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Sulphur Dioxide. Notes on the Electronic Changes which Occur on Coordination

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The sulphur dioxide molecule and the two negative ions, SO_2^- and SO_2^{2-} are studied by *ab initio* SCF–MO methods using a small but flexible gaussian orbital basis set. The calculations were performed for two different geometries and allow some understanding of the electronic changes that accompany the formation of complexes in which the SO_2 molecule acts as a ligand.

Das Schwefeldioxid-Molekül und die beiden negativen Ionen SO_2^- und SO_2^{2-} werden mit Hilfe einer *ab initio* SCF–MO Methode, die einen kleinen aber flexiblen Gauß-Basissatz benutzt, studiert. Die Rechnungen werden für 2 verschiedene Geometrien durchgeführt und erlauben ein näherungsweises Verständnis der Änderungen der Elektronenparameter, die die Bildung von Komplexen mit dem SO_2-Molekül als Ligand begleiten.

Introduction

In this paper we present the results of some calculations on the sulphur dioxide molecule. These calculations were performed with the aim of providing some information about the electronic changes which occur in the molecule when it coordinates to transition metal complexes. There is a great deal of experimental information about the stereochemistry and electronic arrangement of such ligands as CO, NO, O_2, SO_2, olefins, allyls and acetylenes bonded to transition metal complexes, derived mainly from X-ray crystallographic and spectroscopic observations. There have been a number of theories of a largely qualitative nature produced to explain the bonding in such complexes [1–6], but few calculations have been performed. It seems reasonable to suppose that SCF calculations upon such molecules should provide much information about the bonding in them. In the main, the size of the complexes precludes the possibility of MO–SCF calculations by present methods, although $Ni(\pi\text{–}C_3H_5)_2$ [7], $Ni(CO)_4$ [8] and CrO_8^{3-} [9] have been studied recently. Calculations upon a system such as $RhCl(CO)(SO_2)[P(C_6H_5)_3]_2$ are not yet possible, so that a first attempt at understanding the bonding seems to be to study the electronic structure of the ligand of interest, SO_2 in this case, and the possible changes that occur upon coordination.

SO_2 coordinates in two different ways to transition metal systems. On the one hand there is the complex $[RuCl(NH_3)_4SO_2]Cl$ [10] where the Ru–SO_2 group is planar and symmetric, and the Ru–S bond is short at 2.072 Å. On the other hand, the reversible coordination of the complexes characterised by $RhCl(CO)(SO_2)[P(C_6H_5)_3]_2$ [11] with a long Rh–S bond (2.450 Å) and the SO_2 group bonded symmetrically, but with an angle of 30.3° between the Rh–S bond

Table 1. The geometry of SO_2 as the free molecule and in various complexes

Compound	S–O (Å)	O–S–O (deg.)
SO_2 [13]	1.431 (1)[a]	119.0 (5)
$[RuCl(NH_3)_4(SO_2)]Cl$ [10]	1.43 (1)	114 (6)
$RhCl(CO)(SO_2)[P(C_6H_5)_3]_2$ [11]	1.451 (4)	113.8 (3)
$S_2O_4^{2-}$ [12]	1.50 (2)	108

[a] The estimated experimental error in the last significant figure is given parenthetically.

and the normal to the SO_2 plane. This latter coordination parallel that in the dithionite ion, $S_2O_4^{2-}$ [12] which has a very long S–S bond (2.39 Å) linking, at a similar angle, two SO_2 groups, with overall C_{2v} geometry. The geometries of the SO_2 group in these various complexes are listed in Table 1. The variations in geometry that are indicated in the table, together with the different modes of coordination described above, suggest considerable electronic differences between the SO_2 group in the various complexes. The calculations presented here are aimed at going some way toward elucidating these differences.

Calculations

MO–SCF–LCAO calculations were performed for the SO_2 molecule and the negative ions SO_2^- and SO_2^{2-} at two different geometries. The calculation designated (I) employed the geometry obtained for gaseous SO_2 from electron diffraction data [13]. This geometry is identical with that found in an X-ray study of the solid [14]. The second calculation (II) employed the geometry of the SO_2 group in the dithionite ion, determined by an X-ray crystallographic analysis of $Na_2S_2O_4$ [12], averaging the two S–O distances, which agreed within error in the experiment. Details of these two geometries are given in Table 1.

A basis set of 48 uncontracted gaussian functions was employed in all calculations. This is equivalent to two gaussian functions per atomic orbital. A (6*s*, 4*p*) set of gaussian functions for sulphur determined by optimization against the total energy of the ^3P ground state of the sulphur atom (total energy −395.262 a.u.) [15] was supplemented by two *d*-type functions with exponents 0.4 and 2.0. For the oxygen atoms a (4*s*, 2*p*) set was optimized to give a total energy for the atom of −73.900 a.u. [15]. All one- and two-electron integrals were computed exactly. The SCF calculations were carried out by repeated diagonalization, making use of molecular symmetry [16]. All calculations were performed on an ICL 1907 computer using programs written by the authors.

Results and Discussion

Three *ab initio* calculations on SO_2 have been reported in the literature, and it is instructive to compare the results of the present work with these calculations, in order to assess the accuracy of our wavefunction. Some of the results of these

Table 2. Results of some *ab initio* SCF calculations on SO_2

	This work	Ref. [17]	Ref. [18]	Ref. [19]	Observed
Total energy (a.u.)	−543.340	−541.008	−546.831	−547.209	
Dissociation energy (eV)	7.56		5.77	3.85	11.18[a]
Ionization potential (a.u.)	0.413	0.444	0.466	0.491	0.454[b]
Dipole moment (Debye)	−1.26	−0.81	−2.17	−2.28	1.61[c]
S 3*d* population	1.33	1.17	0.55	0.43	

[a] Ref. [19]. [b] Ref. [20]. [c] Ref. [21].

calculations are presented in Table 2. Column 2 gives values obtained by Hillier and Saunders [17] who employed a basis set of 72 gaussian functions contracted in groups of three to a minimal (3*s*, 2*p*, 1*d*) basis for sulphur and (2*s*, 1*p*) for oxygen. It is significant that the present calculation, which uses a smaller basis set of 48 gaussians, yields a total energy some 2.3 a.u. lower, partially as a result of the greater flexibility of the non-minimal bais set, but mainly because the smaller basis set has been subjected to optimization for the free atoms. Columns 3 and 4 give results from the considerably more accurate GTO calculations of Roos and Siegbahn [18] and Rothenberg and Schaefer [19], who both included 3*d* functions of oxygen as well as sulphur, and used considerably more accurate expansions for the core orbitals. These calculations give lower sulphur 3*d* populations, which, as Hillier and Saunders pointed out, is to be expected since the participation of the 3*d* orbitals in both the present calculation and the 3-GTO minimal basis calculation is certain to be exaggerated because of the incomplete *s* and *p* orbital basis sets. The fact that the present calculation apparently gives the best dissociation energy, from comparison with the experimental value, can be explained by this exaggerated 3*d* participation in the wave function, which allows an improved description of the sulphur core orbitals and hence artifically lowers the binding energy. The Koopmans' theorem ionization potential, and the dipole moment calculated from the present wavefunction are in reasonable agreement with the experimental values. Final confirmation of the quality of this wavefunction is given by the energy level ordering it exhibits, which is the same as that of the Roos and Siegbahn wavefunction.

For geometry (II) total energies of −543.340, −543.264 and −542.831 a.u. were obtained for SO_2, SO_2^- and $SO_2^=$ respectively. The figures for geometry (II) were −543.349, −543.304 and −542.903 respectively. The two additional electrons in the SO_2^{2-} calculations resided in the level $3b_1$, whilst the $^2B_1$ wavefunction was the most stable state found for both SO_2^- calculations.

The total energies for the SO_2 ground state in the two different geometries are separated by 0.009 u.a. with the experimental geometry giving rise to the higher figure. This indicates an energy plateau as far as small, symmetric deformations of the isolated molecule are concerned, and we feel that the apparent slight increase in stability when the S–O bonds are stretched and the OSO angle decreased is an artifact of the limited basis set used in the calculations. The most stable virtual orbital of the SO_2 calculations has b_1 symmetry. It is centred mainly on the sulphur atom but with some 2*p* character, and has the symmetry of a

p-orbital perpendicular to the SO_2 plane. The orbital is S–O π-antibonding and O–O π-bonding. When electrons are added to this orbital it is evidently considerably more stable in geometry (II) rather than (I). The orbital energies for this orbital in both the SO_2^- and SO_2^{2-} calculations are 0.031 a.u. lower in (II) than their corresponding values in (I). This is confirmed by the total energies which indicate SO_2^- (II) to be 0.040 a.u. more stable than SO_2^- (I) whilst the difference between the SO_2^{2-} energies is 0.072 a.u. These differences are considerably larger than the small difference between the SO_2 energies, and they agree with the experimental observations of the geometry change in SO_2 when it coordinates as a Lewis acid [11]. The $3b_1$ orbital has the correct symmetry for σ-bond formation between sulphur and another atom in such complexes as $S_2O_4^{2-}$ and $RhCl(CO)(SO_2)(P(C_6H_5)_3)_2$ where the SO_2 group is oriented such that the normal to the SO_2 plane is at about 30° from the line of the S–S or S–Rh bond. In both the SO_2^- calculations the molecular orbital $3b_1$ has atomic orbital components which are 54% sulphur $3p_z$, 17% sulphur $3d_{xz}$ and 29% oxygen $2p_z$ where the SO_2 molecule lies in the xy-plane with the x-axis the 2-fold axis. The presence of electrons in this orbital, whether in the SO_2^- and SO_2^{2-} ion, or in complexes where the orbital is involved in σ-overlap with a suitably directed doubly-occupied metal orbital, will decrease the amount of S–O π-bonding and increase the O–O π-bonding over that found in free SO_2. The geometry changes which will enhance the stability of a system where the SO_2 $3b_1$ orbital is occupied will therefore be S–O bond lengthening and the decrease of the angle between the two S–O bonds. We observe that the other two orbitals which are more stable in the geometry calculations (II), namely $6a_1$ and $8a_1$, are both S–O antibonding and O–O bonding in character, whilst the orbital $5b_2$ and $1a_2$ which are antibonding between the oxygens are less stable in the geometry (II) calculations.

The orbital $8a_1$ is the obvious source of the electron pair needed for σ-bond formation in complexes such as $[RuCl(NH_3)_4SO_2]Cl$ where the SO_2 group acts as a Lewis base. As Roos and Siegbahn have pointed out, this orbital can not be characterized as a lone pair orbital on sulphur, since it has a large oxygen $2p$ component (58% in our calculation) and is S–O antibonding. However, withdrawal of electrons from this orbital on complex formation will stabilize the S–O σ-bonding and will favour back-donation from appropriately directed occupied metal d-orbitals into the vacant $3b_1$ orbital on SO_2 which has the right symmetry for metal-sulphur π-bond formation. Thus we suggest that the electronic configuration of SO_2 in the ruthenium amine complex will resemble that in an excited state of SO_2 that can be qualitatively described as $\ldots(1a_2)^2(8a_1)^1(3b_1)^1$. Since both the orbitals $8a_1$ and $3b_1$ are S–O antibonding and O–O bonding we would expect little or no change in the geometry of the SO_2 group on complex formation of this type. The relevant crystallographic data for $[RuCl(NH_3)_4SO_2]Cl$ (see Table 1) confirm that, within error, the SO_2 geometry is the same as that in the free molecule, whilst the short Ru–S distance indicates the presence of a double bond between these atoms.

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