The Electronic Spectrum and Structure of Tetrasulfur Dinitride

Michael H. Palmer
Department of Chemistry, University of Edinburgh, Scotland

Z. Naturforsch. **38 a,** 74–77 (1983); received August 9, 1982

Ab initio configuration interaction calculations of the ground and singlet A′ and A″ excited states have been performed, with all possible single and double excitations from the 10 highest occupied orbitals to the lowest 17 virtual orbitals being included, the previous C_S symmetry molecular structure being used. Some of the states can be identified with excitation from individual occupied (SCF) orbitals to members of the virtual set, but some are not well represented by single configuration concepts. The results suggest that the three broad UV-spectral maxima observed in solution are not single excitations, but groups of excited states, with a total of 8 states. The closeness of some of these states makes positive assignment difficult. The most probable assignment is 455 nm (1A″), 377 nm (2A″ + 1A′ + 2A′), ~ 277 nm (3A″ + 3A′), 232 nm (4A′ + 4A″).

Introduction

Recently the knowledge of S_4N_2 (I) has been markedly extended with studies of its crystal structure [1], equilibrium (computed) geometry [2] and electronic structure by Hartree Fock [3] and other methods [4], as well as an assignment of the photoelectron spectrum by configuration interaction calculations [3]. The electronic spectrum of S_4N_2 has been known for some time [5], and indeed was known before the compound was finally confirmed as a single substance of cyclic structure (I); recent improved preparative methods have confirmed [4] the earlier electronic spectral data. Following our work on the ground and ionised states of S_4N_2 by configuration interaction studies using a large *ab initio* basis, we now report calculation of the first few A′ and A″ states, by the same methods.

Methods

The S_4N_2 molecule was studied at our previously determined equilibrium geometry [2], which lies very close to that obtained by X-ray diffraction [1]. The S/N basis sets for the initial SCF calculation were the previous ones, of better than double zeta character [3], and the configuration interaction (CI) studies used the ATMOL-SPLICE suite of programs. File size limits on the CDC 7600 computer forced limits on the number of root functions from which the CI could be achieved. The number of active electrons was chosen as 20, ie 10 doubly occupied molecular orbitals (DOMO's); these are the least heavily bound set 5a′ to 10a′, 4a″ to 7a″ in C_S symmetry. The virtual orbital set extended to 21a′ and 14a″, a total of 27 active orbitals. Mulliken analyses of these orbitals [3] showed these to have a range of S(3s/3s′/3p/3p′) and N(2s/2s′/2p/2p′) character, and thus provide a suitable set for the excitation processes.

To restrict the CI to limitations of the available CDC 7600 core size (50 000 octal words), configuration selection was employed [6], with varying thresholds (50, 30 und 15 μH) depending upon the number of configurations occurring. Excitation energies were obtained from differences between the ground and excited states at the same selection level [3].

Results

a) The Configuration Interaction Results

The Ground State SCF wavefunction used [2], and shown diagrammatically in Fig. 1, is essentially similar to that of Chivers *et al.* [4] who used an Xα (Hartree-Fock-Slater) calculation. The most probable excitations (on an orbital basis in the first instance) for comparison with the visible and ultraviolet spectrum ($\lambda_{\max}$ 500, 392, 270, 220 nm) [4, 5] would be between the three highest occupied orbitals (6a″, 10a′ and 7a″) and the three lowest virtual orbitals (11a′, 12a′ and 8a″).

Reprint requests to Herrn Dr. M. H. Palmer, Department of Chemistry, University of Edingburgh, West Mains Road, Edinburg EH9 3JJ, Schottland.

0340-4811 / 83 / 0100-0074 $ 01.3 0/0. – Please order a reprint rather than making your own copy.

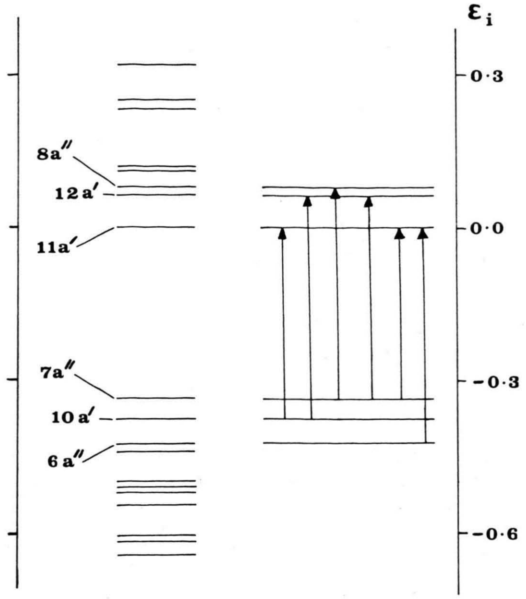


Fig. 1. Ground state energy level diagram and single root function excitation processes.

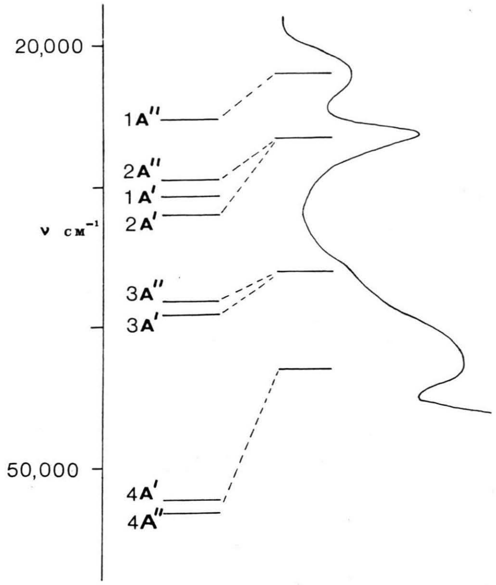


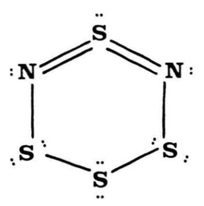
Fig. 2. Final multi-root configuration interaction energy levels and schematic electronic spectrum.

In an initial stage of the CI procedure we thus used a set of single root inputs corresponding to these states, with all single and double excitations, and leading to the results in Tables 1 and 2; the excitation energy order was thus found to be 1A″ (7a″→11a′) < 2A″ (7a″→12a′) < 1A′ (7a″→8a″) ~ 2A′ (10a′→11a′) etc. Each of these states had a leading term as indicated, whose eigenvector (~ 0.9 in each case) corresponded to the input root function. The closeness of the energy levels however required the use of multi-root input to the CI process, ie all single and double excitations from a *set* of reference configurations of same symmetry. The number of configurations rose from around 17 000 (single reference), (Table 2) to 30 000 and 45 000 (double and triple reference). The maximum level using our present computer programme and core available led to the use of configuration selection down to 3000 − 5500 level over the range (Table 3). The triple reference input yielded the same energy order for the states 1A″ − 3A″, 1A′ − 3A′, although all were lowered in energy relative to the single reference calculations of Table 2. This order is not the same as that obtained using static SCF orbital energy (ε_i) differences ($\Delta E = \varepsilon_i - \varepsilon_{j(\mathrm{virt})}$). The final order was thus 1A″ < 2A″ < 1A′ < 2A′ < 3A″ < 3A′; the states are grouped 1 : 3 : 2 in this order (Table 3, Figure 2). Unfortunately we are not currently able to perform detailed analyses of these final states, or able to calculate the transition moments for the processes; hence we are unable to determine which should be weak or strong excitations, and thus assignment of the experimental spectrum where few bands have been observed presents problems.

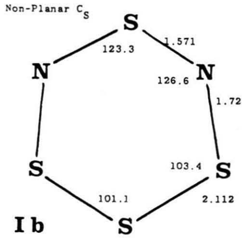
However, we have previously reported Mulliken analyses for the orbitals of interest [3], and here comment upon the nature of these orbitals; the highest occupied orbital (HOMO, orbital 10) is largely of $LP_S(S3+S5)$ character, orbital 98 $LP_S(S3+S5+S4)$, while orbital 8 is $LP_N(N2-N6)$; the virtual orbitals of interest, orbitals 11 − 13 are of local Π^*

Table 1. Orbital numbering system in CI wave-functions.

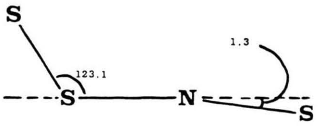
SCF Orbital Label	5a′	6a′	4a″	7a′	5a″	8a′	9a′	6a″
CI Orbital Label	1	2	3	4	5	6	7	8
SCF Orbital Label	10a′	7a″	11a′	12a′	8a″	9a″	13a′	
CI Orbital Label	9	10	11	12	13	14	15	



Ia



Ib



Ic

(N=S=N), LP$^*_S$ and LP$^*_S$ character respectively. On this basis we can estimate the strong groups of transitions as 1A″, 1A′, 3A″. This corresponds to one strong band in each group of states indicated above.

b) Assignment of the Electronic Spectrum

As discussed above, the use of 2 × 3 root functions led to 6 final excited states. The 4A′ and 4A″ were also converged, but since these had leading terms (namely 6a″→12a′ and 7a″→ 9a″) not in the original input set of reference configurations their absolute energy is likely to be too high, and their excitation energy too high. An estimate must put them in the range 45 000 – 52 000 cm^{-1}. The present low resolution solution spectral data yields little information, and we note the need for a gas-phase spectrum. Thus the experimental spectrum with well defined bands at 22 000, 26 500 and 43 100 cm^{-1} and a shoulder near 36 000 cm^{-1} could contain up to 8 singlet excitation processes. Before arriving at an assignment of the spectrum, we need to estimate the accuracy of the CI study reported here. In any CI study the final dominant characteristic must be the SCF orbital basis set [7]; the orbital basis used here is large and almost certainly very adequate for CI studies. The number of active electrons was only 20 out of a valence shell total of 34; since the excitations are in the low energy portion of the electronic spectrum and can be classified roughly as $n \rightarrow \Pi^*$ (eg 10 → 11) or $n \rightarrow \sigma^*$ (eg 9 → 12), the inner valence shell omitted from the CI is probably (relatively) unimportant, as is the upper portion of the virtual set, also not included in the CI. Thus overall, it seems likely that the estimated energies and order of the first 6 states

Table 2. Single reference configuration CI wave-functions and energies (a. u.).

State		Selection level (μH)	Final Config. no.	Energy (+ 1698 a. u.)	Wave-function Eigenvector	Description of occupancy-(leading configurations)	
						Double occupancy	Single
(a) 14 Active Electrons XA′		none	3669	− 0.91036	0.945	$4^2 - 10^2$	
(Ground State)					− 0.081	$5^2 - 9^2$	(4 15)
(b) 20 Active Electrons		15	2068	− 0.94614	0.943	$1^2 - 10^2$	
(i) XA′ (Ground State)					− 0.083	$1^2 - 3^2, 5^2 - 9^2$	(4 15)
		30	1314	− 0.94729	0.944	$1^2 - 10^2$	
					− 0.085	$1^2 - 3^2, 5^2 - 9^2$	
		50	819	− 0.94775	0.946	$1^2 - 10^2$	
					− 0.086	$1^2 - 3^2, 5^2 - 9^2$	
(ii) Singlet Excited	1A′	30	3886	− 0.78718	0.915	$1^2 - 9^2$	(10 13)
					− 0.088	$1^2 - 8^2, 10^2$	(9 11)
	2A′	30	3656	− 0.78505	0.892	$1^2 - 8^2, 10^2$	(9 11)
					− 0.136	$1^2 - 6^2, 8^2 - 10^2$	(7 11)
	3A′	30	3886	− 0.73239	0.865	$1^2 - 8^2, 10^2$	(9 12)
					+ 0.274	$1^2 - 8^2, 10^2$	(9 11)
	1A″	30	3829	− 0.81310	0.884	$1^2 - 9^2$	(10 11)
					− 0.164	$1^2 - 7^2, 9^2, 10^2$	(8 11)
	2a″	30	3911	− 0.79474	0.895	$1^2 - 9^2$	(10 12)
					− 0.159	$1^2 - 9^2$	(10 15)
	3A″	30	3540	− 0.77758	0.673	$1^2 - 7^2, 9^2, 10^2$	(8 11)
					− 0.548	$1^2 - 9^2$	(10 11)
					− 0.329	$1^2 - 4^2, 6^2 - 10^2$	(5 11)

Table 3. Multi-reference configuration CI wave-functions, energies and excitation energies.

Root	Energy (+ 1698.0 eV)	Leading Configurations		Single Occupancy	Excitation Energy	
		Eigenvector	Double Occupancy		eV	cm^{-1}
A′ STATES; Multi-reference Level = 3; Configurations: – Initial = 45 117, Final = 5056, Selection = 50 μH						
1	– 0.80799	– 0.722	$1^2 - 8^2, 10^2$,	(9 11)	3.803	30 678
		– 0.476	$1^2 - 9^2$,	(10 13)		
		+ 0.255	$1^2 - 8^2, 10^2$,	(9 12)		
2	– 0.80222	0.782	$1^2 - 9^2$,	(10 13)	3.960	31 943
		+ 0.415	$1^2 - 8^2, 10^2$,	(9 11)		
		+ 0.212	$1^2 - 8^2, 10^2$,	(9 12)		
3	– 0.76897	0.826	$1^2 - 8^2, 10^2$,	(9 12)	4.865	39 242
		– 0.301	$1^2 - 8^2, 10^2$,	(9 11)		
		– 0.174	$1^2 - 8^2, 10^2$,	(9 15)		
4	– 0.70919	0.890	$1^2 - 9^2$,	(10 14)	6.491	52 364
		– 0.149	$1^2 - 8^2$,	(9 11) (10 14)		
		– 0.133	$1^2 - 6^2, 8^2 - 10^2$,	(7 11)		
A″ STATES; Multi-reference Level = 3; Configurations: – Initial = 42 494, Final = 4668, Selection = 50 μH						
1	– 0.83270	0.828	$1^2 - 9^2$,	(10 11)	3.131	25 253
		– 0.284	$1^2 - 7^2, 9^2, 10^2$,	(8 11)		
		+ 0.190	$1^2 - 9^2$	(10 12)		
		+ 0.186	$1^2 - 4^2, 6^2 - 10^2$,	(5 11)		
2	– 0.81332	0.857	$1^2 - 9^2$,	(10 12)	3.658	29 507
		+ 0.214	$1^2 - 7^2, 9^2, 10^2$,	(8 11)		
		– 0.164	$1^2 - 9^2$,	(10 15)		
		– 0.118	$1^2 - 4^2, 6^2 - 10^2$,	(5 11)		
		– 0.103	$1^2 - 9^2$,	(10 11)		
3	– 0.77419	+ 0.752	$1^2 - 7^2, 9^2, 10^2$	(8 11)	4.723	38 096
		+ 0.340	$1^2 - 9^2$,	(10 11)		
		– 0.300	$1^2 - 4^2, 6^2 - 10^2$	(5 11)		
		– 0.180	$1^2 - 9^2$	(10 12)		
4	– 0.70516	0.664		(8 12)	6.601	53 249
		+ 0.444		(5 11)		
		– 0.264		(9 13)		
		+ 0.164		(8 11)		

is reasonably good, with no progressive errors. Thus we propose the assignment 1A″ (455 nm, 22 000 cm^{-1}), 2A″ + 1A′ + 2A′ (377 cm^{-1}, 26 500 cm^{-1}), 3A″ + 3A′ (~277 nm, 36 000 cm^{-1}), 4A′ + 4A″ (232 mn, 43 100 cm^{-1}).

Conclusions

Large scale CI calculations of the singlet excited states of S_4N_2 yield three groups of states, with the lowest being 1A″. Assignment of these to the poorly resolved solution spectrum is not unambiguous, and may have to be revised if higher resolution disclosed different numbers of excitation processes under the envelope.

Acknowledgements

Thanks are due to Dr. M. F. Guest (Daresbury Laboratory) for advice and assistance with the ATMOL-SPLICE system of programs, and to Dr. N. P. C. Westwood (U.B.C., Vancouver) for information prior to publication.

[1] T. Chivers, P. W. Codding, and R. T. Oakley, J. Chem. Soc. Chem. Comm. **1981**, 584.
[2] M. H. Palmer, J. R. Wheeler, R. H. Findlay, N. P. C. Westwood, and W. M. Lau, J. Molecular Struct. **86**, 193 (1981).
[3] M. H. Palmer, N. P. C. Westwood, and M. W. Lau, Z. Naturforsch., **38a**, 78 (1983).
[4] T. Chivers, P. W. Codding, W. G. Laidlaw, S. W. Liblong, R. T. Oakley, and M. Trsic, J. Amer. Chem. Soc., to be published. Private communication.
[5] J. Nelson and H. G. Heal, J. Chem. Soc. (A) **1971**, 136.
[6] M. F. Guest and W. R. Rodwell, The Bonded Function CI Program, Science Research Council, Atlas Computing Division, September 1977; RL-77-110/B.
[7] R. S. Mulliken and W. C. Ermler, Polyatomic Molecules – Results of ab initio Calculations, Academic Press, New York 1981, Chapter 1.