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Title: SPIN-MAPPING OF COAL STRUCTURES WITH ESE AND ENDOR
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ABSTRACT

Advanced EPR methods -- ESE, ENDOR, and most recently Very High Frequency Electron Paramagnetic Resonance (VHF EPR) -- have demonstrated cability for study of molecular components (including organic sulfur) in coal. We have constructed a unique VHF EPR instrument operating at the W-band (96 GHz), one of only two such instruments in the world, and the only one studying coal. We are employing this instrument, as well as collaborating with scientists at Cornell University who have constructed a 250 GHz EPR spectrometer, to develop a clearer understanding of the relationships between the VHF EPR spectra we observe from Illinois coal and the organic sulfur species present in it.

Work this Quarter for this DOE grant (supplemented by a one-year award through the Illinois Center for Research on Sulfur in Coal and also reported to that agency) has focussed on three main areas: (i) synthesis and analysis of model systems for thiophenic sulfur species in coal; (ii) ESE and VHF EPR of inertinites from an Illinois #6 coal, as well as evaluation of the sensitivity of the signals from this maceral to oxygen; (iii) VHF EPR of iodinated coals.

GENERAL SUMMARY

This program addresses the need for innovative approaches to characterize the organic sulfur in coal with special attention on Illinois Basin coals. With support U. S. DOE, the Illinois Center for Research on Sulfur in Coal, the Petroleum Research Fund (ACS), and the National Institutes of Health, we have developed a unique very high frequency electron paramagnetic resonance (EPR) spectrometer operating at the W-band of microwave frequencies (96 GHz). This instrument has shown special sensitivity to heteroatoms in coal, and we believe the technique can be successfully applied for the **non-destructive, direct determination of organic sulfur in coal.** It supplements the other advanced EPR tools -- ESE and ENDOR -- which have also provided us with insight into coal molecular structure. Preliminary data from Illinois coals and separated macerals indicate that **the VHF method also may be able to distinguish aromatic from aliphatic sulfur, and may be useful in assessing the extent of conjugation in aromatic portions of the coal.**

Our approach utilizes the naturally occurring unpaired electrons in coal as "spies" of their environment. Effects of neighboring atoms on the magnetic energy levels of the electron are reflected in changes in the EPR spectrum, and from this data, conclusions about the structure of the coal can be made. In the case of sulfur, the strongest interaction between the unpaired electron and S atoms usually is the spin-orbit (SO) coupling, which changes the value of the external magnetic field needed to

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cause the unpaired electron to resonate (absorb energy) in the presence of microwave radiation. The spectrometer records this sulfur-induced shift in the position of the EPR resonance, and it becomes a signature for organic sulfur. Because unpaired electrons are naturally occurring in all coal, and because few other species in coal give rise to EPR signals (and none in the region of the organic free electrons), the technique is non-destructive and very sensitive. It also could become relatively quick; a typical EPR spectrum of coal on the W-band instrument takes about one minute to record after the specimen has been loaded and all instrument functions properly set.

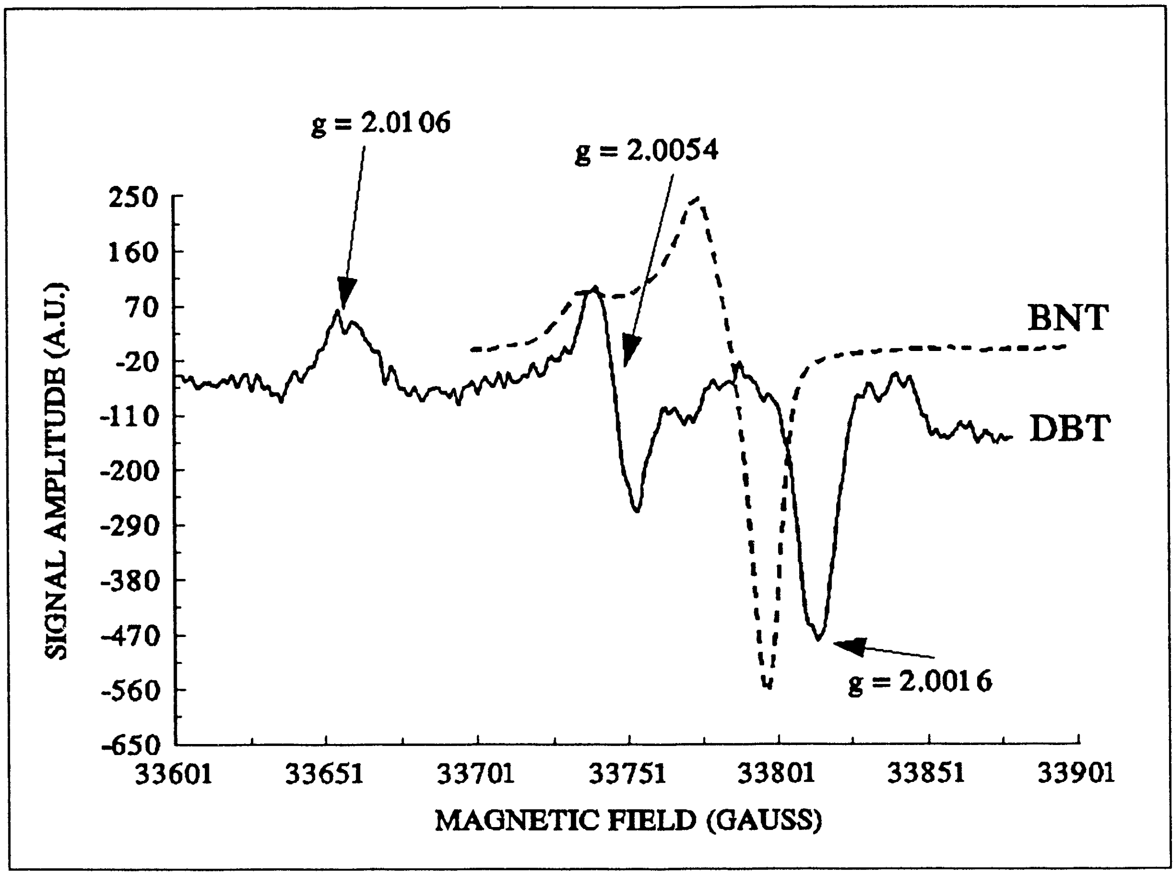


Figure 1. VHF EPR spectra of DBT+ and BNT+ in boric acid glass.

In this Quarter, we have been working on two successful synthetic routes for the creation of radical systems that can serve as models for aromatic organic sulfur species in coal. We have used these preparative methods to synthesize the cation radicals of dibenzothiophene (DBT+), benzonaphthothiophene (BNT+), and dibenzofuran (DBF+), and we have examined them by VHF EPR. Figure 1 shows the spectra from DBT+ and BNT+. Differences in the g-anisotropy in these two compounds is believed to arise from differences in the nature of the spin-orbit (SO) coupling between the unpaired electron in the radical and sulfur, just as we believe occurs in high-sulfur coal. The analysis of such spectra, particularly from the standpoint of the dependence of SO coupling on the aromatic cluster size, is an important step in our work to understand the exact nature of the VHF EPR spectra from organic sulfur in coal.

We also have developed a careful physical characterization of the effects of oxygen on the VHF EPR spectra of fusinite separated from an Illinois #6 coal. We have related this phenomenon to the theory of spin exchange in this maceral, and have performed the EPR experiment over what may be the widest frequency range ever attempted -- 1 GHz to 250 GHz. Variation of the EPR linewidth with frequency/field has helped us to understand the magnitude of spin exchange in this system. It also has allowed us to develop a better appreciation for the importance of stringent sample evacuation prior to examination, and we also may be able to exploit the effect for the non-destructive *in situ* analysis of oxygen in coal.

Finally, we report here initial experiments performed in collaboration with Professor Harry Marsh (University of Newcastle, England) and Drs. Herbert Retcofsky and Kurt Rothenberger (U.S. DOE, PETC) on the use of iodine to probe the chemical structure of coal by means of VHF EPR.

OBJECTIVES

Some of our goals for this funding period can be summarized in three key target areas or phases:

Phase I. Develop a precise model for the analysis of the chemical forms of organic sulfur in coal by very high field EPR spectroscopy.

The W-band EPR spectrometer has been operational for over six months, allowing us to acquire some data on the relationships that exist between the VHF spectra and organic sulfur content. Clearly, we want to improve the precision of this method, and this will be the first priority of Phase I. It also is important to determine how the VHF EPR data relates to the chemical nature of the organic sulfur (e.g. aromatic? average size of conjugated system?). Such additional information would undoubtedly improve the overall analytical reliability of the approach, and might provide "bonus" information that could be used to better understand changes brought about in the organic sulfur by various desulfurization methods.

Phase II. Apply the analytical method to a variety of IBCSP coals and macerals separated from them, as well as to solvent-extracted coals and extracts, determine the chemical forms and content of organic sulfur, and compare these results to data from other analytical techniques whenever possible.

Clearly, the best test of this analytical procedure is to apply it to as many systems as possible. Our goal is to analyze a variety of coal samples from the Illinois Basin Coal Sample Program and from other sources by VHF EPR, in order to develop the data base necessary to evaluate the technique as a non-destructive analytical method for organic sulfur in coal. Whenever possible, we will look at macerals separated from a whole coal, in order to learn more about the distribution of organic sulfur in individual maceral components. Collaborating with Dr. Richard Harvey of the IGS, samples of coal components that have been mechanically separated under a microscope will be studies to further determine the distribution of chemical forms of sulfur, since the great sensitivity of our method allows us to look at less than a milligram of sample. We also will attempt to compare our results with those obtained by other methods, in order to understand better what different techniques actually measure when they report on the "organic sulfur content" in coal. In particular, we will compare our results with destructive chemical analysis data (proximate analysis) and, when possible, with XAFS.

In the latter work, we will collaborate with Prof. G. P. Huffman and co-workers at the University of Kentucky, who has developed unique XAFS methods for sulfur in coal. We also will examine coals subjected to solvent extraction to learn more about the organic sulfur selectivity of these methods (i.e. what types of sulfur are extracted), as well as the extracts themselves, which remain paramagnetic, but which may be chemically altered due to the extraction process. Finally, in collaboration with Mobil Research and Development Corporation, Princeton, NJ, we will examine several heavy petroleum samples with sulfur content ranging from 0.23% to 7.15%. Mobil has carefully examined these residues by a variety of chemical analytical methods, as well as by NMR, and they have made the entire suite of analytical data available to us. This set of samples will be another test for our VHF EPR method, and will add to our understanding of the relationships that exist between our spectra and the chemical forms of organic sulfur.

Phase III. Measurement of Coals subjected to low-temperature pyrolysis.

In very preliminary experiments on the VHF EPR of an Illinois #6 coal subjected to mild pyrolysis, we have seen significant changes in the spectra with sample heating. These changes include variations in the low-field peak associated with organic sulfur. Since so many desulfurization techniques employ temperatures above ambient, we must learn more about the effects of mild heating on coal if we are to properly interpret our data on desulfurized coal samples.

INTRODUCTION AND BACKGROUND

For the past five years, our laboratory has been working on a variety of non-destructive methods for the characterization of organic matter in coal. Our general 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. It has long been known that sulfur has one of the strongest and most characteristic interactions with unpaired electrons, and with funding from the U. S. Department of Energy, the Center for Research on Sulfur in Coal (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) to measure this interaction as a potential avenue to the direct, non-destructive analysis of organic sulfur in coal. This unique instrument is one of only two such devices in the world, and the only one currently operating in the U.S.A.

The fundamental 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. is to improve spectral resolution and sensitivity of the technique to sulfur-containing compounds in order to analyze for sulfur in coal. 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 atomic or molecular orbital of the electron is nondegenerate (L = 0), then the "spin only" energy is given by:

$$\mathcal{H}_{ez} = \beta_e \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S}, \qquad \text{(i)}$$

where $\mathcal{H}_{ez}$ is the spin Hamiltonian (electronic Zeeman interaction only), β_e is the Bohr magneton, **B** is the external magnetic field, **g** is the g-matrix (effective electronic Zeeman coupling matrix), and **S** is the electron spin operator. In this case, when the electron possesses only spin angular momentum, the g-matrix 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:

$$\mathcal{H}_{ez} = \beta_e \mathbf{B} \cdot \mathbf{L} + g_e\beta_e \mathbf{B} \cdot \mathbf{S}, \text{ or}$$

$$= \beta_e \mathbf{B} \cdot (\mathbf{L} + g_e \mathbf{S}). \qquad \text{(ii)}$$

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

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

where λ is the spin-orbit coupling constant, a term proportional to the nuclear charge of the atom (Z) and $1/r_3$, 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:

$$\mathcal{H}_{spin} = \mathcal{H}_{ez} + \mathcal{H}_{so} = \beta_e \mathbf{B} \cdot (\mathbf{L} + g_e \mathbf{S}) + \lambda \mathbf{L} \cdot \mathbf{S}. \qquad \text{(iv)}$$

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 $\mathcal{H}_{spin}$, not by scanning frequency, but by scanning magnetic field. Field positions of resonance lines are related to energies by the simple resonance equation:

$$h\nu = g_{eff} \beta_e B_o, \qquad \text{(v)}$$

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 $g_{eff} = g_e$, 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 ($\mathcal{H}_{so}$) 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:

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

(vi)

Thus, the shift in field, ΔB, of the resonance of our "spy" electrons due to sulfur, is dependent on Δg and ν. 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, 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 EPR instrument, and with it we have observed the ΔB due to sulfur, which is too small to be seen at lower spectrometer frequencies.

EXPERIMENTAL PROCEDURES

A. Preparation of thiophene model systems

Pure samples of dibenzothiophene (DBT) and benzonaphthothiophene (BNT) were purchased from Aldrich Chemical. Cation radicals of these materials, in addition to dibenzofuran (DBF), were prepared by two alternate routes. Each method was developed to produce stable populations of pure cation radicals in a powder or glassy matrix, thus duplicating the disordered state of chemical species in coal. It is essential that this disorder criterion be met for our model systems to provide accurate spectral information that directly relates to spectra from coal without theoretical intervention.

Method 1. Preparation on Houdry catalyst.

In this approach, our method utilizes the oxidation catalyst Houdry M-26, a silica-alumina catalyst developed for petroleum cracking. This catalyst is first activated by calcining in air at 650°C for 12 hours. Alternatively, the catalyst may be activated by heating to the same temperature in a vacuum. Following activation, the catalyst is transferred in a closed tube to a glove bag, where it is opened under an atmosphere of dry oxygen. In the glove bag, an amount of the desired thiophenic sulfur compound is added to the Houdry to make a powdered mixture that is 0.2% by weight in the thiophenic species.

The powder then is placed in a 1mm O.D. quartz tube that has been sealed to a ground glass joint suitable for attachment to a high vacuum system. A stopcock at the top of the apparatus is closed, and the device removed from the glove bag and placed on a vacuum line, where it is opened and evacuated to $P < 10^{-5}$ Torr for several hours. Then the sample stopcock is closed and the sample slowly is heated to the melting point. Sublimation of the thiophenic compound results in an even adsorption throughout the Houdry catalyst, where electron transfer produces a cation radical species (DBT+, BNT+, or DBF+). The small quartz capillary holding the sample then is flame sealed, and is ready for examination in the W-band EPR spectrometer.

Method 2. Preparation in Boric Acid Glass by UV Irradiation

Powdered boric acid and the desired thiophenic compound are mixed together in a 1:100 ratio by weight. The powder then is heated slowly to the melting point of boric acid (ca. 125°C). The glass is allowed to cool, broken into small fragments, and loaded into a quartz sample tube. The tube is placed in a Ray-O-Net irradiation unit and subjected to UV irradiation and 3260 nm for 30 minutes. After this, the sample is removed, sealed with high-purity mass spectrograph grease, and taken to the W-band spectrometer for analysis.

B. Vacuum preparation.

All coal samples were carefully evacuated to a pressure less than 10^{-5} Torr for at least 24 hours prior to being sealed in quartz glass tubes.

C. Spectroscopy

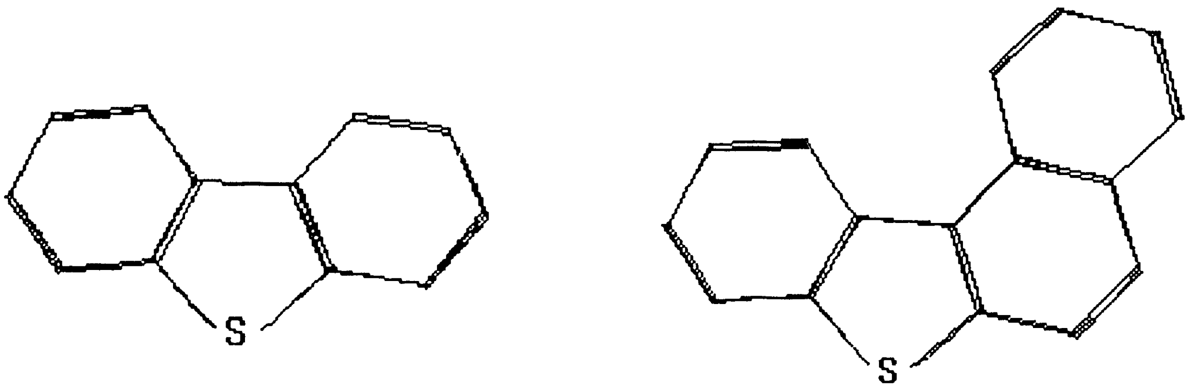
All spectroscopy at W-band (ca. 96 GHz) is done on the instrument constructed in our laboratory and described elsewhere [1]. 250 GHz EPR spectra of coal and maceral samples were obtained through the courtesy of Professor Jack Freed and colleagues at Cornell University. L-, S-, X-, and Q-band EPR spectra were obtained on instruments located in the Illinois EPR Research Center.

RESULTS AND DISCUSSION

A. Model Thiophene Systems

One key theoretical question in the interpretation of VHF EPR spectra of high-sulfur coal is the role that aromatic ring size plays in modulating the magnitude of sulfur spin-orbit coupling contributions to the anisotropic Zeeman interaction. If we recall that in the previous section, the influence of sulfur on VHF EPR spectra was thought to be primarily through this spin-orbit (SO) interaction, then the key form of this interaction was presented in equations (ii) and (iii). The magnitude of $\mathcal{H}_{so} = \lambda \mathbf{L} \cdot \mathbf{S}$ depends on all three terms, λ, $\mathbf{L}$, and $\mathbf{S}$.

Consider the two thiophenic compounds shown in Figs. 2 and 3. The compound



Figures 2 and 3. Dibenzothiophene (2; left) and benzonaphthothiophene (3, right).

on the left, dibenzothiophene (DBT+), is a cation radical formed by the techniques discussed above. Its single unpaired electron is delocalized over a carbon frame containing 12 carbon atoms as well as the sulfur. On the right is a structure for benzonaphthothiophene (BNT+), which also is a cation radical, with one unpaired electron delocalized over 16 carbon atoms. Now the magnitude of the SO interaction depends on the average unpaired electron density found at the sulfur atom in both these compounds. Supposing that the hybridization of the sulfur atom is roughly the same in both species, we would predict that DBT would show a stronger SO interaction than BNT. This prediction should be testable by examining the VHF EPR spectra of the two radicals.

Figure 1. (shown on the General Summary above) shows spectra of the two compounds. As is immediately apparent, DBT has a much more anisotropic spectrum than BNT, which is what our simple model predicted. In fact, the actual change in g-values with the size of the aromatic cluster is not well understood, and we are actively studying the theory of spectra in such compounds to develop a detailed description of the effect. With the development of this theory, it should be possible to analyze VHF EPR spectra and obtain good information on the size distribution of aromatic clusters containing sulfur in coal. Our strong efforts to develop a quantitative description of VHF EPR spectra like those shown in Figure 1. represents ongoing work in accord with goal #1 of this program.

Not only unpaired spin density and hybridization, but also the type of element plays a role in determining the magnitude of SO interactions. Figure 4. shows the molecular structure of dibenzofuran, the oxygen analogue of DBT, while Figure 5 shows its VHF EPR spectrum. Here, the SO coupling constant λ for oxygen is about 40% that of sulfur, and the overall interaction, a combination of λ, unpaired electron density, and atomic orbital hybridization, is very much less than that. While our primary focus always is on organic sulfur in coal, we cannot neglect the effects of other heteroatoms like oxygen on the VHF EPR spectra of coal, and so we are working with DBF+ in order to more correctly account for the role of oxygen compounds in our spectra.

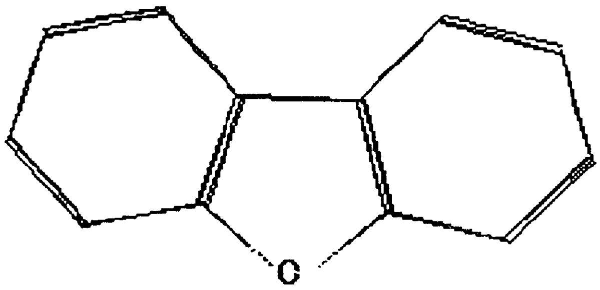


Figure 4. Molecular structure of dibenzofuran.

A comparison of the VHF EPR spectrum of DBF+ with that of BNT+ or DBT+ clearly demonstrates that the combination of effects makes this spectrum much less anisotropic than those of the sulfur-containing species. Next steps in this phase of the work will be to make careful comparisons of the spectra of thiophenic compounds prepared by both synthetic routes, in order to determine whether there is a chemical difference between species formed from the same starting compound by the different procedures. It will be advisable to perform ENDOR spectroscopy on some of these preparations in order to verify their molecular structure. We are pleased of our synthetic achievements, but want to be careful in characterizing these never before studied radicals.

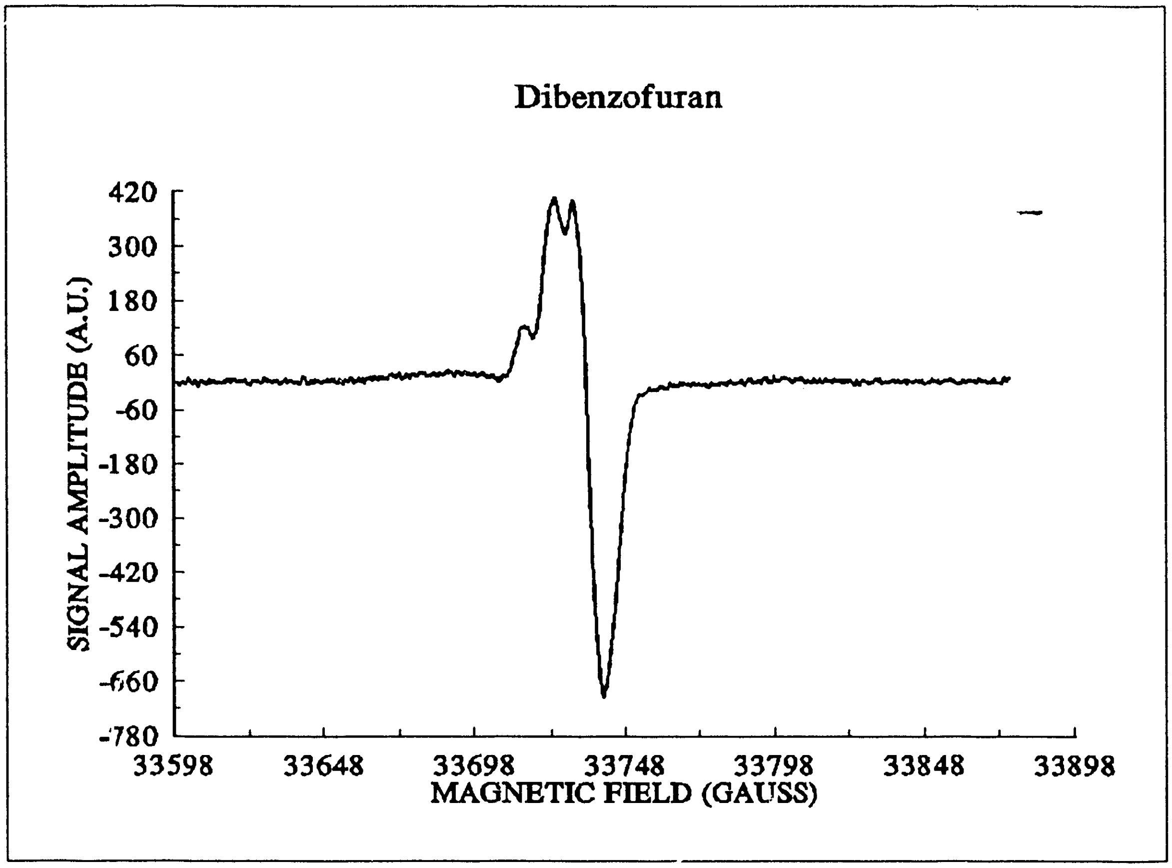


Figure 5. VHF EPR spectrum of dibenzofuran+ in boric acid glass.

While a study of model compounds represents a very important component of our overall program, a word needs to be said about its connection to the analysis of coal and maceral spectra. Figure 6 is a VHF EPR spectrum of Argonne Premium Coal Sample #301, the Illinois #6. This spectrum should be compared to the three previous spectra from model compounds. What becomes evident immediately is that if our hypothesis concerning the origin of the anisotropic spectra in the VHF EPR of coal is correct, the average aromatic organic sulfur species in the Illinois #6 must have an extent of conjugation that is slightly larger than that in BNT. Further, while there are many aromatic oxygen species in this coal, the VHF EPR spectrum at 96 GHz probably cannot resolve them, due to the very small extent of g-anisotropy, as suggested by the DBF+ spectrum, which could be an upper limit on the g-anisotropy in aromatic oxygen compounds, and which is not comparable to the spectrum from the Illinois #6. Higher frequency spectroscopy at 250 GHz may be able to resolve *both* sulfur and oxygen in coal, however, and we are currently working on that experiment in collaboration with Professor Jack Freed and colleagues at Cornell University.

Spectral simulations, by which our theories are tested against experimental data, are being performed utilizing software developed by Belford and his students. This aspect of the work has assumed a much greater importance since our successful development of synthetic methods of producing model compounds for study, and we

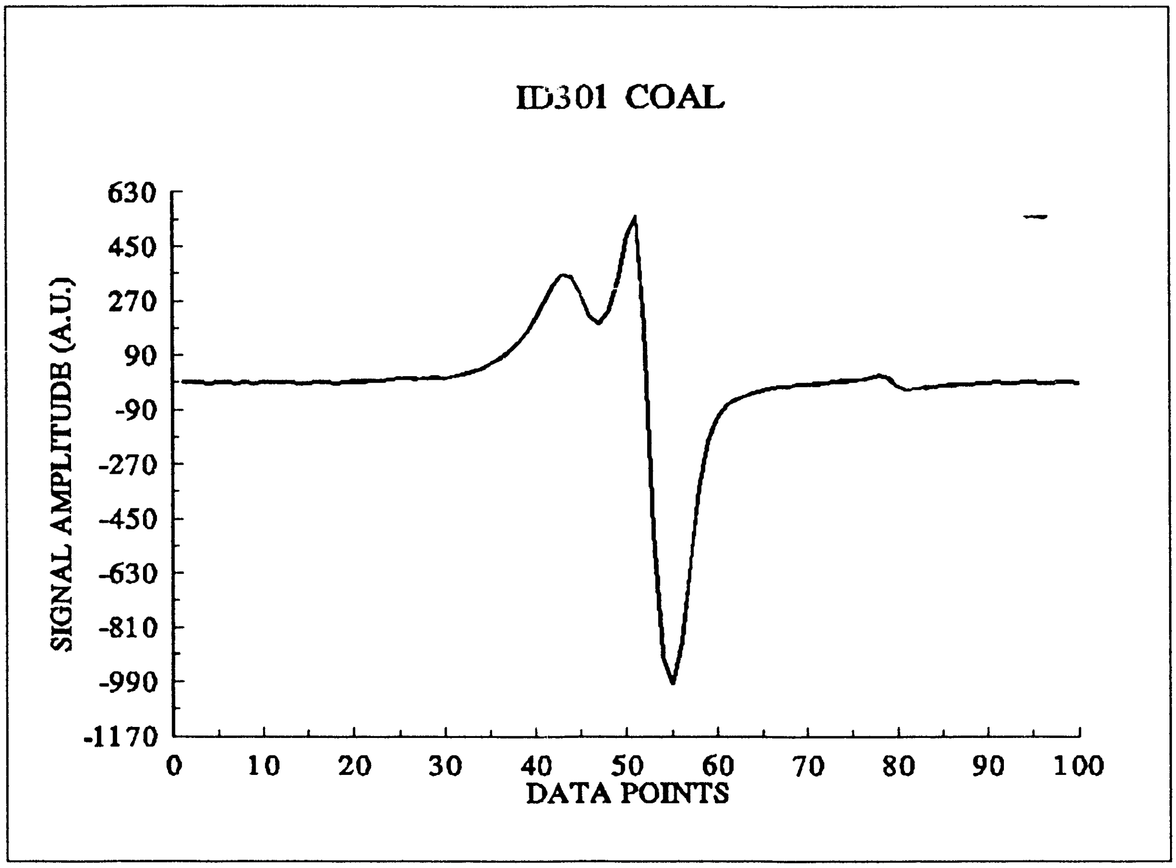


Figure 6. VHF EPR spectrum of APCS #301; and Illinois #6.

hope to report on our progress here in another Quarterly Report.

B. VHF EPR of Separated Inertinites

In the course of studying separated macerals, as planned in Phase II of our project, we have carefully characterized the unique the oxygen-sensitive EPR spectral response of fusinite, an inertinite maceral from Illinois #6 coals. The spectrum of fusinite is characterized by a spin-exchange narrowed lineshape that broadens from 500 mG to over 4 Gauss when the oxygen partial pressure over the material is changed from zero to 200 Torr.

Model.-

Our preliminary model for the effect of oxygen on the EPR lineshape has been built around the idea that, in the limit of fast exchange,

$$\mathcal{J} \gg |g_i - g_j| \beta B_o,$$

where "fast enough" is parameterized in terms of the range of g-values over which one wants to average. If the inequality is obeyed, then the EPR lineshape will be narrowed by exchange interaction. As we increase the magnetic field strength at which our EPR experiment is performed, the inequality should be less and less well-obeyed, since B_0 will increase, while the exchange energy remains constant. Finally, we should see the linewidth increase with increasing B_0 as the exchange narrowing condition fails to be met.

VHF EPR is ideal for evaluating this effect, and we have performed EPR experiments on fusinite separated from an Illinois #6 coal at microwave frequencies from 1 GHz to 250 GHz. Figure 7 shows the variation in linewidth as a function of observation frequency, revealing that above 9 GHz, the strong exchange inequality progressively fails to hold. The importance of understanding this oxygen effect on fusinite cannot be overemphasized -- it is evident that the effect can be used to provide an *in situ* measurement of oxygen pressure. Our work on this class of macerals continues, and we hope to finish the physical characterization of the effect in the next six months.

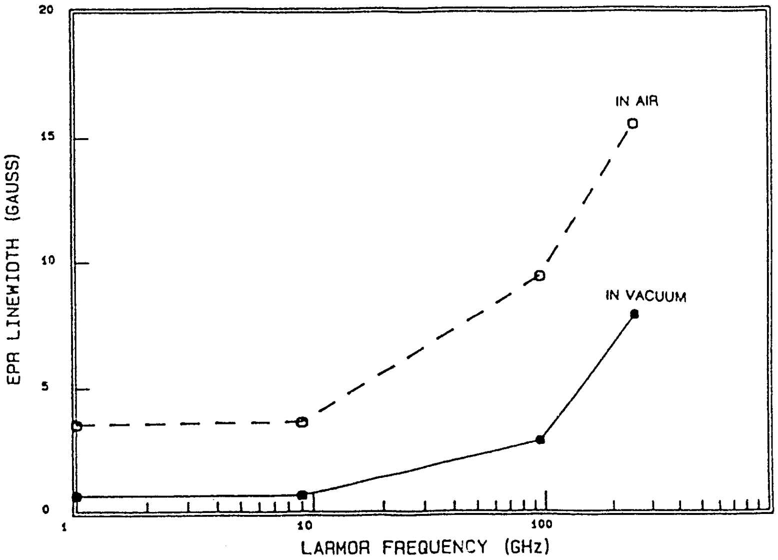


Figure 7. EPR linewidth in fusinite as a function of microwave frequency.

C. VHF EPR of Iodinated Coal

Professor Harry Marsh, University of Newcastle upon Tyne in England, has developed techniques for studying coal structure that employ iodine as a reagent to produce radicals, presumably by means of electron charge transfer from aromatics to the electrophilic I_2. In collaboration with Professor March and Herb Retcofsky of the U. S. DOE (PETC), we have examined some of these iodinated coals by VHF EPR. Figure 8. illustrates spectra of just one of these samples both before and after treatment with iodine. The example is a Gedling coal, which is very weakly coking. It appears that the EPR signal strength in these samples is higher than in the non-iodinated coals, suggesting that new radical centers have been produced or that radicals which were EPR-silent have become EPR-active.

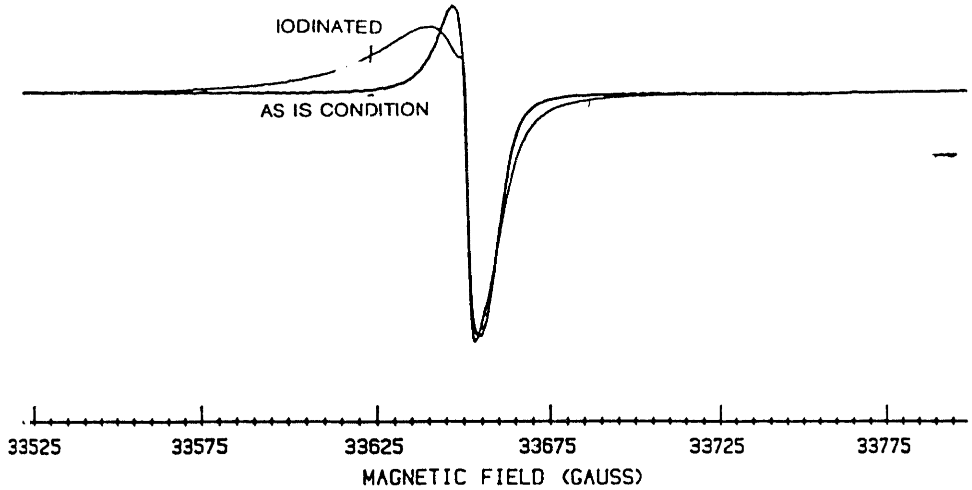


Figure 8. VHF EPR of a Gedling coal, both before and after treatment with iodine.

The anisotropy in EPR signal, which is not observable or not so pronounced at conventional (9.5 GHz) frequencies, is very reminiscent of samples with g-anisotropy due to SO coupling. Considerable variation is noted in going from a good coking coal to this weakly coking sample, suggesting that iodination may be diagnostic of structural differences in the coal that account for its coking properties. We feel this system may provide important insights into the mechanism of SO coupling by giving us another type of g-shifting atom (iodine) for comparison to sulfur, and we plan to investigate the effects of these chemical treatments on sulfur-containing compounds and coals.

CONCLUSIONS AND RECOMMENDATIONS

We are very pleased now to be in a position to synthesize aromatic heterocycles that provide a good model for VHF EPR spectra of high-sulfur coals. Our preliminary hypothesis concerning the relationship between aromatic cluster size and the magnitude of SO interactions seems to be correct, and these results warrant further work in this direction. We are concerned about the exact identity of the species produced by the two synthetic routes, and will concentrate on making more precise measurements in order to insure that our experimental data is unambiguous before we commit to a detailed theoretical analysis.

The effects of oxygen on the VHF EPR spectra of separated fusinite from an Illinois #6 is both exciting and worrisome. We see clearly that the material may provide a direct, non-destructive method of analyzing the oxygen concentration in coal, which could open important avenues for investigating combustion and desulfurization. We also see that these results represent a strong *caveat* concerning the importance of carefully and thoroughly evacuating coal samples for reliable comparisons.

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