Assignment of the Low Energy Photoelectron Spectrum of the Octa-Sulphur Molecule: An ab initio Configuration Interaction Study

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A large basis set *ab initio* configuration interaction study of S_8 has yielded a satisfactory assignment of the first 5 IP's of the UV-photoelectron spectrum for the first time. The ionisation potential order (low to high) is $^2A_1$, $^2E_3$, $^2E_2$, $^2E_1 \ll {}^2B_2$ and follows the orbital ordering of our recent large basis *spd* calculation, via the application of Koopmans' theorem.

Introduction

The UV-photoelectron spectrum (UV-PES) of the octa-sulphur molecule (S_8) has been reported previously [1, 2]; the X-ray PES [3] and photoemission spectrum [4, 5] have also been recorded, but neither show well developed structure in the low IP region (9 – 15 eV) (resolution about 0.6 eV compared with the UV-PES of about 15 meV). In contrast the UV-PES shows a group of 4 IP's around 9.5 eV [1, 2] followed by a single peak (11.4 eV) and then a more complex set of bands (12.5 – 14.4 eV).

Several types of semi-empirical [5 – 7], Xα [2] & *ab initio* molecular orbital [8, 9] calculations have been performed, and several authors have attempted [4, 6, 7] to assign the UV-PES on the basis of *either* Koopman's Theorem ($\mathrm{IP}_i = -\varepsilon_i$, where $\varepsilon_i = \mathrm{M.O.}_{(i)}$ energy) [6, 7], *or* the Xα transition state method [4]. In practice there is no agreement between these methods or with the application of Koopmans' Theorem to recent *ab initio* studies [8, 9] for even the first IP. Hence an *ab initio* study, using configuration interaction to calculate the IP's was desirable, and this is reported in the present paper.

Methods

The high symmetry of the molecule (D_{4d}) [10] leads to a large number of configurations of each state symmetry when single and double excitations from the SCF wave-function are performed. For example, the orbital mixed products $E_i * E_j$ $(i \neq j)$, where $i, j = 1, 2, 3$, yield the following:

$$E_1 * E_2 = E_1 + E_3 = E_2 * E_3\,,$$

$$E_1 * E_3 = B_1 + B_2 + E_2\,.$$

The corresponding symmetrical products $E_i * E_i$ yield even more terms [9]. Thus it was *necessary* to restrict the number of configurations; this was done by two methods.

(i) Although the previous *spd*-basis calculation [9], was significantly lower in total energy than the *sp*-basis (by 0.3629 Hartree, where 1 Hartree = 1 a.u. = 2626 kJ mol^{-1}), the density of each set of 3 *d* orbitals was only 0.1099 *e*. Hence it was decided to work with the *sp*-basis calculation of 152 basis functions rather than 192 (*spd*).

(ii) Configuration selection was employed (as in [9]); the contribution of a particular configuration was estimated from its matrix elements; if less than a thresh-hold (here 50, 30 or 15 μ Hartree), the configuration was rejected but a contribution to the total energy loss was accumulated [11]. As in our other recent work [12, 13] we found that these energy losses varied with the thresh-hold, but only very little between symmetry states. Thus all ionisation energies are obtained by difference between the ground and ionised states, at the same level of selection [12, 13].

The results at each thresh-hold showed similar calculated IP's, thus only those at the most stringent thresh-hold are shown in Table 1, while the numbering system used for the orbitals is given in Table 2.

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Table 1. Final CI results for S_8 and its ions (selection in CI at 15×10^{-6} a.u.).

State	Configurations		Energy (a.u.)		Leading configurations			
	Total	Selected	Selection Loss	Final total (+ 3179.0)	Eigenvector	Wave-function		
						Double occupancy	Single/mixed	
X $^1A_1$	9 077	899	0.00491	−0.95785	0.980	1^2-8^2		
					+0.028	$2^2, 3^2, 5^2-8^2$	(13, 1) (23, 4)	
					−0.026	$2^2, 4^2-8^2$	(13, 1) (24, 3)	
1 $^2A_1$	19 434	1750	0.00517	−0.58905	0.957	2^2-8^2	1	
					+0.060	$2^2, 4^2-8^2$	(15, 3) 1	$(e_1)^2$
					−0.057	$2^2, 3^2, 5^2-8^2$	(16, 4) 1	
1 $^2E_1$	21 079	1834	0.00546	−0.55115	0.955	$1^2, 2^2, 4^2-8^2$	3	
					−0.077	$2^2-6^2, 8^2$	(13, 7) 1	$b_2 e_3$
					+0.068	$2^2-5^2, 7^2, 8^2$	(24, 6) 1	$e_2 e_3$
1 $^2E_2$	21 730	2025	0.00512	−0.55411	0.954	$1^2-4^2, 6^2-8^2$	5	
					+0.078	$1^2-4^2, 6^2, 8^2$	(24, 7) 5	e_3^2
					−0.076	$1^2, 3^2, 4^2, 6^2-8^2$	(13, 2) 5	b_2^2
1 $^2E_3$	21 222	1902	0.00549	−0.58217	0.956	$1^2-6^2, 8^2$	7	
					−0.088	$1^2, 3^2-6^2, 8^2$	(13, 2) 7	b_2^2
					−0.062	$1^2-4^2, 6^2, 8^2$	(20, 5) 7	e_2^2
1 $^2B_2$	19 780	1996	0.00493	−0.49096	0.928	$1^2, 3^2-8^2$	2	
					−0.078	$1^2-5^2, 8^2$	(24, 6) 7	e_{23}^2
					−0.078	$1^2-4^2, 6^2, 8^2$	(23, 7) 5	e_3^2

Table 2. *sp*-basis active set of orbitals and sequence numbers (non-aufbau order).

SCF occupied set							
CI seq. no.	1	2	3, 4	5, 6	7, 8		
Symmetry	3 a_1	2 b_2	3 e_1	3 e_2	3 e_3		
SCF seq. no.	64	57	60, 61	58, 59	62, 63		
SCF virtual set							
CI seq. no.	9	10	11	12	13	14	15, 16
Symmetry	4 a_1	5 a_1	1 a_2	2 b_1	3 b_2	4 b_2	4 e_1
SCF seq. no.	73	82	72	81	65	74	68, 69
CI seq. no.	17, 18	19, 20	21, 22	23, 24	25, 26		
Symmetry	5 e_1	4 e_2	5 e_2	4 e_3	5 e_3		
SCF seq. no.	79, 80	70, 71	75, 76	66, 67	77, 78		

Table 3. Correlation of IP's with calculated data (eV).

State	IP (obs)	IP (calc) by CI	Koopmans' Theorem	
			sp basis	*spd*
$^2A_1$	9.23	10.01	10.51	10.23
$^2E_1$	10.12	11.07	11.47	11.03
$^2E_2$	9.83	10.99	11.50	10.81
$^2E_3$	9.47	10.22	10.74	10.36
$^2B_2$	11.35	12.71	13.56	13.02

Results and Discussion

The leading configuration for the ground state (X^1A_1) and each of the doublet states (Table 1) is the reference configuration. The eigenvector is above 0.92 in each case, leading to 86% of the density from this configuration; the states then can be well represented as one-particle states, and thereby related to those arising from use of Koopmans' Theorem. The order of states $^2A_1 < {}^2E_3 < {}^2E_2 < {}^2E_1 < {}^2B_2$ differs from that of the KT order for the *sp*-basis set SCF calculation on which the CI was based – i.e. a change of order has occurred, and the CI order now mimics the Koopmans' order of our previous *spd*-basis SCF calculation [9]. The relative separations of the first 4 IP's in the CI are now closer to those observed experimentally [1], than for the corresponding Koopmans' set at the *spd*-SCF level: CI separations ($\mathrm{IP}_{n+1} - \mathrm{IP}_n$): 0.22, 0.76, 0.08, 1.63 eV; expt.: 0.24, 0.36, 0.29, 1.23, eV; *spd*-SCF: 0.13, 0.45, 0.22, 1.99 eV. The absolute values of the CI calculated IP's are relatively close to the *spd*-basis SCF Koopmans' values, and both are about 1 eV too large when compared with experiment. Only about 0.3 ~ 0.5 eV of this difference can be directly ascribed to the *sp*/*spd* orbital energy differences, and thus the remaining deficit must arise from *either* slightly larger utilisation of the 3 *d* orbitals during the relaxation accompanying ionisation, *or* the *sp*-basis is still not flexible enough. Comparison of these results with our earlier work on S_4N_2 (3 d_s incorporated, and good numerical agreement with experimental IP's) [12] and S_4N_4 (3 d_s not incorporated, and similar errors to the present work) [14], suggests that the assistance of 3 d_s in relaxation is the dominant reason.

Analysis of the wave-functions from the CI of the doublet states shows a number of consistent effects. By far the most commonly occurring replacement orbitals from the virtual set are 3 b_2 (seq. no. 13; SCF65) – the LUMO, and the next (degenerate) pair 4 e_3 (seq. no. 23, 24; SCF 66, 67). The next orbitals above, 4 e_2, 4 e_1 are also prominent, but relatively little contribution occurs from the higher members. Thus it may be profitable to carry out a relatively large CI, using the *spd*-SCF basis, but restricting the virtual orbital set to perhaps only ten (65–74).

Conclusions

The present CI calculations show that a group of four doublet states are close to one another at the low energy end, and that these are well separated from the next state. It seems reasonable therefore to assign the IP's [1] as follows: 9.23 (1^2A_1), 9.47 (1^1E_3), 9.83 (1^2E_2), 10.12 (1^2E_1) and 11.35 eV (1^2B_2). At present it is not practicable to go beyond this point with either a large *spd*-basis, or a multi-reference set to explore the IP range beyond this. There is every reason to suppose that shake-up states will also occur beyond about 12 ~ 13 eV [12], and these will further complicate the calculations.

The present order of states is the same as that which would be predicted on the basis of Koopmans' Theorem using the large *ab initio spd*-basis set values [9]; this order differs from all previous calculations such as EH[7] or Xα [2] and CNDO-2 [5]. A single inter-change of 3 a_1 and 3 e_3 will convert the CNDO order to the present CI one, but these latter results must be treated with caution, since there are too many e_3 and too few b_1 orbitals given for the occupied set in Table 2 of [5].

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