

Molecular Structure of Nitrogen in Coal from XANES Spectroscopy

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Five major nitrogen chemical structures, present in coals of varying ranks, have been quantitatively determined with the use of nitrogen x-ray absorption near-edge spectroscopy (XANES). Similar studies of the sulfur chemical structures of coals have been performed for the last ten years; nitrogen studies on these fossil-fuel samples have only recently been realized. XANES spectra of coals exhibit several distinguishable resonances which can be correlated with characteristic resonances of particular nitrogen chemical structures, thereby facilitating analysis of these complicated systems. Many model compounds have been examined; for some, the relative peak positions are explained in terms of the orbital description of the lone pair of electrons. All features in the XANES spectra of coals have been accounted for; thus, all the major structural groups of nitrogen present in coals have been determined. A wide variety of aromatic nitrogen compounds is found in the coals; no evidence of saturated amine is found. Pyrroles, pyridines, pyridones, and aromatic amines are found in coal; of these, pyrrolic structures are the most prevalent. Pyridine nitrogen is prevalent in all except low-rank coals. The low pyridine content in low-rank (high-oxygen) coals correlates with a large pyridone content. This observation suggests that, with increasing maturation of coal, the pyridone loses its oxygen and is transformed into pyridine. Aromatic amines are present at low levels in coals of all rank. The spectral effects of aromatic amines are shown by comparing the XANES spectra of coal and petroleum asphaltenes.

Index Heading: X-ray absorption spectroscopy.

INTRODUCTION

Coal is a sedimentary rock, with a complex and inhomogeneous structure, consisting primarily of organic matter as well as mineral matter and water.^{1,2} The organic part of coal originates principally from plant materials, which metamorphose over geological time under the influence of elevated temperature and pressure. Mineral grains and dissolved ions also find their way into the coal beds, forming the inorganic component. The organic and inorganic components of coal contain heteroatoms which are a hindrance to the utilization of this resource. Nitrogen-containing polycyclic aromatic compounds found in coal can poison catalysts during upgrading.³ In addition, nitrogen-containing compounds pose an environmental threat due to their conversion to nitrogen oxides during coal combustion. Heteroatoms are also important in determining the solubility and chemical characteristics of coal fractions.

The extent of metamorphism is described by the rank of a coal; a higher-rank coal is more extensively metamorphosed than a lower-rank coal. Lower-rank coals have a lower carbon and higher oxygen content than higher-

rank coals. ¹³C NMR and IR, as well as various chemical studies, indicate that the carbon aromaticity in coal increases with an increase of carbon content and coal rank.² The aromatic carbon content of a low-rank coal can be as low as 40% of total carbon, and the same figure for a high-rank coal can be as high as 90%.² Hydrogen occurs in coal in both aromatic and aliphatic fractions; the aromatic hydrogen content also increases with increasing rank.² As the rank of coal increases up to the anthracite level, the porosity and the moisture content of coal decrease.¹ Oxygen is the principal heteroatom present in coal; the organic structures occur mostly as furan analogues or as etheric groups attached to aromatic systems.² The fraction of oxygen in dry, mineral-matter-free coal samples is found to decrease with increasing coal rank. Sulfur structures in coal have been studied extensively; x-ray absorption near-edge spectroscopy (XANES) studies on sulfur in coal have been performed for the last ten years and have differentiated and quantified the different forms of sulfur in coal.⁴⁻⁹ Most of the sulfur in coal is found in organic forms; (aromatic) thiophenic sulfur, (saturated) sulfidic sulfur, sulfoxide, and sulfone are the most common organic structures. Inorganic sulfur in the forms of sulfide, elemental sulfur, and sulfate is also found in coals.

It has been rather difficult to identify the nitrogen chemical structures in coals. Largely, the methods used until now have been destructive and indirect. Chromatographic methods are problematic for insoluble or high-molecular-weight samples, and extraction methods do not account for the entire coal sample. Many spectroscopic methods are incapable of resolving the different chemical structures of nitrogen, especially considering the small mass fraction of nitrogen in coals (~1%). X-ray photoelectron spectroscopy studies on coal^{10,11} and coal-derived materials¹² have been informative; however, they suffer from the limited energy separation and large XPS peak widths of different forms of nitrogen. In contrast, XANES methodology, which is nondestructive, offers great promise, as shown in an initial study of asphaltenes and coal,¹³ a detailed study of asphaltenes,¹⁴ and a study of nitrogen in heterocycles in biological molecules.¹⁵ In addition, XPS methods are sensitive to surface conditions of the sample, while XANES methods explore the bulk properties of samples.

The detailed XANES study of nitrogen in asphaltenes has provided substantial information about asphaltenes as well as the small nitrogen-containing compounds used to analyze the asphaltenes.¹⁴ Asphaltene is the heaviest component of petroleum; it is a dark brown to black,

Received 28 December 1992; revision received 29 March 1993.
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infusible solid and consists of a core of condensed aromatic rings with aliphatic and alicyclic side chains.¹⁶ As with higher-rank coals, the principal constituents of petroleum asphaltene are carbon and hydrogen, with small quantities of heteroatoms such as oxygen, sulfur, and nitrogen. XANES methodology has been an effective probe of the structural forms of sulfur in asphaltene.¹⁷⁻¹⁹ As with coal, thiophene (aromatic) is the most common form of sulfur in asphaltene, and sulfidic (saturated) sulfur is the next most abundant form. However, unlike coal, the most common oxidized form of sulfur in asphaltene is the sulfoxide group.¹⁹ Petroleum asphaltene is chemically more reduced than coal, and has a C:H ratio of about 1.1. Unlike coal, petroleum asphaltene does not contain any mineral matter. Nitrogen XANES studies on petroleum asphaltene have revealed that most of the nitrogen in these samples is present in aromatic forms, with negligible quantities of saturated forms; pyrrole and pyridine structures are the aromatic forms of nitrogen found in petroleum asphaltene.¹⁴

In the present report, we employ XANES methods to determine and quantify five different chemical forms of nitrogen in coals of varying ranks. The five different types of nitrogen chemical structures examined are pyridine, pyridone, pyrrole, aromatic amine, and saturated amine. The aromatic nitrogen molecules studied exhibit both π^* and σ -shape resonances, while the saturated amines show only a σ -shape resonance. Analogues of the same nitrogen structure have XANES spectra with characteristic lowest-energy resonances at similar energies. For instance, the lowest energy π^* resonance of all pyridine analogues occurs at ~ 399.7 eV, that of pyridone analogues at ~ 402 eV, that of pyrrole at ~ 403.5 eV, and that of aromatic amines at ~ 405 eV. Thus, a particular nitrogen type can be readily identified by its characteristic resonance absorption energy. The energy of the π^* resonances is determined in part by the orbital description of the lone pair of electrons at the nitrogen site. When the lone pair of electrons at the nitrogen site occupies an sp^2 orbital, as in a pyridine analogue, the nitrogen is slightly negatively charged, and the lowest-energy π^* resonance occurs at a low energy. In the pyrrole analogues, the lone pair is delocalized in the p_z orbital, which decreases electron density from the nitrogen site, and the molecule exhibits a higher-energy π^* resonance. A similar situation prevails in the pyridone case, which shows a π^* resonance near that of pyrrole. The π^* peak of pyridone is slightly shifted to lower energy compared to that for pyrrole, perhaps due to the interaction of the carbonyl group with the aromatic system.

The well-separated energies of the characteristic resonances of the different nitrogen molecules facilitate analysis of the coal spectra, since the coals exhibit differing absorbances in these different spectral regions. In this study, all the main peaks in the spectra of coal have been accounted for. A quantitative analysis performed on the spectra of coals and model compounds shows that most of the nitrogen in coals occurs in aromatic forms, with no detected saturated amine. Pyridines, pyrroles, pyridones, and aromatic amines are the major aromatic compounds in coals. Pyrroles are by far the most dominant chemical structure of nitrogen in all coals (examined). Pyridine is present in appreciable quantities in all

coals except those of the lowest rank. For low-rank coals, the pyridine fraction decreases to nearly zero, while the pyridone fraction increases to large values. This observation suggests that, with the maturation of coal (and the loss of oxygen), pyridone transforms into pyridine. The aromatic amine fraction is small and relatively independent of the rank of the different coals. The spectral effects of aromatic amines are shown in the comparison of coal and asphaltene spectra. In contrast to low-rank coals, petroleum asphaltene tends to possess negligible quantities of pyridone.

EXPERIMENTAL

All XANES measurements were performed on AT&T Bell Lab's soft x-ray "Dragon" beam line U4B²⁰ at the National Synchrotron Light Source, at Brookhaven National Laboratory. Contamination with atmospheric nitrogen was avoided in the experiments using high-vacuum chambers, with the pressure approximately 10^{-9} to 10^{-10} Torr, which was maintained with the help of a cryopump and a turbomolecular pump. All experiments were performed at room temperature. A monochromator containing a fused-silica grating with 600 lines/mm was used for the experiments.

Detection of both x-ray fluorescence and Auger electrons was performed. A thirteen-channel fluorescence germanium detector,²¹ which was operated at liquid nitrogen temperature, and an electron yield detector, with its channeltron voltage of 1000-1500 V, were used for such purposes.

The sample suite consisted of eight coals of varying ranks, a petroleum asphaltene, and several nitrogen model compounds. The coals ranged in rank from lignite to low-volatile bituminous, and were obtained from Argonne Premium Coal Sample Bank at Argonne National Lab.²² These coals have been obtained from seams from different parts of the U.S.A.: a low-volatile bituminous coal from Pocahontas #3, VA (POC); a medium-volatile bituminous coal from Upper Freeport, PA (UF); four high-volatile bituminous coals from Pittsburgh #8, PA (PITT), Lewiston-Stockton, WV (WV), Blind Canyon, UT (UT); and Illinois #6, IL (IL); and a subbituminous from Wyodak-Anderson, WY (WY), and a lignite from Beulah-Zap, ND (ND).

The petroleum asphaltene was precipitated from a crude oil from Kuwait (KUW2). The model compounds consisted of the pyridine group: acridine, 4,7-diphenyl-1,10-phenanthroline, phenanthridine, di-*p*-tolyl pyridine, and 4-polyvinylpyridine-costyrene; the pyridone group: 6-(2,2-diphenyl-2-hydroxyethyl)-2(1H)-pyridone, 2-hydroxyquinoline, 1-hydroxyisoquinoline, 1-methyl-4-pentadecyl-2(1H)-quinoline; the pyrrole group: tetrahydrocarbazole, 2-phenylindole, 9-vinylcarbazole, and carbazole; the aromatic amine group: 2-aminofluorene and 2,7-diaminofluorene; and the saturated amine group: 1,3,5-tribenzylhexahydro-1,3,5-triazine and diaminododecane. These models were obtained from Aldrich Chemical Co. and were used without further purification. All the coals, the petroleum asphaltene, and the model compounds were in powder forms, and samples were run by mounting the powders on nitrogen-free double-sticking tape. All the

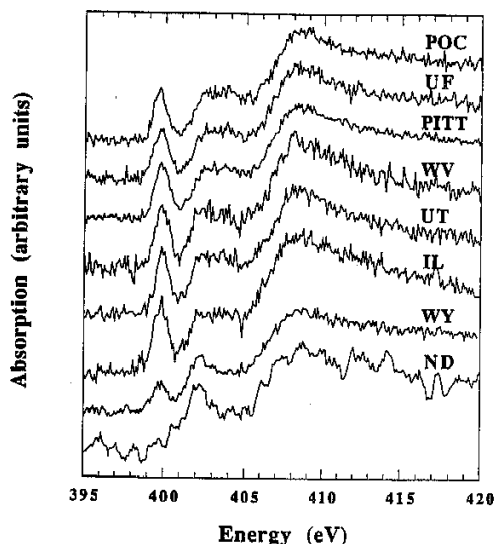


FIG. 1. Fluorescence XANES spectra of coals in order of varying ranks; the spectrum of the highest-rank coal is shown at the top. Five resonance regions are observed in the spectra, at ~ 399.7 eV, 402 eV, 403.5 eV, 405 eV, and 408 eV. These five resonance regions can be used to quantify nitrogen chemical structures in coal. Variations in intensities of various resonance regions are noted for different-rank coals. In particular, dramatic and opposite changes in magnitude of the two resonances at 399.7 eV and 402 eV are noted for the lowest-rank coals. The spectra of higher-rank coals are more uniform, indicating smaller differences in their nitrogen chemical structures.

XANES spectra were calibrated with respect to the first π^* resonance of zinc octaethylporphyrin at 399.72 eV.

RESULTS AND DISCUSSION

Figure 1 shows the XANES spectra of eight coals in order of the coal rank, the highest rank being at the top. The coals exhibit general similarities in their spectra with three well-resolved resonance regions. The magnitude of the resonance at 399.7 eV is variable, being quite small for low-rank coals. A closer analysis shows that the broad central feature spanning 402 eV to 405 eV consists of three resonance regions located at ~ 402 eV, ~ 403.5 eV, and ~ 405 eV. The absorption strength at 402 eV is seen to be quite large for only the low-rank coals; this resonance is large when the 399.7-eV resonance is small, suggesting an interconversion of the two nitrogen types. The 402-eV absorption is evident for the three coals of intermediate rank (WV, UT, IL) but small for the three coals of highest rank. A broad absorption at ~ 403.5 eV is prominent in all coal spectra, indicating a uniformly important nitrogen structure. A spectral valley of varying depth is observed at 405 eV; some variability is indicated by the differing resonance amplitudes at 403.5 and 405 eV. Additionally, all coals show a strong resonance at 408 eV.

In order to analyze the different coal spectra shown in Fig. 1, we obtained XANES spectra of several nitrogen model compounds belonging to five different chemical groups—pyridines, pyridones, pyrroles, aromatic amines, and saturated amines. In Fig. 2, the XANES spectrum of a coal (UT) and a set of model compounds are shown; the models are a pyridine (poly-4-vinylpyridine-co-styr-

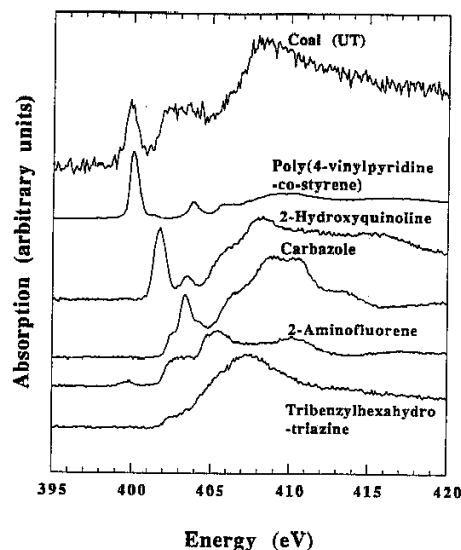


FIG. 2. Fluorescence XANES spectra of one coal (UT) and five different model compounds. The aromatic compounds have both π^* and σ^* resonances, while the saturated compound shows only a σ^* resonance; all the models show well-separated π^* resonances (or σ^* resonances). The first resonance of the coal matches well with the lowest-energy π^* resonance of acridine, a pyridine analogue. The second resonance at 402 eV matches that of a pyridone; the third resonance region at ~ 403.5 eV is at similar energy to carbazole, a pyrrole; and the fourth resonance region at 405 eV matches the lowest-energy π^* resonance of aromatic amine. All the aromatic compounds and the saturated compound, hexahydrotriazine, have a σ -shape resonance at the same energy as the fifth resonance region in the coal spectrum.

ene), a pyridone (2-hydroxyquinoline), a pyrrole (carbazole), an aromatic amine (2-aminofluorene), and a saturated amine (tribenzyl hexahydrotriazine). This figure shows the nitrogen chemical structures which combine in coal to generate the coal spectrum. All the aromatic model compounds have their lowest-energy π^* resonances (or σ^* resonance in the saturated amine case) at well-separated energies, and each resonance feature in the coal spectrum is identifiable with the characteristic resonance of a particular model compound. The π^* resonance of acridine (a pyridine analogue) at 399.3 eV is large and isolated and provides a clear signature of pyridine in coal. The width of this resonance in acridine is less than the corresponding width in the coal spectrum, suggesting the presence of several different pyridine molecules in the coal. The pyridone peak at 402 eV increases in lower-rank coals; this observation is in accord with the large oxygen content of low-rank coals. The broad pyrrole peak at ~ 403.5 eV is adjacent to the pyridone peak but resolvable in energy. For all coals, the pyrrole peak is quite large, illustrating that pyrroles are uniformly a very important class of nitrogen compounds in coal. At 405 eV, aromatic amines show absorption. The coals generally show a slight valley at 405 eV, indicating that aromatic amines are present in only smaller quantities; nevertheless, the valleys at 405 eV for the coal spectra are quite shallow in comparison to those for the model compounds (and asphaltene, as we shall see), indicating that some aromatic amines are present in coals. All models show absorption at 408 eV, but the saturated amine shows

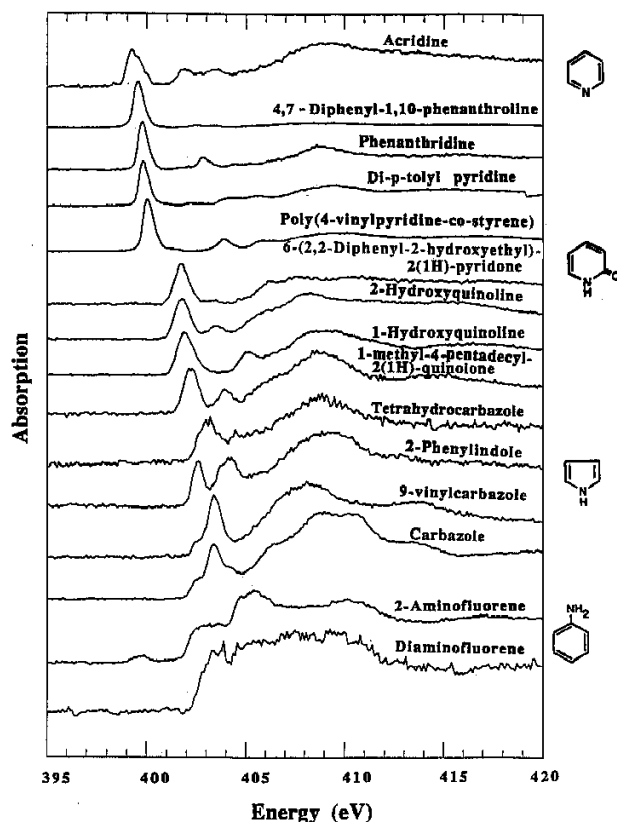


FIG. 3. Fluorescence XANES spectra of many (15) nitrogen model compounds belonging to five different chemical groups. All the model compounds belonging to the same nitrogen structure show lowest-energy π^* resonances at similar energies. Pyridines show their lowest-energy π^* resonances at 399.7 eV, lower than the other model compounds. The pyridone analogues show their lowest-energy π^* resonances at 401.9 eV, and pyrroles show broad absorption at 403.5 eV. The more basic pyridines with their lone pair in an sp^2 orbital have a π^* resonance at lower energy, while the less basic pyrroles and pyridones with their lone pair of electrons in the p_z orbital have their resonances at higher energy. The carbonyl group of the pyridones produces an energy difference in the pyrrole and pyridone resonances. The aromatic amines show broad π^* resonances at ~ 405 eV. The saturated amines have only a broad σ resonance, as discussed in Ref. 14. Because we do not find evidence of saturated amines in coals, we do not show their spectra here.

absorption only at 408 eV. The contribution of saturated amine to the coal spectra must be determined by subtracting from the coal spectra the contribution of all other models to absorption at 408 eV and assigning the remaining absorption to saturated amines.

Figure 3 plots the XANES spectra of many (15) nitrogen model compounds belonging to different chemical groups; for each group several analogues appear. The basic molecular structures of the different nitrogen types are given in the figure. This figure shows that all pyridine analogues produce a resonance at ~ 399.7 eV. Likewise all pyridones produce a resonance at ~ 402 eV, pyrroles at 403.5 eV, and aromatic amine at 405 eV. Thus, a given nitrogen chemical structure has an associated characteristic XANES absorption feature. This property of XANES spectra is enormously important for analyzing

chemical constituents in complex materials and has been applied to the analysis of nitrogen in asphaltenes^{13,14} and sulfur in coals⁴⁻⁹ and asphaltenes.¹⁷⁻¹⁹ This figure also shows the range of energies for resonances corresponding to particular structures. The fact that the pyridine resonance in coals is comparable in width to the range spanned by the pyridine models indicates that many pyridine analogues are present in coals, as expected. The pyridine resonances are well-separated from other resonances so the range of pyridine resonances does not obscure the chemical classification of this absorption feature.

The pyridone and pyrrole resonances are quite close to each other. It is important to establish whether overlap exists in peak locations for these two nitrogen structures. Figure 3 shows that the lowest-energy (π^*) resonances of pyridones are always below 402.2 eV, spanning about 0.5 eV, while for pyrroles the corresponding resonances are always above 402.2 eV, spanning about 1 eV. The spectra ranges of pyridones and pyrroles meet at 402.2 eV, but do not overlap. Perhaps if more models were examined, a small overlap would be found, but it is clear from the large number of pyridone and pyrrole models examined that the lowest-energy π^* resonances of these two chemical structures are resolvable. This result is not surprising, because the two structures are chemically quite distinct, and distinct structures often produce resonances in different regions. Likewise, the lowest-energy peaks of pyrroles and aromatic amines are quite close, but those of pyrroles are always lower in energy. The coals tend to show slight valleys at 405 eV, while the aromatic amines show peaks at this energy, indicating the lesser importance of the aromatic amines in coals.

All pyridine analogues show π^* resonances which occur at ~ 399.7 eV, a much lower energy ($E > 2.5$ eV) than shown by the pyrroles. We have described this difference in the location of resonances of pyridine and pyrrole in terms of the orbital configuration of the lone pair of electrons on nitrogen and in terms of electronegativity.¹⁴ In pyridine, the lone pair of electrons at the nitrogen site in pyridine occupies an sp^2 orbital and is not involved in the π -electron cloud. The higher electronegativity of nitrogen imparts a slightly negative charge at the nitrogen site in the six-membered pyridine molecule. On the other hand, in pyrrole, the lone pair of electrons of the nitrogen is in the p_z orbital and is shared in the aromatic ring, and the molecule moves towards a fivefold symmetry. The resonance structures in pyrrole result in a net loss of electron density at the nitrogen site. The high electron density at the nitrogen site, which is higher in pyridine than pyrrole, results in a significantly lower-energy π^* resonance in pyridine and is in accord with XANES results on other atoms.^{17,19,23} According to these considerations, the π^* resonance of pyridone should be close to that of pyrrole. As in pyrrole, the lone pair of electrons of pyridone is in the p_z orbital and thus is shared in the aromatic ring. This resonance effect in pyridone is similar to what is found in pyrrole, thereby producing similar energies for their π^* resonances. The small energy difference in π^* resonances between the pyridones and pyrroles results from the carbonyl group.

Our arguments regarding the location of the pyridone resonance rest on the supposition that the pyridones

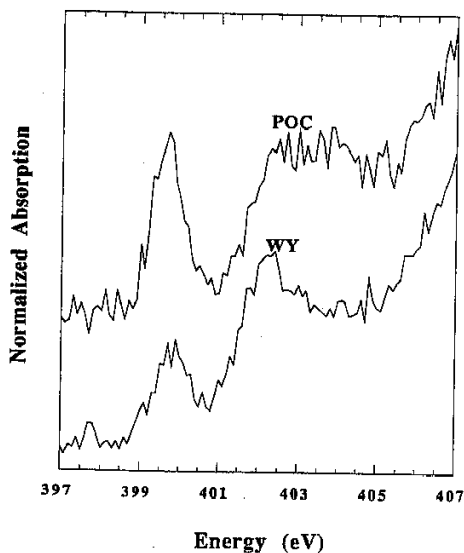


FIG. 4. Fluorescence XANES spectra of a high-rank coal (top) and a low-rank coal (bottom). With maturation, the pyridine peak (399.7 eV) grows and the pyridone peak (402 eV) decreases. This observation correlates with the significant loss of oxygen with maturation. The implication is that, with coal maturation, pyridone is converted to pyridine.

exist in the keto form as opposed to the enol form. We would anticipate that the enol form would produce an absorption peak close to that of the pyridines, not the pyrroles. Infrared spectroscopy²⁴ has been used to establish that 2-quinolone (2-hydroxyquinoline) does in fact exist in the keto form. Our data imply that the other pyridones used here, such as 1-quinolone, also exist in the keto form.

In Fig. 1, the two lowest-rank coals are seen to have very small pyridine peaks and very large pyridone peaks. Correspondingly, the highest-rank coals have large pyridine peaks and much smaller pyridone peaks. Figure 4 shows the spectra of a low-rank and a high-rank coal on a scale expanded in the pyridine and pyridone scale. The spectral impact of a large pyridone fraction in the low-rank coal and of a large pyridine fraction in the high-rank coal is evident. It is clear that the relative peak heights of pyridine and pyridone are very different for these two coals. Low-rank coals are relatively high in their (nonwater) oxygen content and, with maturation, coals lose most of this oxygen. The suggestion is that the pyridone is converted to pyridine with increasing maturation.

The effect of aromatic amines on the coal spectra is somewhat difficult to display in the raw data because, as will be discussed shortly, the coals have relatively small and invariant fractions of aromatic amines. Nevertheless, the effect of aromatic amines can be observed when coal spectra are compared with the spectrum of a related system, petroleum asphaltene. Figure 5 shows, on an expanded scale, the spectra of a high-rank coal and of a petroleum asphaltene. The petroleum asphaltene shows a shallow spectral valley at 405 eV, while the coal shows almost no valley. The aromatic amines exhibit a peak at 405 eV (see Fig. 3). Coals and petroleum asphaltenes are

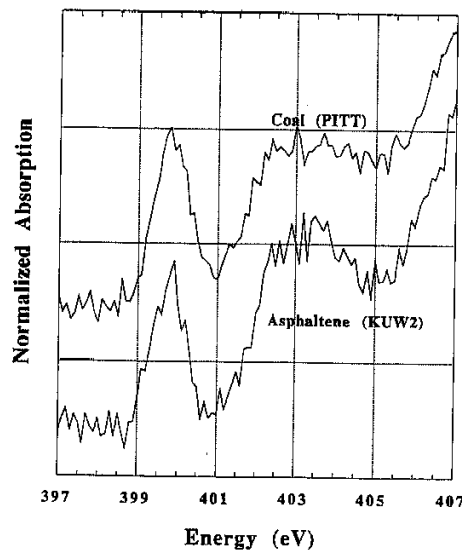


FIG. 5. Fluorescence XANES spectra of a high-rank coal and a petroleum asphaltene. The coal shows only a slight spectral valley at 405 eV, while the asphaltene shows a much more noticeable decrease in absorption at this energy. Aromatic amines possess an absorption maximum at 405 eV. The aromatic amine content of coals, lacking in asphaltenes, causes the increased absorption at 405 eV. (Although pyrroles have their peak absorption at 403.5 eV, they also absorb at 405 eV.)

similar with regard to their high concentrations of varied pyrroles and pyridines. However, coals evidently also have an aromatic amine fraction which produces absorption at 405 eV, thereby "filling in" the spectral valley at this energy. Aromatic amines are known constituents in coal-derived materials.²⁶

Least-squares fitting analyses were performed on all the spectra of the nitrogen model compounds and the fossil fuel samples. Each model-compound spectrum was fitted with a superposition of a number of Lorentzian peaks to account for the resonances, and an arc-tangent step function which represents electronic transition to the continuum. Figure 6 illustrates the fitting of three model compounds—a pyridine, a pyridone, and a pyrrole. In order to maintain consistency, both the position (~ 408.6 eV) and the width (1.5 eV) of the arc-tangent functions were held nearly the same for all the spectra, the exact position chosen to yield the best fit. The area-to-step-height ratios for resonances of all pyridine models were determined, and average values for different energy resonances of pyridines were obtained. Likewise, the area-to-step-height ratios for resonances of pyridones were determined, again, yielding average values for different energy resonances. In a similar manner, area-to-step-height ratios were determined for pyrroles, aromatic amines, and saturated amines. These ratios were used in the analysis of the coal spectra.

Concentration (thickness) effects in the fluorescence data of the model compounds were corrected for, with the use of the atomic subshell photoionization cross sections of carbon, hydrogen, nitrogen, and oxygen;²⁶ the corrections were made in a manner similar to that for earlier work on sulfur in fossil-fuels^{19,23} and of nitrogen in asphaltenes.¹⁴ With the exception of the diphenyl

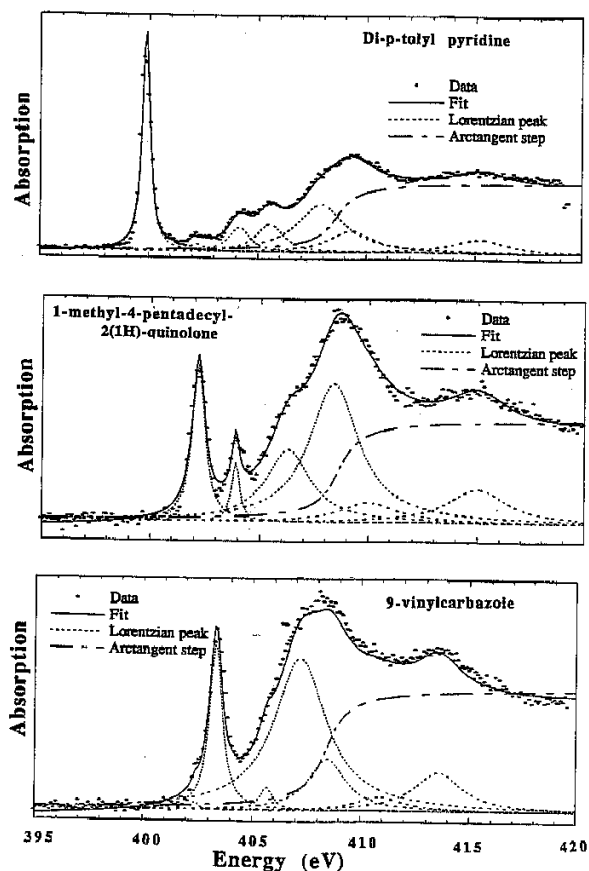


FIG. 6. The fitting used for three model compounds—di-*p*-tolyl pyridine, 1-methyl-4-pentadecyl pyridone, and 9-vinyl carbazole. The energies of the lowest-energy resonances of pyridines are 399.7 eV; pyridones, 401.9 eV; and pyrroles, 403.5 eV.

phenanthroline, the concentration effects were less than 10%. Therefore, the model compounds did not suffer from significant concentration problems. All the fluorescence spectra of the model compounds were, nevertheless, first corrected for thickness effects before the coal spectra were analyzed.

All coal spectra were fitted with eight Lorentzian peaks and an arc-tangent step function. The fitting is illustrated in Fig. 7 for a high-rank coal (top) and a low-rank coal (bottom). The seven lowest-energy peaks used to fit the coals were identified with particular nitrogen chemical structures. The relevant peaks are 399.8 eV, $\Delta\nu = 0.8$ eV (pyridine); 401.9 eV, $\Delta\nu = 0.97$ eV (pyridone); 402.6 eV, $\Delta\nu = 1.3$ eV and 403.7 eV, $\Delta\nu = 1.9$ eV (pyrrole); 405.0 eV, $\Delta\nu = 2.0$ eV (aromatic amine); and 406.2 eV, $\Delta\nu = 1.4$ eV and 407.9 eV, $\Delta\nu = 2.9$ eV (all models including saturated amines). A continuum resonance was included to produce better fits to the data but was not used in our analysis procedure; its location was 412.8 eV, $\Delta\nu = 3.2$ eV.

Areas of the different resonances in the spectra were normalized with respect to the arc-tangent step height. The normalized area of the 399.7-eV resonance in the spectrum of each coal was attributed to the pyridinic

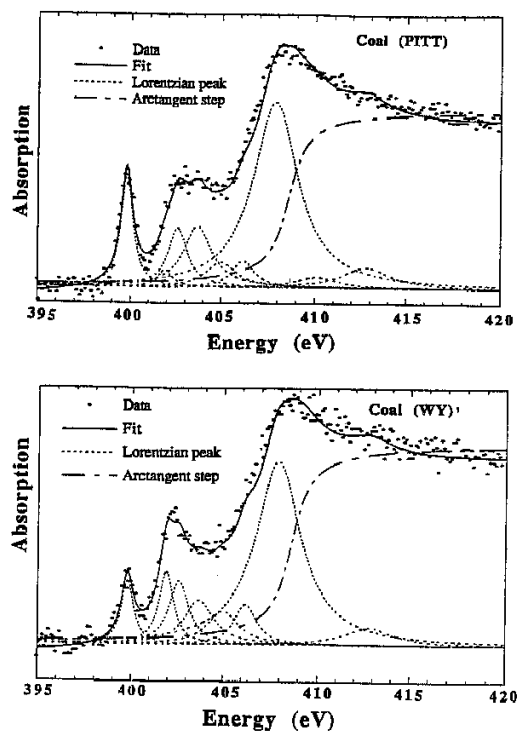


FIG. 7. The fitting used for a high-rank coal (PITT) and a low-rank coal (WY). The fit to the data is quite good, and the constituent peaks are shown. For fitting all coal spectra, the same peak positions and widths were used in order to more clearly establish trends. Note the difference in magnitude of the pyridine peak at 399.7 eV and the pyridone peak at 401.9 eV for the two coals.

nitrogen, and the total pyridine concentration in the fossil-fuel sample was determined with the use of the area-to-step-height normalization values obtained from the pyridine models. Next, the pyridone fraction was determined. The 401.9-eV peak area of each coal spectrum has a small contribution from the pyridinic nitrogen. This pyridinic contribution was subtracted, and the remaining peak area of the 401.9-eV peak was assigned to pyridone. The fraction of pyridone was determined with the use of the area-to-step-height ratio determined with the pyridone models. Next, the pyrrole fractions of all the coal samples were determined. The contributions to the 402.6- and 403.7-eV peak areas from pyridine and pyridone were subtracted, and the remaining peak area of these two peaks was assigned to pyrrole. The pyrrole fraction was determined with the use of the area-to-step-height normalization values obtained from the pyrrole models. In the absorption region of the aromatic amines at ~ 405 eV, the pyrrole fractions also show considerable absorption. The absorption of the pyrroles at 405 eV is accounted for by the 403.7-eV peak with its 1.9-eV peak width. Thus, the entire peak area of the 405-eV peak obtained in the coal fitting procedure was assigned to aromatic amine. Finally, all nitrogen chemical structures exhibit a σ resonance at ~ 408 eV. In order to determine the contribution of saturated amines to the spectra of coals, the contributions of all other nitrogen structures were subtracted from the sum of the 406.2-eV and the

TABLE I. Percentages of different nitrogen structures found in coals of different ranks.

Coal sample	Elemental composition (%) ^a				Nitrogen chemical structure (%) ^b			
	C	H	O	N	Pyridine	Pyridone	Pyrrrole	Aniline
POC	91.81	4.48	1.66	1.34	18	8	66	8
UF	88.08	4.84	4.72	1.60	18	8	66	8
PITTT	84.95	5.43	6.90	1.68	20	6	65	9
WF	85.47	5.44	6.68	1.61	20	16	55	9
UT	81.32	5.81	10.88	1.59	17	15	60	8
IL	80.73	5.20	10.11	1.43	20	19	54	7
WY	76.04	5.42	16.90	1.13	10	29	51	10
ND	74.05	4.9	19.13	1.17	2	42	50	6

^a Mass fraction from K. S. Vorres, Users Handbook for the Argonne Premium Coal Sample Program, Argonne National Lab, Argonne, IL.

^b Normalized by nitrogen content.

407.9-eV peaks. For all coals, there was no remaining peak area after subtraction of aromatic contributions from the σ resonance; that is, we found no evidence of saturated amine in any of the coals.

The results of quantification of the different nitrogen structures present in the coal samples are tabulated in Table I. The headings pyridine, pyridone, pyrrole, and aniline are meant to include all analogues with the corresponding chemical structure. In coal, most of these structures will have fused aromatic rings. For all the coals, the pyrrolic nitrogen is the dominant nitrogen fraction. Significant quantities of pyridinic nitrogen are found for higher-rank coals. For lower-rank coals, little pyridine is found; instead, large quantities of pyridone are found. All coals are found to contain small but significant quantities of aromatic amine. This amine fraction is nearly constant for all coals. No evidence of saturated amines was found in any of the coals; thus, no saturated amine is listed in Table I.

The data from Table I are plotted in Fig. 8; the fraction of nitrogen structures for each coal is plotted against the oxygen content for dry, mineral-matter-free coal samples. The dominance of pyrrolic nitrogen for all but the lowest-rank coal is observed. The correlation of a large pyridone fraction with a small pyridine fraction is evident. For higher-rank coals, pyridine is the second most abundant nitrogen type. The small but constant aromatic amine fraction is seen for these coals.

We estimate the error of the numbers listed in Table I to be approximately $\pm 12\%$; nevertheless, the trends shown in Fig. 8 are reliable and are directly evident in the data. Likewise, the magnitude of the small aromatic amine fraction is not certain, but the effect of the aromatic amine is seen directly in the data, as shown in Fig. 5. Several sources of error exist. We have obtained the XANES spectra of only a limited number of model compounds for each chemical class of nitrogen; thus, some uncertainty exists in both the energy range and the magnitude of the corresponding resonances. In our fitting procedure applied to coals, the assigned location of the peaks is somewhat arbitrary (only partially constrained by model spectra). If we fit the coal spectra with peaks at somewhat different energies, we would obtain different values of nitrogen fractions, thereby adding to the uncertainty. Again, trends would remain the same.

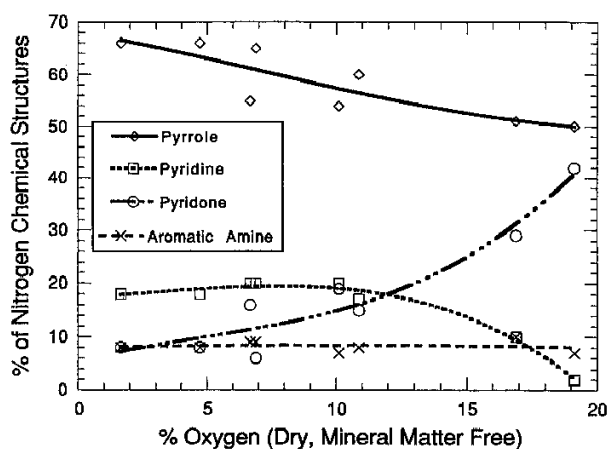


FIG. 8. The fractions of different nitrogen chemical structures are plotted against (dry, mineral-matter-free) oxygen content for all of the coals. Pyrroles are the most dominant nitrogen chemical structure of coals. For low-rank (high-oxygen) coals, the pyridine fraction is small and the pyridone fraction is large. Evidently maturation converts pyridone to pyridine. Aromatic amines are present in small but significant quantities in all coals.

There is an apparent increase in the pyrrole fraction as the oxygen content of the coals diminishes. This observation may result from the conversion of oxidized pyrrole to (reduced) pyrrole with maturation. We have not formally included oxidized pyrrole in our analysis. If the oxidized pyrrole ring maintains an aromatic nature (no sites of saturation), then it could appear quite similar to pyridone. Perhaps the XANES spectrum of this oxidized pyrrole would overlap with pyridone. This matter is currently under investigation.

CONCLUSIONS

XANES methodology has proven to be an excellent analysis tool to elucidate the different nitrogen structures in coals. The coal XANES spectra exhibit five well-resolved resonances, identifiable with five different chemical structures of nitrogen. The π^* resonances in the spectra of nitrogen model compounds belonging to different chemical structures occur at well-separated energies, facilitating the analysis of the coal spectra. Nitrogen in coals occurs in aromatic forms with negligible quantities of saturated forms. Pyrrolic nitrogen is most abundant in coals; pyridine, pyridone, and aromatic amines are also found in coals. For the lowest-rank coals, the pyridine fraction declines to very low values while the pyridone fraction increases considerably. This result correlates with the high oxygen content of low-rank coals. The clear implication is that pyridone is converted into pyridine with maturation of low-rank coals. A comparison between the coals and a petroleum asphaltene reveals the impact of aromatic amines on coal spectra. Investigation of a large number of model compounds shows that analogues having the same chemical structure show π^* resonances at similar energies. The less basic pyrroles and pyridones have higher-energy π^* resonances than the more basic pyridines. The π^* resonances of pyrroles and pyridones occur at somewhat different energies probably due to the carbonyl group of pyridones.

Future nitrogen XANES studies of coals should provide a wealth of information regarding the chemical properties of coal and related materials.

ACKNOWLEDGMENTS

The authors are grateful to Dr. Jan F. Branthaver of Western Research Institute for enlightening conversations. This research was performed at Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Division of Material Science and Division of Chemical Science S.P.C. acknowledges support by Lawrence Berkeley Lab, LDRD Exploratory Research Fund and by the National Institutes of Health, Grant GM-44380, and the National Science Foundation, DMB-9107312.

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