Project Title: Studying Coal Molecular Structure with ESE Spectroscopy  
ICCI Project Number: 86-87/2.2A-8  
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ABSTRACT

The object of this research is to develop non-destructive analytical methods for determining the atomic and molecular composition of organic components in coal, particularly those containing sulfur. Our general approach is to use the naturally occurring free radicals in coal as probes of their environment by means of magnetic resonance techniques such as Electron Paramagnetic Resonance (EPR), and Electron Spin Echo (ESE) spectroscopies. These spectroscopic techniques are used to study: 1) the structure of radicals, which we believe is representative of the organic phases in which they are found, and, 2) the atomic environment surrounding the radicals. Model systems, which exhibit many of the same properties as coal, also are studied to gain a better understanding of the factors effecting spectra and to develop the most appropriate methods of spectral analysis.

During the grant year, we have focussed on constructing a special spectrometer capable of performing the EPR experiment in a pulsed mode at microwave frequencies of between 2 and 4 GHz (the S-band of frequencies). This novel instrument, perhaps the only one of its kind in the world, is designed to be especially sensitive to the radical signals from coal, including the nuclear modulation of the electron spin echo envelope (ESEEM), which is proving to be most useful in the study of coal molecular structure. Our S-band instrument is now in its final test stage, and we are pleased with the preliminary results thus far obtained from it.

While building the spectrometer, we have been performing a variety of experiments on coal and model coals in order to: 1) learn more about the relationships between hyperfine couplings and molecular structure in compounds thought to exist in coal, 2) develop better theories for the analysis of spectral data, and, 3) observe radiation-induced radicals in coal. Results from these three areas, as well as from the spectrometer construction project, will be found in this Annual Report.
EXECUTIVE SUMMARY

The development of efficient and low cost techniques for removing sulfur from Illinois coals is a complex task requiring detailed information on coal structure. Among the most important information needed in desulfurization development is knowledge of the molecular environment of organic sulfur in coal -- the bonding and structure of the sulfur-containing organic species. Aided by specific information on its molecular environment, research into the best choice of solvents, temperatures, pressures, and mechanical properties for the removal of organic sulfur could be more systematically accomplished. Information on the distribution of organosulfur species among different coal macerals might allow the design of desulfurization techniques tailored for specific components. Such information also could help to determine if the separation of coal into maceral types prior to desulfurization is a useful procedure. Finally, knowledge of the changes in the molecular environment of sulfur in coal brought about by various desulfurization techniques could be very useful in assessing the effectiveness of different processes, and could guide researchers to achieve greater efficiency in sulfur removal technology.

For the last two years, our laboratory has been addressing these needs by developing magnetic resonance techniques for the determination of organic molecular structure in whole coal. Our work has been sponsored through grants from the ICDB/CRSC, the U. S. DOE, the National Institutes of Health, and by private industrial support. We have discovered that one technique, Electron Spin Echo Spectroscopy (ESE), is particularly well suited for studying coal molecular structure, and we have begun construction of a special ESE spectrometer optimized for this work on coal. The instrument construction, which is funded in part by the ICDB, will be completed by the Fall of 1987, and will be the first of its kind in the world. Used in conjunction with other techniques available in our laboratory such as multi-frequency Electron Paramagnetic Resonance (EPR) and Electron-Nuclear Double Resonance (ENDOR) spectroscopy, ESE is a powerful probe of coal structure.

Magnetic resonance spectroscopic techniques have shown great promise for the elucidation of organic molecular structure in coal and coal-derived materials. NMR methods such as CP/MAS and zero-field NMR have begun to observe resonances that can be attributed to specific compounds and functional groups [1, 2], while ESE has measured hyperfine interactions in Illinois coal that are characteristic of several types of conjugated aromatic compounds [3, 4], as well as of carbon-electron distances in coals and macerals [5]. NMR studies have often been hampered by sensitivity and linewidth problems, limiting resolution and making the observation of sulfur extremely difficult in whole coal. These difficulties are due, in part, to the high concentration of organic free radicals in coal. ESE spectroscopy uses the naturally occurring radicals in coal as paramagnetic probes of the environment, and thus is able to achieve much better sensitivity. As we shall see, ESE also can be sensitive to the presence of sulfur in a radical, thus providing information on both molecular structure and sulfur content.
The key features we measure by ESE spectroscopy are 1) hyperfine interactions, and 2) electron g-values. Hyperfine interactions give us information on the type, number, and geometric arrangement of nuclei with magnetic moments that are interacting with the unpaired electron in coal radicals. This information helps us map the organic molecular structures present in whole coals and separated macerals. Figure 1 illustrates a typical ESE spectrum of an Illinois #6 whole coal measured in our laboratory. Hyperfine interaction energies are manifested in this spectrum by spectral peaks at various frequencies. Comparison of the interactions observed with those measured in pure compounds allows us to analyze the coal molecular structure.

Figure 1. FT-processed ESE spectrum of an Illinois #6 whole coal.

The second important spectral feature we measure is the electronic g-value. This parameter characterizes the magnetic field/microwave frequency ratio at the center of the EPR spectrum of a radical under investigation. Because of a strong interaction of unpaired electrons with sulfur, the g-value of organosulfur radicals is higher than that of purely hydrocarbon radicals, thus allowing us to distinguish between the two classes of compounds based on differences in g-values.

In order to combine the measurement of these two parameters in one experiment, we have developed a technique we call two-dimensional ESE spectroscopy. We take ESE spectra at several hundred different values of the static magnetic field (B₀) spanning the EPR spectral width of the coal signal under study, and then process the data to determine the field dependence of individual hyperfine interaction peaks. The results can be seen in Figure 2, where the field dependencies two hyperfine peaks are plotted. The non-coincidence of the two plots indicates that these two hyperfine interactions arise from different radicals with different g-values. We believe that one of the species contains sulfur and one does not. By correlating the g-values associated with individual hyperfine interactions, we may be able to distinguish between molecular structures that do and do not contain sulfur, and thus identify organosulfur compounds in coal.

The instrumentation required to obtain data that can result in spectra like those shown in Figures 1 and 2 is not commercially available. In the past, we have relied on the hospitality of groups at the Argonne National Laboratory (Drs. Norris and Bowman) and at the Albert Einstein
Medical Center (Drs. Peisach and McCracken) for assistance in making the ESE-measurements. Both of these centers have built pulsed EPR spectrometers operating at 9.5 GHz (X-band). The data we have thus far obtained suggests that for the observation of proton hyperfine interactions in coal, X-band is not the optimal frequency range. Therefore, we have this year constructed a pulsed spectrometer operating in the range 2 to 4 GHz (S-band). This instrument should be much better suited for resolving the weak echo envelope modulation resulting from electron-proton interactions in coal, and we are currently doing final tests on it. The S-band pulsed EPR instrument should allow us to make much more rapid progress in our study of coal by this technique, since we will now be able to make these studies in our own laboratory. We will continue to collaborate with the other groups, however, in order to make measurements at X-band frequencies.

Analysis and interpretation of ESE spectral data is another area of research which we have been pursuing this year. In order to gain a better understanding of the factors influencing ESE data, we have studied several model systems, using X-band ESE and Electron-nuclear Double Resonance (ENDOR) spectroscopies. ENDOR often gives complementary information to ESE, and can be extremely useful in analyzing the spectra of radicals in disordered solids. We have studied conjugated aromatic hydrocarbon radicals like perylene (+) and heterocyclic sulfur compounds like thianthrene(+) and dibenzothiophene(+) [6, 7]. We also have used these model systems to study the relationships between hyperfine interactions and molecular structure, which is a necessary theoretical link in the interpretation of coal spectra. Our work has identified the need to develop a library of interpreted ENDOR spectra from known compounds which have been suggested as likely to exist in coal macerals. These will serve as a basis from which to develop an interpretation of spectra from whole coal. We have completed the analysis of ENDOR results from several compounds, and plan to study several more before attempting a detailed interpretation of whole coal data.

The distribution of naturally occurring radicals in organic components of coal has always prompted discussion among coal scientists. Do the radicals fairly represent all of the organic phase in which they are found, or do they give a chemically biased view of macerals? Are radicals uniformly distributed throughout organic material, or are they clustered selectively in certain macerals? To begin to answer these questions and
others related to radicals in coal, we have studied radicals formed in coal by ionizing radiation. We have studied the effects of gamma rays and electron bombardment on the EPR signals observed in coal, and have seen major effects only from electron bombardment. The energy of the electron beam seems to influence spectral changes - spectra after irradiation by 2.0 and 2.5 MEV electrons are different. We have developed a technique for irradiating coal samples with electrons, keeping samples at 77K so that heating effects will be minimized and so that very reactive radiation-induced radicals will persist long enough to be measured. Using this approach, we believe that it will be possible to get answers to the questions stated earlier - answers which will be important in understanding the significance of our ESE data from unirradiated coals.

In conclusion, we feel that this year has been one of real progress in our study of the structure of coal. Using our new S-band ESE spectrometer, we look forward to making even more progress on this complex problem in the coming years.
OBJECTIVES

Our research plan this year has focused on the following tasks:
2. Development of a library of hyperfine interactions for compounds thought to exist in coal (e.g., naphthalene, anthracene, pyrene, perylene, dibenzothiophene, thiophene, etc.), using EPR, ENDOR, and ESE.
3. Measure whole coal, separated macerals, synthetic coals, and model systems by ESE and 2-D ESE.
4. Interpret ESE spectra by comparison to hyperfine interaction library.

Step #1 in the plan of experiments should be completed in the next several months. Step #2 has begun to develop the experimental and theoretical information needed to interpret the spectral information obtained from coal samples. Step #3 has obtained information on a variety of materials as well as whole coal. It may enable us to determine the organic molecular composition of separated macerals, for example, aiding in the evaluation of maceral separation as a component of coal cleaning and desulfurization. Step #4 has made use of the information collected in #2, and may be the key to interpreting the spectra from whole coal.

INTRODUCTION AND BACKGROUND

The goal of this research is the application of ESE, ENDOR, and EPR spectroscopies to the determination of the molecular environment of organic sulfur in whole coal, separated macerals, desulfurized coal, synthetic coals, and model systems. Our approach uses the naturally occurring free radicals in coal as paramagnetic probes of their environment, is non-destructive, and requires only that the samples be evacuated for a few hours and then cooled to liquid nitrogen or liquid helium temperatures for observation.

The physical principle underlying the technique is that unpaired electrons in free radicals interact with neighboring magnetic (I>0) nuclei by means of the hyperfine interaction, and that the energies associated with this interaction can be analyzed to determine the structure of molecules in the sample. ENDOR and ESE spectroscopies have proven to be uniquely suited to measure the hyperfine interaction energies in coal, and thus provide us with the means to study organic molecular structure in the sample. In this section we first will discuss the hyperfine interaction and its measurement in more detail; then we will relate the measurements to molecular structure in coal.

A. The Hyperfine Interaction.

The EPR spectrum of a hydrocarbon radical such as those believed to occur naturally in coal is customarily described in terms of a spin-Hamiltonian:
\[ H = \sum_{i} S_{i} \cdot g_{i} \cdot B(t) - \sum_{k} A_{i_k} \cdot I_{k} \cdot B(t) + \sum_{i,k} A_{i_k} \cdot I_{k} + H_{ss} + H_{s_{1}} + H_{i_{1}} + H_{i_{1}}(i) \]

In this equation, which is the meeting ground between a mathematical model for the system and the experimental spectral data, the first term describes the interaction of the unpaired electronic spins \([S_{i}]\) with the dc and high frequency magnetic field \([B(t)]\), the second describes a similar interaction between nuclei with non-zero spins \([I_{k}]\) and the external field, and the third accounts for the electron-nuclear hyperfine interactions. Interactions of the electron spins with each other \((H_{ss})\), electron spin-lattice interactions \((H_{s_{1}})\), nuclear spin-lattice interactions \((H_{i_{1}})\), and lattice energy \((H_{i_{1}})\) are assumed to be small or constant contributions to the energy of the system and will henceforth be neglected.

In the case of coal radicals, spectral information related to molecular structure and environment is contained in each term of the Hamiltonian, but the hyperfine terms are especially useful in characterizing a particular species. Let us take, as an example to illustrate this point, the perylene radical, which has been identified in both aqueous and organic solvent extraction solutions obtained from whole coal \([8]\), and which has proven to be a useful coal model compound in our work \([4]\). For a perylene cation or anion radical formed by the loss or addition of an electron, the hyperfine interactions are characterized by three interaction terms - one for each unique proton in the system - as well as by electron-nuclear dipole-dipole interactions between the unpaired electrons and non-bonded nuclei with nuclear spin (e.g. \(^1\text{H}, ^{13}\text{C}, \text{and} ^{27}\text{Al}\)). Proton hyperfine interactions are responsible for the fine structure seen in the EPR spectra of aromatic hydrocarbon radicals. The orientation dependencies of the Zeeman and internal interactions of the radical are described by the coupling matrices \(g\), \(g_{n}\), and \(A_{i_k}\)'s in equation \((i)\). For radicals tumbling rapidly in solution, these orientation-dependent terms can average to zero, resulting in a sharply resolved, isotropic EPR spectrum like that shown in Figure 3.

**Figure 3.** X-band EPR spectrum of perylene cation radical in solution

In the case of many polycyclic aromatic hydrocarbon radicals, \(g\) and \(g_{n}\) are so nearly isotropic that we may write them as scalar constants. Roughly speaking, each matrix, \(A_{i_k}\), carries the information on the variation of the hyperfine coupling between \(I_{k}\) and \(S_{i}\) as a function of the orientation of the external magnetic field, \(B_0\), relative to the line of centers of the \(I_{k} - S_{i}\) interaction pair. The through-space dipole-dipole interaction couples the unpaired electron and more distant, non-bonded nuclei of non-zero nuclear spin, giving rise to so-called matrix interac-
tions, which also can provide us with important information in the study of coal structure. Then, for a simple system comprised of a single electron and proton \((S=1/2, I=1/2)\) at a high field strength where the electronic Zeeman interaction dominates, these interactions result in a set of magnetic spin energy levels like that shown in Figure 4. Because the samples encountered in the study of coal are powders, all orientations of the molecular system relative to the external magnetic field are observed in the spectra. This fact, coupled with other mechanisms such as heterogeneous sample environment, causes inhomogeneous line broadening.

\[ \text{Figure 4. Energy level diagram for an } I=1/2, S=1/2 \text{ system. Major NMR, EPR, and ENDOR transitions are shown as arrows.} \]

that increases observed linewidths and often obscures spectral features such as the weak \(\beta\)-proton hyperfine contribution to the cw EPR spectra of many polycyclic aromatic hydrocarbon radicals believed to exist in coal. The information about molecular structure found in the hyperfine interactions, \(A_{ij}\), thus may be lost in the EPR spectra of disordered solids (powders, polycrystalline samples, glasses). Figure 5 illustrates this point by again showing EPR spectra of the perylene radical, but this time immobilized on an alumina surface.

\[ \text{Figure 5. EPR spectra of perylene cation radical on an alumina powder.} \]

Moreover, valuable information on the environment of the radical contained in the even weaker dipole-dipole interactions is extremely difficult to deduce from such EPR measurements, since linewidths and lineshapes, which are the usual manifestation of such interactions in conventional spectra, are now potentially influenced by so many factors, making modeling of the lineshape a very difficult and uncertain calcula-
tion. Fortunately, there are two related spectroscopic techniques which can help to overcome many of the problems introduced by inhomogeneous line broadening in disordered solid samples by providing alternate experimental routes to a measurement of weak hyperfine and dipole-dipole interactions. The older of the two, Electron-Nuclear Double Resonance (ENDOR) spectroscopy, was first performed by Feher in 1957 on $^{29}$Si nuclei in a semiconductor sample [9]. The second, Electron Spin Echo (ESE) spectroscopy, is based on the electronic analog of nuclear spin echoes, discovered by Hahn in 1950, and has become a more versatile technique in recent years due to the development of very fast digital control devices [10]. We have found these two techniques to be very useful in the characterization of radicals formed on disordered solids. Let us consider each in order to understand how they can be applied to the question of the nature and environment of radicals found in coal.

The ENDOR Technique --- A good general review of the ENDOR technique is to be found in the book by Kevan and Kipsert [11]. For the discussion here, we need to remember that: 1) ENDOR improves the resolution of inhomogeneously broadened lines in disordered solid samples by observing the homogeneous spin packet substructure (a resolution enhancement of $\approx \text{He}/\mu_n$, which for protons is about 800); 2) In solids, ENDOR gives us information on the anisotropic as well as the isotropic part of the hyperfine interaction. Recalling Figure 4, the typical proton ENDOR spectrum consists of pairs of resonance lines positioned symmetrically about the Larmor precessional frequency for protons, $\nu_p = g_n g_0 B_0$:

$$f(\text{ENDOR}) = \nu_p \pm A/2,$$  \hspace{1cm} (ii)

where $A$ is the effective hyperfine splitting for the specific magnetic field orientation with respect to the molecule.

For ENDOR spectra of radicals in solution, the rapid tumbling of the molecules usually averages out the anisotropic portion of the hyperfine interaction, producing an isotropic spectrum consisting of a pair of resonance lines for each interaction. In solids, all the information of the anisotropic portion of the interaction is retained in the powder spectrum, producing a much more complex and informative pattern, which must be analyzed by means of a mathematical model or simulation. Such analysis can, as we shall see in the next section, provide very detailed information about the molecular structure of the radical being observed by obtaining from the experimental data the absolute values of the important elements of the hyperfine interaction matrix. If the molecule should contain several magnetically inequivalent protons, the combination of experiment and theory could obtain the important elements of each hyperfine interaction. For the case of polycyclic aromatic hydrocarbon radicals on surfaces such as alumina and silica-alumina, we have successfully made such measurements and analysis, as will also be discussed in the next section.

In addition to hyperfine interactions between the unpaired electron and nuclei chemically bonded to it in the molecule, there also are electron-nuclear dipole-dipole interactions between the electron and more distant nuclei. These give rise to an effect called distant ENDOR or matrix ENDOR, which is manifested by the appearance of additional ENDOR resonance lines located at the nuclear Larmor frequency [12]. What makes the matrix ENDOR effect so important for us is that it can identify the
nature of $^{14}$O nuclei near a radical. We thus can use the naturally occurring radicals in coal as probes of their immediate environment, obtaining information on neighboring atoms. Furthermore, one can model the lineshape of the matrix line and obtain information about the number of nuclei of a specific type neighboring the radical (cf. Kevan13). We believe this matrix ENDOR effect (and a similar effect seen in ESE spectroscopy) can provide much useful information about the atomic structure of individual macerals, and we have results from an Illinois #6 coal demonstrating the feasibility of the approach for $^1$H and $^{13}$C matrix interactions, which we will discuss in the next section.

The ESE/ESSEEM Techniques -- The other, and in many ways complementary, technique we intend to use to study coal molecular and atomic structure is Electron Spin Echo (ESE) spectroscopy. By observing the modulation due to anisotropic hyperfine interactions in the electron spin echo decay envelope (an effect known as ESSEEM), one can get information on weakly coupled nuclei. Some features that make ESE particularly attractive for this work are: 1) ESE, like ENDOR, improves resolution for inhomogeneously broadened lines by a factor $\approx \mu_e/\mu_n$; 2) unlike ENDOR, the sensitivity of ESE is not dependent on the nuclear gyromagnetic ratio, and hence it is equally sensitive to all nuclei; 3) ESE allows the direct measurement of the dynamical spin variables, making it uniquely suited for studying such problems as the diffusion of oxygen through the pore structure of coal; correlation of these variables with, eg., coal rank can give clues to the environment of unpaired electrons, as Thomann has recently reported [14]. We have already demonstrated that we can obtain excellent electron spin echoes from the naturally occurring radicals in coal, and in the next section, we will discuss some of our most recent results.

Although the ideas behind ESE techniques are as old as magnetic resonance itself (1946), the general application of spin echo methods to paramagnetic systems has occurred in only the last few years with the advent of very high speed digital electronics under computer control. Unlike the familiar continuous wave (cw) EPR experiment, which has been available in commercial instrumentation for nearly 20 years, ESE spectroscopy is not yet a commercially available technique, and only a dozen or so laboratories throughout the world currently perform the experiment. For an excellent review of theory and early applications of ESE spectroscopy, the book by Kevan and Schwartz is recommended [15].

Unlike cw EPR, ESE is a pulsed microwave experiment. Very short microwave pulses excite the paramagnetic spin system, and the time evolution of the magnetization is monitored. Certain pulse schemes, characterized by the number of degrees the magnetization vector is tipped by each pulse, are known to generate a strong instantaneous magnetization in the sample following the sequence. Typical pulse schemes known to induce this rephasing or "echo" effect are $90^\circ$-T-$180^\circ$ (Hahn echo sequence) and the $90^\circ$-$t$-$90^\circ$-T-$90^\circ$ (stimulated echo sequence). We have found the stimulated echo sequence, diagrammed in Figure 6, to be most useful in our coal studies.

ESE spectroscopy has many advantages over the more conventional cw EPR. Chief among the advantages for our coal work is that, like ENDOR, the technique may be used to obtain spectra which resolve hyperfine structure that is obscured in cw spectra by inhomogeneous line broadening.
Figure 6. Timing diagram of stimulated-echo pulse sequence. Typical pulse ~40 nsec; times t and T range from 1 μsec to 1 msec.

In order to understand how ESE can be made to accomplish this task, let us look at the characteristics of the information obtained in the experiment.

In a typical stimulated echo experiment done on coal, the time interval t between the first and second 90° pulse is set at a fixed value during the experiment, while the interval T between the second and third pulses is incremented in steps, as shown in Figure 7. The amplitude of the echo induced by the sequence is measured as a function of the delay time T between the second and third pulses. In the absence of any interactions between the unpaired electrons being observed and neighboring nuclei with non-zero magnetic moments, the variation of the echo amplitude V with the delay time T is given by the simple exponential function:

\[ V_{\text{echo}}(2t + T) = V_0 \exp \left( \frac{(2t + T)}{T_m} \right), \]  

where \( T_m \) is the phase memory time of the individual spin packets. The exponential decay curve describing the echo amplitude as a function of T is called the electron spin echo envelope.

If our unpaired spins experience hyperfine interactions with neighboring nuclei, these interactions will manifest themselves as modulation patterns in the ESE envelope. This phenomenon is thus known as electron spin echo envelope modulation (ESEEM). For an \( S=1/2, I=1/2 \) system with isotropic g-values (a very good approximation in the case of coal) and two hyperfine interactions characterized by frequencies \( f_a \) and \( f_b \), the ESEEM pattern (without echo decay) is given by:
\[ V_{\text{mod}}(2t+T) = 1 - k\left(\sin^2\left(\frac{f_a t}{2}\right)\sin^2\left[\frac{f_b(t+T)}{2}\right] + \sin^2\left(\frac{f_b t}{2}\right)\sin^2\left[\frac{f_a(t+T)}{2}\right]\right) \]

In this expression, \( k \) is the so-called modulation depth parameter, proportional to \( B_0^{-2} \) in the limit of small hyperfine interactions (\( B_0 \) being the value of the static external magnetic field). For more than one nucleus, \( V_{\text{mod}} \) is the product of the modulation functions of the individual nuclei:

\[ V_{\text{mod}} = V_{\text{mod}}(I_1) \cdot V_{\text{mod}}(I_2) \cdot V_{\text{mod}}(I_3) \cdots \]  

Thus, for the case of \( n \) like nuclei coupled identically to an electron spin, the overall modulation is given by the modulation function for one nucleus raised to the \( n \)th power. The overall modulated signal in the time-domain spectrum is then the product of these two functions:

\[ V_{\text{echo}}(2t + T) = V_{\text{decay}} \cdot V_{\text{mod}} \]  

A Fourier transform of the ESEEM pattern results in a frequency domain spectrum exhibiting linewidths that are characteristic of individual spin packets rather than of the entire envelope of spin packets comprising the inhomogeneously broadened lines observed by cw EPR. Since the modulation frequencies can be analyzed by an ENDOR-like theory, this technique provides us with a powerful alternative way of resolving the hyperfine interaction energies normally obscured in the cw spectra of whole coal. This information, in turn, allows us to study the environment experienced by radicals in coal, as well as giving us information on the structure of the radicals themselves. ESE and ENDOR thus provide two complementary routes to the study of coal molecular and atomic structure.

B. Studying Coal Organic Molecular Structure via Hyperfine Interactions

For the past two years, work in our laboratory has centered on developing a reliable instrumental method for measuring proton hyperfine interactions in coal and other disordered solids, and on creating techniques to analyze the data obtained with this tool. Because the literature does not contain extensive prior work on proton hyperfine interactions in powdered or disordered samples, we decided to embark on a program of measuring and analyzing ENDOR and ESE data from pure compounds believed to exist in the organic phases of coal. Among hydrocarbons, we chose perylene as a starting point because of its frequent observation in the analysis of coal by-products and coal pile runoff [8]. For sulfur-containing materials, we consulted the report of Attar and Dupuis, who stated that the distribution of organic sulfur compounds in Illinois coals conformed to the following table [16]:

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<th>R - SH</th>
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Guided by such information, we have begun this phase of our work with two conjugated aromatic heterocycles, dibenzothiophene and thianthrene, which are...
representative of the largest class of organic sulfur compounds in coal. In the future, we plan to study anthracene, naphthalene, pyrene, several aryl thioethers, and other sulfur and hydrocarbon compounds in order to develop a library of ESE and ENDOR spectra of molecules likely to be present in coals. As we shall discuss later in this section, this library of spectra will play an important role in our interpretation of hyperfine data obtained from Illinois coals.

Our work on these model compounds has already progressed to the publication of ENDOR spectra and spectral simulations for the perylene cation radical formed on an activated silica-alumina catalyst [6]. The silica-alumina catalyst support creates cation radicals by electron transfer, and samples prepared in this manner closely resemble coal samples in many important ways. We also have obtained EPR and ENDOR spectra from thianthrene and dibenzothiophene on the same support, and currently are analyzing these spectra. Because the hyperfine interactions in all these materials is anisotropic, interpretation of the results is complex, and a satisfactory understanding of the data cannot be achieved without theoretical modeling. Figure 8 illustrates an ENDOR spectrum from the perylene radical, together with a theoretical simulation.

![Figure 8. ENDOR Spectrum of perylene radical on Al/Si catalyst. — is experimental, ---- is theoretical [6].](image)

A preliminary ENDOR spectrum of the thianthrene radical on silica-alumina is shown in Figure 9. The substantial differences between the two spectra can be related directly to differences in the structure of the two species. Each ENDOR

![Figure 9. ENDOR spectrum of thianthrene cation radical on Al/Si powder.](image)

spectrum has associated with it an analogous ESE spectrum, which contains the same information in a different format. Figure 1 showed one presentation of the
ESE spectrum of an evacuated sample of Illinois #6 whole coal. In a manner similar to that used in mass spectroscopy, we will analyze coal spectra by referencing hyperfine peak patterns to our library of spectra from known compounds. In this way, we will be able to determine the organic molecular structures present in a coal or separated maceral. It also should be possible to determine the relative concentrations of different species using the same data.

In addition to ENDOR and ESE spectra derived from the hyperfine interactions of molecules in coal, we are fortunate to have at our disposal another piece of information that can inform us about the sulfur content of the molecules we are observing. Figure 10 shows EPR spectra of perylene and thianthrene. It can be seen that the centers of the two spectral patterns do not coincide.

![Figure 10. X-band EPR spectra of perylene and thianthrene, showing the non-coincidence of spectral centers.](image)

This phenomenon is due to the fact that thianthrene contains sulfur, while perylene does not, and it can be used to distinguish the presence and amount of sulfur in any organic radical molecule. The theory of the effect is well understood, and we are able to predict the amount of spectral shift between sulfur and non-sulfur organic molecules with good precision. Why, then, do we not simply observe the EPR spectra of coals and analyze for organic sulfur species based on this effect?

Figure 11 shows the EPR spectrum of an evacuated Illinois #6 whole coal. The resonance line is a single, almost featureless absorption peak, lacking the detailed features of the spectra shown in Figures 8 and 9. This lack of detail

![Figure 11. X-band EPR spectrum of evacuated Illinois #6 whole coal.](image)
is due in part to the mechanisms discussed in Section A of this part of the Report. It also is due to the fact that an EPR spectrum from coal is a superposition of spectra from several different radical species, further obscuring details. We use ESE and ENDOR spectroscopies instead of EPR to study molecular structures in coal precisely because of this fact -- ESE and ENDOR techniques resolve hyperfine details obscured in ordinary EPR spectra. Does this mean we cannot benefit from the spectral shift phenomenon when studying organic sulfur in coal? The answer, fortunately, is that we still can use the effect, thanks to a new development in our laboratory -- two-dimensional ESE spectroscopy.

As was pointed out in the Executive Summary, 2-D ESE is really a combination of EPR and ESE techniques, in which the ESE experiment is repeated many times at different fixed values of the magnetic field. Data obtained in this way can be analyzed to determine the field dependence of the intensity of a particular hyperfine feature; Figure 2 showed plots of two such spectra. The non-coincidence of these two peaks is due to the same mechanism that is responsible for the effect in conventional EPR spectra -- it arises from the presence of sulfur (or, to a lesser extent, oxygen and nitrogen) in one of the molecules being observed. Thus, by 2-D ESE, we can learn about the sulfur content of individual radical species in coal as well as about their molecular structure.

EXPERIMENTAL PROCEDURES

In this section, we will discuss certain key techniques which are employed in the research. The technical description of these is best divided into three main sections. The first will deal with the novel S-band ESE spectrometer we have nearly completed building, and the experimental methodology required in its operation. The second part will describe sample preparation and specialized chemical methods. The third will discuss data analysis methods.

A. THE S-BAND ESE SPECTROMETER

Electron spin echo spectroscopy and ESE spectrometers have been the subjects of several recent and comprehensive review articles [17, 18]. Consequently, or discussion here will not be comprehensive, but will emphasize some important aspects of this technique.

Unlike the cw EPR experiment, ESE is a time-domain technique, analogous to time-domain methods commonly used in modern nuclear magnetic resonance. Very short microwave pulses are used to excite the paramagnetic spin system, and the time evolution of the magnetization is detected. Figure 6 illustrated the most common sequence of microwave pulses used in this experiment -- the 90-s-90-T-90 stimulated echo sequence. Here, 90 refers to the angle through which the net magnetization is tipped by the microwave pulse. In this experiment, the value t is typically kept constant (ca. 100-500 nsec), and the value T is stepped in 5-10 nsec intervals. The information of interest is contained in the amplitude of the echo and in how this amplitude changes as we step T. Figure 7 illustrated how the experiment is performed by stepping T and showed the time-dependence of the echo amplitude.

The echo amplitude modulation curve shown above is referred to as ESE Envelope Modulation (ESEEM); this curve contains the desired electron-nuclear interaction information. More specifically, in the absence of any interaction between the unpaired electrons and any neighboring nuclei, the ESE envelope will
show no modulation pattern but will show an exponential decay given by

\[ V_{echo}(2t + T) = V_0\exp\left(\frac{-2t + T}{T_m}\right) \] (vii)

where \( T_m \) is the phase memory time of the individual spins. More interesting to our purpose is the case where the unpaired electrons do experience hyperfine interactions with neighboring nuclei. In this case, the electron-nuclear interaction is observed as an ESEEM pattern. If we deconvolute the effect of the exponential decay, then for a \( S = 1/2 \) system with isotropic \( g \) (a good approximation for the organic radicals in coal) and hyperfine interactions characterized by frequencies \( f_a \) and \( f_b \), the ESEEM pattern is given by

\[ V_{mod}(2t + T) = 1-k[\sin^2(f_a t/2)\sin^2(f_b(t+T)/2) + \sin^2(f_b t/2)\sin^2(f_a(t+T)/2)] \] (viii)

In this expression, \( k \) parametrizes the depth of the modulation wiggles on the echo envelope. This parameter is proportional to \( B_0^{-2} \) (\( B_0 \) is the value of the static applied magnetic field). An important aspect of our spectrometer is that we will use a \( B_0 \) of about 1000 Gauss in our 2-4 GHz spectrometer, as compared to about 3300 Gauss in a typical X-Band (9 GHz) ESE spectrometer. As a consequence, we can increase the depth of these ESE modulations, effectively increasing our signal-to-noise ratio. This is particularly useful for coal samples that typically show relatively shallow modulations.

Figure 12 illustrates a block diagram for our ESE spectrometer. Considering

Figure 12. Block diagram of the S-band ESE spectrometer.
our brief discussion above, the necessity of several of the spectrometer elements is clear. First, we need a computer-interfaced pulse programmer to control the fast microwave pulses, the time-stepping of these pulses, and the acquisition of the data. We also need sufficient microwave power to generate 90-degree pulses in our sample. This power is achieved by amplifying the weak (10-50 mW) signal of the microwave source to tens or hundreds of watts with a TWT amplifier. In addition, the ability of the cavity to concentrate these microwave pulses at the sample is important. Finally, detection and amplification of the weak spin echo signals is required.

Through this instrumentation program, we will soon have operational a unique magnetic resonance instrument optimized for the study of hyperfine interactions in coal and related materials. In order to gain additional information and to clarify questions of spectral interpretation, we will continue to collaborate with Drs. James Norris and Michael Bowman at the Argonne National Laboratory, and Drs. Jack Pelsach and John McCracken at the Research Resource for Pulsed EPR Spectroscopy in New York. Each of these groups has an X-band ESE spectrometer. The ability to perform ESE experiments at several microwave frequencies has been seen as an ideal method of resolving ambiguities in interpretation -- we are indeed fortunate to have the willing collaboration of two such outstanding groups in the work we are doing on coal.

B. SAMPLE PREPARATION AND MANIPULATION

Our typical experimental procedure when working on coal is to first carefully evacuate samples that have been ground to 50-100 mesh (although we have performed ESE experiments on large fragments). We have noted that the presence of adsorbed oxygen has a significant effect on \( T_m \), reducing it by more than a factor of two and making the experiments more difficult to perform. Similar effects of oxygen on ENDOR spectra of coal have been reported by us [19]. Samples evacuated to pressures less than \( 10^{-6} \) Torr for several days are then sealed in quartz glass tubes for study. Experiments typically are performed at liquid helium temperatures in order to make \( T_m \) and \( T_1 \) as long as possible.

One important sample preparation option needs special mention. Because we use naturally occurring organic radicals in coal as probes of the environment, we are very interested in learning whether these radicals sample a typical maceral environment, or whether they represent a unique and atypical portion of the organic phase. One approach to answer this question is to create radicals which are not naturally occurring, and which have a random distribution throughout macerals. To attempt this radical generation, we have irradiated coal samples with \( \gamma \)-radiation. Like the literature, our results to date are inconclusive. The only published radiation effects in American bituminous coals which appear unambiguous are those reported by Retcofsky, et. al. using an electron beam [20]. We plan to adopt a similar approach, using the 2 MEV electron beam from an accelerator located in the Materials Research Laboratory at the University of Illinois/Urbana. Samples will be kept at liquid nitrogen temperatures during the brief irradiation period, and changes in the ESE spectra brought about by new radicals will be screened. By creating radicals randomly throughout macerals, we hope to gain information concerning the distribution of naturally occurring radicals in coal.

C. DATA ANALYSIS

Experimental data from an ESE experiment is "time domain" information -- data that records the time variation of our observables. Since the more customary
format for spectroscopic information is in the frequency domain -- variation of observables as a function of frequency -- we often Fourier transform our primary data to achieve this usual presentation. As the report in Appendix A more carefully discusses, direct Fourier transformation of ESE data sometimes leads to distortions that can complicate spectral interpretation.

We have been studying the problem of ESE data handling for over a year, and we now feel that the most reliable approach is to simulate the time domain data without recourse to Fourier transformation. This method obtains all the information we need in this study. It does not produce "spectra" in the usual sense of frequency domain data plots, and we still will make these spectra using several new techniques, including the Windowing approach of Mims [21].

The analysis of ELDOR spectra by computer simulation also poses unique challenges. We have written programs to simulate powder spectra of fully anisotropic systems (anisotropic g and A tensors), and these run on the VAX computer in the Department of Chemistry as well as on IBM PC/AT systems in our laboratory. A graduate research assistant in Professor Belford's research group currently is studying the problem of computer optimization of the choice of spectral parameters needed to fit experimental data to theoretical calculations, and an approach utilizing the simplex technique is showing great promise. This method already has been successfully applied to the simulation of ESE time domain data, with a great savings in human time. The successful creation of a really reliable computer optimization strategy for ELDOR as well as ESE data will result in an even greater savings of time, allowing researchers to be more productive.

ESE and 2-D ESE data will be analyzed by comparison to ELDOR spectral library data, using a spectral simulation route. Empirically determined contributions from different molecular structures will be summed, and the time domain ESE data simulated. Theoretical modeling, making use of variables like interatomic distance, number of nuclei, and atomic positions, will generate spectral simulations which also will aid us in the overall analysis of the atomic structure of coal macerals. As stated in the previous section, the overall goal of this analysis is the more complete understanding of the organic molecular environment of sulfur in coal.

RESULTS AND DISCUSSION

The purpose of this section is two-fold. Key experimental results thus far obtained on coals and model coals using ELDOR and ESE spectroscopies will be summarized, and the experimental rationale of our approach to the study of coal will be explained, providing a context in which to view the different experiments as logical steps directed toward the goal of elucidating molecular and atomic structural information.

The first ELDOR and ESE results on whole coal were reported by Kevan and colleagues [22], focusing on proton matrix ELDOR effects. Retcofsky, et al. published ELDOR spectra from several Pennsylvania coals, resolving hyperfine interactions between unpaired electrons and protons bonded to the radicals [23]. These spectra held out the promise of identifying the radical species in coal based on the hyperfine couplings. Two principal points complicated interpretation: 1) ELDOR spectra from whole coals are the result of contributions from several different radical species, and, 2) ELDOR spectra from radicals in disordered solids exhibit significant hyperfine anisotropy, requiring the full
theoretical simulation of spectra in order to arrive at an accurate interpretation. Because these two points each represent a complex problem in spectral interpretation, we decided to approach them separately, by using model compounds thought to exist as radicals in coal.

We adopted a technique whereby cation radicals of conjugated aromatic molecules are formed on the surface of activated silica-alumina and alumina powders. Samples prepared in this way have many of the spectroscopic characteristics of the radicals in coal. Because the ENDOR spectra of radicals in coal represent a "powder-like" pattern, and because there is considerable hyperfine anisotropy in conjugated aromatic radicals, it is impossible to obtain the principal elements of the hyperfine coupling tensors by simple inspection of the experimental results. A computer simulation of the results needs to be made, and a best fit of experimental and calculated spectra sought. This best fit then defines the $A_x$, $A_y$, and $A_z$ values for each interaction. Our original ENDOR spectral simulations followed closely the approach used by Dalton and Kwiram [24], who simulated ENDOR using perturbation theory. A more rigorous simulation approach on which we now are working diagonalizes the spin Hamiltonian matrix rather than using perturbation theory expressions. The inclusion of $g$-anisotropy and quadrupole interactions also makes this new calculation more comprehensive. While our earlier calculations [6] of experimental ENDOR spectra developed reliable values for the $A$ matrices, it is hoped the new ENDOR simulations will give more reliable information on line intensities, and thus allow a better fit between simulation and experiment. An experimental and theoretical ENDOR spectrum of our first model compound, perylene, are shown in Figure 13.

Figure 13. Experimental (----) and theoretical (-----) ENDOR spectra; perylene$^+$ radicals formed on activated alumina. T=110K [6]

As we develop a more thorough understanding of the ENDOR spectral characteristics of radicals formed from model compounds, we plan to build a library of spectra on which to base the simulation of ENDOR and ESE spectra whole coal and separated macerals. Using the experimental and theoretical techniques developed for our work on perylene, we now are analyzing radicals formed from anthracene, naphthalene, pyrene, and dimethylanthracene. This selection of compounds should span a significant percentage of the aromatic hydrocarbon radicals found naturally in coal. We also are studying dibenzothiophene in order to learn the characteristics of sulfur heterocycles, thought to be important forms of organic sulfur in Illinois coals. We believe that this approach, using ENDOR to study intermolecular hyperfine interactions in model systems, affords us the most direct route to an improved understanding of the more complex spectra obtained from coal.
A detailed theoretical understanding of the proton hyperfine couplings in the radicals found in coal is needed if we are to use them to probe the molecular structure of organic sulfur. This is true for both ENDOR and ESE measurements. Most fundamental is the theory linking 1) a particular molecular geometry and bonding pattern and, 2) the hyperfine couplings observed by ENDOR or ESE spectroscopy. In order to develop this structural theory of hyperfine couplings for radicals that are models of coal composition, we have calculated the theoretical couplings in the perylene radical. Two methods were used. The first was developed by McConnell and Strathdee [25]. In this method, the isotropic hyperfine contribution to the spin Hamiltonian is simply made proportional to the \( \pi \)-electron spin density on the carbon. The anisotropic hyperfine interaction is approximated by a magnetic dipole interaction between the proton and an electron spin magnetization centered on the carbon in a \( p \)-orbital.

There are several problems with this method. First of all, the electron is not really in a \( p \)-orbital on an isolated carbon atom: it actually is delocalized in a \( \pi \)-orbital. Also, each electron - proton interaction is treated as a C-H fragment. Thus, in the McConnell-Strathdee treatment, the dipolar interactions of neighboring electron spin density is ignored. In spite of these problems, the method gives excellent qualitative and reasonable quantitative results when compared to the ENDOR experimental values.

In order to include interactions of the additional electron spin magnetization on the other carbons, the method of hyperfine calculation proposed by O'Malley and Babcock has been used [26]. The inclusion of these neighbor interactions caused substantial deviation from the values expected for an isolated C-H fragment. In this calculation, which we have just completed for the perylene radical, all carbon atoms with a spin density within 5 Å of the proton of interest have been included as point dipole interactions. The interaction of the proton connected directly to a carbon is approximated as an isolated C-H fragment and the other interactions are added after transformation to a common axis system. In addition to changing the hyperfine tensor components, inclusion of the additional interactions causes a rotation of the principal axis system. In the original system, the y-axis is taken as the C-H bond, the x-axis is perpendicular to it in the plane, and the z-axis is out of the plane of the molecule. With the inclusion of neighbor interactions, the axis system is rotated for each proton, the effect being most pronounced for the \( \beta \)-proton, which has the smallest spin density on its bonded carbon.

If ENDOR spectroscopy is the method of choice for the resolution of strong hyperfine interactions, ESE is uniquely sensitive to weaker, intramolecular interactions. In the first published account of ESE measurements in coal, Kevan, et. al. studied matrix proton interactions, calculating a mean distance between unpaired electrons and protons in an SRC of \( r = 0.5 \pm 0.03 \) nm, and an apparent interaction shell occupancy of \( n = 16 \pm 2 \) protons [13]. Das, et. al. found a value of \( r = 0.36 \pm 0.04 \) nm (not reported) from a similar analysis of two-pulse ESE experiments performed on a low-sulfur Pittsburgh bituminous coal [27]. The matrix interaction, it will be remembered, is the essentially electron-nuclear dipole-dipole coupling between non-bonded atoms, and thus reflects the density of nuclei in the immediate neighborhood of the unpaired electron. The model used for these first analyses was a spherical shell, depicted in Figure 14. Such information, when correlated with specific maceral types, should provide us with a much more precise measurement of the atomic structure of coal, and may be diagnostic of structural changes brought about by various coal beneficiation technologies.
We have performed experiments on powdered Illinois #6 whole coal using a three-pulse ESE sequence, and have analyzed the matrix ESEEM by the spherical shell model. Figure 15 shows our data and best-fit simulation using $r = 0.75 \pm 0.05$ nm and $n = 40$ protons [4]. Variations in $r$ and $n$ among the three reported measurements may be due to differences in the structure of the samples studied; more likely sources of variations are the differences in experimental techniques (two-pulse, three-pulse), and different spectrometer characteristics (pulse power, cavity Q, etc.) used in the three studies. We currently are making a detailed study of these effects using whole coals and coal model systems in an effort to better understand the role of experimental factors in the results obtained. We also are studying the utility of more realistic model geometries (e.g., layered structure) and the sensitivity of ESEEM simulations to the choice of geometry.

In 1984, we first reported the observation of matrix ESEEM from $^{13}$C nuclei in natural abundance in coal [28]. Since that time, we have worked to understand the experimental and theoretical characteristics of this important effect, and we have recently developed criteria to optimize experimental sensitivity [29].
Because, to zeroth order, ESE sensitivity does not depend on the nuclear gyromagnetic ratio, this spectroscopy is much better suited for the observation of "low gamma" elements such as carbon and sulfur, which present severe problems for ENDOR and NMR. Data on $^{13}\text{C}$ ESEEM thus far suggests that in an Illinois #6, $r = 0.31 \pm 0.01$ nm, and $n = 2$. Clearly, the opportunity to map the carbon skeleton of coal with this technique represents a great opportunity; it also is clear that much more work is needed to fully understand and correctly interpret such data.

Although ESE spectroscopy is well-suited for studying nuclei weakly coupled to unpaired electrons, it also is capable of examining stronger hyperfine interactions like those existing between nuclei bonded to the radical. Data from these measurements essentially have the ENDOR format and are analyzed by the same theory. Because ESE is a time-domain technique (similar in some ways to FT-NMR), the data obtained from these experiments may be Fourier transformed or else simulated before meaningful interpretation can be done. We have extensively studied the problems involved in the analysis of time-domain data from coal, and our results suggest that in many instances, data simulation is a safer route than FT techniques. Figure 16 illustrates a Fourier transformed ESE spectrum of whole coal, revealing several spectral peaks corresponding to resolved proton hyperfine interactions. From data like that in Figure 16, we are learning information about

![Figure 16. FT-processed ESE spectrum of a whole Illinois #6 coal.](image)

the structure of radicals in coal, using the same theoretical approach developed for ENDOR.

Several hybrid schemes have been employed by our laboratory to increase the ability of ESE to discriminate between hyperfine interactions arising from different macerals. We classify these techniques as 2-dimensional ESE, in that they develop information on the intensity of hyperfine coupling signals as a function of magnetic field. Figure 17 illustrates one representation -- plots of two discrete ESE line intensities (individual hyperfine frequencies) as functions of $B_0$. It will be seen that the centers of the two lines are not coincident, indicating that the radicals giving rise to the interactions are different (have different g-values). This resolution of individual hyperfine couplings into groups with different g-values may provide the basis for determining the maceral origin of components of the complex hyperfine patterns observed in whole coal. It also may allow the deconvolution of the composite spectra from whole coal into spectra from individual components.

Another type of 2-D ESE experiment is illustrated in Figure 18. Here, the
hyperfine intensities across a wide range of radiofrequencies are plotted as a function of magnetic field. Most prominent are those peaks from \(^1\)H and \(^{13}\)C matrix interactions. It can be seen that the two peaks go through a minimum near the center of the EPR signal. We believe this demonstrates the existence of an effect called instantaneous diffusion [30], and we have suggested that it can be used to calculate the concentration of radicals in a particular maceral in coal.

ESE time-domain spectra like the one shown in Figure 15 contain information on the hyperfine interactions in the ESEEM pattern. In many instances, the depth of this echo envelope modulation is very shallow, resulting in a low signal-to-noise ratio for the data to be analyzed. Since all the work thus far was performed at X-band (ca. 9.5 GHz) frequencies, it was reasoned that because of the \(B_0^{-2}\) dependence of the ESEEM depth parameter in Equation (iv), better quality proton ESEEM would be obtained by working at lower frequencies (and fields). This is one of the primary reasons we undertook to build an ESE spectrometer operating at S-band (2 – 4 GHz) frequencies. This program, funded by the CRSC, is now nearing completion, and we plan to use this unique spectrometer extensively in the study of coal structure here proposed. Figure 12 shows a block diagram of the spectrometer. The instrument has the additional advantage that the frequency range spanned by the nuclear Zeeman interactions in coal samples is smaller at lower fields, thus allowing a more complete excitation of the spectrum, and hence a better time-domain representation of the complete range of hyperfine interactions present in the coal.
Low gamma nuclei like $^{13}$C and $^{33}$S have correspondingly low ESEEM modulation frequencies. For these nuclides, higher field strengths should aid in the separation of signal modulations and instrumental artifacts. Because of our certainty that the atomic information from these nuclei will be vital for the study of coal structure, we have designed an accessory to our S-band ESE spectrometer that will operate at K-band (18 - 24 GHz), and in this proposal we ask for funds to construct the unit. In design, it is similar to the block diagram of Figure 13, except that it will not employ a single digital phase shifter, but will switch between two microwave arms set 180° apart in phase. Not only will this additional frequency range aid in the study of elements like carbon, nitrogen, and sulfur, it also will assist us in the theoretical analysis of data by providing an additional frequency for experimental observation.

We continue to study coal by means of cw EPR. We currently have spectrometers operating at L-band (1 - 2 GHz), X-band (9.5 GHz), and Q-band (35 GHz). X- and Q-band instruments are commercial spectrometers; the L-band instrument was built by us. We currently are working on a W-band (ca. 96 GHz) instrument, under a grant from the NIH, and we believe that this new, superconducting spectrometer will be a powerful addition to our spectroscopic arsenal in the study of coal. Because the g-values of radicals in coal are nearly identical, the EPR signals overlap at normally used field strengths (0.34 T.). Observing these resonances at 3.4 T. will separate the lines, perhaps making possible a direct deconvolution of the complex spectra from whole by spectral dispersion. ENDOR at this high field also is possible, and we intend to pursue the possibilities for coal.

One area in which cw EPR is important to us is the study of radiation-induced radicals in coal. As was stated in the Executive Summary of this Report, key questions concerning the representative nature and distribution of naturally occurring radicals in coal may be answered through an investigation of radicals created by ionizing radiation. We have subjected Illinois #6 coals to both gamma ray and electron irradiation. Figure 19 shows the EPR spectrum of one such coal both before and after irradiation by 11.6 Mrad of gamma rays from a $^{137}$Cs source. A comparison of spectra (a) and (d) show no change as a result of the radiation dose. Figure 20 shows a similar coal before and after irradiation by 2.5 MEV electrons for 53 minutes. Comparison of spectra (a) and (d) now show profound

Figure 19. EPR of Illinois #6 coal before and after irradiation by gamma rays.
changes in the spectrum, indicating the creation of radicals different from those naturally occurring in the coal. This is the effect we have been seeking, and represents an opportunity for future work.

CONCLUSIONS AND RECOMMENDATIONS

Several key conclusions can be drawn from our work. Let us briefly consider each, and then make recommendations for further work.

1. We have been able to construct a working S-band ESE spectrometer, as we outlined in our proposal.

2. Results from ESE experiments thusfar indicate that the structure of radicals in coal are predominately aromatic in character. Proton hyperfine coupling constants are in a range expected from two, three, four, and five-ring conjugated aromatic structures. No proton hyperfine coupling constants suggestive of aliphatic carbons have been seen.

3. 2-D ESE experiments can differentiate between hyperfine couplings arising from radicals with different g-values, giving us reason to believe that this spectroscopic approach can be used to identify and study sulfur-containing species in whole coal.

4. Anisotropic hyperfine interactions are the rule in coal radicals. Therefore, detailed theoretical simulations of the spectra are needed, at least initially, to allow accurate interpretation of the results.

5. Simulation of the time-domain ESEEM data gives detailed information on the carbon-proton and carbon-carbon distances in macerals. We have been able to simulate both proton and $^{13}$C signals using a theory developed in our laboratory. This information may be very useful in studying changes in coal structure brought about by various desulfurization procedures.

6. Parallel studies of model compounds using ENDOR spectroscopy are necessary to allow detailed study of electron-nuclear interactions, and to facilitate the development of procedures for the interpretation of data.
7. A library of interpreted ENDOR spectra from model compounds believed to exist in coal is necessary to permit the modeling of spectra from whole coal.

8. Electron bombardment of coal samples produces new radicals in the structure. This technique will allow us to address the questions of radical distribution and chemical selectivity, hopefully permitting a more accurate interpretation of data on coal structure.

Based on these conclusions, we recommend that additional work be performed in the areas of ESE and ENDOR spectroscopies of coal. Particularly, we believe that the new S-band spectrometer, funded by the CRSC, will provide better data for the study of coal structure, and we urge the Center to support work on that instrument. We also suggest that the Center use its good offices to provide better communication between groups working in areas like coal characterization. Particularly, our work would benefit from collaboration with groups engaged in the separation of macerals. We also would be interested in obtaining samples of coals subjected to various desulfurization procedures, in order to assess the sensitivity of our techniques to changes in coal structure and composition.

REFERENCES


