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X-ray Emission Spectra and Electronic Structure of the Disulphide Anion

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The $K\beta$ and $L_{2,3}$ X-ray emission bands of the disulphide anion are discussed in terms of a molecular orbital model. The bonding between the sulphur atoms, that is consistent with the spectra, is essentially 3p in character, but 3d orbitals help to stabilise the antibonding π orbitals. 3s orbitals play no significant part in bonding. The weakness of high energy emission bands is consistent with antibonding π-orbital participation in covalent Fe—S_2 bonding. Extensive covalent bonding to the iron atom is also indicated by Mössbauer spectroscopy.

Introduction

In X-ray emission spectroscopy[1] a vacancy is made in an inner orbital of an atom. When the atom relaxes from this excited state the vacancy is filled by an electron from an outer orbital and a quantum of X-radiation is emitted. Valence shell orbitals can be perturbed by chemical bond formation and this can cause corresponding changes in the energy of the emitted X-quantum.[2]

The contribution of an atomic orbital (Φ_r) to a molecular orbital (ψ_i) is indicated in the LCAO approximation by the coefficient a_{ri} in the equation, $\psi_i = \Sigma a_{ri}\Phi_r$ (summation over n possible atomic orbitals).

Now if a p orbital, for example, from atom Z contributes to a variety of molecular orbitals, then the transition to an s vacancy on Z would be possible from all such orbitals but the intensity of the transition would depend upon the size of a_{ri} and the number of electrons in the orbital. The energies of the transitions would depend upon the (molecular orbital - 1s orbital) ionisation energy differences. The effect of chemical combination is to create the possibility of quite a complex emission spectrum, depending upon the bonding inovlvements of particular orbitals. Conversely an investigation of the structure of such peaks can be used in the study of the bonding roles of atomic orbitals.

In this paper the disulphide anion of iron pyrites is studied in some detail. Since this is an ionic compound with discrete S_2^{2-} anions a molecular orbital model should provide a fairly clear interpretation of the X-ray emission spectra although some features of the spectra might well be due to Fe^{2+}, S_2^{2-}-interactions.

Experimental Section

All possible X-ray emission spectra from sulphur in the disulphide anion of FeS_2 were recorded. These are the $K\alpha_{1,2}$ ($2P_{3/2,1/2} \rightarrow 1S_{1/2}$) the $K\beta$ ($3P_{3/2,1/2} \rightarrow 1S_{1/2}$) and $L_{2,3}$ ($3D_{5/2,\,3/2}$ and $3S_{1/2} \rightarrow 2P_{3/2,\,1/2}$) spectra. Because of the wide differences in energy between the K and L photons, two different spectrometers were used. The $L_{2,3}$ emission band was measured using a concave grating spectrometer which has been described in detail elsewhere[3]. The grating has 600 lines per mm and a radius of 2m. The blaze angle is 1° 31′ and the angle of incidence 85°. A Bendix M 306 photomultiplier was used as a detector. The average resolution of the instrument was 0.9 eV. Spectra were excited by direct electron bombardment (3kV, 1.5 mA). Vacuum conditions within the spectrometer were 10^{-6} torr and about 10^{-7} torr within the X-ray tube. During the course of the experiments no changes in intensity distribution were found, indicating that the iron pyrites did not decompose under the influence of the electron impact.

The sulphur $K\alpha_{1,2}$–doublet and the $K\beta$–emission band were measured[4] using a vacuum spectrograph of the Johann type[5]. The photographic plates were re-evaluated by the present authors. The diffracting crystal was quartz $(10\bar{1}1)$ bent to a logarithmic spiral of about 1m radius giving an average dispersion of 5.0 XE. mm^{-1} or 2.2 eV. mm^{-1} for the $K\alpha$ lines and 6.0 XE. mm^{-1} or 3.0 eV. mm^{-1} for the $K\beta$ emission band. A reflecting area of 10×40 mm^2 was used. The crystal was maintained at a temperature of 30 ± 0.03°C throughout the experiments.

The measurements were performed using radiation from a copper X-ray tube (12kV, 120 mA) and photographic – photometric registration. The overall resolution is about 0.8 eV; the instrumental window

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(1) A. H. Compton and S. K. Allison, « X-ray in Theory and Practice », Van Nostrand, New York, 1963; D. S. Urch, *Quart. Rev.*, 1971, *25*, 343.

(2) D. S. Urch, *J. Phys. Chem., Solid. State Phys.*, 1970, *3*, 1275.

(3) G. Weich, *Z. Physik*, 1966, *193*, 490.

(4) W. Koppen, unpublished results - Diplomarbeit, Univ. of Munich, 1967.

(5) H. H. Johann, *Z, Physik*, 1931, *69*, 185.

being 0.4 and the width of the sulphur 1s level 0.36 eV[6].

Results

The results for the sulphur Kβ and $L_{2,3}M$ emission bands are shown in Figure 1. The low energy tail and some of the breadth of the peaks in the $L_{2,3}$ spectrum is due to Auger broadening of the lower-lying energy levels. A further reason for broad $L_{2,3}$ peaks is the nearness in energy (∼ 1.1 eV) of the two possible vacancy states, $2P_{3/2}$ and $2P_{1/2}$-transitions to these states are not resolved one from another. The energy of the sulphur $K\alpha_1$ line has been used to relate the Kβ and $L_{2,3}$ spectra, (S $K\alpha_1$, 5360.99XE = 2307.86 ± 0.02 eV; S $K\alpha_2$, 5363.60 XE ≡ 2306.72 ± 0.01 eV). The sulphur $K\alpha_{1,2}$ doublet in S_2^{2-} is shifted to longer wavelengths by 0.11 XE (−0.05 eV) by comparison with the element (S_8).

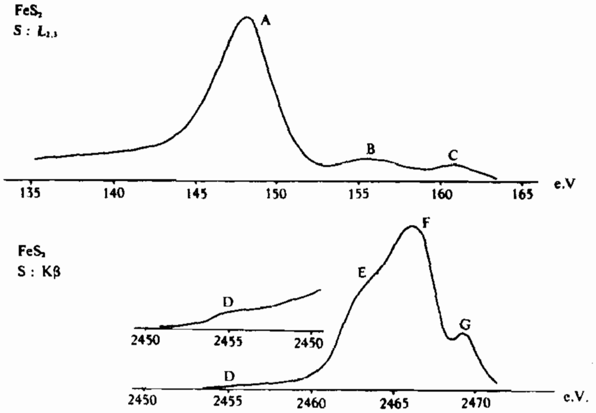

Figure 1. Sulphur X-ray emission spectra from iron pyrites. Upper curve $L_{2,3}$ and lower curve K spectra. Vertical scale in arbitrary units. Inset shows D region, Kβ′, with vertical scale amplified.

Molecular Orbital Model. In order to interpret this data a molecular orbital energy level diagram should be constructed. This has been attempted in Figure 2. The interactions between the valence shell atom orbitals of the two sulphur atoms are considered in two stages. In the first stage molecular orbitals are formed from 3s, 3p, and 3d orbitals independently and classified according to the irreducible representations of the disulphide point group $D_{\infty h}$. The amount of interaction between 3s–3s and 3p–3p orbitals indicated in the Figure for stage 1 has been arranged to agree with the X-ray emission spectra. One main peak only is found in the $L_{2,3}$ spectrum. This indicates that 3s character is not widely spread through many orbitals and that the two molecular orbitals (i) and (ii) where most 3s character is concentrated are not widely separated in energy. On the other hand the Kβ structure extends over about 10 electron volts with considerable intensity. This suggests much stronger interactions between 3p orbitals and this has been indicated in the Figure. This Figure is essentially qualitative and is intended to show the general features of the bonding rather than quantitative ionisation energies. In the second stage interactions are considered between stage 1 molecular orbitals belonging to the same irreducible representations.

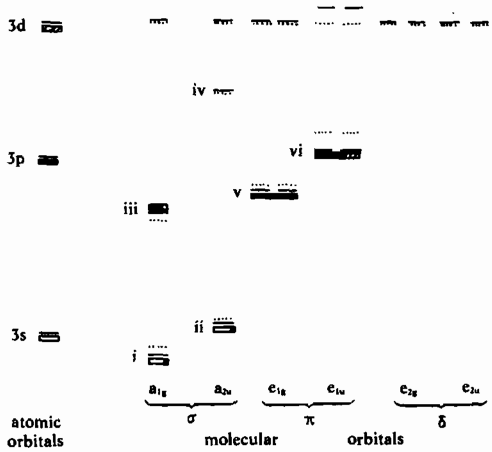

Figure 2. Qualitative molecular orbital energy level diagram for the S_2^{2-} anion. Stage 1 orbitals (see text) are indicated by ....., stage 2 orbitals by —. An indication of atomic orbital contribution to occupied molecular orbitals is given using the symbols 3s ▭ , 3p ■ , 3d ▨ . Most tightly bound orbitals are at the bottom of the diagram.

The interactions between the "3p" and "3s" molecular orbitals of a_{1g} symmetry will be greater than between those of a_{2u} symmetry because they are closer in energy. Thus a greater 3p contribution will be found in m.o. (i) than in (ii). A small 3s contribution will be found in (iii), equivalent to the 3p contribution to (i). The possibility of 3d interaction may be considered in the same way. The anti-bonding π orbitals e_{1g} will be nearer in energy to 3d molecular orbitals of the same symmetry than the bonding π orbitals e_{1u}. The greatest amount of 3d character is therefore to be anticipated in orbitals (vi). The effect of 3d interaction is to make (vi) less anti-bonding, thereby helping to stabilise the anion. Other 3d interactions in other symmetry classes have been ignored, either because the energy difference between the molecular orbitals was too great or because no symmetry partners are available (e_{2g} and e_{2u}).

Discussion

Using this diagram it is now possible to interpret the X-ray emission spectrum of the disulphide anion. The main Kβ peak (F) will be due to the four electrons in (v) and low energy shoulder (E) to the two electrons in (iii). The small 3s component of (iii) gives rise to the weak peak B in the $L_{2,3}$ spectrum. The small 3p contribution to (i) is seen as the weak low energy Kβ′ satellite D. It is interesting to observe that this peak lies directly under A. This is just what would be expected if A were a composite peak from orbitals (i) and (ii). Peaks C($L_{2,3}$) and G(Kβ)

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[6] L. G. Parratt, *Rev. Mod. Phys.*, 1959, *31*, 616.

are related vertically in Figure 1 and are therefore associated with the same molecular orbital (vi). This demonstrates experimentally the 3d character anticipated in the discussion above. Whether the 3d contribution is so large as to explain the low intensity of F is uncertain (3d participation in (vi) cannot be estimated by comparison with A and B since the intensity integrals involving 3s and 3d orbitals will be different). It seems more reasonable to suggest that some covalent bond formation takes place between Fe^{2+} and S_2^{2-}. Since it will be the least tightly bound orbitals in S_2^{2-} that will contribute most readily the electron density around the sulphur atoms in (vi) will be diminished. Transitions C and F would therefore be weakened in intensity. Covalent bond formation, by taking electrons from an anti-bonding orbital, will also stabilise the S_2 anion.

The possibility of covalent bonding between iron and sulphur can also be investigated by Mössbauer spectroscopy ($\delta = +0.5$ mm sec^{-1}). Walker *et al.*[7] placed FeS_2 on the ferric curve in such a position as to require an isolated Fe^{3+} ion. However there is no reasonable evidence to support the necessary corrollary of S_2^{3-}. It is more reasonable to assume that the iron is basically in the ferrous state. Using Walker's curves it is then necessary to postulate about 40% of an electron in the 4s orbital. Danon's[8] revised correlations would require about 60% of a 4s electron whilst if Goldanskii's[9] interpretations are followed a whole electron should be present in the Fe4s orbital of iron pyrities. Clearly, whichever is correct, the Mössbauer evidence strongly supports the idea of considerable electron donation (*i.e.* covalent bond formation) from the S_2^{2-} anion to Fe^{2+}.

Simple molecular orbital theory thus provides a satisfactory framework for the discussion and interpretation of the X-ray emission spectra of disulphide. The data also provides a most interesting insight into the bonding rôles of the various sulphur orbitals. 3s orbitals are seen to be essentially non-bonding. This is in accord with other indirect arguments about the bonding potential of these orbitals. The bond angle H_2S (92°)[10] for example has long been held as evidence that the sulphur bonding in this molecule is essentially p in character. Also the supposed reluctance of 3s orbitals to enter into strong chemical bonds has been used as the basis of an argument suggesting a rather important bonding rôle for 3d orbitals in oxy-anions.[11] The result obtained in this work on disulphide provides experimental confirmation of these ideas. The bonding in the anion is mostly 3p in character in both σ and π bonds but some 3d participation is found.

(7) L. R. Walker, G. K. Wertheim and V. Jaccarino, *Phys. Rev. Lett.*, 1961, *6*, 98.

(8) J. Danon « Applications of the Mossbauer Effect in Chemistry and Solid State Physics ». Tech. Report Series No. 50, page 89. Published by International Atomic Energy Agency, Vienna, 1966.

(9) V. I. Gol'dankii, « The Mossbauer Effect and its Applications Chemistry », English translation published by Consultants Bureu, New York, (1964).

(10) H. C. Allen and E. K. Plyler, *J. Chem. Phys.*, 1956, *25*, 1132.

(11) D. S. Urch, *J. Inorg. Nucl. Chem.*, 1963, *25*, 771.