Nitrogen Chemical Structure in Petroleum Asphaltenes and Coal by X-Ray Absorption Spectroscopy

Sudipa Mitra Kirtley,[@*] Oliver C. Mullins,[@] Jan van Elp,[*] & Stephen P. Cramer[*#]
[@]*Schlumberger-Doll Research, Ridgefield, CT 06877;*
[*] *Lawrence Berkeley Laboratory, Berkeley, CA 94720;*
[#] *University of California, Davis, Davis, CA 95616*

Keywords: nitrogen, XANES, fossil-fuel

ABSTRACT

Nitrogen chemical structure in fossil-fuel samples has been determined using x-ray absorption near-edge structure (XANES) spectroscopy. XANES data on three petroleum asphaltenes, a coal, and a number of nitrogen model compounds have been analyzed by comparing normalized areas under corresponding resonances in the spectra of the fossil-fuel samples and the model compounds. In the asphaltene and coal samples, we find that nitrogen occurs mostly in aromatic forms; very little or no evidence of saturated amines is found. The coal and asphaltenes show substantial quantities of pyrrole and pyridine fractions, and the pyrrole content is found to be greater than or equal to the pyridine content in all cases. XANES methodology is shown to be promising for the investigation of nitrogen structures in fossil-fuels, similar to its success in determining sulfur forms in similar samples over the past decade.

INTRODUCTION

Heteroatom chemistry of the heavy ends of petroleum and of coals has long been of interest for both processing and environmental concerns.[1,2] However, the study of the heteroatom chemistry in these fossil fuels is problematic. Nondestructive chromatographic methods are largely precluded due to the high molecular weights of these materials. Spectroscopic studies, particularly of nitrogen and sulfur, are difficult due to the low concentration of the heteroatoms and the elemental nonspecificity of many spectral methods. X-ray methods are element specific, and x-ray photoelectron spectroscopy (XPS) methods have been employed to study nitrogen in coals. However, XPS studies to date have suffered from the lack of resolution; peak separations from different chemical forms of nitrogen are comparable to or less than peak widths.[3,4] Additionally, XPS is particularly sensitive to surface effects. Here we report the study of nitrogen chemistry in three petroleum asphaltenes and in a coal using x-ray absorption near-edge structure (XANES). Nitrogen K-edge XANES spectra are found to have distinct and well resolved features which allow identification of the corresponding chemical forms of nitrogen. The fossil fuel spectra are satisfactorily interpreted in terms of two different kinds of aromatic model compounds, pyrrole and pyridine analogues. In both the asphaltene and coal samples, these aromatic nitrogen fractions

account for all of the nitrogen, and there are no indications of saturated amines. The coal and asphaltene samples differ in that the asphaltene has a greater fraction of pyrrolic nitrogen while the coal has comparable fractions of pyrrolic and pyridinic nitrogen fractions.

Over the past decade, XANES has emerged as perhaps the most powerful tool[5] for the analysis of sulfur in coals,[6-11] coal macerals,[10] and petroleum asphaltenes.[12,13] This is a moderately sensitive, nondestructive and element-specific method that relies on changes in positions and shapes of spectral features near the K-edge (or other edge), that depends on the chemical environment. In coals,[7,10] the organic and inorganic fractions of sulfur have been determined. In both coals[8-11] and asphaltenes,[12,13] the fractions of sulfidic and thiophenic forms of sulfur have been resolved. Different oxidized forms of sulfur have been readily identified in coals[8-10] and asphaltenes.[13] Although x-ray absorption methods have been very useful in the determination of the chemical forms of sulfur,[5-13] the application of XANES to the study of nitrogen in asphaltenes and coals is more difficult due to the low energy of the nitrogen K edge. Recent availability of high resolution soft x-ray beam lines[14] and of efficient fluorescence detectors[15] facilitates nitrogen XANES studies.

EXPERIMENTAL SETUP

Measurements were performed at the National Synchrotron Light Source at Brookhaven National Laboratories using the AT&T Bell Lab's 'Dragon' beam line (U4B).[14] Typical incident x-ray resolution in the experiments was 0.14 eV. The powdered samples were placed on silicon supports using nitrogen-free double-stick tape. The sample was then placed in the vacuum chamber fitted with a cryopump which maintained the pressure at $\sim 10^{-9}$ torr. Energy calibration was performed using zinc octaethylporphyrin which has a resonance at 399.72 eV. Fluorescence detected x-ray absorption spectra were obtained using a seven element Ge detector,[15] with single channel analyzers set to select the shaped pulses corresponding to the nitrogen $K\alpha$ emission.[15] The coal sample was obtained from Argonne National Labs (Pittsburgh #8), the asphaltenes were prepared from crude oils from California, USA (CAL), France (FRA), and Kuwait (UG8), by 40cc/g dilution with n-heptane, and the pure model compounds were obtained from the Aldrich Chemical Company.

RESULTS AND DISCUSSION

Figure 1 compares the fluorescence excitation spectra of the petroleum asphaltenes and Pittsburgh #8 coal.[16] (Figure 1 also shows the composite spectrum consisting of the weighted sum of the spectra of acridine and carbazole, see below). Three distinct spectral regions are apparent in all spectra, at 399.5 eV, 403 eV, 408 eV. To assign these features, we have resorted to the fluorescence detected x-ray absorption spectra of model compounds, as shown in figure 2. Acridine, a pyridine analogue, has a particularly strong resonance at ~399 eV which is assigned to a $1s \rightarrow \pi^*$ transition.[17] Carbazole, a pyrrole analogue, has a strong resonance at ~403 eV which is also assigned to a $1s \rightarrow \pi^*$ resonance.[17] 1,3,5-

tribenzylhexahydro-1,3,5-triazine, a saturated amine, exhibits only a broad σ resonance at ~408 eV, a slightly lower energy than the σ resonances of the aromatic compounds.[17] The π* resonances of the two different types of aromatic compounds are well resolved which is advantageous for interpreting the data.

There is a clear correspondence in the spectra between the peaks of the aromatic compounds with peaks of asphaltenes and coal in figure 1. Assuming the oscillator strengths of these transitions remain in constant ratio with post threshold continuum absorption at 420 eV, these spectra can be used to quantitatively determine the various nitrogen fractions. Small energy shifts between peaks in the spectra of models and fossil fuel samples are observed. Furthermore, peak widths in the spectra of the fossil fuel samples are somewhat larger than for the pure model compounds. Therefore, we did not simply fit the asphaltene and coal spectra with sums of model spectra. We fit all spectra with a sum of Lorentzian peaks and an arc-tangent step function. We used peak areas normalized by the step height to determine nitrogen fractions in the fossil fuels. For the asphaltene and coal spectra, the area of the lowest energy resonances at ~399.7 eV was assigned to the pyridine analogue, thereby determining the pyridine fraction. The resonances near 403.5 were assigned to both pyridine (already determined) and pyrrole. The contribution of pyridine to the area of the broad peak centered at ~403.5 eV was subtracted and the remaining peak area was assigned to the pyrrole analogue, thereby determining the pyrrole fraction. Likewise, the peak area of the 409 eV peak was assigned to both aromatics (already determined) and the saturated amine. The contribution of the aromatics to the very broad peak at ~409 eV was subtracted and any remaining, unaccounted for peak area was assigned to the saturated amine.

The fitting procedure resulted in the following peak positions (listed in eV). UG8 asphaltene: 399.3, 399.8, 402.55, 403.4, 406.77, 408.0, 410.8, 412.5, 415.5 and step 408.6; FRA asphaltene:399.6, 402.2, 403.2, 406.5, 407.8, 412.8, and step 408.6; CAL asphaltene: 399.8, 402.4, 403.5, 406.2, 407.4, 412.3, 416.9, and step 408.3; Pittsburgh #8 coal: 399.5, 400.05, 402.7, 404.05, 407.08, 408.2, 412.9, and step 408.6; acridine: 399.25, 399.6, 401.8, 403.3, 406.4, 407.9, 408.9, 412.9 and step 408.6; carbazole: 402.3, 403.2, 404.2, 406.1, 408.0, 410.4, 413.3, 418.4, and step 408.4; and tribenzylhexahydrotriazine: 402.3, 402.9, 405.3, 407.5, 410.0, 413.3, and step 408.5.

The normalized fractional forms of nitrogen are for CAL: 50% pyridine, 48% pyrrole, and saturated amine 2%, for FRA: 40% pyridine, and 60% pyrrole, for UG8: 37% pyridine, 63% pyrrole, and for coal: 47% pyridine, 53% pyrrole. The error estimate, based on the unnormalized nitrogen fraction, is considered to be about 10%. Figure 1 shows the similarity of the overall features of the spectra of the fossil fuels, although there are some differences in peak positions and widths. For the sake of comparison, a weighted spectral sum with 42% acridine and 58% carbazole (fractional values intermediate between coal and asphaltene results) is also shown. Examination of a greater selection of model compounds may reduce

discrepancies between spectra of fossil fuels and the spectral sum of model compounds. The coal and the three asphaltenes exhibit appreciable fractions of both pyrrolic and pyridinic nitrogen, with the pyrrolic nitrogen content being either greater than or equal to the pyridinic content in all four samples. Little evidence of saturated amine is found in any sample. XPS methods employing pyrrole and pyridine models have been used to study coal-derived materials,[3,4] and coals.[4] Coal asphaltenes[3] were found to contain 49-62% and coals[4] 65-85% pyrrolic nitrogen, the rest being assigned to pyridine analogues in both cases. Our determination of pyrrolic and pyridinic nitrogen fractions for our asphaltene samples is similar to the XPS results for coal asphaltenes, and the pyrrolic estimate for our coal is somewhat lower than the XPS coal results. Uncertainties exist in the XPS results as a result of resolution difficulties. For all asphaltenes and coals, the nitrogen is much more aromatic than the (organic) sulfur where large sulfidic fractions are found. Additionally, for asphaltenes, the fraction of aromatic nitrogen is much larger than the fraction of aromatic carbon (~40%), whereas in coal, such a comparison can not be easily made, since the aromatic carbon content varies significantly among different coals.[18]

CONCLUSIONS

Nitrogen XANES methods are powerful for determining different chemical forms of nitrogen in asphaltenes and coals. The high degree of specificity of this technique coupled with the well resolved resonances of various forms of nitrogen provide one of the best methods for differentiating nitrogen chemical forms in fossil fuels. Aromatic pyrrolic and pyridinic nitrogen are the most prevalent forms of nitrogen found in the asphaltenes and coal; pyrrolic nitrogen is generally more abundant than pyridinic nitrogen, although considerable variability is observed in the pyrrole and pyridine fractions of nitrogen in the asphaltene and coal samples. Little evidence of saturated amines is found in these fossil-fuel samples. Non-destructive and direct XANES methodology for nitrogen characterization in amorphous fossil-fuel samples is shown to be very successful, and holds promise for further work in this area.

Acknowledgments

Research carried out at the National Synchrotron Light Source at Brookhaven National Laboratory which is supported by U.S. Dept. of Energy, Division of Material Science and Division of Chemical Science. SPC acknowledges support by Lawrence Berkeley Lab, Exploratory Research Fund and by the National Institutes of Health, Grant GM-44380.

References

1) Coal Science II, H.H. Schobert, K.D. Bartle, and L.J. Lynch Eds., ACS symp. Series #461 Amer. Chem. Soc., Washington D.C., (1991)

2) Chemistry of Asphaltenes, J.W. Bunger, N.C. Li, Eds., Amer. Chem. Soc., Washington, D.C., (1981)

3) S. Wallace, K.D. Bartle, D.L. Perry, Fuel, 68, 1450, (1989)

4) P. Burchill, Intl. Conf. Coal Science, J.A. Moulijn et al eds., Elsevier Pub., Amsterdam, 5, (1987)

5) L.M. Stock, R. Wolny, B. Bal, Energy & Fuels, 3, 651, (1989)

6) Z. Hussain, E. Umbach, D.A. Shirley, J. Stohr, J. Feldhaus, Nucl. Instrum. Methods. Phys. Res. 195, 115, (1982)

7) C.E. Spiro, J. Wong, F. Lytle, R.B. Greegor, D. Maylotte, S. Lampson, Science 226, 48, (1984)

8) G.P. Huffman, F.E. Huggins, H.E. Francis, S. Mitra, and N. Shah, Coal Science and Tech.16: Proc. and Util. of High Sulfur Coals III, 21, (R. Markuszewski et al eds.), 21, (1990)

9) M.L. Gorbaty, G.N. George, S.R. Kelemen, Fuel, 69, 1065, (1990)

10) G.P. Huffman, S. Mitra, N. Shah, S. Vaidya, and F. Lu, Energy & Fuels, 5, 574, (1991)

11) G.N. George, M.L. Gorbaty, S.R. Kelemen, and M. Sansone, Energy & Fuels, 5, 93, (1991))

12) G.N. George, M.L. Gorbaty, J. Amer. Chem. Soc., 111, 3182, (1989)

13) G.S. Waldo, O.C. Mullins, J.E. Penner-Hahn, S.P. Cramer, Fuel, 71, 53, (1992)

14) C.T. Chen, Nucl. Instrum. Methods Phys. Res. A, 256, 595 (1987); C.T. Chen, F. Sette, Rev. Sci. Instrum. 60, 1616, (1989)

15) S.P. Cramer, O. Tench, M. Yocum, H. Craner, L. Rogers, V. Radeka, O.C. Mullins, and S. Rescia, X-Ray Absorption Fine Structure - Proc. 6th Intl. XAFS Conf., S.S. Hasnain, Ed., Ellis Horwood Chichester, 640, (1991)

16) Using x-ray absorption tables (J.J. Yeh, I. Lindau, Atomic Nuc. Data Tables, 32, 1, (1983)), maximum nonlinearities from concentration effects in the model compound spectra are calculated to be ~7% and were corrected

for in the data using Eqn. 23, in J. Goulon, C. Goulon-Ginet, R. Cortes, J.M. Dubois, J. Physique. 43, 539, (1982)

17) J.L. Dehmer, A.C. Parr, S.H. Southworth, Ch. 5 in Handbook on Sychrotron Radiation, Vol. 2, G.V. Marr Ed., North-Holland, Amsterdam, (1987)

18) R.M. Davidson, Coal Science, Vol. 1, I. G. Dryden Ed., Academic Press Inc., 83, (1982)

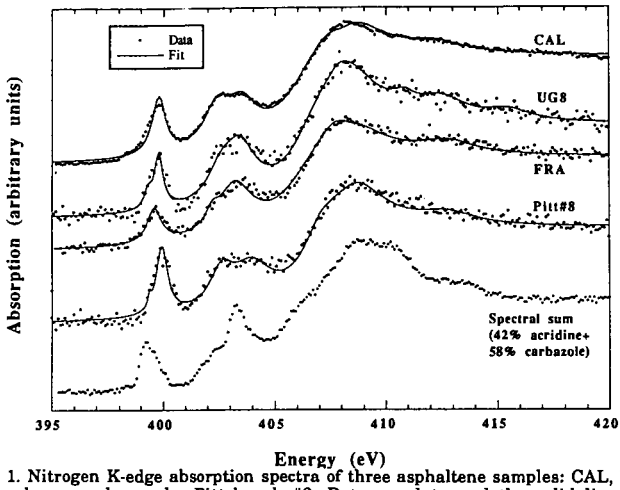

Figure 1. Nitrogen K-edge absorption spectra of three asphaltene samples: CAL, FRA, and UG8, and one coal sample: Pittsburgh #8. Dots are data and the solid lines are fits consisting of a sum of lorentzians and an arc-tan function. Also shown (at the bottom) is the weighted sum of the spectra of a pyridine analogue, acridine (42%), and a pyrrole analogue, carbazole (58%).

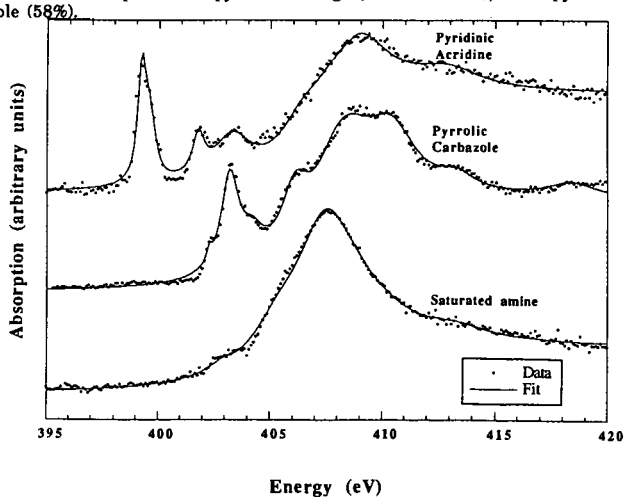

Figure 2. Nitrogen K-edge absorption spectra of three model compounds used to fit the fossil fuel spectra, acridine - a pyridine analogue, carbazole - a pyrrole analogue, and tribenzylhexahydrotriazine - a saturated amine. Dots are data and the solid lines are fits consisting of a sum of lorentzians and an arc-tan function.