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A Molecular Orbital Study of the Changing Role of *d*-Orbitals in Transition Metal Compounds: ZnS, FeS and CrS

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SCF-MO studies as FeS, CrS and ZnS illustrate the changing role of *d*-orbitals along a transition series, where they become at first good acceptors playing an important role in the bonding, then so stable that their electrons behave essentially as "core" electrons in agreement with the conjecture of Phillips and Williams [1].

Key words: Transition metal compounds – FeS – CrS – ZnS

1. Introduction

The chemistry of the transition elements can be rationalised in a very appealing way by considering the changing behaviour of the *d*-orbitals [1]. Early in each series and for low oxidation states in the middle of each series, it is supposed that the *d*-orbitals are fairly high in energy and diffuse; as the oxidation number increases, or as one goes across a particular series, they become at first effective acceptors playing an important role in the bonding, and then so stable that their electrons behave essentially as "core" electrons. Thus the features characteristic of transition metal chemistry – variable valence, colour, formation of complexes with hydride or organic ligands – are associated with Fe or Ni rather than with Sc or Zn.

In this paper we explore the assumption of varying behaviour of *d*-orbitals along one transition series. A constant oxidation state (+2) and ligand (S^{2-}) are chosen, and Molecular Orbital (MO) calculations performed on the closed shell configurations of lowest energy for the gas-phase compounds CrS, FeS and ZnS. In addition we study FeS in several different electronic configurations in order to quantify what differences can be expected in the behaviour of *d*-orbitals in different spin states.

We find that the properties studied depend almost exclusively on which *d*-orbitals are occupied. Likewise the variations shown by FeS in different spin states show up clearly in these properties and appear to be of almost equal magnitude to the changes shown across the series CrS – FeS – ZnS, and can be interpreted by rather similar arguments. A careful study of the MO energy correlation diagrams shows a systematic trend in the bonding role of the *d*-electrons across this series as postulated by Phillips and Williams [1].

2. Calculations

We first discuss the problem of different spin states, then go on to compare FeS, CrS and ZnS for the *same* spin state. To a first approximation the energy levels of FeS will be determined by the energy levels of the Fe^{+2} ion as perturbed by an S^{-2} ion. The degeneracy of the *d*-orbitals is lifted in FeS and from simple MO considerations one would expect the σ component to have the same orbital energy as in the free ion whilst the σ and π components will be raised in energy by interaction with the ligand donor orbitals. In fact the order is expected to be $E(\delta) \ll E(\pi) < E(\sigma)$ [2] and so the closed shell configuration of lowest energy will be $\sigma^2\delta^4$, either of the triplet states arising from the configurations $\delta^4\pi^2$ or $\delta^4\pi^1\sigma^1$ could be the lowest energy low-spin states and the ground state is most likely to be a high-spin state (e.g. $\sigma^1\pi^2\delta^3$) [3].

SCF-MO calculations were performed on the University of Manchester CDC 7600 computer. Gaussian basis sets were used throughout, being the large and small sets of Roos *et al.* [4] for Fe, Cr and Zn contracted according to Dunning's [5] principles. The basis sets used for S have been reported previously [6]. In detail the contraction schemes used were as follows:

1) FeS small basis set; S(11, 8)→[6, 5]; Fe (10, 5, 4)→[6, 3, 2]
2) large basis set; S(11, 8, 2, 1)→[6, 5, 2, 1]; M(12, 7, 5)→[8, 5, 3].

Orbital exponents and contraction coefficients are available on request from the authors.

Using the smaller basis set pilot SCF-MO calculations were performed on FeS at a fixed bond length for the closed-shell configurations $\sigma^2\delta^4$ and $\sigma^2\pi^4$ together with some Unrestricted Hartree Fock calculations on configurations with $M_\Sigma = 0,\ldots,3$ where M_Σ is the component of total spin along the internuclear axis. The $M_\Sigma = 0$ calculation converged to a state which is a linear combination of ${}^1\Gamma$ and ${}^1\Sigma$ arising from the low-spin configuration $\pi^4\delta^2$, $M_\Sigma = 1$ did not converge whilst $M_\Sigma = 2$ and $M_\Sigma = 3$ converged to high-spin states approximating to ${}^5\Delta$ ($\sigma^1\pi^2\delta^3$) and ${}^7\Sigma(\sigma^1\pi^3\delta^2)$ respectively. The lowest energy state found was ${}^5\Delta$, just as the ground state of Fe^{2+} is ${}^5D$ [7]. Bagus and Preston [8] have reported large-scale calculations on FeO using extensive configuration interaction. Their only positive conclusion is that the ground state is not ${}^5\Sigma$, which does not appear to contradict our findings for FeS.

The orbital energy correlation diagram (Fig. 1) for 3 of the 5 configurations investigated by us shows that it is not possible to arrange the d_σ, d_π and d_δ orbitals in a constant order of orbital energy, since the order varies with configuration. The diagram does show however that the MOs arising from Fe 3*d* (and 4*s*) atomic orbitals are indeed very similar in energy to those arising from S 3*p* and 3*s*.

One encouraging feature of the population analysis[1] (Table 1) is that the atomic charge on Fe is fairly constant for 4 of the 5 states. The π overlap population

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[1] See appendix of Ref. [6] for nomenclature used.

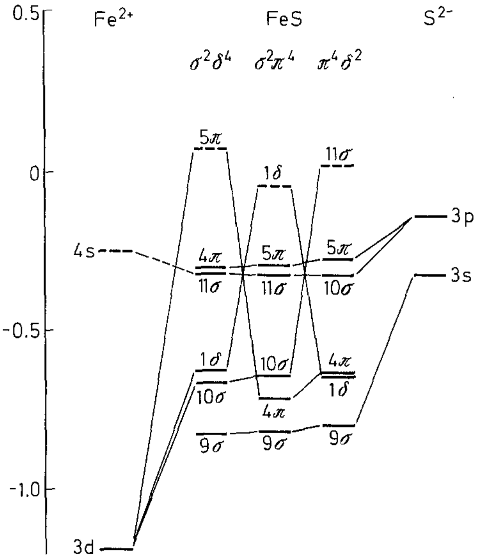

Fig. 1. Orbital energy correlation diagram for some low-spin configurations of FeS. Occupied orbitals are shown by a solid horizontal bar, virtual orbitals by a dashed bar. Orbitals composed of similar basis functions are connected by diagonal lines, and there is in addition a considerable mixing together of orbitals of the same symmetry types

is very small for $\sigma^2\pi^4$ and $\pi^4\delta^2$, intermediate for $^7\Sigma$ and $^5\Delta$ and substantial for $\sigma^2\delta^4$. This is to be expected, for the d_π orbital can act as an acceptor only if it is vacant. On the other hand for the low-spin states the σ-overlap population is almost constant, since the vacant 4s orbital on Fe is acting as an acceptor as well as the d_π and can compensate if the latter is occupied.

The Table also gives a dipole moment analysis. Note that the homopolar dipole opposes the overall polarity Fe^+S^- (especially for the $\sigma^2\pi^4$ configuration), whereas in the low-spin states the S atomic density enhances it. There is a reasonable correlation between the dipole moment function (μ/R) and the atomic charge population for the low-spin states but not for the high-spin ones.

We now discuss the differences shown by the electronic distributions of FeS, CrS and ZnS. MO calculations were performed using the larger basis set.

There is fairly complete data on the dissociation energies of the divalent sulfides for the first transition series [9] and a plot against atomic number shows a double maximum superimposed on a general upward trend, as expected for high-spin complexes, but the interesting feature is that the maxima occur for the d^4 and d^9 ions, whereas simple ligand field theory [2] gives d^2 and d^7. This implies that the metal π-orbitals are not strongly antibonding (which in turn implies that the filled ligand π-orbitals are not strongly bonding, whatever their overlap populations may suggest).

The orbital correlation diagrams for CrS and ZnS (Figs. 2 and 3) confirm in a pleasing way the arguments of Phillips and Williams [1] on the changing role of *d*-electrons across a transition series. In CrS the MO's arising from Cr 3d (1δ, 10σ, 4π) lie well above the 9σ orbital which is essentially pure S 3*s*. On the other

Table 1. FeS: population analysis for different configurations, together with dipole moment analysis

	$^7\Sigma$	$^5\Delta$	$\pi^4\delta^2$	$\sigma^2\pi^4$	$\sigma^2\delta^4$
hartree	−1658.4057	−1658.4997	−1658.3005	−1658.0948	−1658.2806
Overall indices					
Fe-S overlap pop.					
σ	−0.526(−0.117)	0.139(.137)	0.425(0.277)	0.472(0.350)	0.430(0.280)
π	0.201(.074)	0.152(0.046)	0.048(0.010)	0.048(0.010	0.314(0.116)
S net	16.761	16.768	16.779	16.683	16.591
S valence	−0.211	0.082	0.187	0.159	0.349
Fe net	25.563	24.956	24.747	24.797	24.664
Fe valence	−0.113	0.197	0.287	0.361	0.396
Atomic charge	0.550	0.846	0.966	0.843	0.940
Gross populations					
S s	5.945	5.967	5.979	5.988	5.988
S p_σ	3.924	2.982	3.023	2.888	3.377
S p_π	6.681	7.897	7.964	7.967	7.574
Fe s	7.113	7.011	6.734	7.178	6.648
Fe p_σ	3.989	3.991	3.990	3.991	3.992
Fe p_π	7.999	7.999	7.999	7.999	7.998
Fe d_σ	1.029	1.050	0.275	1.956	1.995
Fe d_π	3.320	2.104	4.037	4.034	0.428
Fe d_δ	0.000	3.000	2.000	0.000	4.000
Dipole moment					
μ(heteropolar)	2.515	3.803	4.266	3.962	4.046
μ(homopolar)	−0.205	−0.250	−0.210	−0.423	−0.100
μ(atomic, Fe)	−0.003	−0.040	−0.061	−0.028	−0.059
μ(atomic, S)	−0.370	0.081	0.482	0.371	0.360
μ	1.938	3.513	4.476	3.882	4.247
μ/R	0.461	0.836	1.066	0.924	1.011

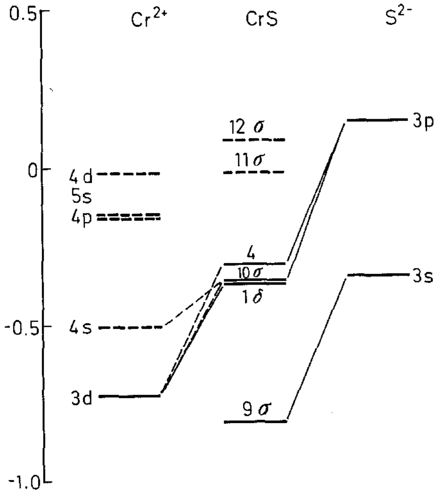

Fig. 2. Orbital energy correlation diagram for Cr(δ^4)S

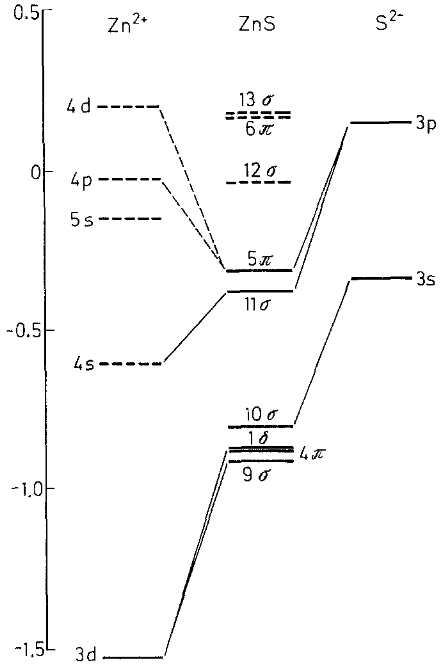

Fig. 3. Orbital energy correlation diagram for ZnS

hand the S 3*p* orbitals interact strongly with Cr 3*d* and 4*s*. In FeS ($\sigma^2\delta^4$) the $9\sigma/10\sigma$ energy gap is much smaller, and there is some Fe d_σ mixed into S 3*s* in the 9σ orbital. The two orbitals arising from S 3*p* now lie slightly above the band of filled Fe 3*d* orbitals. In ZnS the band of Zn 3*d* orbitals lies below the 10σ (S 3*s*), and although there is some intermixing in the $9\sigma/10\sigma$ orbitals this is not expected to produce an energy lowering since both bonding and antibonding MOs are filled. There is a large energy gap between the 10σ orbital and the band of S 3*p* orbitals (5π, 11σ) which now interact with Zn 4*s* and 4*p* rather than Zn 3*d*. Thus the 3*d* electrons act as valence electrons for Cr (II) and Fe(II), but as core electrons for Zn(II).

For the sake of completeness we will mention that the calculated SCF-MO energies were $-1\,440.292\,4$, $-1\,659.376\,7$ and $-2\,174.741\,2$ hartree for Cr (δ^4) S, Fe ($\sigma^2\delta^4$) S and Zn ($\sigma^2\pi^4\delta^4$) respectively using the larger basis sets. A study of the population analysis indices (not shown) gives atomic charges of 0.878, 0.846 and 0.753 for Cr, Fe and Zn respectively, whilst the calculated dipole moments (3.766, 3.571 and 3.269 atomic units) go in the same order as the atomic charges.

3. Conclusions

Whereas the bonding in CrS involves mainly the partially filled 3*d* orbitals of Cr, and in FeS a combination of 3*d* and 4*s*, in ZnS the "valence orbitals" on Zn are 4*s* and the 3*d* electrons behave as "core" electrons. This agrees with expectation [1] and also with the available experimental data: thus Men'shikov and Nemnonov [10] in their study of the $K\beta_5$ X-ray emission bands of various

Cr compounds infer that one component (dominant for CrS) is due to localised, covalent bonds involving $d(t_{2g})$ electrons of the Cr. Bhide *et al.* [11] correlate Mössbauer isomer shifts with Pauling ionicity; the curvature of their plot suggests an especially high $4s$ density for FeS. Hazony [12] has made an especially ambitious attempt to relate Mössbauer isomer shifts to the behaviour of the $3d$ electrons, but his work has been criticised [13] precisely because of his neglect of the influence of the Fe $4s$ orbital.

Many workers have attempted to estimate the atomic charges q in crystalline solids. Kramer and Klein [14] estimate q_M as 0.43 in FeS whereas Nefedow [15] obtained $q_L = -0.71$ for *S* in Fe S and $q_L = -0.66$ or -0.86 for S in ZnS. These results by themselves do not assist greatly in answering the problem of whether Zn S is more or less polar than FeS, but they do suggest that the calculated Löwdin-Daudel atomic charges are reasonable – one would expect a smaller atomic charge on the metal in the solid phase because of its higher coordination number.

We conclude that our calculations strongly support Phillips' and Williams' [1] conjecture as to the changing role of *d*-orbitals across a transition metal series. This is revealed especially clearly in the molecular orbital energy correlation diagrams.

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