Ab Initio Calculations, including *d*-Orbitals, of the Electronic Structure of the Sulphate Ion

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Summary *Ab initio* molecular orbital calculations using a Gaussian basis set, of the electronic structure of the sulphate ion reveal the importance of 3*d*-orbitals in describing the bonding in this ion.

TABLE

	s and *p* sulphur basis set	*s*, *p*, and *d* sulphur basis set
Total energy (a.u.)	−687·489	−688·327
Diagonal elements of Fock matrix (a.u.)		
3*s*	−1·57	−1·57
3*p*	−0·66	−0·69
θ_{xx} (a.u.)	−31·0	−32·1
Atomic populations		
Sulphur		
3*s*	1·35	1·19
3*p*	3·28	2·84
3*d*		2·58
Oxygen		
2*s*	1·92	1·83
2*p*	4·94	4·54
Orbital energies (a.u.)		
$5t_2$	0·27022	0·09681
$1t_1$	0·26607	0·17720
1*e*	0·20367	0·00437
$4t_2$	−0·02906	−0·13663
$5a_1$	−0·12248	−0·23013
$3t_2$	−0·68420	−0·79217
$4a_1$	−0·93320	−1·0032

THE nature of the bonding, particularly the importance of 3*d*-orbitals, in molecules containing latter second-row elements such as sulphur, is still a matter of some speculation.[1,2] Semi-empirical molecular orbital calculations give varying degrees of *d*-orbital participation depending upon the parameters used.[3,4] For this reason, and because of the lack of non-empirical studies on sulphur-containing molecules (except for H_2S[5] and COS[6]), we here report the results of *ab initio* molecular orbital calculations of the sulphate ion. A Gaussian basis set was used in which three such functions are used to describe each member of a minimal basis set of Slater-type orbitals.[7] The orbital exponents of the latter, except for that of the 3*d*, were taken as the best atom values given by Clementi.[8] In view of the large amount of computer time required for such calculations, it was not possible to optimize the 3*d*-orbital exponent. A value of 1·2 was chosen, following the suggestion of Craig *et al.*[2] Such a value is in line with the optimum 3*d* exponents found for some phosphorus compounds.[9,10] The results of the two calculations with and without *d*-orbitals are summarized in the Table. The decrease of nearly 1 a.u. in the molecular energy compared with *ca* 0·05 a.u. in the case of H_2S[5] shows the importance of the 3*d*-orbitals, which is further illustrated by the large 3*d* population obtained by a Mulliken analysis. The introduction of 3*d*-orbitals lowers the energy of the 1*e* molecular orbitals by removing their non-bonding characteristic, and the mixing of the 3*d*-orbitals into the $5t_2$-orbitals brings about a reversal in the order of the $5t_2$- and

t_1-orbitals. The population analysis which yields a negative charge on the sulphur atom when *d*-orbitals are included gives an exaggerated picture of the charge redistribution which occurs on expansion of the basis set. Owing to the diffuseness of the *d*-orbitals, their population should to a large extent be associated with the oxygen atoms. This is shown by the small change both in the sulphur 3*s* and 3*p* diagonal elements of the Fock matrix at self-consistency, and the non-vanishing components of the quadrupole moment on the introduction of *d*-orbitals.

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