

EXAFS INVESTIGATION OF ORGANIC SULFUR IN COAL

G. P. Huffman*, F. E. Huggins*, N. Shah*, D. Bhattacharyya*,
R. J. Pugmire**, B. Davis+, F. W. Lytle++, and R. B. Greggor++.

*University of Kentucky, 401 Patterson Office Tower,
Lexington, KY 40506; **University of Utah,
Fuel Science Department, Salt Lake City, UT 84112;
+Kentucky Energy Cabinet Laboratory, Lexington, KY 40512;
++The Boeing Company, Seattle, WA 98124

ABSTRACT

EXAFS spectroscopy is shown to be a very promising technique for investigating the molecular structure of organically bound sulfur in coal and coal derivatives. The current paper presents sulfur K-shell EXAFS results for a number of a maceral separates prepared by density gradient centrifugation and for several biodesulfurized coals. Both the near-edge structure and the radial structure functions exhibit some similarities to dibenzothiophene. However, a broad peak occurs in the XANES region of the coal spectra that is not observed for the molecular structures usually ascribed to organic sulfur in coal. This is believed to arise from resonant photoelectron scattering from second and third nearest neighbor carbon shells and from sulfur bonded to oxygen.

Introduction

Numerous techniques are available for investigating the structure of the inorganic forms of sulfur in coal and coal derivatives. These include ^{57}Fe Mössbauer spectroscopy,^(1,2) computer-controlled scanning electron microscopy,^(3,4) and x-ray diffraction,^(5,6) to mention a few. The development of techniques to determine the structural forms of organic sulfur, however, has proven more difficult. Recently, it has been demonstrated that X-ray absorption fine structure spectroscopy, usually referred to as EXAFS spectroscopy, is a very promising method for investigating the molecular structure of organic sulfur in coal.^(7,8) In this article, some recent EXAFS results obtained from maceral separates and other samples containing little or no pyrite are summarized.

Experimental Procedures

EXAFS spectroscopy provides information on the electronic bonding and atomic environment of an element through detailed analysis of the fine structure associated with an X-ray absorption edge of that element. When a synchrotron radiation source is used, individual elements can be investigated at dilute levels (~ 100 ppm to 1%) in complex samples. The current experiments were conducted during a dedicated run at the Stanford Synchrotron Radiation Laboratory using wiggler beam-line VII-3. Electron energies were 3 GeV and beam currents were typically 40 to 80 mA. A Si(111) double crystal monochromator was used to vary the X-ray energy from approximately 100 eV below to 600 eV above the sulfur K-shell absorption edge (2472 eV). To minimize absorption of these relatively soft X-rays, an all helium pathway from the beam pipe to the sample and detector was constructed and thin (6 μ m) mylar windows were used wherever possible. The experiments were done in the fluorescent mode, using a fluorescent ionization detector described elsewhere.⁽⁹⁾

Most of the samples examined were maceral separates prepared by density gradient centrifugation (DGC). Discussions of the DGC methods are given elsewhere.⁽¹⁰⁻¹²⁾ EXAFS measurements were made on exinite, vitrinite and inertinite separates from coals of several ranks. In addition to maceral separates, several coals from which all pyrite had been removed by biological desulfurization⁽¹²⁾ were examined. The EXAFS specimens were prepared in the form of pellets by hydrostatically pressing the coal powder into a boric acid cylinder or, in some cases, adding an epoxy binder.

Results and Discussion

EXAFS spectroscopy determines the electronic structure and atomic environment of an element by analysis of the fine structure associated with an X-ray absorption edge of that element. The spectra are normally divided into two regions. The region within about 20 to 50 eV of the absorption edge is called the X-ray absorption near edge structure, or XANES (see Figures 1 and 2). The peaks and other structure in this region are derived primarily from two sources: photoelectron transitions to vacant, bound levels,^(13,14) and low-energy scattering resonances.⁽¹⁵⁻¹⁷⁾ The XANES spectra are quite sensitive to the detailed nature of the electronic bonding and can frequently serve as fingerprints to identify different compounds or types of binding.

The extended X-ray absorption fine structure, or EXAFS, is the oscillatory structure that begins at 30 to 50 eV above the edge and extends to fairly high energies (~ 500 to 1000 eV). These oscillations arise from interference between the outgoing and backscattered photoelectron wave functions. They can be subjected to a Fourier transform analysis to yield a radial structure function (Figure 3) from which interatomic distances and coordination numbers for the atomic neighbor shells of the absorbing atoms can be determined.^(18,19)

Typical sulfur K-shell EXAFS data are shown in Figures 1 to 3. The XANES of several standard compounds appear in Figure 1. The zero of energy is taken at the first peak in the differential of the spectrum of elemental

sulfur. The first large peak in the XANES, the so-called "white line", probably arises from a transition of the photoelectron from the 1s level to hybridized p levels - 3p/3d-4s for pyrite and 3p/2p for the remaining compounds. The subsequent broader peaks, located between approximately 5 and 30 eV for pyrite and dibenzothiophene (dbt), and from 15 to 40 eV for the sulfur-oxygen bonded compounds, probably arises from low energy scattering resonances.(15-17) It is evident that the increase in valence of the sulfur ions bonded to oxygen in sulfosalicylic acid and ferrous sulfate causes a significant positive shift in the white line and other XANES features.

XANES spectra of several maceral separates from a high volatile bituminous coal (PSOC 733, HVAB, Appale, PA) are shown in Figure 2. The first two peaks, which are relatively sharp, occur at the same locations and have similar intensities to the corresponding peaks in the XANES of dbt. Presumably, they represent s \rightarrow p transitions characteristic of an aromatically bound sulfur atom. Thianthrene, however, which contains two aromatically bound sulfurs, exhibits only the first of these two sharp peaks, at approximately 3 eV. This could reflect the increase in symmetry of the sulfur sites in thianthrene.

The broad peak at 10-11 eV was observed for all coal specimens examined, but was not present in the XANES of any standard compounds in which S is bonded to C and H. It is in approximately the same location as the strong white line in the XANES of the standard compounds that contain S bonded to O (sulfosalicylic acid and various sulfates). Consequently, sulfur oxidation may be partially responsible for this feature. However, it is seen in Figure 1 and Table I than sulfur-oxygen bonded species also exhibit significant secondary XANES structure between 20 and 30 eV that is not evident in the coal spectra. It seems likely, therefore, that low energy resonant scattering of the photoelectron by second and third neighbor shells may be the primary origin of the broad peak at 10-11 eV. As discussed elsewhere,(15-17) the position of such scattering peaks can be related to interatomic distance. It has previously been noted(16,17) that an $ER^2 = \text{constant}$ relation frequently holds for such XANES features, where E is the energy at which the peak occurs and R is the distance from the absorbing atom to the neighbor shell which gives rise to the scattering resonance. Dependent on what reference point the peak energy is measured from, the effect of phase shifts on the E - R relation, and multiple versus single scattering, distances of approximately 2.5 to 4 Å could be compatible with the peak in question. Work is now in progress to establish suitable energy vs. distance calibration curves from analyses of the XANES of various standard sulfur compounds.

Typical radial structure functions (RSF's) produced by Fourier transformation of the EXAFS of maceral separates are shown in Figure 3. It appears that two atomic shells, and possibly three, can be resolved. Assuming that the atoms surrounding the sulfur in coal are primarily carbons, the standard back transform analysis of the RSF peaks was carried out using an empirical S - C phase shift determined from the EXAFS data for dbt. The interatomic distances determined in this manner seem reasonable (Table II).

Conclusions

The current results demonstrate that EXAFS spectroscopy is an excellent method for direct, non-destructive, investigation of the molecular structure of organic sulfur in coal. Future studies will concentrate on development of calibration relationships for interpretation of the XANES, and conducting in situ studies of the changes in sulfur structure resulting from pyrolysis, hydrogenation, and oxidation.

Acknowledgements

This research was sponsored by the Department of Energy under DOE Contract No. DE-FG22-86PC90520, and under DOE Contract No. DE-FC22-86PC90017. The latter contract supports the research program of the Consortium for Fossil Fuel Liquefaction Science. We would also like to acknowledge the staff of the Stanford Synchrotron Radiation Laboratory, sponsored by DOE.

References

1. G. P. Huffman and F. E. Huggins, *Fuel* **57**, 592 (1978).
2. F. E. Huggins and G. P. Huffman, in: *Analytical Methods for Coal and Coal Products*, Vol. III, Chapt. 50, pp. 371-423, Ed., C. Karr, Jr., Academic Press, 1981.
3. F. E. Huggins, D. A. Kosmack, G. P. Huffman, and R. J. Lee, *Scanning Electron Microscopy/1980/I*, 531-540, SEM Inc., AMF O'Hare, Chicago, IL.
4. F. E. Huggins, G. P. Huffman, and R. J. Lee, in: *Coal and Coal Products: Analytical Characterization Techniques*, ACS Symposium Series **205**, Ed., E. L. Fuller, Jr., pp. 239-258, Amer. Chem. Society., 1982.
5. R. G. Jenkins and P. L. Walker, Jr., in *Analytical Methods for Coal and Coal Products*, Vol. II, Chapt. 26, pp. 265-292, Ed., C. Karr, Jr., Academic Press, 1978.
6. C. Prosada Rao and H. J. Gluskoter, *Illinois State Geol. Survey Circ.* No. 476, 1973, 56 pp.
7. C. E. Spiro, J. Wong, F. Lytle, R. B. Greeger, D. Maylotte, and S. Lampson, *Science* **226**, 48-50, 1984.
8. G. P. Huffman, F. E. Huggins, N. Shah, D. Bhattacharyya, R. J. Pugmire, B. Davis, F. W. Lytle, and R. B. Greeger, in *Processing and Utilization of High Sulfur Coals II*, Eds. Y. P. Chough and R. D. Caudle, pp. 3-12, Elsevier, 1987.
9. F. W. Lytle, R. B. Greeger, D. R. Sandstrom, E. C. Marques, J. Wong, C. L. Spiro, G. P. Huffman, and F. E. Huggins, *Nuclear Instruments and Methods* **226**, 542-548 (1984).
10. J. Karas, R. J. Pugmire, W. R. Woolfenden, D. M. Grant, and S. Blair, *Int. J. Coal Geology* **5**, 315-338 (1985).
11. R. Keogh, S. Poe, B. Chawla, and B. Davis, in *Coal Science and Technology*, Vol. II, Eds., J. A. Moulijn, K. A. Nater, and H. A. G. Chermin, Elsevier, 1987, pp. 289-294.
12. Cooperative Research in Coal Liquefaction Infratechnology and Generic Technology Development, Final Report on DOE Contract No. DE-FC22-85PC80009, submitted by the Consortium for Fossil Fuel Liquefaction Science, June 29, 1987.

13. J. Wong, F. W. Lytle, R. P. Messmer, and D. H. Maylotte, Phys. Rev. B 30, 5596-5610 (1984).
14. F. W. Kutzler, C. R. Natoli, D. K. Misemer, S. Doniach, and K. O. Hodgson, J. Chem. Phys. 73, 3274 (1980).
15. F. Sette, J. Stohr, and A. P. Hitchcock, Chem. Phys. Letters 110, 517-520 (1984).
16. A. Bianconi, E. Fritsch, G. Calas, and J. Petiaw, Phys. Rev. B 32, 4292-4295 (1985).
17. F. W. Lytle, R. B. Gregor, and A. J. Panson, "Discussion of XANES: Application to Cu in High T_c Superconductors," submitted to Phys. Rev. B.
18. D. E. Sayers, F. W. Lytle, and E. A. Stern, Phys. Rev. Lett. 27, 1204 (1971).
19. P. A. Lee, P. H. Citrin, P. Eisenberger, and B. M. Kincaid, Rev. Mod. Phys. 53, 769-806 (1981).

TABLE I. Energies (eV) of the first three peaks observed in the XANES of some standard compounds and coal specimens. Peak 1 is the most intense XANES feature.

Sample	Peak 1		Peak 2		Peak 3	
	Position (eV)	Area [†] (%)	Position (eV)	Area (%)	Position (eV)	Area (%)
K ₂ SO ₄	11.5	62	15.1	6	17.3	32
thianthrene	3.3	66	9.4	34		
4,4 thiodiphenol	2.5	26	4.1	15	10.7	52
sulfamic acid	9.0	41	11.5	31	18.0	27
sulfosalicylic acid	10.3	83	16.9	17		
dibenzothiophene	2.8	60	4.8	9	8.3	31
2,2 thiodiacetamide	2.6	17	7.8	27	18.5	56
thioacetamide	0.1	42	2.4	13	5.8	46
pyrite	0.9	94	8.9	3	11.8	3
pyrrhotite	-0.5	7	6.8	32	12.0	54
W. KY #9, run 6, biodesul.	2.9	37	5.0	6	11.4	57
W. KY #9, run 5, biodesul.	2.9	32	4.9	4	11.7	64
PSOC 733 (e)	2.8	47	4.9	7	11.3	46
PSOC 733 (v)	2.9	43	4.7	6	11.3	51
PSOC 733 (i)	2.9	41	4.9	3	11.6	56
PSOC 1111 (e)	3.3	41	5.1	23	10.2	36
PSOC 1111 (v)	3.3	39	5.0	24	10.0	37
PSOC 1111 (i)	3.3	43	5.0	24	9.9	33
PSOC 1110 (e)	3.0	46	4.8	20	9.8	34
PSOC 1110 (v)	2.4	26	4.1	9	9.1	73
PSOC 1108S (v)	2.5	21	4.2	9	9.4	78
W. KY #9 (e)	2.9	41	4.8	4	10.8	55
W. KY #9 (v)	2.9	40	5.0	5	10.8	55
W. KY #9 (i)	2.9	35	4.9	1	11.2	64
W. KY #9 (v)	2.9	44	4.9	10	11.2	46
W. KY #9 71095 (v)	2.9	48	4.9	6	11.2	46
W. KY #3 (v)	2.2	38	4.2	5	9.9	57
W. KY #5 (v)	2.2	38	4.1	5	10.3	57
W. KY #6 (i)	2.1	45	4.0	5	10.7	50

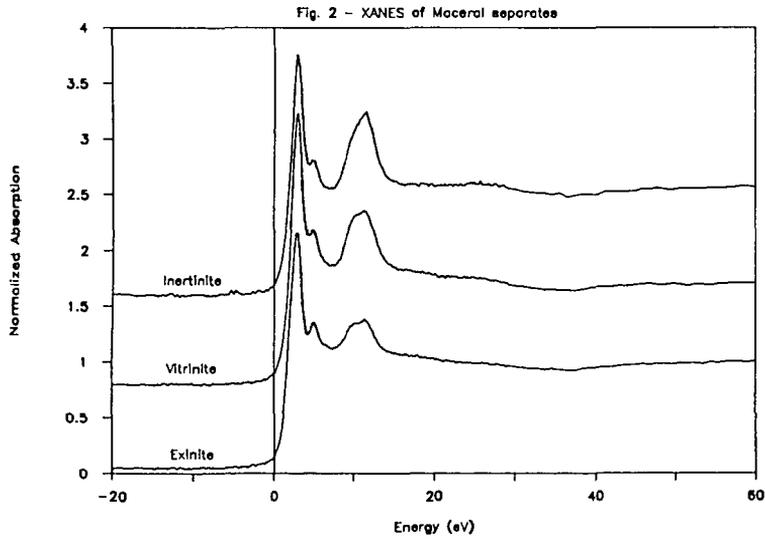
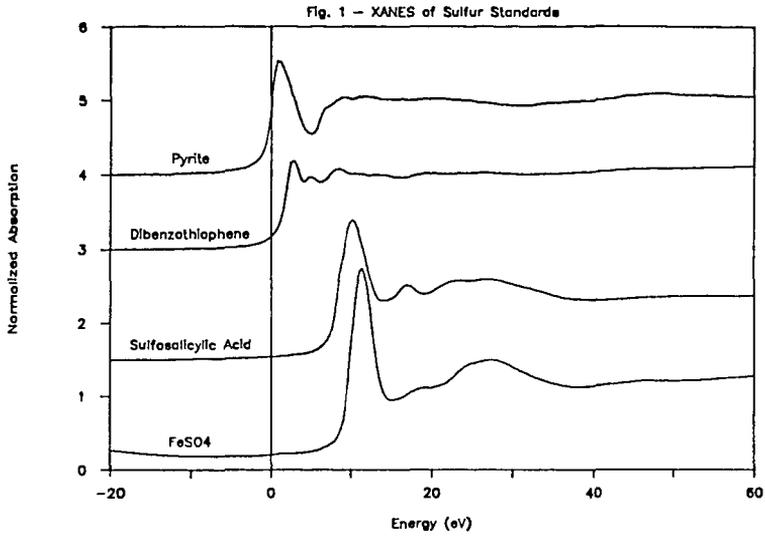
*(e), (v), and (i) denote exinite, vitrinite, and inertinite separates prepared by DGC.

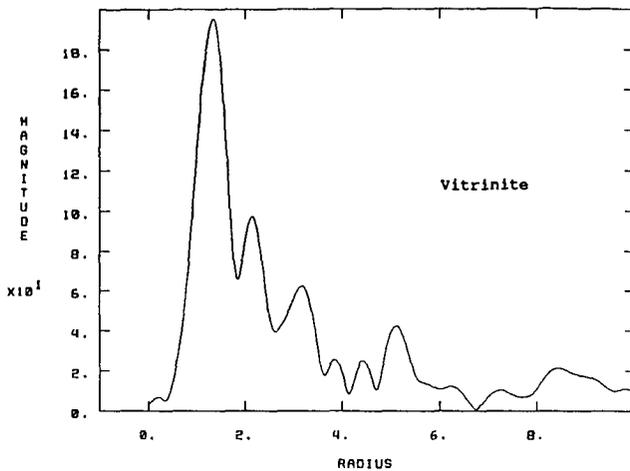
[†]The area percentages are determined by a program developed by one of the authors (R. B. Gregor) that fits the XANES peaks with Lorentzians and the edge step by an arctangent function. The analyses were carried out from -10 to +20 eV.

TABLE II. Distances (Å) from the sulfur atom to its nearest neighbor shells in dibenzothiophene and a variety of coal specimens.

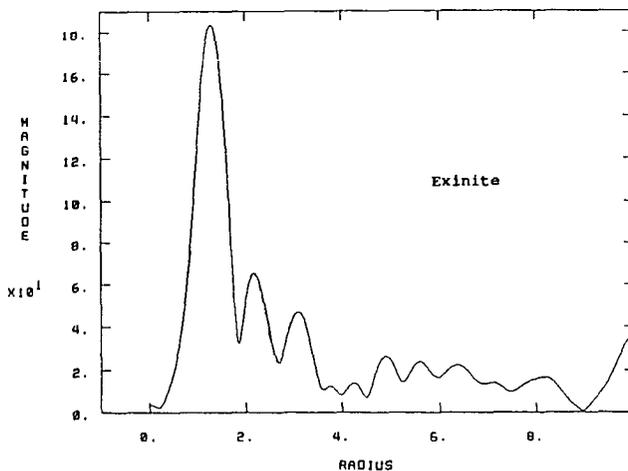
Sample*	Shell 1	Shell 2	Shell 3
dibenzothiophene	1.74	2.71	4.02
W. KY #9, run 6, biodesul.	1.75	2.75	
PSOC 733 (e)	1.75	2.75	4.02
PSOC 733 (v)	1.74	2.74	4.02
PSOC 1111 (e)	1.74	2.74	4.02
PSOC 733 (i)	1.74	2.73	
PSOC 1111 (e)	1.74	2.75	4.05
PSOC 1111 (i)	1.74	2.73	4.02
PSOC 1110 (e)	1.74	2.76	
PSOC 1110 (v)	1.74	2.75	
PSOC 1108S (v)	1.74	2.75	
W. KY #9 (e)	1.78	2.74	
W. KY #9 (v)	1.75	2.74	
W. KY #9 (i)	1.75	2.82	
W. KY #9 (v)	1.75	2.73	
W. KY #9 71095	1.75	2.75	
W. KY #3 (v)	1.75		
W. KY #5 (v)	1.75	2.77	
W. KY #6 (i)	1.74	2.80	

*(e), (v), and (i) denote exinite, vitrinite, and inertinite separates prepared by DGC.





SHACAD.303 3/1 11-JAN-88



SHACAD.308 3/1 11-JAN-88

Figure 3. Radial structure functions obtained from the EXAFS of maceral separates from PSOC 733.