the CI (Series III, Table 3), the Koopman's state corresponding to ionisation from $1b_{1u}^2$ exclusively does not occur; the first five roots of $^2B_{1u}$ have leading terms corresponding to (ionisation + excitation) from each of the first five orbitals in turn, i.e. to the process $(i)^2 \rightarrow 2b_{1u}^1$ where $i = 1b_{3g}$, $1b_{2g}$, $2b_{2u}$, $2b_{3u}$ and $3a_g$. There are no orbitals of A_u states involve the pseudo-e″ pair of orbitals, $1b_{2g}$ and $1b_{3g}$ and the LUMO ($2b_{1u}$).

The only states (Table 3) in which over 50% of the density corresponds to direct ionisation from one orbital (Koopmans' states) are: 1^2A_g (68%), 1^2B_{3g} (83%), 1^2B_{2g} (83%), 1^2B_{2u} (83%) and 1^2B_{3u} (82%) (Group I); these correspond to the highest 5 orbitals with calculated IP's in the range 9.8–13.7 eV. There is another group (Group II) where although the proportion is less than 50%, the Koopmans' configuration is either leading or at least prominent (Table 3); these include 3^2A_g (31%), 2^2B_{1g} (43%), 1^2B_{1u} (44%). Both sets of states agree with the main conclusions from the GF/TDA study [4]. The order of the first group also agree with the GF results [4] while the TDA values in the same order cover a much wider range. However, the differences between the CI and GF results are significant; (i) the first group of 3 IP's are more equally and closely spaced in the CI (range 0.3 eV) than GF (0.68) or TD (0.55), the two latter methods indicating a 2 : 1 and 1 : 2 ratio; the experimental envelope (Figure 1a) is complex (as discussed below) and more than one interpretation of the envelope is possible; (ii) the first ^2A_g state is found over 1 eV to lower IP than GF, with the TDA value differing by 1.27 eV; (iii) the present 1^2B_{1u} state is 3.35 eV to lower binding energy than the TDA and in contrast to the TDA this is not too dissimilar to a Koopmans' state. Thus the present calculation leads to a markedly different assignment of 1^2B_{1u}: here it is coupled with 1^2A_g at 14.4 eV, in contrast to 17.5–20.0 eV (TDA) [4].

Assignment of the Photoelectron Spectrum

From the above it is clear that the differences between the CI results and the GF or TDA ones [4] differ progressively as the energy of the state increases. In Fig. 1, we have assembled the 16 TDA and 5 GF data points from [4] with the observed UV-PES in diagrammatic from and the Koopmans' Theorem (KT) plus CI results from the present work. The most obvious feature from the experimental spectrum (Fig. 2) is the high density of states from 15–20 eV; this is only brought out in the CI-III results; the TDA results lead to a large number of states, but the bulk of these lie at higher calculated energy. The most likely interpretation is that the smaller basis of the TDA calculations has led to less low energy virtual orbitals, and hence less states in the low IP region.

We now consider the various regions of the UV-PES assignment in more detail. Those calculated IP's where a high level of singly excited configurations occur can be expected to yield strong UV-PES lines (Koopmans' states); the five GF lines and those TDA values with high pole strength come in the same category.

The order and grouping 3 : 1 of the first 4 calculated IP's is the same by all three methods; these are clearly assigned to the broad band centred on 10.8 eV and the well resolved multiplet at 12.3 eV. The assignment of the individual IP's of the 10.8 eV band has been discussed previously [12]; the first band (adiabatic IP 10.41 eV) was assigned to a π-level on the basis of well resolved fine structure, not seen previously (Fig. 3) with intervals of 470 and 810 cm^{-1}. This same IP is reduced in intensity relative to the 10.8 eV band by He(II) radiation [1], this is indicative of higher $3p_S$ in the 10.4 eV band which is assigned to $^2B_{3g}$; this assignment was previously given [1, 4, 12] and is a reversal of the KT order of the highest (pseudo e″) orbitals. The origin of the second IP, which probably does not

have well resolved five structure must lie near 10.8 eV, since the high energy fine structure of IP_1 is lost; this is the other pseudo E″/e″ state/orbital. The long tail, starting at 11.07 eV is then the highest $^2\Sigma^-$ state $^2B_{3u}$, and largely LP_N^- in character.

The well resolved band (adiabatic 12.1, vertical 12.29 eV) is generally assigned [1, 4, 12] as $^2B_{2u}$ in agreement with the present work. This is LP_S^- in nature. It is interesting to note that 1,2,5-thiadiazole (**5**) which is related to S_2N_2 by replacement of −S− by −CH=CH− (a well-established procedure in organic chemistry) shows marked fine structure of a band at 13.39 eV; this was assigned to $14a_1$ [13] – an orbital rich in LP_S character. The thiazoles and other thiadiazoles show some similar fine structure on IP's in the 12−13.5 eV region, and these were all assigned [13] to orbitals rich in LP_S character. The variation in IP for these orbitals varies considerably owing to various amounts of mixing with LP_N and in the case of S_2N_2, of the linear combinations LP_S^+ and LP_S^-. Thus it appears that LP_S shows better resolved fine structure than LP_N in these planar systems.

Beyond 13 eV the UV-PES of S_2N_2 shows two major broad peaks (14.40 and 16.77 eV) and at least four groups of weak peaks; the former most probably contain at least one Koopmans' type IP (i.e. high level of single one-electron excitation configuration) and the latter are largely shake-up satellites. The present calculations indicate a nearly degenerate pair of semi-Koopmans' type peaks (i.e. Group I + II above) $1^2A_g + 1^2B_{1u}$; these occur in the TDA method (at lower energy) with relatively high pole strength, while only the former is found by the GF method at higher energy. Asignment to the broad IP at 14.40 eV together with two shake-up peaks seems reasonable. The latter are the first doublet states of A_u symmetry (1^2A_u), calculated to lie at the low IP end of this peak, with 1^2B_{1g} at the high end.

No further GF IP's have been given; two high pole strength states 2^2A_g and 2^2B_{1g} [4] were previously assigned to the weak band at 15.5 eV; these are better assigned to the major band at 16.75 eV, where the present calculations place 3 semi-Koopmans' Group II IP's together with a close set of shake-up peaks. The absence of the latter in the TDA calculation forced the assignment cited above, which seems unrealistic on intensity grounds. Indeed the 16.75 eV peak is assigned [4] to a group of 3 shake-up peaks of singularly low pole strength.

The one remaining CI state of relatively high single excitation type is 4^2B_{1u}, in which the Koopmans' state is the leading configuration (33%); this must be correlated with the 2^2B_{1u} TDA line and assigned to the remaining relatively strong peak at 19.6 eV, together with a considerable number of satellites to either side.

Conclusions

Generally then it seems that the TDA method has failed to find enough states at low IP; only 16 are calculated [4] down to 19.5 eV, compared with 36 in the present work. It is conceivble that even more could arise with even larger basis set CI calculations. The TDA values are significantly lower than experiment with the CI relatively closer. The GF values are very close to experiment for the first few values. There are, however, difficulties in the region where change-over between the GF and TDA methods occurs. This is typified by the 1^2A_g state (calculated values: TDA, 13.8; GF, 15.1 eV) assigned at 14.4 eV. The present method whilst more expensive in computing facilities is both more rigorous, has no discontinuities, and probably locates more of the ionic states.

With the exception of the first two nearly degenerate orbital energies, $1b_{3g}$ and $1b_{2g}$, derived from the degenerate pair of $C_4H_4^=$ in D_{4h}, the order of high intensity states follows the Koopmans' theorem order down to 16.7 eV. Thus the main conclusions of our previous paper [1] remain; however, the large number of shake-up states identified by this method suggests that the new approach is probably worth persuing with related molecules.

There is a fundamental problem in assignment of the high IP valence shell region – low experimental signal to noise. The need for higher quality data, with extensive signal averaging and high stability is apparent.

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