d-Orbital Participation in the Bonding in Molecules Containing Phosphorus, Sulphur, and Chlorine Studied by *ab Initio* SCF–MO Calculations

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Summary *d*-Orbital participation in the bonding in molecules containing phosphorus, sulphur, and chlorine is discussed with the aid of *ab initio* SCF–MO calculations on ClO_2^-, ClO_3^-, ClO_4^-, PF_3O, SO_2F_2, and ClO_3F.

It is now recognised that 3*d* orbitals can play an important role in the bonding in molecules containing the later second-row elements silicon, phosphorus, sulphur, and chlorine. *Ab initio* self-consistent field molecular orbital (SCF–MO) calculations, in which a minimal basis of Slater type orbitals (STO) is expanded to include 3*d* orbitals, give a substantial decrease in the total molecular energy for a number of molecules and yield molecular properties such as dipole moments and ionization potentials in better agreement with experiment than is obtained from calculations without 3*d* orbitals.[1] However, the extent to which *d*-orbital participation is dependent upon the choice of second row atom, and also upon the number and type of atoms attached to the second row atom has not been fully investigated.

We here present the results of *ab initio* SCF–MO calculations of the ions ClO_2^-, ClO_3^-, and ClO_4^-, and the isoelectronic series PF_3O, SO_2F_2, and ClO_3F.

The atomic orbital bases for these calculations consisted of STO's with best atom exponents of Clementi and Raimondi[2] except for the fluorine 2*p* orbital where an atomic orbital was used. This basis was augmented by five 3*d* orbitals on the second row atoms. To assess the size of the 3*d* orbital in such molecules, the exponent was optimized in PF_3, yielding a value of 1·77. This value was used for PF_3O, the 3*d* exponent for the other molecules being taken to be 1·8. For computational convenience each STO was expanded in three Gaussian type functions (GTF) and the fluorine 2*p* orbital in four GTF's. Polarization and expansion or contraction of the 3*d* orbitals were allowed for as previously described.[3] The calculations were performed using the ATMOL system on the Manchester University Atlas computer.

Those results pertinent to a discussion of 3*d* participation are summarized in Tables 1 and 2. In the series ClO_2^-, ClO_3^-, ClO_4^- the 3*d* population increases uniformly as the co-ordination number of the chlorine atom increases and to a good approximation the population is 0·5e per Cl–O bond, although that for ClO_4^- is rather larger than this value. The contribution of the 3*d* orbitals to the total molecular energy also increases through this series and is about 4ev per Cl–O bond, that for ClO_4^- again being rather larger than this value. As the *d* orbitals cannot contribute to the energy of the isolated atoms, their importance to the binding energy is thus very large and approximately additive as the number of oxygen atoms is varied.

Table 1

The bonding in chlorine oxides

	3*d* population	Calculated molecular energy (a.u.) With 3*d* orbitals	Without 3*d* orbitals	ΔE
ClO_2^-	1·04	−602·2928	−601·9792	0·31
ClO_3^-	1·55	−676·0903	−675·6068	0·48
ClO_4^-	2·24	−749·9037	−749·1073	0·80

Table 2

3d *Participation in* PF_3O, SO_2F_2, *and* ClO_3F

	3*d* population	Contribution of 3*d* orbitals to overlap population X–O	X–F
PF_3O	1·32	0·64	0·32
SO_2F_2	1·73	0·66	0·29
ClO_3F	2·07	0·63	0·25

The calculations for the isoelectronic series PF_3O, SO_2F_2, and ClO_3F show a steady increasing 3*d* population as the atomic number of the central atom increases. We believe the dominating factor controlling these 3*d* populations is the difference between the sum of the valencies of the ligands and the valency of the central atom, the latter being calculated assuming only 3*s* and 3*p* central atom orbital involvement in bonding. This difference measures the excess valency forced upon the central atom by the ligands, and takes the values of 2,4, and 6 for PF_3O, SO_2F_2, and ClO_3F, respectively, and correlates well with the contribution of the 3*d* orbitals to the bond overlap populations through this series. These populations are approximately independent of the second row atom, but for bonds involving an oxygen atom are about twice that for bonds involving a fluorine atom.

The inclusion of 3*d* functions also has an appreciable effect on the calculated observable molecular properties. Thus, the calculated dipole moment of ClO_3F is 1·56D in the absence of 3*d* functions, but is reduced to 1·08D on their inclusion. Furthermore, the observed photoelectron spectrum[4] of this molecule can only be interpreted in terms of the calculated orbital energies from the calculation including 3*d* functions.

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[1] I. H. Hillier and V. R. Saunders, *Chem. Phys. Letters*, 1969, **4**, 163.

[2] E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, 1963, 38, 2686.

[3] I. H. Hillier and V. R. Saunders, *Chem. Comm.*, 1970, 316.

[4] D. R. Lloyd, unpublished results.