

HIGH RESOLUTION X-RAY FLUORESCENCE SPECTROSCOPY
A POTENTIALLY USEFUL TECHNIQUE FOR CHEMICAL BONDING STUDIES
IN FOSSIL FUELS

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Introduction

One of the key problems in fossil fuel analysis is the determination of various functional groups associated with C, N, S, and O atoms. While a number of analytical techniques have been utilized to accomplish this objective, to date none of these techniques provide bulk information in a non-destructive manner. Thus, for example, when photoelectron spectroscopic methods are used in a non-destructive mode, because of the nature of the photoelectron escape depth ($\sim 10 \text{ \AA}$), they provide useful information only about surface composition. In order to get bulk analysis with these techniques, it is necessary either to average a large quantity of surface data by running different samples, or to destroy the sample, layer by layer, and average the resultant data. Of course, any sort of surface layer destruction is bound to alter the sample and provide inaccurate chemical bonding information. Mass spectrometric methods, which constitute another way of studying coal samples, are destructive by nature and do not yield totally reliable answers.

Aside from the above considerations, another problem presents itself if one considers coal to be an ensemble of randomly variable huge macromolecules. The size of the macromolecule by itself guarantees that the valence electron structure will be very complex, i.e., that there is a "forest" of valence molecular orbitals. Consequently, any spectroscopic technique which provides only a single valence electron spectrum per molecule is practically useless. It is, for this reason that UV absorption, UV and X-ray valence photoelectron spectroscopies are not effectively useful in coal functional group analysis. What is needed is a spectroscopic method which is able to provide different views of a complex "forest" of valence molecular orbitals. While it is certainly correct to say that X-ray core photoelectron spectroscopy provides some useful information because for each kind of atom (with $Z \geq 3$) there exists at least one specific and characteristic core photoelectron signal, it is equally true that the correlation between core photoelectron shifts due to changes in valence electron structure are not always readily decipherable in the case of large organic macromolecules.

It is the objective of this paper to present X-ray fluorescence in a new role at high optical resolution, namely, as a potentially useful tool for a direct determination of the valence electron structures around the different kinds of atoms of interest. Stated somewhat differently, it will be shown that XFS is an atomic probe to sample molecular valence electron structure, and because of the very nature of this probe, the complex "forest" of molecular orbitals becomes more decipherable than with any other technique.

Theory and Background Information on Pure Substances

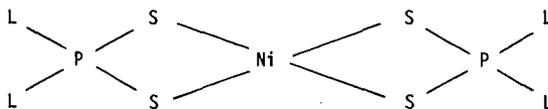
While Urch (1) has recently reviewed the overall capabilities of XFS for chemical bonding studies, his review did not direct the reader toward the analytical

possibilities of this technique. Thus, it appears to be useful to show how molecular XFS "works." Figure 1 is a comprehensive view of the energy level diagram of a hypothetical diatomic molecule A-B, where both atoms A and B have filled core levels, K, L₁, L₂, L₃, and where the molecule AB possesses a manifold of filled molecular orbitals ψ_i 's and a manifold of unfilled (antibonding) ψ_i 's. The various spectroscopic techniques are illustrated by appropriately labelled arrows, with each arrow representing a typical one-electron transition. Besides XFS, XPS (X-ray photoelectron spectroscopy), XAS (X-ray absorption spectroscopy), UAS (ultraviolet visible absorption spectroscopy) and UPS (ultraviolet photoelectron spectroscopy) transitions are shown.

As stated before, one of the fundamental differences between XFS and other spectroscopic methods used for electronic structural studies of molecules is that with all of the other methods one obtains a single spectrum per molecule. If one were interested in studying the valence electron structure of 10-thioxanthone (a likely constituent to be found in coal) by UAS, UPS, and XPS, each of the techniques would yield a single valence electron spectrum. Using XFS a carbon K emission spectrum, an oxygen K emission spectrum, as well as sulfur K and sulfur L emission spectra, can be obtained.

With XFS not only is there a heteroatom capability and possibly even multiple spectra per each heteroatom, but also electric dipole selection rules provide additional simplification in case the symmetry is high enough. Simplified spectra are obtained especially if the core vacancy is on an atom with a centro or pseudo centrosymmetric position.

The use of XFS to determine the position and type of heteroatom has enormous practical analytical consequences (2-5). If the core vacancy is on a central atom, and if the valence electron charge density is sufficiently localized, then XFS can be used for ligand identification. Thus, if the central atom A is in a 4-fold coordination with ligands L₁, L₂, L₃, L₄ and if L₁ = L₂ = L₃ = L₄, namely, A-(L₁)₄ but it is changed to L₂-A-(L₁)₃, then the XFS spectra will reflect this substitution of L₂ for one of the L₁-s by showing a new transition. Note that the ligands can be atoms or molecular fragments. Additional examples were studied by Whitehead (6). The central atom in this case was sulfur and S-K β spectra were obtained for Na₂SO₄, KHSO₄, Na₂SO₃, NaHSO₃, KC₂H₅SO₄, (C₄Hg)₂SO₂, (CH₃C₆H₄)₂SO₂, and C₆H₅SO₂NH₂. Typical examples are shown in Figures 2 through 5. Identical capability is achieved when the core vacancy is on a pseudo-central atom. The PK β spectrum of a large molecule of the type II shows individual transitions that correspond to the



II

different ligands as the ligand is changed from -OCH₃, to OC₂H₅, to CH₃ to C₂H₅. What is significant is that it is possible (4,5) to identify "fingerprint" transitions of the type: P_{p3}-S_{3p}; P_{3p}-S_{3p}; P_{3p}-O_{2p}C_{2p}; P_{3p}-O_{2p}C_{2p}C_{2p}; P_{3p}-C_{2p}; P_{3p}C_{2p}-C_{2p}; P_{3p}-O_{2s}; P_{3p}-C_{2s}.

Another interesting and unique aspect of using XFS as an atomic probe to characterize valence electron structure can be illustrated when the initial state core vacancy is on a ligand atom which itself is attached to a ring system. This was demonstrated by Whitehead (6,7). The Cl-K β spectra of p-chloroaniline, p-dichlorobenzene, and p-nitrochlorobenzene were different precisely because of the difference in the electron donating and withdrawing powers of the -NH₂, -NO₂, and -Cl functional groups. Equally interesting was Whitehead's demonstration of the ability of XFS as a ligand atom probe to differentiate among the o,m-, and p-chlorobenzoic acid isomers by studying the Cl-K β emission spectra.

It is appropriate to indicate the power of XFS as a heteroatom probe when studying sulfur bearing heterocycles since several types are present in coal. Phillips (8) studied the S-K β spectra of 19 different sulfur-bearing heterocycles which included thiophene, saturated sulfur heterocycles, various mono- and di-substituted thiophenes and a few heterocycles containing both sulfur and nitrogen. Figure 6 shows the S-K β spectrum of thiophene. Accordingly, there are several prominent features, namely, band A at 2456 eV corresponding to a transition from a σ bond of S(3p_x)-C(2s) character, band B at 2460 eV reflecting σ bonding of S(3p_y)-C(2p)-C(2p) character, band C around 2464 eV reflecting π bonding with S(3p_z)-C(2p_z) as well as S(3p_y)-C(2p_y) character, band D at 2466 eV reflecting π S(3p_x)-C(2p) σ bond, and the only sharp band E at 2468 eV corresponding to the nonbonding S(3p_z) orbital. In reality each of the broad bands A, B, and C involve several unresolved transitions, and the lack of resolution is primarily due to the initial state--S-K level broadening.

In going from thiophene to the other heterocycles, the overall pattern in terms of the number of bands and the relative positions of the bands remains the same. This should not be too surprising since the basic C-S-C structure is retained. The relative peak heights for bands A and B also remain the same. However, in going from an unsaturated to a saturated sulfur heterocycle, inserting a nitrogen into the ring system, or using dichloro substitution in the ring, the amount of S-3p character in molecular orbitals corresponding to transitions C, D, and E is altered. For the spectra of thiophene and tetrahydrothiophene (Figure 7), the integrated intensity ratio of D/E changes from 1.4 to 0.8. The introduction of a nitrogen atom in the ring, or dichloro substitution causes the D/E ratio to decrease to 0.9.

When the immediate environment of S is drastically altered from C-S-C to C-S-N as in isothiazole (Figure 8), or to N-S-N as in 2,1,3 - benzothiadiazole, then new bands appear, corresponding to C(2p)-S(3p)-N(2p) or N(2p)-S(3p)-N(2p) bonding, etc. The D/E intensity ratio for saturated sulfur heterocycles is in the range of 0.7 to 0.8, and since for unsaturated sulfur heterocycles this ratio is in the range of 1.2 to 1.4 with the exact value depending upon the nature of the substituent, it appears that this ratio gives a reliable value for the relative amount of saturated sulfur heterocycles. The introduction of one or more nitrogen atoms adjacent to S drastically alters the S-K β spectra and the S-N and N-S-N functional content also appears to be discernible. Consequently, it appears that there may be several useful analytical capabilities attainable from the S-K β emission spectra of sulfur heterocycles.

Another problem in electron structural studies is to examine whether or not a particular technique is capable of distinguishing between different kinds of carbon-oxygen bonding. This area was investigated by Burkard and Kim (9,10). The following substances were studied by Burkard: p-benzoquinone (PBQ), anthraquinone (AQ), acridone (ACR), acenaphthalenequinone (ANQ), and phenanthrenequinone (AQ). The oxygen K α spectra of all of the quinones show three basic features, namely, an intense and relatively sharp band around 527 eV corresponding to transitions from lone pair (lp) orbitals, a relatively diffuse and broad π band region about 2 eV below the lp peak, plus a very broad and diffuse σ region around 522 eV. There are significant differences in all of the spectra. For ACR the lone pair peak, probably due to the presence of the N heteroatom causes a low energy shift for the lone pair lp band. Moreover, the widths of the lp bands as well as their contours seem to provide useful lp-lp interactions. One of the more obvious lp-lp interactions, as illustrated in Figures 9 and 10, is due to ortho vs. para positions of the oxygen atoms yielding a very broad lp band for ANQ as compared with AQ. There appears to be some limited analytical potential in using O-K α emission spectra to distinguish among various quinones.

Kim's C-K α and O-K α studies included lithium carbonate, urea, lithium acetate, magnesium oxalate, and squaric acid. The spectra for the latter three are illustrated in Figures 11-13. According to the spectra, it appears that when there is a monocarboxylic acid (LiAC) as compared with a dicarboxylic acid, the halfwidth of the lone pair band A is considerably narrower. Thus, the halfwidth of the lone pair may be a useful tool for differentiating between mono and polycarboxylic

acids. Finally, as shown in Figure 13 for squaric acid, XFS can differentiate between C=O and C-OH functional groups (see bands A vs. A' and D vs D', respectively, in the O-K emission spectrum).

Instrumentation and Experimental Procedures

All of the S-K β , Cl-K β and P-K β spectra were obtained on a double crystal instrument developed by Andermann's group at the University of Hawaii (11). This instrument represents the addition of a second crystal to a standard Norelco vacuum emission spectrograph. Using calcite crystals, the instrumental broadening was about 0.7 eV. Spectra taken on this instrument were obtained point by point typically in 2 to 4 hours.

All of the O-K α and Cl-K β spectra were obtained on a 5M focal length grating spectrometer also developed by Andermann's group (12-14). The instrumental resolution at O-K α can be as low as 0.05 eV, and at C-K α , as low as 0.02 eV. These resolution limits are not achievable with the present photographic and scanning photoelectric detection methods, but the use of position sensing detection, etc. should allow the utilization of the instrument at the high resolution limits with exposure times well below 1 hr. (15).

With the double crystal spectrometer, helium was used to allow optical transmission, but with the grating spectrometer, vacuum has to be employed for O-K α and C-K α studies. It should be noted, that with the grating spectrometer a sample chamber pressure of 10^{-2} torr is adequate. Cryogenic sample handling currently under development will allow the irradiation and analysis of samples, such as coal, which contain volatile compounds.

Discussion of Analytical Capabilities for Functionality Characterization

While it may be premature to assert with any degree of certainty the potential analytical capabilities of XFS for characterizing the nature and amount of different functional groups, a few generalizations are in order. Judging from the position of the oxygen lone pair peaks in squaric acid, it should be feasible to distinguish between -C=O and -C-OH groups. In the case of carboxylic acids the C-K emission is highly simplified and the halfwidth of the lone pairs should provide a handle on the presence and quantity of mono or polycarboxylic acids. An unsaturated ring system provides a unique C $_{2p}$ -C $_{2p}$ π band, and conceivably, the integrated intensity might yield useful information about the extent of unsaturation. XFS to determine sulfur functionality, as discussed before, appears to provide a unique capability in determining the degree of saturation in the sulfur heterocyclic substances, as well as the capability in determining the nature of the atoms directly linked to the sulfur atom.

While the above fundamental studies appear to be encouraging, clearly it will be necessary to evaluate directly the analytical capabilities of XFS for coal characterization. Preliminary studies are currently under way.

Acknowledgement

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References

1. Urch, D.S., X-ray Emission Spectroscopy, "Electron Spectroscopy, Theory, Techniques and Application," Acad. Press, N.Y. 3, 1-39 (1979).
2. Myers, K., M.S. Thesis, University of Hawaii (1972).
3. Myers, K., Andermann, G., Chem. Comm. 16, 934 (1972).
4. Myers, K., Andermann, G., J. Phys. Chem. 76, 3915 (1972).
5. Myers, K., Andermann, G., J. Phys. Chem. 77, 280 (1973).

6. Whitehead, H.C., Ph.D. Dissertation, Univ. of Hawaii (1975).
7. Whitehead, H.C., Andermann, G., J. Phys. Chem. 378, 2592 (1974).
8. Phillips, D., Ph.D. Dissertation, University of Hawaii (1976).
9. Burkard, F., M.S. Thesis, University of Hawaii (1981).
10. Kim, R., M.S. Thesis, University of Hawaii (1986).
11. Whitehead, H.C., Layfield, J., Andermann, G., Rev. Sci. Instr. 43, 50 (1973).
12. Andermann, G., Bergknut, L., Karras, M., Griesehaber, G., Spectr. Letters, 11 (8) 571 (1978).
13. Andermann, G., Bergknut, L., Karras, M., Griesehaber, G., Rev. Sci. Instr. 51 (6), 814 (1980).
14. Andermann, G., Burkard, F., Kim, R., Fujiwara, F., Karras, M., Spec. Letters, 16 (12), 891 (1983).
15. Andermann, G., Kim, R., Burkard, F., AIP Conf. Proceed. 75, 309 (1981).

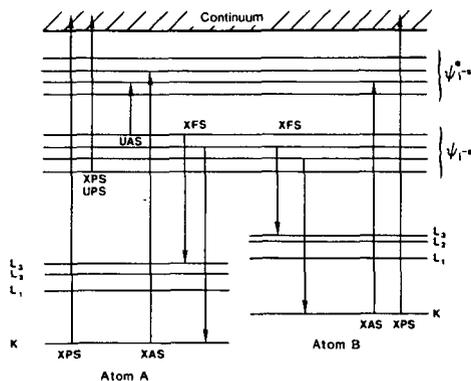


FIGURE 1. Energy Level Diagram For Diatomic Species A-B.

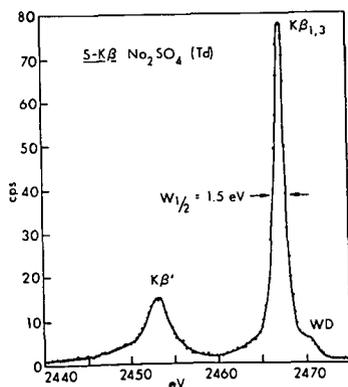


FIGURE 2. S-K β Spectrum of Na₂SO₄.

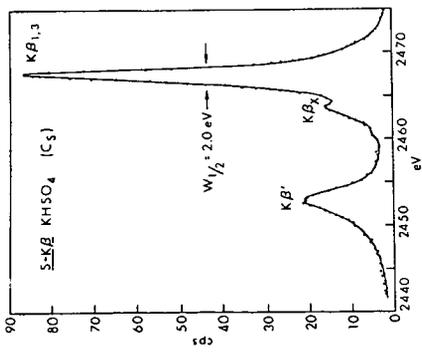


FIGURE 3. S-K α Spectrum of KHSO $_4$.

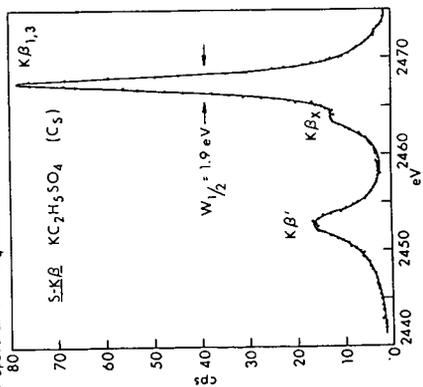


FIGURE 4. S-K α Spectrum of KC $_2$ H $_3$ SO $_4$.

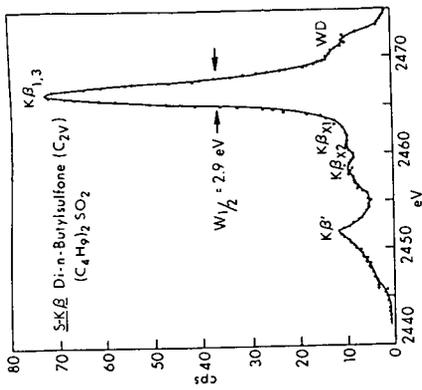


FIGURE 5. S-K α Spectrum of Di-n-Butylsulfone.

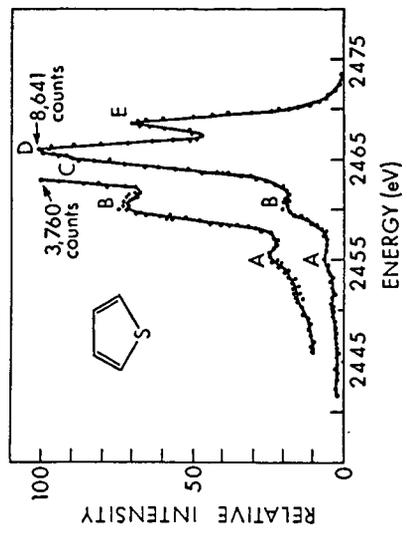


FIGURE 6. S-K α Spectrum of Thiophene.

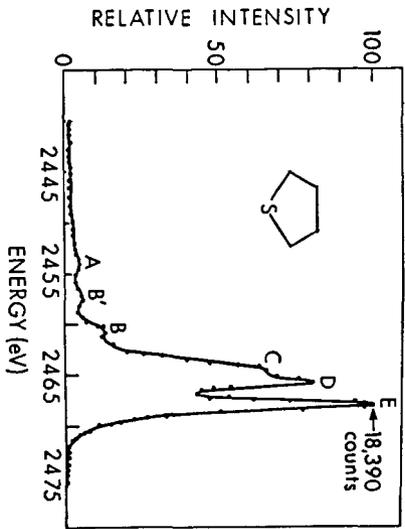


FIGURE 7. S-K α Spectrum of Tetrahydrothiophene.

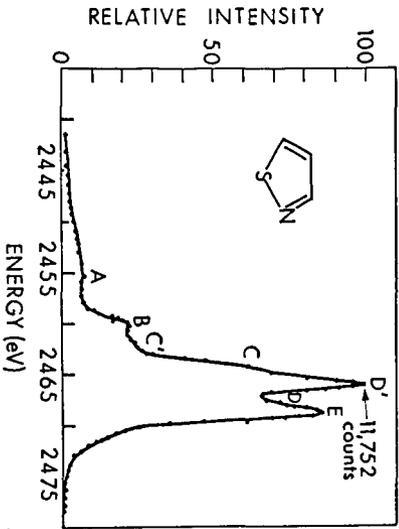


FIGURE 8. S-K α Spectrum of Isothiazole.

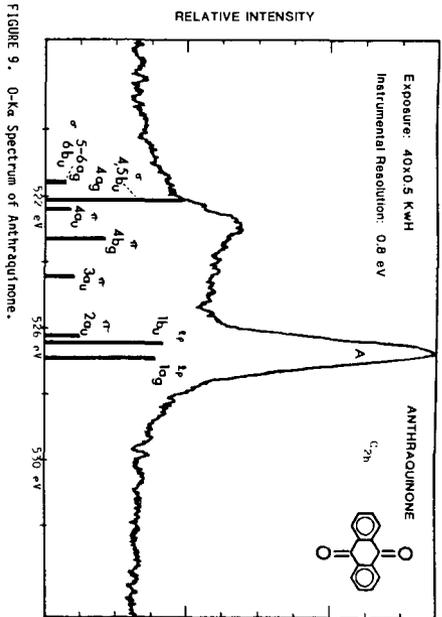


FIGURE 9. O-K α Spectrum of Anthraquinone.

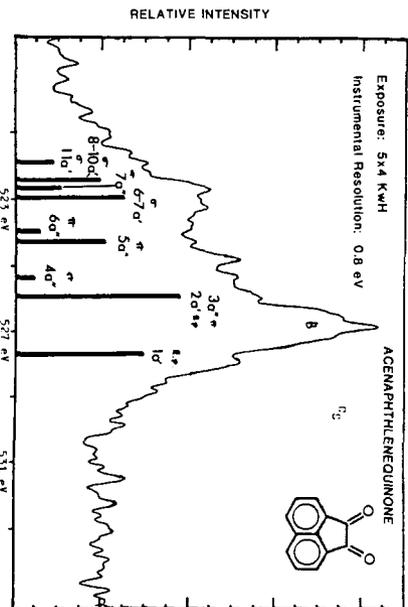


FIGURE 10. O-K α Spectrum of Acenaphthenequinone.

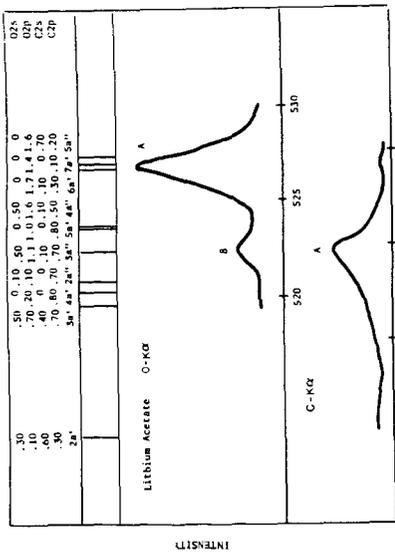


FIGURE 11. Lithium Acetate Combined Spectra of Oxygen K and Carbon K.

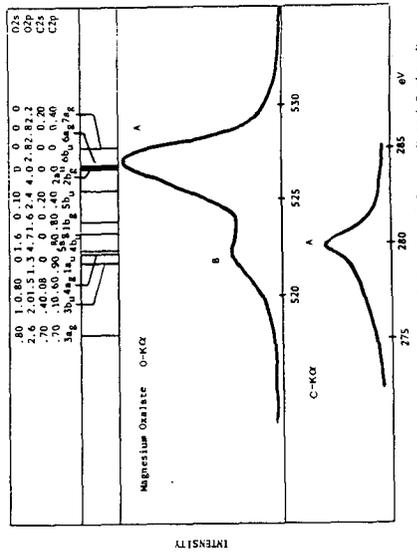


FIGURE 12. Magnesium Oxalate Combined Spectra of Oxygen K and Carbon K.

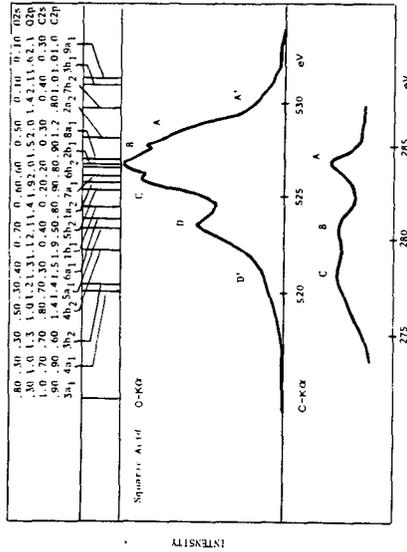


FIGURE 13. Squaric Acid Combined Spectra of Oxygen K and Carbon K.