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Hartree-Fock Calculations and Photoelectron Spectra of SSO and NSF

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Results from *ab initio* Hartree-Fock calculations on the ground states of SSO and NSF are reported. The calculations employ large basis sets of Gaussian functions of essentially double zeta quality. The photoelectron spectra of the bent triatomic molecules with 18 valence electrons, i.e. SSO, NSF, O_3, SO_2, NSCl are compared. Further experimental details of the photoelectron spectrum of SSO are presented and an assignment of the observed ionic states of $SSO^{\oplus}$ is attempted. The calculated dissociation energies, dipole moments and the population analyses are given. The correlation effect is qualitatively discussed in connection with the applicability of Koopmans' theorem for the bent tri-atomic molecules.

Key words: SSO, photoelectron spectra of ~ – NSF, photoelectron spectra of ~

1. Introduction

Disulphur oxide (SSO) and thiazyl fluoride (NSF) represent bent 18 valence electron triatomic molecular systems which correlate with the valence isoelectronic molecules ozone (O_3), sulphur dioxide (SO_2), thiazyl chloride (NSCl) or nitrosyl fluoride (FNO) within the well known Walsh rules [1]. This empirical scheme based on a qualitative molecular orbital theory has been successfully used for the prediction of equilibrium molecular geometries. The close symbiosis between qualitative molecular orbital theory and LCAO-MO-SCF approach allows one to identify the calculated molecular orbitals as the quantitative counterparts to the empirical orbitals discussed by Walsh. Moreover, the experimental ionisation potentials from photoelectron (PE) spectra are connected via Koopmans' theorem [2] with the calculated orbital energies. It is therefore of interest to compare the Hartree-Fock molecular orbitals, Walsh empirical orbitals and the PE spectra of the aforementioned molecules in order to see what parallels can be drawn between their electronic structures.

The PE spectra of NSF, SO_2, O_3, and NSCl have been investigated by several authors [2–10]. The assignments of some observed states of the corresponding molecular ions, however, are still open to considerable doubt [5, 8, 10]. Recently,

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the interpretation of the SO_2 PE spectrum has been substantially improved [8] by new experimental results, by comparison with ab initio SCF calculations on SO_2 [11–14] and by PE spectroscopic correlation with NSF. The PE spectra of SO_2 and NSF are very similar to the PE spectrum of the bent and valence isoelectronic SSO [15, 16], so that comparison of the ionisation patterns of these molecules might furnish further insights into the assignment of the ionic states.

Theoretical studies of the molecular properties of SO_2 have been given by several authors. Hillier and Saunders [11, 12] have performed *ab initio* SCF calculations on SO_2 using Slater-type orbitals (STO's) approximated as a linear combination of Gaussians. Roos and Siegbahn [14] as well as Rothenberg and Schaefer [13] have reported *ab initio* Hartree-Fock calculations on SO_2 with medium and large basis sets of Gaussian-type orbitals (GTO's). The only *ab initio* SCF study on NSF has been published by Dekock *et al.* [5] and this calculation is similar in philosophy to those carried out by Hillier and Saunders on SO_2. So far no *ab initio* calculations on SSO have been reported in the literature.

2. Method

The calculations of the SSO and NSF ground states were carried out at experimental geometries with $d_{S-S} = 1.884$ Å, $d_{S-O} = 1.465$ Å, $\sphericalangle \mathrm{SSO} = 118°$ [17], $d_{N-S} = 1.446$ Å, $d_{S-F} = 1.646$ Å and $\sphericalangle \mathrm{NSF} = 117°$ [18], respectively.

In the previous calculations with GTO's on SO_2 [13, 14] two different basis sets for the sulphur atom were employed, the 10*s*, 6*p* set proposed by Roos and Siegbahn [19] and the 12*s*, 9*p* set of Veillard [20]. The published 10*s*, 6*p* set contains a misprint for one of the inner shell exponents. The exponent of the fifth *s* function should read 79.0448 instead of 97.0448 [21]. Using the published uncontracted set one calculates for the sulphur ^3P state an energy of -397.233 a.u. deviating from the published value -397.400 [19].

Our calculations on disulphur oxide employed two different basis sets. The basis set A consisted for sulphur of the 12*s*, 9*p* set of Veillard [20] contracted to $s(6,2,1,1,1,1)$ and $p(5,1,1,1,1)$. This contracted basis yields an energy of -397.4815 a.u. for the sulphur atom, compared to the Hartree-Fock value -397.50487 a.u. [23]. In addition, we used a set of *d* functions with exponent 0.6 [13] on each sulphur atom. For oxygen Huzinaga's 9*s*, 5*p* set [24] has been contracted to $s(5,1,1,1,1)$ and $p(4,1)$. This contraction yields an energy of -74.8005 a.u., compared to the Hartree-Fock value -74.80939 a.u. [23]. A set of d functions with exponent 0.8 [22] has also been added for the oxygen. The basis set *B* was that of Roos and Siegbahn [19] and consisted for sulphur of a 10*s*, 6*p* set contracted to $s(4,2,1,1,1,1)$ and $p(2,2,1,1)$. For oxygen the 7*s*, 3*p* set [19] was contracted to $s(4,1,1,1)$ and $p(2,1)$. On all atoms *d*-functions have been considered [22]. The calculation with this basis set yields for SSO an energy of -867.247 a.u. due to an error in the inner shell exponent, as mentioned above. For thiazyl fluoride a basis set of a quality similar to that of the basis set *A* for disulphur oxide has been used. Exactly the same basis as for SSO has been employed for the sulphur atom. For nitrogen and fluorine 9*s*, 5*p* sets of Huzinaga [24] have been contracted to $s(5,1,1,1,1)$ and $p(4,1)$. These contractions yield an energy of -54.3943 a.u. for nitrogen, compared to the Hartree-Fock value -54.40093 a.u. [23], and -99.3945 a.u. for fluorine (Hartree-Fock value: -99.40933 a.u. [23]), respectively. On all atoms sets of *d*-functions with exponents given by Roos and Siegbahn [22] have been added. The sum of our calculated SCF energies for one S plus two O atoms exceeds the Hartree-Fock sum of these atoms by 0.0556 a.u. Similarly, the sum of energies obtained for N, S, and F atoms lies 0.0448 a.u. above the corresponding Hartree-Fock sum. The basis are therefore seen to be of essentially double-zeta near Hartree-Fock quality.

3. Energy Quantities, Dipole Moments, and Population Analyses

The calculated total energies, virial quotients, dissociation energies and dipole moments for SSO and NSF are summarized in Table 1.

The experimental dissociation energy of SSO has been estimated by adding the SO dissociation energy 5.357 eV [25] to the SSO predissociation limit 3.9 eV (without zero point energy correction) [26] under the assumption that SO + S are the dissociation products. The calculated dipole moments and dissociation energies are of a quality similar to the results of Rothenberg and Schaefer for SO_2 [13]. Our calculations suggest that the dipole moment of NSF should lie between the experimentally known dipole moments of SO_2 (1.63 D [29]) and SSO (1.47 D [17]).

From the total electron density contours [37] one can deduce that the fluorine atom in NSF retains a substantial portion of its atomic character similarly to FNO [30]. From the nine valence molecular orbitals only two of them strongly contribute to the bonding interaction between sulphur and fluorine.

In Table 2 the total atomic population and the total *d*-population are summarized. The relative importance of *d* functions has been stressed in the

Table 1. Energy quantities and dipole moments of SSO and NSF (basis set *A*)

	SSO ($\tilde{X}\,^1A'$)	NSF ($\tilde{X}\,^1A'$)
Total energy	−869.8447 a.u.	−551.3368 a.u.
Virial quotient	−1.00040	−1.00028
Dissociation energy	2.21 eV	1.81 eV
exp.	9.4 eV [26]	
Dipole moment	2.06 D	2.18 D
exp.	1.47 D [17]	

Table 2. Population analyses for SSO, NSF and OSO (basis set *A*)

	SSO ($\tilde{X}\,^1A'$)		NSF ($\tilde{X}\,^1A'$)		OSO ($\tilde{X}\,^1A'$) [13]	
Total atomic population						
	S	16.193	N	7.357	O	8.565
	S	15.226	S	15.210	S	14.869
	O	8.580	F	9.433		
Total *d*-population						
	S	0.071	N	0.031	O	0.063
	S	0.311	S	0.309	S	0.425
	O	0.042	F	0.003		

calculations on SO_2 [11–14]. The sulphur *d* function population, 0.425 electrons in SO_2 [13], is much larger than *d* function populations on both oxygen atoms. Similarly, as deduced from Table 3 the *d* functions are required to describe the distorted central S atoms in NSF and SSO, whereas the spherical symmetry of the fluorine atom seems to be only slightly perturbed.

4. PE Spectra of SSO, NSF, and SO_2, and their Assignment

The He(I) spectrum of SSO published simultaneously by Frost *et al.* [15] and by us [16] consists of five well defined band systems. The overall pattern of the observed states of the $SSO^{\oplus}$ radical cation is in remarkably good agreement with the empirical orbital diagram given by Walsh [1] for bent triatomic molecules with 18 valence electrons and shows close similarities with the PE spectra of other valence isoelectronic molecules (Fig. 2). The interpretation of the SSO PE spectrum is aided by comparison with those of NSF [3–5] and SO_2 [6–8]; the observed ionisation potentials and the vibrational spacings are compared in Table 3.

Only the first two band systems of $SSO^{\oplus}$ exhibit vibrational fine structures (Fig. 1). As in NSF [3, 31], the ν_1 and ν_2 vibrations in the SSO molecule are presumably localized, more or less corresponding to S–O and S–S stretching modes [32]. The ν_3 bending mode is tentatively assigned at about $388 \pm 10\,\mathrm{cm}^{-1}$ [32]. Our assignment of all observed vibrational spacings differs from that given by Frost *et al.* [15] and is thoroughly discussed in the following paragraphs.

Orbital energies, calculated with basis sets *A* or *B*, and vertical ionisation potentials of SSO are presented in Table 4. Because only the valence orbital energies can be compared with the ionisation potentials obtained from the He(I)

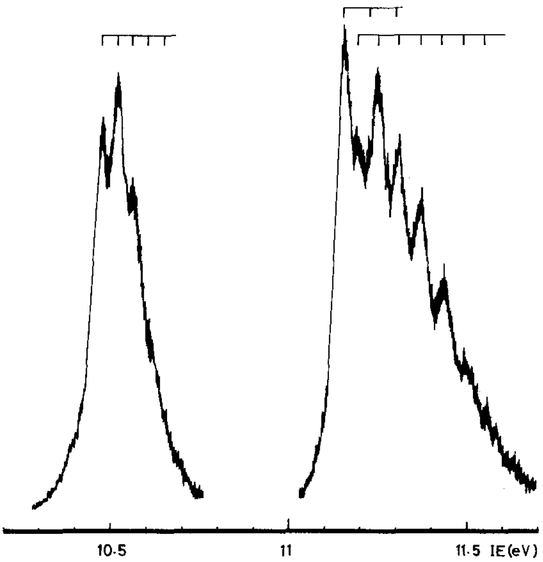

Fig. 1. Expanded records of the first and second band systems in the He(I) PE spectrum of SSO

Table 3. Vertical ionisation potentials IP(eV) and vibrational spacings $\tilde{\nu}^{\oplus}$ (cm^{-1}) for SSO, NSF and OSO

	SSO (C_s) [16]		NSF (C_s) [3–5]			OSO (C_{2v}) [6–8]		
State[a]	IP	$\tilde{\nu}^{\oplus}$	State[a]	IP	$\tilde{\nu}^{\oplus}$	State[a]	IP	$\tilde{\nu}^{\oplus}$
$\tilde{X}\,^2A'$	10.52	370±40	$\tilde{X}\,^2A'$	11.89	300±50	$\tilde{X}\,^2A_1$	12.31	403±20
$\tilde{A}\,^2A'$	11.22	570±40	$\tilde{A}\,^2A'$	13.54	820±40; 460±50	$\tilde{A}\,^2A_2$	13.01	1090±30; 403±20
$\tilde{B}\,^2A''$	11.34	480±40	$\tilde{B}\,^2A''$	13.90	1060±40; 695±40; 365±40	$\tilde{B}\,^2B_2$	13.30	470±20
$\tilde{C}\,^2A'$	14.62		$\tilde{C}\,^2A'$	15.64	895±30	$\tilde{C}\,^2B_2$	16.0	782±20 363±20
$\tilde{D}\,^2A''$	14.82		$\tilde{D}\,^2A''$	16.56		$\tilde{D}\,^2A_1$	16.0	936±30
$\tilde{E}\,^2A'$	15.80		$\tilde{E}\,^2A'$	17.24		$\tilde{E}\,^2B_1$	17.5	
$\tilde{F}\,^2A'$	18.5		$\tilde{F}\,^2A'$	21.1		$\tilde{F}\,^2A_1$	20.65	
Vibrational modes of the neutral molecules	$\tilde{\nu}_1 = 1160$ [32] $\tilde{\nu}_2 = 679$ $\tilde{\nu}_3 = 388 \pm 10$		$\tilde{\nu}_1 = 1372$ [31] $\tilde{\nu}_2 = 640$ $\tilde{\nu}_3 = 366$			$\tilde{\nu}_1 = 1151$ [33] $\tilde{\nu}_2 = 518$ $\tilde{\nu}_3 = 1361$		

[a] The assignments are tentative.

PE spectra, the inadequate description of the inner shells in basis set *B* plays no important role.

For NSF the experimental ionisation potentials and the orbital energies, calculated by Dekock *et al.* [5] and in this work are given in Table 5. Comparison of both calculations shows that the large GTO's basis set does not change the orbital ordering in the approximated STO's basis set. This supports the explanation by Dekock *et al.* [5] that the observed difference between calculated and experimental ionisation potentials (Table 5a) could be due to the inadequacies of Koopmans' theorem.

The first band system in the PE spectrum of SSO at 10.52 eV obviously originates from an ionisation to the $^2A'$ ground state of the radical cation. The decrease of the first ionisation potential of SSO relative to SO_2 reveals the strong influence of the terminal sulphur atom on this ionisation. Actually, the corresponding molecular orbital $16a'$ in SSO is mainly localized on the terminal sulphur atom. According to Walsh [1] the removal of an electron from the highest filled orbitals of SSO, SO_2, and NSF molecules is expected to induce an increase in the bond angle. The vibrational progressions observed in the first band systems of SO_2 and NSF have been identified in accordance with the Walsh prediction as excitations of the bending modes (Table 3). Frost *et al.* [15] observed for SSO a frequency of 480 cm^{-1} and assigned it to the S–S stretching vibration. On the contrary, we found a vibrational spacing of only 370 cm^{-1} (Fig. 1) which can be assigned to the $SSO^{\oplus}$ bending mode (Table 3).

The second band systems in the PE spectra of SO_2 and NSF both include ionisations to two excited states lying close together. These two excited states of $SO_2^{\oplus}$ have been assigned as $^2A_2$ and $^2B_2$ respectively [6–8] on the basis of the observed decrease in the ν_1 frequency, which was attributed to the $d-\pi$

Table 4. Orbital energies and vertical ionisation potentials IP (a.u.) of SSO

Symmetry	Orbital energies		IP [16]
	Basis set *A*	Basis set *B*	
$1a'$	-92.169	-91.627	
$2a'$	-92.012	-91.463	
$3a'$	-20.604	-20.636	
$4a'$	-9.139	-9.026	
$5a'$	-8.997	-8.875	
$6a'$	-6.828	-6.837	
$1a''$	-6.827	-6.836	
$7a'$	-6.826	-6.834	
$8a'$	-6.686	-6.687	
$2a''$	-6.684	-6.684	
$9a'$	-6.683	-6.683	
$10a'$	-1.433	-1.431	
$11a'$	-1.095	-1.077	
$12a'$	-0.819	-0.802	0.680
$13a'$	-0.639	-0.629	0.581
$14a'$	-0.635	-0.621	0.545[a]
$3a''$	-0.611	-0.600	0.537[a]
$15a'$	-0.459	-0.446	0.417[b]
$4a''$	-0.415	-0.402	0.412[b]
$16a'$	-0.405	-0.393	0.387

[a, b] Reversed symmetry ordering possible.

Table 5. Orbital energies and vertical ionisation IP (a.u.) of NSF

Symmetry	Orbital energies		IP [5]
	Dekock *et al.* [5]	This work	
$1a'$		-92.149	
$2a'$		-26.307	
$3a'$		-15.656	
$4a'$		-9.123	
$5a'$		-6.813	
$1a''$		-6.810	
$6a'$		-6.809	
$7a'$		-1.617	
$8a'$	-1.164	-1.283	
$9a'$	-0.888	-0.874	0.775
$10a'$	-0.693	-0.702	0.633
$2a''$	-0.684	-0.694	0.609
$11a'$	-0.656	-0.665	0.575
$12a'$	-0.546	-0.552	0.511[a]
$3a''$	-0.522	-0.517	0.498[a]
$13a'$	-0.446	-0.463	0.437

[a] Reversed symmetry ordering possible.

backbonding in the a_2 orbital [12, 14]. For NSF$^{\oplus}$ Dixon *et al.* [4] assigned the weak band at 13.34 eV to the 00←01 hot band and interpreted the observed progressions as not belonging to the N–S stretch [3]. For the first excited state of NSF$^{\oplus}$ progressions of increased ν_2 and ν_3 have been found. The second excited state shows a decrease of ν_1, an increase of ν_2 and unchanged ν_3. Due to the observed significant decrease of ν_1 in the second state, the first excited state was assigned [5] as ${}^2A'$ and the second one as ${}^2A''$ contrary to the calculated sequence of the molecular orbitals, $3a''$ followed by $12a'$. Removal of an electron from the $12a'$ orbital, antibonding between N and S, should produce a moderate increase of ν_3 and the change in ν_3 observed for the second ${}^2A'$ state of $NSF^{\oplus}$ seems to agree with this prediction.

For SSO the comparison with the PE spectra of the valence isoelectronic molecules as well as the calculated orbital energies both support an assignment of two states within the second band system. However, the observed fine structures render an identification of two states difficult. Frost *et al.* [15] interpreted the progressions as being a simple series of S–O stretching vibrations for two different states. At variance with their results our calculations predict the $4a''$ orbital of SSO to be strongly S–S bonding and S–O antibonding, the $15a'$ orbital S–S bonding and S–O antibonding. The strong bonding participation of the terminal sulphur atom in these states is experimentally supported by the decrease of the second and third ionisation potentials relative to SO_2 (Table 3). The calculated S–O antibonding interaction seems to rule out the assignment by Frost *et al.* [15] of a decreased S–O stretch to the observed progressions (Fig. 1 and Table 3). Moreover, the distance between the two most intense peaks in this band systems differs by about $200\,\mathrm{cm}^{-1}$ from the other relatively regular spacings assigned by Frost *et al.* [15] to the same progression. We believe that the clearly discernible vibrational components on the high energy side of this band system have to be assigned to the second excited state of $SSO^{\oplus}$ and therefore to a strongly decreased S–S stretching or increased SSO bending mode. The fact that no vibrational fine structure has been observed on the low energy side of the band system might be explained by a preferential adiabatic transition between the neutral ground state and the first excited state of the $SSO^{\oplus}$ radical cation, which would implicate only small changes in the corresponding potential surface of this state relative to that of the neutral molecule. Nevertheless, a moderately decreased S–S stretch on the high energy side seems to be excited in this state (Fig. 1).

In the PE spectra of SO_2 and NSF, which show different patterns of the corresponding band systems, progressions of the bending modes have been observed for the $\tilde{A}$ and $\tilde{B}$ states (Table 3); while in the PE spectrum of SSO there is no evidence for such a simultaneous excitation. It is questionable whether or not the Koopmans' ordering of the $\tilde{A}$ and $\tilde{B}$ states in $SSO^{\oplus}$ is valid due to the extremely small separation of both states in the PE spectrum.

The assignment of the third band system of SO_2 which extends from 16 eV to 17.5 eV has been thoroughly discussed [8]. The correlation with the PE spectrum of SSO suggests in the same way as the correlation with the PE spectrum of NSF that the third band system of SO_2 must contain three states. Although the corresponding states in $NSF^{\oplus}$ and $SSO^{\oplus}$, i.e. $\tilde{C}, \tilde{D}, \tilde{E}$ are close in energy, the vertical ionisation potentials can be clearly identified. The only observed progression with a strongly anharmonic spacing of ν_1 has been found for the band at 15.64 eV in $NSF^{\oplus}$, which was assigned to the ionisation from the $11a'$ orbital. The $3a''$ orbital in SSO is calculated to be delocalized and totally bonding, whereas the $2a''$ orbital in NSF is almost totally localized on the fluorine atom.

The $3a''$ orbital in SSO lies above the $14a'$ orbital, contrary to the calculated ordering in NSF, i.e. $11a'$ followed by $2a''$. In both molecules the corresponding σ orbitals – $14a'$ and $13a'$ in SSO, $11a'$ and $10a'$ in NSF – are very similar. Based on the comparison of the PE spectrum of SSO with those of SO_2 and NSF we tentatively assign the $\tilde{C}$ state as $^2A'$, the $\tilde{D}$ state as $^2A''$ and the $\tilde{E}$ state as $^2A'$ (Table 3).

The last observed bands within the He(I) region are extremely weak for all three molecules (Tables 3). The calculations show that the $12a'$ orbital in SSO is S–S antibonding and S–O bonding, the $9a'$ orbital in NSF N–S antibonding and S–F bonding. In the He I PE spectrum of SSO no further bands were detected.

5. Discussion

The PE spectroscopic valence ionisation patterns of the bent triatomic molecules with 18 valence electrons, presented in Fig. 3, indicate that one may refer to the general ABC orbital correlation diagram developed empirically by Walsh [1]. The corresponding correlation diagrams based on *ab initio* SCF calculations for several molecules are shown in Fig. 2.

The discrepancies between the calculated and predicted ordering have been thoroughly discussed in the literature, e.g. SO_2 [13], O_3 [34], or CF_2 [35]. Apparently, in all molecules of Fig. 2 the position of the orbitals antisymmetric to the molecular plane, i.e. the π orbitals is at variance with the Walsh prediction. If the spacings between the observed vertical ionisation potentials are compared with those from Koopmans' ionisation potentials (Figs. 2 and 3, Tables 3–5) one recognizes that in particular A' and A'' states should be differently influenced

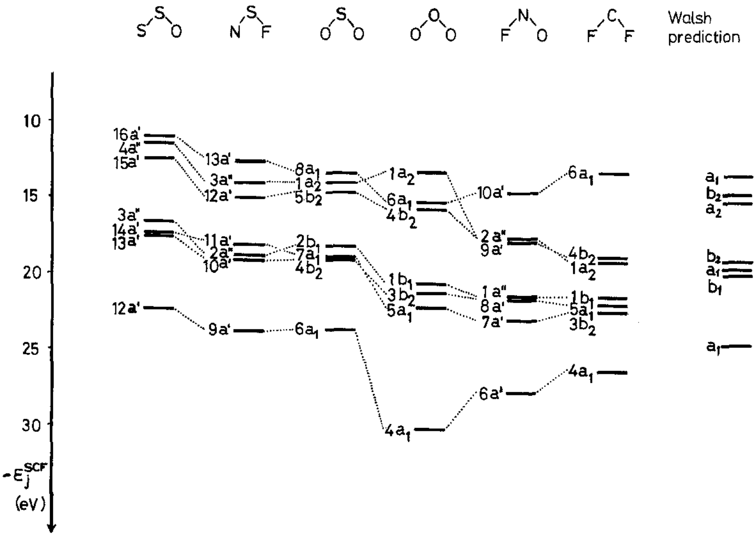

Fig. 2. Ab initio eigenvalues $-\varepsilon_J^{SCF}$ (eV) for triatomic bent molecules with 18 valence electrons compared to the Walsh prediction for AB_2 systems

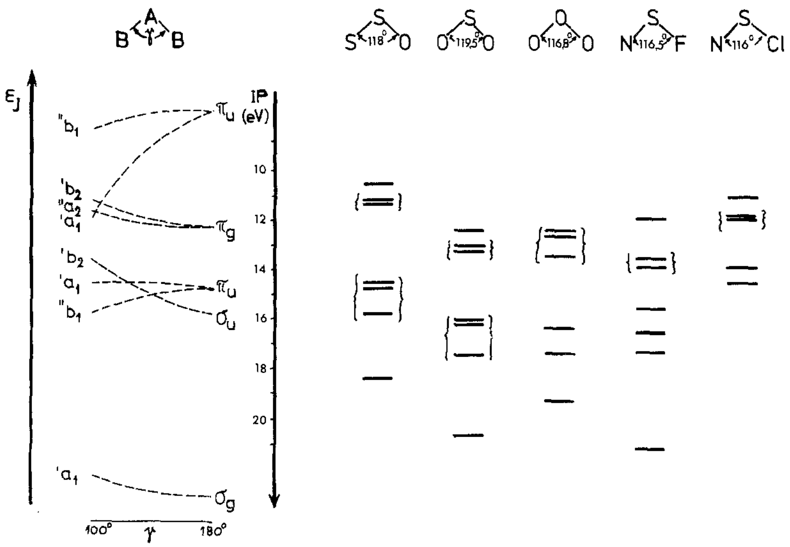

Fig. 3. Walsh correlation diagram AB_2 and ionisation potentials of SSO, OSO, OOO, NSF, and NSCl

by the rearrangement and correlation energy contributions. For the lowest ${}^2A''$ excited states of SSO$^\oplus$ and NSF$^\oplus$ we have obtained the following restricted Hartree-Fock energies: $\tilde{A}\,{}^2A''$ SSO$^\oplus$ -869.4613 a.u.; $\tilde{A}\,{}^2A''$ NSF$^\oplus$ -550.8521 a.u., which yield for both states almost the same rearrangement energy of about 0.132 a.u. Unfortunately, due to the convergence difficulties for ${}^2A'$ states a comparison with other low lying states was not possible. Nevertheless, experimentally observed vertical energy differences between $\tilde{A}$ and $\tilde{B}$ or $\tilde{C}$, $\tilde{D}$, and $\tilde{E}$ states are very small and clearly make necessary further work beyond the Hartree-Fock approximation. It is to be expected that $\tilde{A}$, $\tilde{B}$ pairs and two components of the $\tilde{C}$, $\tilde{D}$, $\tilde{E}$ states are degenerate ${}^2\Pi$ states in the linear ABC$^\oplus$ systems and for this reason knowledge of correlated angular potential curves for the corresponding radical cations would be of great interest. The comparison of the above ionic states with the ground states of the neutral molecules shows that the ions lose the correlation σ- other and π-other electrons respectively. Furthermore, the extension of the orbital space for the correlation between all other electrons may result in significant differences between the correlation energies for A' and A'' states. The Hartree-Fock approximation and Koopmans' theorem, for instance, yield a reversal of the observed spectroscopic order for the ground state ($\tilde{X}\,{}^2\Sigma_g^+$) and the first excited state ($\tilde{A}^2\,\Pi_u$) of the nitrogen radical cation $N_2^\oplus$ [36]. A similar effect has been observed for $(CN)_2^\oplus$ [27, 28], HCCCN$^\oplus$ [27, 28] and $S(CN)_2^\oplus$ [44]. The estimation of the correlation contributions by Verhaegen *et al.* [38] for $N_2^\oplus$ show that the reversal of these states is due to much higher correlation contribution to the energy of the ${}^2\Sigma_g^+$ state than to the ${}^2\Pi_u$ state. The extensive calculations on $N_2^\oplus$ made by Meyer [39] reveal that two different correlation effects mainly account for the differences in the overall correlation corrections to the restricted Hartree-Fock energy values: the droping out of the correlating between the removed and all other electrons (${}^2\Sigma_g^+$ $+0.064$ a.u.,

$^2\Pi_u + 0.080$ a.u.) and the change in correlation of all other electrons due to the extension of the orbital space ($^2\Sigma_g^+ - 0.057$ a.u., $^2\Pi_u - 0.018$ a.u.). The total correlation energy contributions for $^2\Sigma_g^+$ and $^2\Pi_u$ states therefore differ by about 0.055 a.u. Similar results have also been found using the approximate propagator technique by Cederbaum *et al.* [40]. The corrections to the Koopmans' ionisation potentials calculated by this method include perturbationally estimated changes in correlation energy and the orbital relaxation. We used this procedure [41] within the semiempirical CNDO method [42] for SO_2, NSF, and SSO molecules [43] with the result that all corresponding σ orbital corrections are much larger than the corrections connected with the ionisations from π orbitals and are large enough to cause a reversal of A' and A'' states. This could support the tentative assignments of the PE spectra of NSF and SSO as given Table 4, in disagreement with the predictions made by Koopmans' theorem.

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Note added in proof: Recently, for O_3 new PE-data have been published by Brundle, C.R.: Chem. Phys. Letters **26**, 25 (1974) which are in nice agreement with those of other valence isoelectronic molecules.

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