DOE Technical Report No. DOE/ PC/ 88921-16
Final Technical Report on Research Grant No. DE-FG22-88PC88921
Title: SPIN-MAPPING OF COAL STRUCTURES WITH ESE AND ENDOR
Principal Investigators: R. L. Belford and R. B. Clarkson
Institution: University of Illinois at Urbana-Champaign
Date: September 1, 1992; revised June 1, 1993
US/DOE Patent Clearance is not required prior to publication of this document.

EXECUTIVE SUMMARY

A nondestructive method to determine the atomic and molecular structures present in the organic (maceral) components of whole coal and coal products has been sought for many years. The proposal (1988) for this project outlined a program of research designed to address that analytical need by applying advanced electron magnetic resonance techniques to the determination of coal molecular structure.

Structural information was to be obtained by using the naturally occurring unpaired electrons in coal as "observation posts" from which to survey neighboring atoms through the electron spin-magnetic field interactions and the electron-nuclear hyperfine interactions. Such an overall approach has been termed "electron spin mapping" of coal structure. Advanced techniques like ENDOR (electron-nuclear double resonance), ESE (electron spin echo), and multifrequency EPR (electron paramagnetic resonance) spectroscopies were to be employed in the determinations. During the course of this study, these methods were applied, but the multifrequency EPR techniques proved to be the most useful.

The multifrequency studies were to use two unique instruments designed and constructed at the University of Illinois - an S-band (2 to 4 GHz) ESE spectrometer and a very high frequency (W-band, 94 to 96 GHz) EPR spectrometer. During the course of the study, both were used. The W-band system provided the most dramatic results.

The first materials to be studied initially were Illinois #6 coals and well-separated macerals obtained by density-gradient separation in order to reduce the heterogeneity of the samples. Some other coals and fossil fuel samples also were to be studied as opportunities arose. Typical EPR-active aromatic model compounds thought to exist in coals were to be prepared and studied by these techniques with the ultimate object of building libraries of spectra to aid in the coal analyses. In fact, all of these proposed sample types were studied during the project; moreover, some treated (including beneficiated) coals were included as well.

During the course of the project, several instrumentation improvements were made, methods investigated, and certain related aspects of the EPR behavior of coals and chars such as sensitivity to air and oxygen studied.

The following report consists of a Project Summary highlighting components of the work accompanied by a set of abstracts of publications and presentations resulting, in whole or in part, from this project.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

sp

PROJECT SUMMARY

Several kinds of electron paramagnetic resonance (EPR) spectra of coal (including whole coal, separated macerals, density-gradient separated fractions, and treated coals) and of model organic compounds thought to be molecular constituents of coals were acquired and analyzed in order to probe the molecular structure and surface properties of coals and of model systems. Typically, the model compounds under investigation and their analogues are found in coals as stable free radicals which give rise to an EPR signal. In some cases, the model compounds were selected because they have some characteristic, such as a particular functional group or heteroatom which may be found in coals, which fits them to serve as test materials for methods development.

Two critical instruments for this work — the W-band EPR spectrometer and the S-band ESE spectrometer — were built in this laboratory and were both further developed as part of this project. The ENDOR spectrometer also has been improved. During the course of this project, the W-band EPR system has proven to be the most fruitful tool for probing the chemical structures of coal, with the ESE system providing the most valuable auxiliary data.

While this research group continues to catalogue and analyze EPR and ESE spectra of coal, coal maceral, and model compound samples, it has very recently also made progress in technique development and application. In particular, this project has seen considerable progress in the general examination of the applicability of W-band EPR and of low-frequency ESE (electron spin echo) spectroscopy to characterization of heteroatoms in a heterogeneous environment. Nitroaromatic, thiophenic, furanic, and other aromatic radicals catalytically produced in the presence of oxygen as asymmetric surface species on particulate catalyst surfaces and as solid matrix centers were probed by both techniques, and it is shown that the electronic structure in the vicinity of the nitrogen, sulfur, and oxygen atoms can be elucidated in this way.

The following report summarizes highlights of these studies. It provides some background, rationale, and selected data and results. Finally, a list of papers and presentations is provided together with abstracts of all of them.

PROJECT REPORT - HIGHLIGHTS

There is a present and growing need for non-destructive methods to analyze coal structure on the molecular level. Future developments in coal processing and utilization require better information concerning patterns of chemical bonding, functional group distribution, and organic heteroatom concentrations and types, to name a few areas of significant need for coal research and engineering. Because coal is an opaque solid with relatively low volatility at room temperature, few analytical techniques can provide information on its molecular structure in a non-destructive fashion. Because coal structure is sensitive to thermal and chemical modification, the requirements for truly non-destructive methods are stringent, a fact that is especially important in analyzing for effects of processing or cleaning.

The naturally occurring unpaired electrons in coal have always offered an attractive route to the non-destructive study of coal structure. In a typical Illinois #6 coal, for example, there are about 10^{19} unpaired spins/gram. Because coal is highly aromatic (in this Illinois #6, ca. 77% C, it is estimated that 65 - 70% of the carbon is aromatic, with an average aromatic cluster size of 20 - 25 carbon atoms [1]), unpaired electrons delocalize over many carbons. Thus, the unpaired electrons in an Illinois #6 *interact directly with 1% of all the carbon, and 2% of the aromatic carbon in the coal*. For the ENDOR and ESE versions of EPR, long-range interactions between the electrons and neighboring nuclei with magnetic moments (e.g. ^1H) can extend the "field of view" to include more than 10% of all the atoms in the coal. This good coverage of the atoms in coal, together with a reasonably uniform distribution of unpaired electrons throughout all maceral components and the exceptional sensitivity of electron paramagnetic resonance (EPR) spectroscopy (10^3 times the sensitivity of ^1H NMR) makes the paramagnetic spins very attractive natural observation posts from which to non-destructively analyze coal molecular structure.

The problem that had prevented the EPR approach to coal structure analysis from being more successful was one of resolution. Information about molecular structure and atomic environment was hidden within the EPR spectral lineshape of typical data obtained at 9.5 GHz and 0.34 T. (X-band EPR), and in most cases it could not be deconvolved. This lack of spectral resolution was especially maddening in the case of heteroatom (N, O, S) analysis, where indications of the effects of atomic spin-orbit coupling between the unpaired electrons and heteroatoms were even seen in X-band spectra [2], and which higher magnetic field strength experiments were predicted to resolve. In 1990, our laboratory pioneered in the development of a novel 95 GHz, 3.4 T. (W-band) EPR instrument[†], and demonstrated that this prediction was correct by examining the suite of Argonne Premium Coal samples, as well as a vitrinite, sporinite, and inertinite maceral separated from an Illinois #6 coal by density gradient centrifugation [3]. Figure 1 illustrates the emerging resolution of a low-field feature in an Illinois coal as the magnetic field strength is increased from 0.34 T. to 3.4 T. The technique, termed very high frequency EPR (VHF EPR), seems uniquely sensitive to the effects of heteroatoms, particularly sulfur.

[†]This is the only spectrometer of its kind in the United States, and one of only two in the world.

Figure 1. EPR spectra of a whole Illinois #6 coal at (a) 0.34 T. (X-band), (b) 1.2 T. (Q-band), and 3.4 T. (W-band). Shaded area is believed to be due to organic sulfur species.

Figure 2. Above: Illinois #6, 2.38% organic sulfur. Below: Sporinite, 4.25% organic sulfur. In each figure, solid line is experimental data; dashed line is simulation.

What makes this discovery useful as well as interesting is the fact that spectra like those shown in Figure 1 can be understood theoretically, thus allowing for the development of a *technique* to analyze for organic sulfur in coal. Further, information from organic sulfur model compounds like dibenzothiophene and benzonaphthothiophene allow theory to be tested on ideal molecular systems with properties thought to be very similar to important species found in whole coal. During this project, we developed chemical techniques to synthesize coal model sulfur compounds, and thus are in a position to develop this analytical component of the work with much better precision. This process started under the DOE grant and continues even after the expiration of this grant (see end of this section). Spectra from compounds such as these form the basis of our understanding of the more complex spectra obtained from coal.

Three examples will be given to illustrate some of the potential in the VHF EPR method, as it has been developed in this project. The first, shown in Figure 2, compares the VHF EPR spectra at W-band of an Illinois #6 coal from the Argonne Premium Coal Sample program, and a sporinite separated from it by density gradient centrifugation. Careful destructive chemical analysis suggests that the whole coal contains 2.38% organic sulfur [4], while the sporinite contains 4.25% [5]. We analyzed the VHF EPR spectra of these samples by computer simulation of the spectra, assuming a two-species model of axial symmetry, assuming the total spectrum can be treated as the sum of contributions from sulfur and sulfur-free species. Areas under the simulated sulfur-containing spectra from the two samples were in the ratio 1.76 (sporinite/whole coal), while the ratio of organic sulfur concentrations was 1.79. Such excellent agreement indicates that the magnetic resonance method is accurate, while also remaining non-destructive and quick. Similar good agreement between chemical and VHF EPR analyses was found for a high-sulfur Rasa coal. Individual coals do show variations in spectral parameters, however, and very important additional information on the molecular structures and sizes contributing to the overall VHF EPR lineshapes are still to be understood. This method now should be further developed in order to improve its quantitative accuracy and structure sensitivity for organic, aromatic sulfur forms in coal.

Figure 3 compares two "before and after" samples in order to demonstrate the effects of two desulfurization methods on an Illinois #6. In Figure 3(a), the coal was subjected to biodepyritization by action of *thiobacillus ferrooxidans* bacteria (samples obtained from Dr. Greg Olson, Coal Cleaning Group, PETC). What makes this result significant is that since our method rigorously excludes pyritic sulfur from analysis, the decrease in the low-field spectral feature associated with organic sulfur means that this biologic cleaning method altered or removed nearly 45% of the *organic* sulfur. Our results now have been corroborated by XANES data on this sample, giving us greater confidence in the effectiveness of VHF EPR in evaluating the effects of biodesulfurization. Figure 3(b) shows spectra of the Illinois #6 before and after low-temperature (285°C) pyrolysis for two hours. The greatly reduced low-field peak in the pyrolyzed coal suggests that this treatment significantly altered and removed aromatic organic sulfur, as has been reported by Kruse, et al. We propose to investigate such desulfurization processes with VHF EPR in order to learn details of the processes, as well as to assess their effectiveness.

Fig. 3(a). W-band spectra of an Illinois #6 before and after biodesulfurization.

Fig. 3(b). W-band spectra of an Illinois #6 before (solid) and after (dashed) low temp. pyrolysis.

Figure 4(a) 94 GHz and 250 GHz VHF EPR spectra of a sporinite separated from Illinois #6.

Figure 4(b). VHF EPR spectral simulations of a C_{20} thiophene radical at 94 and 140 GHz.

Figure 4(a). shows VHF EPR spectra taken at 94 GHz and 250 GHz of the sporinite shown in Figure 2. (the 250 GHz spectra were obtained on a quasi-optical, 9 T. instrument built by Prof. Jack Freed and co-workers at Cornell University, with whom we collaborate).

Resolution of the low-field region of the spectrum is much improved at the higher frequency (and field). An analysis of these two spectra, based on theoretical simulations of model compounds, reveals that an unambiguous interpretation of the sulfur and oxygen-containing molecular forms contributing to the total VHF EPR spectral data set will benefit from at least one other VHF spectrum at a third field/frequency value. The need for multi-frequency data in the analysis of powder EPR spectra of coal has been considered in detail by Belford, et. al. [6, 7]. For this reason, we intend eventually to construct a unique VHF EPR spectrometer operating at 140 GHz, 5 T. (D-band), and optimized for coal research. (This would become the second D-band spectrometer in the United States, and the only one targeting coal research). Figure 4(b) shows 94 GHz and 140 GHz spectral simulations of a model compound, illustrating the better resolution expected from D-band.

Additionally, we have explored relaxation processes in coals and have prepared to consider the role of nitrogen in the chemistry of aromatic compounds in coal by studying the magnetic (hyperfine) interactions between nitrogen nuclei and unpaired electrons, utilizing a unique S-band pulsed EPR spectrometer built in our laboratory especially for coal-relevant research. During the period of the DOE grant, considerable progress was made in developing the use of this ESE instrument to locate the positions and electronic state of nitrogen atoms near EPR-active sites. With multifrequency, especially VHF, EPR observations, as well as information on electron-nuclear interactions, we have built the basis to develop a library of reliable spectral parameters for model systems, and from this theoretical base to analyze the concentration and structure of the major organic sulfur (and perhaps oxygen and nitrogen) species contributing to the spectra. Thus two major goals have emerged to guide our work during the latter stages of the reporting period and in the near future: (1) development of the VHF EPR method (experimental and theoretical), together with other advanced magnetic resonance techniques, into a more powerful analytical approach for the quantitative determination of aromatic sulfur in coal, as well as for molecular structural information concerning organic species containing sulfur, oxygen, and nitrogen (e.g., number of aromatic carbons associated with sulfur) and, (2) application of the method to a systematic evaluation of the effects of desulfurization on organic sulfur content and coal structure.

Our DOE/PETC research program recently was reviewed by the U. S. DOE in a full Peer Review in Pittsburgh organized by Oak Ridge National Lab. Not only was our approach judged "creditable and logical", but reviewers said of our work, "...support is crucial to maintaining a viable program in this area, with possible high benefit-to-cost ratio in the area of method development."

SCIENTIFIC DISCUSSION

Over the past few years, our laboratory has been working on a variety of non-destructive methods for the characterization of organic matter in coal. Our approach is to use the naturally occurring unpaired electrons in coal as "spies" of their local environment; they report on the number, positions, and types of atoms with which they come in contact or close proximity, and we translate this information into models of coal structure. Unpaired electrons in coal occur

naturally in all organic phases with an abundance that is excellent for our spectroscopic method. Their typical concentration (see Introduction) is ideal — high enough to be of value in examining the structure and to yield very strong EPR signals yet just low enough to prevent spin-spin interactions from destroying the spectroscopic detail from which information is obtained. Their distribution by maceral types is not uniform, but does scale as the weight fraction of individual maceral types [1]. There is, of course, the question to what extent these unpaired electrons spy on a representative distribution of local structures in each maceral. We have some evidence that if the distribution is not uniform, it is at least biased toward the sulfur-containing aromatic structures.

It has long been known that sulfur and oxygen have strong and characteristic interactions with unpaired electrons. With funding from the U. S. Department of Energy, the Center for Research on Sulfur in Coal (now Illinois Clean Coal Institute under IDENR), the Petroleum Research Fund (ACS), and the National Institutes of Health, as well as from an industrial sponsor, we have built a unique, Very High Frequency Electron Paramagnetic Resonance (VHF EPR) spectrometer operating at the W-band of microwave frequencies (ca. 96 GHz). This spectrometer is capable of measuring these interactions, providing a potential avenue to the direct, non-destructive characterization of organic heteroatomic species in coal. In the discussion that follows, we will focus our attention on organic sulfur in coal, while keeping in mind that the very same arguments also apply to oxygen.

The fundamental fossil fuel motivation for building a spectrometer to perform the EPR experiment at a magnetic field of 3.4 T. instead of at the usual 0.34 T. was to improve spectral resolution and sensitivity of the technique to sulfur-containing compounds - especially thiophenics and thiobenzene rings - (and, perhaps, to oxygen-containing compounds like furans and phenolics) in order to characterize organic sulfur in coal. This expectation has been borne out during the course of this DOE project. (There is corresponding fundamental motivation for the planned, but as yet unfunded, addition of yet a higher frequency, ~145 GHz: yet more resolution will be available at the higher frequency and that new, independent data will be obtained which will increase information content and reduce the ambiguities which remain, including the role of oxygen in the spectra and differences in spectral parameters from different coals.)

The relationship between magnetic field strength and sensitivity to sulfur can be better understood by considering the energy of an unpaired electron in an external field, B . If the orbital occupied by the electron is nondegenerate ($L = 0$), then the "spin only" energy is given by:

$$\mathcal{H}_{\text{sz}} = \beta_e B \cdot g \cdot S \quad (\text{i})$$

where $\mathcal{H}_{\text{sz}}$ is the spin Hamiltonian (electronic Zeeman interaction only), β_e is the Bohr magneton, B is the external magnetic field, g is the g -tensor, and S is the electron spin operator. In this case, when the electron possesses only spin angular momentum, the g -tensor is isotropic and has the free electron value $g_e = 2.00232$. When the electron is in an orbital with angular momentum ($L > 0$), either by itself or via coupling to excited states, then the orbital angular momentum mixes with the spin angular momentum. Our Zeeman spin Hamiltonian now contains another term, reflecting this additional interaction:

$$\mathcal{H}_{\text{ez}} = \beta_e B \cdot (L + g_e S). \quad (\text{ii})$$

In addition to modifying the electronic Zeeman energy, the orbital angular momentum of the unpaired electron (or magnetic dipole moment induced by the orbital motion) also interacts directly with the unpaired electron, creating an additional energy term:

$$\mathcal{H}_{\text{so}} = \lambda L \cdot S \quad (\text{iii})$$

where λ is the spin-orbit coupling constant, a term proportional to the nuclear charge of the atom (Z) and $\langle 1/r^3 \rangle$, where r is the orbital radius. λ may be positive or negative, reflecting the fact that the local orbital field may add to or subtract from the external static field.

The total spin energy for this system now is written:

$$\mathcal{H}_{\text{spin}} = \mathcal{H}_L + \mathcal{H}_S = \beta_e B \cdot (L + g_e S) + \lambda L \cdot S \quad (\text{iv})$$

The effect of orbital angular momentum is to alter the energy of the spin in an external magnetic field. We now must remember that in the EPR experiment, we measure the energy represented by $\mathcal{H}_{\text{spin}}$ by scanning magnetic field rather than frequency. Field positions of resonance lines are related to energies by the simple resonance equation:

$$h\nu = g_{\text{eff}} \beta_e B_\nu \quad (\text{v})$$

where all symbols have their customary meaning, and g_{eff} is an "effective g-value" that characterizes the position of the line (analogous to the chemical shift parameter in NMR). If $L = 0$, then $g_{\text{eff}} = g_e$ as can be seen in Equ. (iv); if $L > 0$, then g_{eff} will deviate from g_e in a way determined by L and λ . In the coal system, spin-orbit coupling ($\mathcal{H}_L$) is primarily responsible for this deviation, and this key fact allows us to observe the presence of organic sulfur compounds in the EPR spectra.

Since g_{eff} differs from the free electron g-value, g_e by an amount Δg , which is sensitive to the presence of sulfur, it is important to know what we can do experimentally to optimize our ability to measure this effect. It can be seen from equation (v) that, at a constant ν , the change which sulfur makes in the magnetic field position of the EPR resonance line, B , is given by:

$$B_1 - B_2 = \Delta B = h\nu/\beta(1/g_1 - 1/g_2) = h\nu/\beta \{ (1/g_e) - (1/(g_e + \Delta g)) \} \quad (\text{vi})$$

Thus, the shift in field, ΔB , of the resonance of our "spy" electrons due to sulfur, is dependent on Δg and ν .

Deviations of g factors (g-shifts) from the free-electron value (2.0023) and direction-dependence in g factors (g-anisotropies) result from admixture of orbital angular momentum (and therefore magnetic moment) into the spin angular momentum to augment (or diminish) the spin-only Zeeman splitting. An unpaired electron in an orbital Φ which includes some p, d, or f character on atom A is subjected to a spin-orbit coupling interaction characteristic of that particular atomic orbital; that interaction mixes excited-state spin orbitals into the ground-state spin orbitals $\Phi\alpha$ and $\Phi\beta$. As a rule, organic radicals which contain sulfur atoms display particularly strong g-shifts and g-anisotropies for the following reasons. Generally, 2p oxygen-atom orbitals are much more effective at spin-orbit coupling than carbon-atom orbitals, and 3p (or 3p,3d hybrid) sulfur-atom orbitals are a great deal more effective than oxygen. Moreover, sulfur heteroatoms in an aromatic pi-system radical tend to trap the electron spin density more than oxygen heteroatoms, thus enhancing the intrinsic relative effectiveness of sulfur atoms in causing g shifts. The g-anisotropies arise because the excited-state orbitals which are mixed into the ground-state semi-occupied molecular orbital have directional properties. Finally, g-shifts may be positive or negative depending on the type of excited state which spin-orbit coupling mixes into the ground state; $\chi^2\Phi^1 \rightarrow \chi^1\Phi^2$ and $\chi^0\Phi^1 \rightarrow \chi^1\Phi^0$ transitions cause g-shifts of opposite sign.

The sulfur "g-shift", Δg , is a feature of the coal sample; we cannot change this parameter without changing the chemistry of the sample itself. The experimental frequency, ν , is ours to choose, however, and the higher the better (within very practical limitations imposed by instrumentation and linewidth behavior), since the larger ν is, the larger ΔB will be, and the more sensitive our experiment will be to the presence of sulfur. It is for this reason that we have constructed a very high frequency (94 GHz) EPR instrument, and with it we have observed the

ΔB due to sulfur and oxygen, which produces shifts much too small to be seen at lower spectrometer frequencies.

We have verified the effectiveness of this VHF-EPR approach by taking survey W-band spectra of many coals, including all in the Argonne Premium Coal Sample program [8]. Coals with higher heteroatom concentrations give wider, multi-component spectra, as shown in Fig. 5.

Fig. 5. W-band EPR spectra of three APCS coals. a) Illinois #6, b) Blind Canyon, c) Beulah-Zap

The differences in spectral lineshapes of these three coals are believed to originate in differing concentrations of heteroatoms, principally oxygen and sulfur, and also in differences in the molecular forms containing the heteroatoms. Understanding the relationships between these spectral lineshapes (obtained by several advanced EMR methods) and the concentrations and structures of organic heteroatomic species in coal became an important scientific goal this proposed work. In order to gain more information on the nature of the differences in coal structure revealed by VHF-EPR spectra (and also to reduce spectral complexity), we began to study macerals separated by density gradient centrifugation from the Illinois #6. Preliminary spectra from separated vitrinite, sporinite and fusinite fractions are shown in Figure 6.

The fusinite signal in Figure 6(c) is so different from the other two maceral spectra, it must reflect a dominant interaction that is not as important in the other components. This interaction usually is assumed to be electron spin exchange, resulting in a narrowing of the resonance line [9, 10]. We have tested this hypothesis by performing S-band pulsed EPR measurements on the fusinite, and observe only a free induction decay (FID), as shown in Figure 7. A very strong dependence of T_{1e} and T_{2e} on adsorbed oxygen was observed in these measurements, and the fusinite sample whose FID is shown in Figure 7. was carefully evacuated. The observation of an FID, combined with the absence of echoes, lends strong support for the spin exchange model, particularly since the maceral contains almost as much hydrogen (4.24%) as the vitrinite and sporinite, which give strong spin echoes and proton ESEEM. Fourier

transformation of the FID yields a frequency domain spectrum with linewidth nearly identical to that observed in the sample by CW EPR at 3, 9, and 96 GHz, again in agreement with the prediction of a linewidth independent of B_0 for exchange narrowing in the limit $B_e \gg B_0$ or $B_e \ll B_0$, where B_e is the exchange field [4], although multi-frequency VHF EPR data at higher frequencies is needed for a complete understanding of the effect.

Figure 6. W-band EPR spectra of a) Vitrinite, b) sporinite, and c) fusinite macerals separated from an Illinois #6 coal.

Figure 7. S-band pulsed EPR spectrum of evacuated fusinite from Illinois #6.

We also began a program to measure the static magnetic susceptibility of coals at different temperatures (1.5K to 290K) and different magnetic fields (2 T to 5.9 T) utilizing a superconducting SQUID magnetometer. Non-resonance measurements confirm the presence of a moderate exchange field in fusinite.

Chemical evidence strongly suggests that the complex lineshapes seen in the VHF EPR spectra of a coal like Illinois #6 (and fusinite and sporinite macerals separated from it) are the result of contributions from several molecular populations, some of which contain sulfur. In order to analyze experimental spectra in a quantitative fashion, we have begun work to create a general-purpose computer technique, based on the simplex multi-variable optimization strategy, to simulate experimental data in order to obtain spectral parameters (g-values, linewidths, and composition coefficients) which can be correlated to chemical structure. The first tests of this approach have utilized a model of axial symmetry in which all the contributors to the VHF EPR spectrum are grouped into two classes – sulfur and non-sulfur species – called the two-species model. Theoretical modeling is based on the very successful QPOW algorithm for powder EPR spectral simulation developed by Belford and co-workers [11]. Graphical results of the application of the technique to VHF EPR spectra from an Illinois #6 coal and sporinite separated from it were shown in Fig. 2, and results from several coals are summarized in Table I.

TABLE I. SUMMARY OF TWO-SPECIES SIMULATION OF FOUR COALS

COAL TYPE	$g_1(I)$	$W_1(I)$ (Gauss)	$g_2(I)$	$W_2(I)$ (Gauss)	$g_1(II)$	$W_1(II)$ (Gauss)	$g_2(II)$	$W_2(II)$ (Gauss)	A_1	%S
RASA	2.00429	18.94	2.00294	3.22	2.00354	13.22	2.00308	5.86	420	11.4
Sporinite	2.00418	21.81	2.00257	6.83	2.00290	18.18	2.00236	7.34	180	4.25
Illinois #6	2.00406	18.35	2.00307	10.81	2.00288	10.38	2.00235	12.57	102	2.38
Blind Canyon	2.00418	16.18	2.00284	4.51	2.00309	14.39	2.00268	6.88	63	0.37

(Simulation assumes two species, each with axial symmetry. g_1 and g_2 are the two g-values associated with each axial species. Numerals I and II refer to the two species. $W_{1,2}$ refer to the linewidths of the two components of the spectrum of each species. A_1 is the integrated intensity of species I, which is assumed to contain sulfur. %S is the literature value for the dry, mineral free content of organic sulfur in each coal as determined by chemical analysis.)

In three of the coals (Rasa, Ill#6, and sporinite from Ill#6), good correlation exists between the parameter A_1 and the sulfur content of coals as determined by chemical analysis. Blind Canyon, a lower rank coal, fits the general trend, but not very precisely. This observation, coupled with differences in the other spectral parameters (g-values and linewidths) suggest that much of the structural information contained in these spectra is yet to be understood, and that the VHF EPR technique, in conjunction with other EMR methods, can learn much more about coal structure than simply the content of organic sulfur.

The multi-frequency approach is one very important experimental technique that must be applied in order to take advantage of the structural information contained in VHF EPR spectra. For example, a vitrinite separated from the Illinois #6 coal was run at 250 GHz in the laboratory of Professor Jack Freed (Cornell University). Figure 4(a) shows a comparison of the

96 and 250 GHz spectra and confirms that the low-field peak is, indeed asymmetric and part of one or more overlapping anisotropic spectra, as presumed in the two-species model. Furthermore, the changes in spectral lineshape of the sample at 250 GHz could indicate the presence of a distribution of heteroatomic forms. Recent XAFS results from the groups of Gorbaty [12] and Huffman [13] have suggested that large amounts of organic sulfur in coal are in the form of thiophenes, with a dependence on rank that approaches 100% thiophenic for high-rank coals like Pocahontas. In Illinois #6, thiophenes account for between 50% and 70% of all organic sulfur. If we recall that our VHF EPR method is quite selective for conjugated aromatic forms; then it will be seen as likely that our spectra largely reflect the concentrations and structures of these thiophenes, and the distribution seen at 250 GHz may be an indication of the range of aromatic ring sizes over which our *spy* electrons are delocalized. Further, the striking similarity between VHF EPR spectra at W-band for the Illinois #6 sporinite maceral fraction and the Rasa coal offers more evidence that in these samples, the dominant species seen by our technique are thiophenes, in agreement with XANES and XPS data. Certainly in the Rasa coal, there is on average one sulfur in every aromatic cluster over which the unpaired electrons are delocalized, possibly producing a quite simple VHF EPR spectrum. Higher field/frequency experiments are needed to further investigate this possibility. We have started work to develop a detailed theoretical model of the effects of aromatic ring size on the VHF EPR spectra of coal (with the help of model thiophenic compounds), in order to exploit this effect to assess the size distribution of thiophenic condensed ring structures, and to better understand heterocyclic structure and aromaticity in coal.

Comparison of vitrinite and sporinite spectra (Figs. 6(a) and (b)) illustrate how separated macerals can provide important information on any multi-species model of VHF EPR coal spectra, since features with identical *g*-values appear with different intensities in the two systems, suggesting differing contributions from sulfur and non-sulfur components. The lower two *g*-values (*g*₁ and *g*₂) of the vitrinite are, in fact, just those observed for many different conjugated aromatic radicals, and predicted theoretically by Stone [14], and it is tempting to see the spectrum as a composite formed from pure hydrocarbon and heteroatomic radical contributions. In all probability, the low-field shoulder in this spectrum is associated with heteroatomic radicals, since spin-orbit ("SO") coupling to sulfur (or oxygen) is the most likely mechanism to account for the higher value of *g*₃. The rather poor low-field fit of the single species simulation then could be a reflection of this composite character. Clearly, this issue of spectral and sample heterogeneity is of utmost importance for the correct interpretation of EPR spectra of fossil fuels, even when well-separated and purified, and we presently are working on several approaches designed to shed more light on the problem, including ESE and high-field ENDOR, as well as multi-frequency VHF EPR.

A promising avenue of investigation which we propose systematically to develop involves comparing multi-frequency VHF EPR spectra from coal with spectra obtained from model compounds believed to typify organic structures in coal. One aim of a comparison study of coals and model compounds is species analysis – i.e., to set up a scheme for analysis of an arbitrary coal sample by representing the spectra (*S*) of that sample as a weighted sum of the spectra (*S*_{*j*}) of its component species. That is, one can write a system of linear equations,

$$S_i(B) = \sum_j f_j S_{j,i}(B), \text{ where}$$

B is the magnetic field (the abscissa points in each spectrum), *v* is the spectrometer frequency

and f_j is the fraction of species j in the coal specimen. The equations then need to be solved for the unknowns, which are the fractions, f_j . Ideally, the system is overdetermined, because there are far more data points (for example, around 1000 B points per spectrometer frequency) than unknowns. However, a question which needs to be answered is, of course, how much linear independence there is in the subspecies spectra. Each significantly different (VHF) frequency, ν , provides a new set of equations, which should reduce linear dependences and uncertainties in the solutions. While we are in the process of acquiring W-band (96 GHz) spectra of component (model) species, it seems clear that we can only obtain a partial solution from that frequency alone, and that at least one (and better, two or more) significantly different frequencies would greatly increase information content. The necessity of such an approach is illustrated by the comparison of experimental and theoretical spectra for 94 GHz and 250 GHz spectra from the Illinois #6 sporinite maceral, illustrated in Figure 8. Utilizing a simple model which assumes a spectrum dominated by thiophenic forms, a distribution of anisotropic g -values (reflecting a distribution of contributing thiophenic structures) was employed to simulate the spectra at the two frequencies. Significant error on the low-field side of the 250 GHz simulation may be due to any of a number of factors, including contributions of non-sulfur species (e.g., furans), incorrect choice of g -value distribution (g -strain model), or even instrumental phase errors. An equally bothersome discrepancy between theory and experiment occurs in the mid-spectral region of the W-band data. Unfortunately, improvements in the model (and the identification of possible instrumental artifacts) requires at least one additional field/frequency observation; we hope to develop such a facility in the future.

Figure 8. 250 GHz and 94 GHz spectra of sporinite. (—) experimental; (---) theoretical.

The method of utilizing model compound spectra to simulate complex coal VHF EPR spectra is illustrated in the following data. Figure 9(a) shows a spectrum from perylene cation radicals, together with a preliminary theoretical simulation. The simulation used $g_1 = 2.0024$, $g_2 = 2.0030$, and $g_3 = 2.0032$, proton hyperfine values obtained experimentally by ENDOR [15], and spin packet linewidths determined by electron spin echo measurements [16]. Figure 9(b) shows the perylene(+) spectrum superimposed on a vitrinite W-band spectrum, to illustrate how a portion of the coal resonance line shape might originate from conjugated aromatic hydrocarbon radicals containing no heteroatoms.

Figure 9 W-band spectra of a) model coal hydrocarbon, perylene(+). b) perylene(+) superimposed on vitrinite. (—) experimental; (---) theoretical.

Figure 10a,b. W-band spectra of a) model sulfur heterocyclic, dibenzothiophene(+)(DBT), (—) experimental; (---) simulation; (b) Comparison of DBT and BNT VHF EPR spectra.

Figure 10(a) shows a W-band spectrum of dibenzothiophene (DBT) cation radicals, together with a preliminary simulation ($g_1 = 2.0016$, $g_2 = 2.0054$, $g_3 = 2.0106$). The effect of SO coupling with sulfur is seen in the higher g -values and much more asymmetric line shapes. Figure 10(b) compares W-band EPR spectra of DBT and benzonaphthothiophene(+) (BNT), illustrating how additional carbon atoms in the thiophenic aromatic cluster reduce g -anisotropy. This dependence of g on aromatic cluster size provides a basis for determining the distribution of aromatic sulfur species in coal through an analysis of multi-frequency VHF EPR spectra. Attar and Dupuis [17] reported that thiophenes are the most abundant form of organic sulfur in Illinois coals (thiophenic, 58%; Ar-S-Ar, 20%; R-S-R, 18%; Ar-SH, 15%; R-SH, 7%), and Gorbaty, et. al [6] and Shah, et. al. [7] have obtained similar organic sulfur distributions employing XANES; this model compound approach should allow us to carefully evaluate sulfur-species distributions as observed by EPR, and to compare the results with those obtained from other non-destructive methods.

This brings up an interesting point which requires examination: is the g -anisotropy a monotone-decreasing function of size of the fused-ring system? A naive view would say yes, but

we have found (cf Wei et al., 1992 in our publication list) that the situation is much more complicated. We are now carrying out quantum-mechanical calculations of heterocyclic fused-ring radical systems in an attempt to establish a method for predicting the g matrices from structure. No truly satisfactory calculation has ever been done. Space does not allow further discussion of this. Suffice it to say that we think we understand why previous theory has been unsatisfactory in this and are using both semiempirical and *ab initio* methods (with Prof. Kathleen Robins at UNLV) in attacking the problem.

Because conjugated aromatics are the predominant structural types for organic sulfur in this coal, and because unpaired electrons are expected to be most abundant (and stable) in such chemical environments, it seems likely that EPR spectra from coal will strongly reflect the delocalization of electrons. This implies that a very small number of sulfur (or oxygen) atoms can exert a large effect on spectral line shapes, making this technique uniquely sensitive to heteroatoms with larger SO coupling constants (λ). Since the effect of a sulfur atom on g -values decreases as an electron is delocalized over a larger and larger number of carbon atoms (and the S/C ratio falls), the precise line shapes from sulfur in coal will depend on the size of the aromatic structures, as well as on the type of bonding. As we have mentioned, this fact represents another opportunity for the nondestructive analysis of high-sulfur coals by W-band EPR, since it may be possible to model the spectra in order to get more detailed chemical information about the forms of organic sulfur that are present. To illustrate this concept, Fig. 10(c) shows a W-band spectrum of vitrinite. Superimposed on it is a composite spectrum constructed by adding the spectrum from perylene(+) and a portion of that from dibenzothiophene(+). While the agreement between data and construct is not perfect, a comparison does suggest that molecular forms like perylene and dibenzothiophene are contributing to the experimental spectrum. The incorporation of additional species in a composite model can reliably

Fig. 10(c) W-band spectrum of vitrinite from an Illinois #6. Solid line - exptl; dashed, simulation. be developed only if several field/frequency VHF EPR data sets are available. In the future, we hope to use spectral addition methods in a more quantitative way to gain a better understanding of the molecular structure of the organic heteroatomic components of coal, including organic sulfur.

Nitrogen has a spin-orbit coupling constant much smaller than either sulfur or oxygen, and cannot easily be studied by exclusively VHF EPR techniques. Its role in the heteroatom chemistry of coal is important, however, and we have been preparing to study it with two other

advanced EMR techniques, electron spin echo (ESE) and electron-nuclear double resonance (ENDOR) spectroscopy, which we have developed for coal science in our laboratory. These approaches investigate the molecular environment of nitrogen by measuring magnetic (hyperfine) interactions between the nitrogen nucleus and nearby unpaired electrons. Our work in this area has begun, utilizing as a model *m*-dinitrobenzene radicals formed on activated alumina powders. W-band EPR spectra of this system show *g*-anisotropy that is predictably smaller than that seen in sulfur and oxygen compounds. Making use of our unique S-band pulsed EPR spectrometer (designed and built to study coal), we have observed electron spin echo envelope modulation (ESEEM) which we have analyzed by theoretical simulations and fourier transformation (FT) techniques. Figure 11 shows FT spectra of this compound at three field/frequency values near the conditions of "exact cancellation" for this system, where pure nitrogen quadrupole transitions can be observed as strong, sharp spectral lines. The first three peaks in the spectra are assigned as pure nuclear quadrupole transitions of ^{14}N nuclei, while the fourth peak is a nuclear transition from another spin manifold. Because of the structure sensitivity of NQR transitions to chemical structure, this approach offers some potential for studying nitrogen bonding in coal. For heterocyclic nitrogen, a combination of ESE and ENDOR techniques are being employed. The combination of Zeeman-sensitive techniques (VHF EPR) and hyperfine-sensitive techniques (ESE and ENDOR) provides much more detailed information than any single experimental approach, and is proving useful in understanding the structure of other coal-related heteroatomic species (e.g. furans, semiquinones) as well as nitrogen.

Figure 11. Fourier transformed ESEEM spectra of *m*-dinitrobenzene on alumina at 4.2 K. Experimental frequencies are: A, 3.85 GHz; B, 3.23 GHz; C, 3.01 GHz.

Finally, we mention an outgrowth of this work, supported by DOE/PETC through the Illinois Clean Coal Institute. The computerized spectral simulation optimization technique referred to above (see Table I and associated text) for VHF-EPR spectra of coals based on the axial two-species model was applied to coals and coal blends to check how well the method can work as an analytical tool. Table II summarizes results from two coal macerals - vitrinite and sporinite - separated from Illinois #6 coal and two blends.

TABLE II. SUMMARY OF TWO-SPECIES SIMULATIONS

Maceral	$g_1(I)$	$W_1(I)$ (Gauss)	$g_2(I)$	$W_2(I)$ (Gauss)	$g_1(II)$	$W_1(II)$ (Gauss)	$g_2(II)$	$W_2(II)$ (Gauss)	A_1	%S
Sporinite	2.00430	19.41	2.00281	8.38	2.00301	15.74	2.00261	8.17	67	4.25
1:1 (S:V)	2.00405	20.42	2.00336	10.06	2.00308	11.73	2.00262	9.77	52	3.57
1:2 (S:V)	2.00422	17.20	2.00256	6.86	2.00312	16.84	2.00256	16.84	47	3.35
Vitrinite	2.00399	20.36	2.00370	9.95	2.00318	12.39	2.00257	8.45	40	2.90

Graphical results of the application of the technique to VHF EPR spectra from these samples are shown in Fig. 12. The simulation assumes two species, each with axial symmetry ($1=x, 2=z$). The parameters g_1 and g_2 are the two g-factors (magnetogyric ratios) associated with each axial species. Numerals I and II in Table II refer to the two species. $W_{1,2}$ refer to the linewidths of the two components of the spectrum of each species. A_1 is the normalized integrated intensity of species I, which is assumed to contain sulfur. %S is the literature value for the dry, mineral free content of organic sulfur in each coal as determined by chemical analysis.

The VHF-EPR spectra of such blends and their compositions are shown in Fig. 12. Sporinite and vitrinite were separated from Illinois Herrin No. 6 by researchers at Southern Illinois University at Carbondale and their characterization is reported elsewhere.

The A_1 values correlate with proximate organic sulfur content to better than $\pm 0.5\%$. They are computed using the equation:

$$\frac{(A_1 W_1 S)}{M_1} \left(\frac{A_1}{A_1 + A_2} \right) (C) (100\%) = \%S \text{ of Coal}$$

Here C is the average aromatic fraction of carbon which for Argonne Premium coals averages ca. 0.75, according to NMR data. M_1 is the average molecular weight of the aromatic carbon species (species I) in coals; it can vary from 250 to over 500. Our previous studies showed that the g-anisotropy in coal is representative of a six-aromatic-ring thiophenic containing 22 to 30 carbon atoms. Di-anthracene thiophene (M.W. 384) is one such example. Using a slightly larger number ($M_1=397$) which we previously determined for whole coals, we arrive at $\%S=0.03918 \times A_1$. Fig. 13 shows the linear correlation of the %S determined from this equation with that determined by other methods. The confidence value is better than 99%.

Figure 12 W-band spectra of macerals and maceral blends.

... Experimental

Simulated; Simplex-optimized

Figure 13

Percent sulfur from our EPR analysis vs. percent sulfur from other methods.

LITERATURE CITATIONS

1. D. L. Wertz, *Am. Chem. Soc. Div. Fuel Chem. Prepr.*, **36**, 1147 (1991).
2. H. L. Retcofsky, in: Coal Science, M. L. Gorbaty, J. W. Larson, and I. Wender, eds., Academic Press, New York, 1982, Vol. I, Chapter 3, pp. 43 - 82.
3. R. B. Clarkson, W. Wang, D. R. Brown, H. C. Crookham, and R. L. Belford, *FUEL*, **69**, 1405 (1990).
4. K. S. Vorres, *Users Handbook for Argonne Premium Coal Sample Program*, U. S. DOE, 1989.
5. J. Crelling, Southern Illinois Coal Characterization Laboratory, 1992, unpublished data.
6. R. L. Belford, R. B. Clarkson, J. B. Cornelius, *et. al.* in: Electron Magnetic Resonance of the Solid State, J. A. Weil, ed., Chemical Institute of Canada, Ottawa, 1987, pg. 21.
7. R. L. Belford and R. B. Clarkson, in Magnetic Resonance of Carbonaceous Solids, R. Botto and Y. Sanada, eds., ACS Advances in Chemistry Series No. 229, American Chemical Society, Washington, 1993, 107 - 138.
8. R. B. Clarkson, W. Wang, D. R. Brown, H. C. Crookham, and R. L. Belford, *FUEL*, **69**, 1405 (1990).
9. S. Schlick and L. Kevan, in Magnetic Resonance. Introduction, Advanced Topics, and Applications to Fossil Energy, L. Petrakis and J. P. Fraissard, eds., D. Reidel Publishers, Dordrecht, 1984, p. 655.
10. Silbernagel, B. G., Gebhard, L. A., and Dyrkacz, G. R., In Magnetic Resonance. Introduction, Advanced Topics, and Applications to Fossil Energy. Petrakis, L. and Fraissard, J. P., Eds.; D. Reidel: Dordrecht, 1984; p. 645.
11. R. L. Belford, P. H. Davis, G. G. Belford, and T. M. Lenhardt, in *Extended Interactions Between Metal Ions in Transition Metal Complexes*, L. V. Interrante, ed.; ACS Symposium Series No. 5, American Chemical Society: Washington, 1974; pp 40 - 50.
12. M. L. Gorbaty, G. N. George, and S. R. Kelman, *FUEL*, **69**, 939 (1990).
13. N. Shah, R. A. Keogh, F. E. Huggins, G. P. Huffman, A. Shah, B. Ganguly, and S. Mitra, *ACS Div. Fuel Chem. Preprints*, **35**, 784 (1990).
14. Stone, A. J. *Mol. Phys.* 1964, **7**, 311.
15. R. B. Clarkson, R. L. Belford, K. Rothenberger, and H. C. Crookham, *J. Catalysis*, **106**, 500 (1987).
16. P. A. Snetsinger, J. B. Cornelius, R. B. Clarkson, M. K. Bowman, and R. L. Belford, *J. Phys. Chem.*, **92**, 3696 (1988).
17. Attar, A. and Dupuis, F. *Am. Chem. Soc. Div. Fuel Chem. Preprints*, **24**, 166 (1979).

ABSTRACTS OF PAPERS AND TALKS ARISING WHOLLY OR PARTLY FROM THIS DOE RESEARCH GRANT.

A list of papers and presentations follows. Each entry is numbered, and the corresponding abstract is shown, keyed to the list with the same number.

PAPERS OF R. L. BELFORD AND R. B. CLARKSON
FROM THE IERC DATABASE
1988 TO 1993

(Updated JULY 21, 1993)

IN ORDER BY YEAR, THEN IN ALPHA ORDER BY FIRST WORD OF TITLE

1988

- 1.) "Electron Spin Echo Envelope Modulation Studies of Natural Abundance Carbon-13 and Aluminum-27 in Two Disordered Systems," Snetsinger, P.A., Cornelius, J.B., Clarkson, R.B., Bowman, M.K., Belford, R.L., *J. Phys. Chem.*, 92:3696-3698, 1988.
- 2.) "ENDOR of Perylene Radicals Adsorbed on Alumina and Silica-Alumina Powders. II. The Matrix Effects," Rothenberger, K.S., Crookham, H.C., Belford, R.L., Clarkson, R.B., *J. Catalysis*, 115:430-440, 1988.

1989

- 3.) "Enhancement of Nuclear Modulation in Electron Spin Echo at Low Magnetic Fields: S-band ESE Spectrometer," Clarkson, R.B., Timken, M.D., Brown, D.R., Crookham, H.C., Belford, R.L., *Chem. Phys. Lett.*, 163: 277-281, 1989.

1990

- 4.) "A SAW Oscillator-Based Modulator/Mixer for Frequency Modulated ENDOR," Clarkson, R.B., Belford, R.L., Reiner, C., *Rev. Sci. Instrum.*, 61:3356-3359, 1990.
- 5.) "Electron Spin Echo Envelope Modulation Angle Selection Studies of Axial Pyridine Coordination to Copper(II) Benzoylacetate," Cornelius, J.B., McCracken, J., Clarkson, R.B., Belford, R.L., Peisach, J., *J. Phys. Chem.*, 94:6997-6982, 1990.
- 6.) "Influence of Organic Sulfur in Very High Frequency EPR of Coal," Clarkson, R.B., Wang, W., Nilges, M.J., Belford, R.L., in *Processing and Utilization of High-Sulfur Coal*, R. Markuszewski and T. D. Wheelock, eds., Elsevier, Amsterdam, p. 67-79, 1990.
- 7.) "Multi-Frequency EPR Studies of Argonne and Illinois Sample Bank Coals," Clarkson, R.B., Wang, W., Brown, D.R., Crookham, H.C., Belford, R.L., *FUEL*, 69:1405-1411, 1990.

1991

- 8.) "Multi-Dimensional EMR of American Coals," Clarkson, R.B., Boyer, S., Nilges, M.J., Wang, W., Belford, R.L., *Coal Science Proceedings*, eds. IEA Coal Research, Butterworth-Heinemann, Oxford, 68-71, 1991.

1992

- 9.) "EPR Spin Labeling of Silica, Alumina, Titanium, Molybdenum, and Zirconium Metal Oxide Surface Hydroxyls, and Use in Studying Surface Molecular Dynamics vs. Temperature, Solvent, and Polymer Additive," Auteri, F., Belford, R.L., Robinson, B., Clarkson, R.B., *Colloids and Surfaces* (invited), in press, 1992.

10.) "S-Band Electron Spin Echo Spectroscopy," Clarkson, R.B., Brown, D.R., Cornelius, J.B., Crookham, H.C., Shi, W.J., Belford, R.L., *Pure and Applied Chemistry* 64:893-902, 1992.

11.) "Simultaneous Multi-Site EPR Spectroscopy *In Vivo*," Smirnov, A.I., Norby, S.W., Clarkson, R.B., Walczak, T., Swartz, H.M., *Magn. Res. Med.*, in press, 1992.

12.) "Very High Frequency EPR Spectra of Organic Sulfur Compounds," Wang, W., Clarkson, R.B., Auteri, F.P., Kovacs, P., Williamson, M.V., Belford, R.L., *Am. Chem. Soc. Preprints, Fuel Chem.*, 37:1141-1150, 1992.

1993

13.) "Electronic Magnetic Resonance of Standard Coal Samples at Multiple Microwave Frequencies," Clarkson, R.B., Wang, W., Brown, D.R., Crookham, H.C., Belford, R.L., in *Magnetic Resonance of Carbonaceous Solids*, R. Botto and Y. Sanada, Eds., *ACS Advances in Chemistry Series*, Vol. 229, Chapter 27, pp. 507-528, 1993.

14.) "Multifrequency Electron Paramagnetic Resonance Spectroscopy," Belford, R.L., Clarkson, R.B., in *Magnetic Resonance of Carbonaceous Solids*, R. Botto and Y. Sanada, Eds., *ACS (Advances in Chemistry) Series*, Vol. 229, Chapter 6, pp. 107-138, 1993.

Reprints + Preprints removed

END

**DATE
FILMED**

9/23/93