The He^I Photoelectron Spectrum of Sulphur Trioxide

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The He^I photoelectron spectrum of sulphur trioxide is presented and comparisons are drawn with the available photoelectron spectra of sulphur dioxide and boron trifluoride. The results indicate substantial stabilization of the sulphur lone pair in SO_2 and the possible involvement of central atom *d* orbitals in SO_3.

THE He^I photoelectron (p.e.) spectrum of sulphur trioxide is of interest because of the high symmetry of the molecule (D_{3h}), the consequent relationship between the valence structure and that of BF_3, and the possibility of treating the molecule as an acid–base adduct of atomic oxygen plus sulphur dioxide. These attributes of sulphur trioxide make it of special interest to our laboratory as we have been concentrating on the p.e. spectra of highly symmetric inorganic molecules,[1] including BF_3 [2] and the acid–base adduct pairs NF_3,ONF_3 and PF_3,OPF_3.[3] While the corrosive nature of the compound has limited our study to medium resolution, its p.e. spectrum does throw interesting light on the relationship of its electronic structure compared to that of SO_2 and BF_3.

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[1] P. J. Bassett and D. R. Lloyd, *J. Chem. Soc.* (*A*), 1971, 641.

[2] P. J. Bassett and D. R. Lloyd, *J. Chem. Soc.* (*A*), 1971, 1551.

[3] P. J. Bassett and D. R. Lloyd, *J.C.S. Dalton*, 1972, 248.

EXPERIMENTAL

The sulphur trioxide sample was obtained from Hardman and Holden Ltd., and was vacuum distilled prior to use. Breakseal techniques were used throughout to eliminate contact with vacuum grease. Early spectra showed the presence of SO_2 [4,5] but this was easily removed with continuous pumping on the sample. Infra-red studies [6] have shown that little of the sulphur trioxide trimer exists in the vapour. Since the pressure in our experiment is appreciably lower (3 Nm^{-2}) than in the i.r. studies, we expect no contamination from the formation of trimer.

He^{I} (584 Å, 21·22 eV) studies were carried out with a 127° cylindrical deflection analyser (Perkin-Elmer PS15) with a resolution (full width at half maximum) of 0·05 eV on the argon doublet. A direct inlet system was employed and calibration carried out with standard gases as described earlier.[7] The sample temperature was maintained at 0 °C and the final inlet pressure controlled with a Teflon valve.

Sulphur trioxide readily attacked the electron multiplier (EMI 9643/2B), resulting in a loss of sensitivity. Shifts in the analyser potential were also evident, and may be partly responsible for the large standard deviations in the measured ionization potentials.

RESULTS

The p.e. spectrum is presented in Figure 1 and the ionization data are collected in Table 1. Four bands are definitely observed and perhaps a fifth to the high ionization potential (i.p.) side of the fourth band. The first band is sharp and intense with a measured adiabatic i.p. of 12·73(5) eV. The second band is extremely broad while the third is more intense and exhibits vibrational fine structure with an interval of 920 (100) cm^{-1}. The fourth band shows vibrational fine structure with an interval of 800 (100) cm^{-1} although only two components are definitely observed, at 17·88 and 17·98 eV.

TABLE 1

Ionization data for SO_3

Band number	Ionization potential *	Band number	Ionization potential *
1	12·73(5) a	3	14·92 (4) a
	12·82(5) v		15·08(4) v
2	13·82(5) a	4	17·88(2) a,v
	14·4(1) v		18·3(1) v?

* a, Adiabatic, onset; v, vertical, maximum.

DISCUSSION

Assignment, and Relationship to the BF_3 *Spectrum.*—The general appearance of the p.e. spectrum (Figure 1) is similar to that of BF_3, and of BCl_3, particularly in the first three bands.[2,8] The total intensity of the first band is less than that of the second, and the third band has a very high intensity. By comparison with BF_3 the second and third bands are considerably broader while the first band is somewhat sharper. Whereas in BF_3 the fourth band is weak and broad (with well resolved fine structure), in SO_3 the fourth band is intense and less broad. When allowance is made for the fall-off of analyser sensitivity with decreasing electron energy [9] the fourth band has a similar intensity to that of the third, similar to the fifth band in BF_3. The weak shoulder at 18·3 eV may then correspond to the fourth band of BF_3.

The fine structure on the third and fourth bands is assigned to $\nu_1'(a_1)$ both reduced from $\nu_1'' = 1068$ cm^{-1}.[10] The reduction in frequency may indicate the S–O bonding nature of the orbitals from which ionization has taken place, analogous to the situation found for BF_3.[2,8]

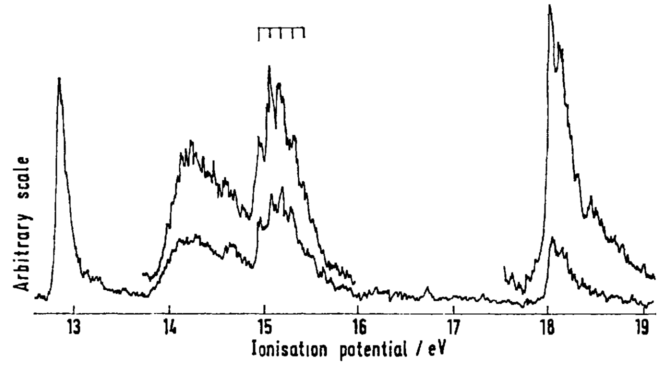

FIGURE 1 The He^{I} photoelectron spectrum of sulphur trioxide

From the similar intensity pattern in the first three bands of BF_3 and SO_3 we deduce the same assignment,* $1a_2' > 1e'' > 3e'$. This assignment is based upon a comparison of the p.e. spectrum of BF_3 with that of the other boron trihalides [2,8] and *ab initio* LCAO–MO–SCF calculations on SO_3,[11] BF_3,[12] and on the various states of BF_3^+.[13] The assignment of the topmost orbital as $1a_2'$ is further supported by the electron spin resonance of NO_3 which shows that the ground state of this radical is $^2A_2'$.[14] From the high intensity and relatively small width, the fourth band is unlikely to be due to ionization from the π orbital $1a_2''$ as in BF_3, so we assign this band as due to the degenerate orbital set $2e'$. In BF_3 the corresponding (fifth) band is very broad from the B 2*p*–F 2*p* σ-bonding character, but the narrower band in SO_3 may be rationalized as due to mixing of O 2*p* and O 2*s* in the sets of $1e'$ and $2e'$. Such mixing causes the orbitals $2\sigma_u$, $2\sigma_g$ in CO_2 to be almost non-bonding,[15] and similar arguments have been advanced for $2a_1'$ of

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* Orbital numberings for all molecules discussed do not include core electrons.

[4] D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, 'Molecular Photoelectron Spectroscopy,' Wiley–Interscience, London, 1970, p. 84.

[5] J. H. D. Eland and C. J. Danby, *Internat. J. Mass Spectroscopy Ion Phys.*, 1968, **1**, 111.

[6] R. W. Lovejoy, J. H. Colwell, D. F. Eggers, jun., and G. D. Halsey, jun., *J. Chem. Phys.*, 1962, **36**, 612.

[7] D. R. Lloyd, *J. Phys.* (*E*), 1970, **3**, 629.

[8] A. W. Potts, H. J. Lempka, D. G. Streets, and W. C. Price, *Phil. Trans. Roy. Soc.* (*A*), 1970, **268**, 59.

[9] O. Klemperer and M. E. Barnett, 'Electron Optics,' 3rd edn., Cambridge University Press, Cambridge.

[10] H. Gerding, W. J. Nijveld, and G. T. Muller, *Nature*, 1936, **137**, 1033, *Z. phys. Chem.*, 1937, **B35**, 193.

[11] A. Breeze, D. W. J. Cruickshank, and G. A. D. Collins, personal communication, 1971.

[12] D. R. Armstrong and P. G. Perkins, *Theor. Chim. Acta*, 1969, **15**, 43.

[13] T. E. H. Walker and J. A. Horsley, *Mol. Phys.*, 1971, **21**, 939.

[14] T. W. Martin, L. L. Swift, and J. H. Venable, jun., *J. Chem. Phys.*, 1970, **52**, 2138.

[15] Ref. 4, p. 69.

BCl_3.[2] The weak shoulder at 18·3 eV may then be assigned as $1a_2''$, and the orbital $2a_1'$ is expected to be beyond 21 eV from its S 3*s* character; the corresponding orbital in SO_2 does not ionize before 20 eV [16,17] and in NSF the corresponding i.p. is 21·1 eV.[18]

All the bands are observed at lower i.p. in SO_3 than in BF_3. This is a reflection of the fact that the ionization is taking place from orbitals which are composed predominantly of oxygen 2*p* rather than fluorine 2*p* orbitals.

Relationship to the Spectrum of SO_2.—The success of the earlier studies [3] upon the acid–base pairs NF_3,ONF_3 and PF_3,OPF_3 prompted an attempt at treating SO_3 as being derived from atomic oxygen and SO_2. The situation is slightly different from the earlier cases as the symmetry increases on going from $SO_2(C_{2v})$ to $SO_3(D_{3h})$ rather than retaining the same point group symmetry. A correlation table $D_{3h} \longrightarrow C_{2v}$ is given in Table 2.

TABLE 2

Correlation table $D_{3h} \longrightarrow C_{2v}$ [a]

D_{3h}	C_{2v}	D_{3h}	C_{2v}
A_1'	A_1	A_1''	A_2
A_2'	B_2	A_2''	B_1
E'	$A_1 + B_2$	E''	$A_2 + B_1$

[a] In both cases the molecule is taken to lie in the *yz* plane. In D_{3h} orbitals of A_1'', A_2'', and E'' symmetry change sign under the σ_h operation. In C_{2v} orbitals of B_1 and A_2 symmetry change sign under the $\sigma_v(yz)$ operation.

The p.e. spectrum of SO_2 has been obtained by two groups,[4,5] and one of these reports illustrates the nodal properties of the valence molecular orbitals.[4] For an AO_2 system, the general form of the molecular orbitals is largely determined by the C_{2v} symmetry constraint.[19] Brundle *et al.*[17] have shown that the p.e. spectra of several triatomic species can be understood on such a qualitative basis. Extensive calculations on SO_2 have confirmed this general picture of the molecular orbitals.[20] Addition of the 2*p* electrons of a third oxygen atom results in extra b_1 and b_2 molecular orbitals in C_{2v} symmetry. The general effect of these oxygen orbitals on the SO_2 molecular orbitals is illustrated in Figure 2.

Figure 3 shows a correlation diagram between the i.p. of SO_2 and SO_3.* The $4a_1$ orbital (sulphur ' lone pair ')

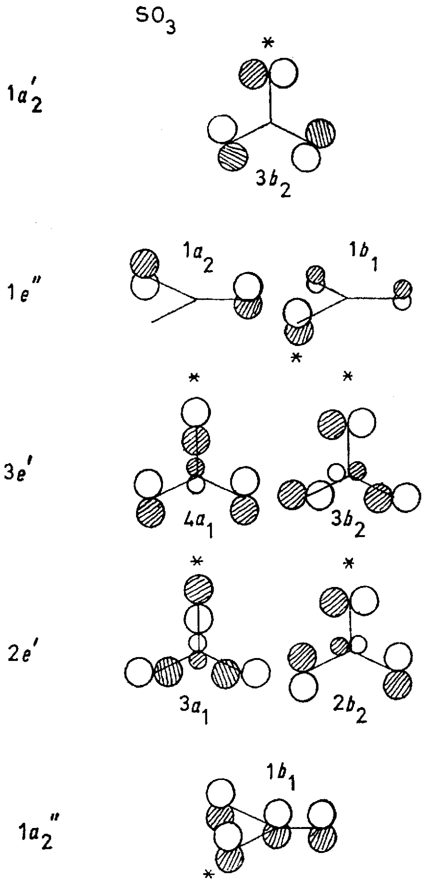

FIGURE 2 Orbital representations for sulphur trioxide. Labels are also given for the sulphur dioxide fragment and the ' new ' oxygen atom is labelled (*)

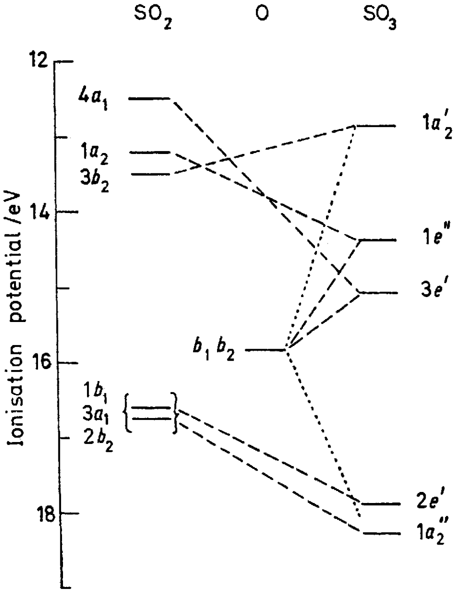

FIGURE 3 Orbital correlation diagram based upon the photoelectron spectrum, utilizing Koopmans' theorem

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* Figure 3 shows strictly a group theoretical correlation derived from Table 2. In this system, the a_2' orbital of SO_3 correlates both with the b_2 orbital of SO_2 and with a ' new ' b_2 orbital. The position of the oxygen atomic i.p. is rather arbitrary and in Figure 3 is given as the valence state ionization potential.[21] It could be argued that one should consider only the i.p. of ^1D and ^1S oxygen atoms if SO_3 is to be considered as an adduct of singlet oxygen and singlet SO_2. This would have the effect of lowering the averaged i.p. of atomic oxygen to about 14·5 eV,[22] a factor which does not affect the assignment discussion.

[16] Ref. 4, pp. 126—129.

[17] C. R. Brundle, D. Neumann, W. C. Price, D. Evans, A. W. Potts, and D. G. Streets, *J. Chem. Phys.*, 1970, **53**, 705, 1970.

[18] R. L. DeKock, D. R. Lloyd, A. Breeze, G. A. D. Collins, D. W. J. Cruickshank, and H. J. Lempka, *Chem. Phys. Letters*, 1972, **14**, 525.

[19] R. S. Mulliken, *Rev. Mod. Phys.*, 1942, **14**, 204.

[20] I. H. Hillier and V. R. Saunders, *Mol. Phys.*, 1971, **22**, 193; M. F. Guest, I. H. Hillier, and V. R. Saunders, *J.C.S. Faraday II*, 1972, **68**, 114.

[21] H. Basch, A. Viste, and H. B. Gray, *Theor. Chim. Acta*, 1965, **3**, 458.

[22] G. Herzberg, ' Atomic Spectra and Atomic Structure,' Dover, New York, 1944, p. 163.

is stabilized dramatically (2·7 eV) upon co-ordination of an additional oxygen atom. This effect is similar to that observed previously for NF_3,ONF_3 and PF_3,OPF_3.[3] The diagram in Figure 2 illustrates why this is so as there is a positive bonding interaction between this lone pair orbital in SO_2 and the empty $2p$ orbital on the approaching oxygen atom.

The SO_2 $1a_2$ molecular orbital is stabilized much less (1·4 eV) as it is a π type orbital and hence subject to weaker interactions than the $4a_1$ molecular orbital. A probable mechanism for its stabilization involves S–O d_π–p_π bonding (advocated for SO_2).[20]

The $3b_2$ molecular orbital of SO_2 is seen to be destabilized upon addition of an oxygen atom (Figure 3). The nodal properties of the orbitals given in Figure 2 illustrate that this is entirely plausible since this orbital is O–O antibonding in SO_3. The destabilization is in fact quite small (0·42 eV) indicating that these O–O interactions are comparatively weak.

The next orbitals in the correlation diagram of Figure 3 are the b_1 and b_2 orbitals of the incoming oxygen atom. Their major correlation is with the $1e''$ and $3e'$ orbitals of SO_3 as these b_1 and b_2 orbitals will be destabilized from those in neutral oxygen due to the negative charge on oxygen in SO_3. Alternatively, if one compares the i.p. of the $1e''$ and $3e'$ orbitals to that of oxygen ^1D or ^1S (*ca.* 14·5 eV), the slight stabilization of the $3e'$ orbital can be construed as evidence for S–O bonding in this orbital.

The p.e. spectrum of SO_2 is complicated between 16 and 17·5 eV; definite evidence for two ionizations was obtained, assigned to orbitals $1b_1$ and $3a_1$,[4,5] and one report suggested a third ionization.[5] Calculations upon SO_2 indicate that $2b_2$ lies very close to $1b_1$ and $3a_1$,[20] and in the isoelectronic NSF three ionizations are predicted and observed in this region,[18] so $2b_2$ has been included close to $1b_1$ and $3a_1$ on Figure 3. These three orbitals correlate with $1a_2''$ and $2e'$ of SO_3; there is a stabilization of these orbitals by *ca.* 1·5 eV between SO_2 and SO_3. The stabilization may be due to bonding interactions, but may also be electrostatic in origin since the donation of charge to the new O atom stabilises the orbitals of the other two O atoms.

Double Bonding in SO_3.—It is usually assumed, to account for the short S–O distance, that the S–O bonds have considerable p_π–p_π and p_π–d_π character;[23] support for this may be drawn from the above assignment. In the absence of π bonding, orbitals $1a_2'$ and $1e''$ are essentially O $2p$ non-bonding, slightly destabilised by O–O interaction. Since the first band is sharp the O–O antibonding is probably small, and from the SO_2–SO_3 correlation, the associated destabilization may be *ca.* 0·5 eV. Referred to this energy zero $1a_2''$ is stabilized by nearly 5 eV, indicating very strong p_π–p_π bonding (there can be no d contribution to $1a_2''$). The separations of $1e''$ and $3e'$ from $1a_2'$ are much larger than in BF_3 and the bands are broader. In the case of $1e''$ any bonding character can only arise from d_π–p_π interaction, and the same interaction may also stabilize $3e'$, though here p_π and d_π interactions are not distinguished by symmetry. Thus there is one orbital with strong S $3p_\pi$–O_π $2p$ bonding and four where there may well be S $3d_\pi$–O $2p_\pi$ interactions.

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[2/2200 *Received, 20th September*, 1972]

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[23] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Wiley, London, 1972, p. 445.