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Title: SPIN-MAPPING OF COAL STRUCTURES WITH ESE AND ENDOR
Principal Investigators: R. L. Belford and R. B. Clarkson
Institution: University of Illinois at Urbana-Champaign
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ABSTRACT

Work reported this quarter (1) continues the study of organic sulfur species in coal with Very High Frequency (VHF) EPR spectroscopy and (2) includes some pulsed EPR work on coals carried out with the S-band ESE spectrometer. A detailed VHF study of one coal from the Illinois Coal Sample Bank is reported, including spectra from separated macerals and solvent extracted coal. Further refinements in the two-species model for interpreting these spectra are presented. It is increasingly apparent that while the organic sulfur species seen by VHF EPR in coal may be thiophenic, they do not have spectra that directly implicate either thiophene or dibenzothiophene as unique molecular forms. The emerging picture seems to indicate a thiophenic sulfur species in which the unpaired electron is delocalized over a more extensive aromatic cluster. VHF EPR may be quite specific for aromatic organic sulfur.

Spectra from eight coals in the Argonne Premium Sample program also have been studied by VHF EPR, and analysis is now under way to determine how well the two-species model accounts for the general features of these spectra. Pulsed electron spin resonance has been performed on the Argonne coals in order to determine their electron phase memory times (T_M) at ca. 1000 G magnetic fields.

EPR and NMR imaging experiments on Illinois coals are currently focussing on developing better resolution through improvements in the spectrometer hardware.

II. GENERAL SUMMARY

During the Symposium on Coal Chemistry and Characterization that took place at the PACIFICHEM '89 meeting of the American Chemical Society (12/89), Herbert L. Retcofsky, Director of the Division of Coal Science at the U. S. DOE's Pittsburgh Energy Technology Center gave two presentations. The theme that was common to both talks, aside from their usual scientific excellence, was the call for innovative new approaches for the analysis of sulfur and oxygen in American coals. Retcofsky pointed out that the standard ASTM methods that are currently used for sulfur analysis were developed as trustworthy guides for the buying and selling of coal, but that these procedures never were intended to address the more complex issues of the distribution of functionalities and heteroatoms (S, O, N) that have become important issues in the current period. Indeed, Retcofsky suggested that because the ASTM method for organic sulfur is indirect and destructive, there are great doubts about the meaning of the data it produces. "Better information about the nature of organic sulfur in coal is urgently needed if we are to do a better job predicting sulfur reactivity and designing coal cleaning strategies that are more economically feasible, not to mention assessing the effectiveness of coal cleaning in the context of likely new Federal regulations," Retcofsky said.

MASTER

Our work this quarter addresses the need for innovative approaches to characterize the organic sulfur in coals. With support from the U. S. DOE, augmented by additional funding from the CRSC (State of Illinois), the Petroleum Research Fund (ACS) and especially from the National Institutes of Health (Research Resource), we have developed a very high frequency electron paramagnetic resonance (EPR) spectrometer (described in previous quarterly reports) operating at the W-band of microwave frequencies (96 Ghz), one of only three such instruments in the world, and the only one in the U.S.A. This instrument has shown exquisite sensitivity to small variations among radicals such as are caused by heteroatoms in coal, and we believe the technique can be successfully applied for the **non-destructive, direct determination of organic sulfur in coal.** Preliminary data from Illinois coals and separated macerals indicate that **the 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 approaches utilize 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 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 the presence of 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 is relatively quick; a typical EPR spectrum of coal on the W-band instrument takes about one minute to record.

In order to illustrate our method, consider Figure A, which shows EPR spectra of an Illinois #6 whole coal taken at three different microwave frequencies: 9, 35, and 96 GHz. The rather simple resonance lineshapes at 9 and 35 GHz represent the state-of-the-art for the EPR of coal before the construction of our 96 GHz instrument. In these lower frequency spectra, sulfur atoms are shifting a portion of the EPR resonance, but the shift is too small to be resolved. The key to resolution of the effects of sulfur is higher field strengths (and higher frequencies). Thus, at 96 GHz, we see an EPR spectrum with two peaks. The resonance occurring at lower field strength, which is highlighted in Figure A(c), is due to heteroatoms, and we have strong evidence that it is largely the result of organic sulfur.

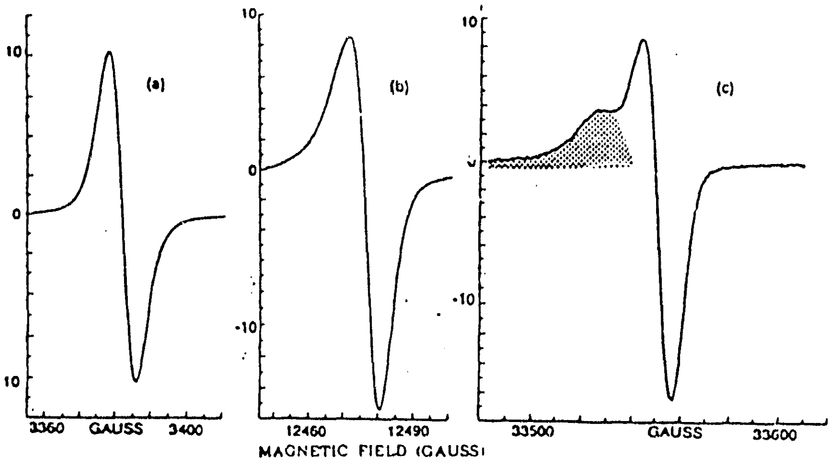

Figure A. EPR spectra of a whole Illinois #6 coal taken at (a) 9 GHz, (b) 35 GHz, and (c) 96 GHz [1]. Highlighted portion of (c) is due to S (and perhaps O).

In order to learn more about the origin of the low-field peak, we studied macerals separated from this coal by density gradient centrifugation. Figure B shows the W-band EPR spectra from the vitrinite and sporinite components, together with simulations based on a simple model. Destructive chemical analysis of these two samples determined that the vitrinite contained 2.9% organic sulfur by weight, while the sporinite contained 4.25%.

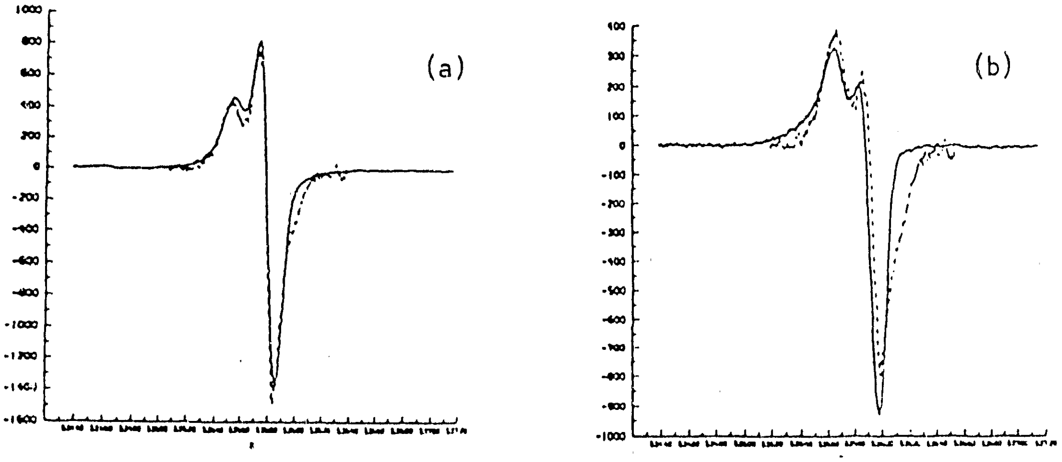

Figure B. (a) Vitrinite (2.9% S) and (b) Sporinite (4.25% S) separated from an Illinois #6. (______)Experimental, (---) Theoretical.

Oxygen composition was identical for the two macerals. The simulations shown in Figure B. required the inclusion of about 1.5 times as much sulfur in the case sporinite as for vitrinite, which is almost precisely the ratio of sulfur contents of the two components as determined by careful chemical means. While more work is needed to develop this very high frequency EPR method into a routine, reliable method to determine the chemical forms and quantities of organic sulfur in coal, we feel these preliminary data show the great potential of our approach.

The overall method used in this work, employing EPR and NMR techniques at a variety of magnetic field strengths (0.05 to 4.7 T) has been termed **multi-frequency electron magnetic resonance**, and has as its primary goal the measurement of structure in complex and disordered systems. Examples of this are the S-band pulsed EPR measurements we have recently made on Argonne Premium Sample coals. These measurements, for which we use the same instrument constructed for the ESE spectroscopy, were aimed at determining electronic phase memory times (T_M or T_2^*) in order to gain a better understanding of the relationships between coal rank and the dynamics of unpaired electrons. Our approach has yielded new information on this poorly understood aspect of coal chemistry.

Finally, we have continued to develop EPR and NMR imaging of coal and to work on the acquisition and interpretation of ENDOR spectra.

III. OBJECTIVES

The broad goals of this project are to determine by nondestructive means the chemical and physical structure of organic sulfur in native and treated coals, and to follow the course of coal cleaning processes with microscopic spatial resolution. In working towards these goals, we must test our new instrumentation and methods on benchmark systems and on model systems as well as on whole, separated, and treated coals.

IV. INTRODUCTION AND BACKGROUND

Multi-frequency EMR is the method of making electron magnetic resonance measurements (eg EPR, ENDOR, ESE) on the same material at several, substantially different, microwave frequencies. Previous applications of the approach to EPR spectroscopy of coal have demonstrated its effectiveness, even over a modest two-frequency range (9.5 GHz and 35 GHz) (2 - 3), and the entire subject recently has been reviewed by Belford and co-workers (4). Multi-frequency studies of complex systems often can facilitate reliable interpretations of structure, bonding, and magnetic interactions that would otherwise remain uncertain or impossible to analyze in single-frequency experiments. These authors point out that an examination of the principal terms of the spin Hamiltonian provide a useful starting point for understanding the utility of multi-frequency experiments.

Let the spin Hamiltonian, $\mathcal{H}_s$, be written as the sum of electronic and nuclear spin operators,

$$\mathcal{H}_s = \mathcal{H}_e + \mathcal{H}_n, \tag{1}$$

in which

$$\mathcal{H}_e = +|\mu_B|\mathbf{B}_0 \bullet \mathbf{g}_e \bullet \mathbf{S}, \qquad S = \tfrac{1}{2}, \tag{2}$$

and

$$\mathcal{H}_n = -g_n|\mu_n|\mathbf{B}_0 \bullet \mathbf{I} + \mathbf{S} \bullet \mathbf{A} \bullet \mathbf{I}, \qquad I = \tfrac{1}{2}; \tag{3}$$

B_0 denotes the external magnetic field while **A** represents the hyperfine interaction matrix. The first term in each part of $\mathcal{H}_s$ describes the Zeeman interaction (electronic or nuclear), and is characterized by a dependence on B_0 and expressions containing g-values. The second term in $\mathcal{H}_n$ describes the hyperfine interactions between electrons and nuclei.

Information on structure and bonding is contained in both the Zeeman and hyperfine interactions, which together form the basis for an experimentally observed electron magnetic resonance spectrum. Because of the complexity frequently seen in spectra from disordered, heterogeneous systems like coal, it can be very difficult to analyze or unambiguously interpret the data. For example, the EPR linewidths of coal spectra can include contributions from g-anisotropy and hyperfine interactions, and it usually is difficult to determine the relative importance of each contribution. In this case, one would like to "switch off" the hyperfine interaction for one observation, and then compare the resulting spectrum with a conventional one containing both Zeeman and hyperfine terms in order to separate the two contributions. Magic-angle spinning attempts to do just this, for example, by averaging away the dipolar portion of $\mathbf{I}_1 \bullet \mathbf{I}_2$ interactions in NMR spectroscopy, and other NMR techniques address different portions of $\mathcal{H}_s$ to effect spectral simplifications. Unfortunately, the much more rapid electronic relaxation rates exhibited by paramagnetic systems have thus far made it impossible to apply these techniques to EMR. What is needed for EMR is a method to vary the importance of terms in the spin Hamiltonian that does not depend critically on relaxation rates -- a goal which the multi-frequency approach accomplishes. By performing EPR, ENDOR, or ESE at different microwave frequencies (and hence in different B_0 ranges), it is possible to emphasize or de-emphasize Zeeman interactions relative to hyperfine terms, allowing a more critical evaluation of many spectral effects, among which are the following: g-dispersion (EPR) (5); nuclear Larmor frequencies, orientation selection (ENDOR) (6); echo envelope modulation depth (7), orientation selection (8 - 9), exact cancellation (10) (ESE); relaxation rates (seen in all methods). For example, Figure 1 shows EPR spectra of an Illinois #6 coal taken at three different frequencies (4). As g-dispersion increases with B_0, the appearance of a low-field shoulder becomes obvious. In this instance, important chemical information contained in the electronic Zeeman term could be revealed only at higher frequencies.

Figure 2 shows another example of the utility of the multi-frequency approach. Here, the electron spin echo envelope modulation (ESEEM) from the same Illinois coal is shown at two frequencies. The depth of the ESEEM pattern is greater at lower frequencies due to a reduction in the energy separation between electronic spin states and a corresponding increase in double (electron-nuclear) spin flip transitions.

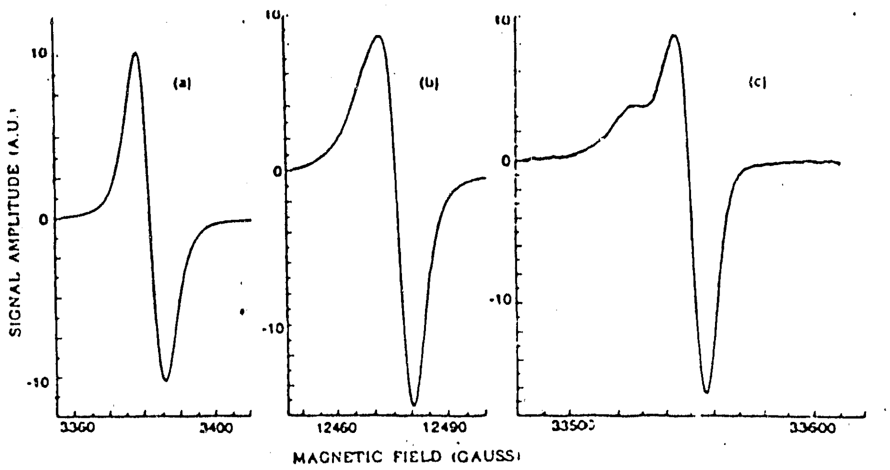

Figure 1. EPR of an Illinois #6 coal at (a) 9.5 GHz, (b) 35 GHz, and (c) 94 GHz. (10).

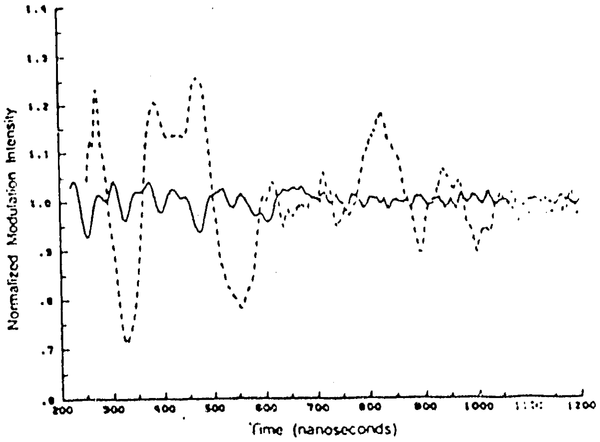

Figure 2. ESEEM patterns from an Illinois coal taken at 3 GHz (---), and 9.4 GHz (______)(6).

In this report, we review our recent very high frequency (96 and 250 GHz) EPR work (4, 11) and report new low frequency (3 GHz) pulsed EPR results on Argonne Premium Sample Coals. Other related ongoing work in our laboratory includes multi-frequency ENDOR of coal and coal-related compounds.

V. EXPERIMENTAL

Samples of coal from the Argonne Premium Coal Sample Program were received in sealed glass ampoules under nitrogen. The compositions of these eight samples have been reported (12). For EPR at 96 GHz (VHF EPR), the ampoules were opened in air just prior to taking spectra. Samples were loaded into 0.5mm I.D. capillaries and placed in the cavity of the spectrometer. The W-band (96 GHz) instrument has been described elsewhere (4). Field strengths were measured with an NMR gaussmeter (Metrolab model 2025); frequencies, with a digital frequency counter (EIP model 578) A variety of sharp, solution phase samples were used to insure precise g-calibration.

A sample of Herrin No. 6 (Illinois #6) coal from the Illinois Coal Basin Sample Program (ICBSP #1, Southern Illinois University registry No. 1822) was separated by density gradient centrifugation prior to study, and vitrinite, sporinite, and fusinite maceral fractions were analyzed prior to taking EPR spectra. The analysis data for these samples is given in Table I.

Table I. Elemental and Proximate Data for SIU 1822
Dry Ash Free Basis

Sample	Dry %C	Dry %H	Dry %N	Dry %S	Dry %O
1822 whole	76.86	4.86	1.29	3.27	13.70
Vitrinite	75.68	5.25	1.41	2.59	11.57
Sporinite	76.18	5.90	1.11	3.87	12.94
Fusinite	79.61	4.24	1.35	2.03	12.77

The maceral composition of the SIU #1822 coal was determined to be 87% vitrinite, 4.4% liptinite, and 8.6% inertinite. The separated vitrinite from this coal was also studied on a 250 GHz spectrometer built by Freed et. al. at Cornell University (13).

Model compounds (perylene, dibenzothiophene, and dibenzofuran) were prepared as cation radicals either by adsorbing the materials as gasses onto an activated silica-alumina catalyst (Houdry M-46) (14), or by UV irradiating boric acid glasses containing the compounds in 10 - 50 mM concentrations.

Samples for pulsed EPR study were evacuated for 24 hours at room temperature and pressures $< 10^{-4}$ Torr in 5mm thin-walled NMR tubes. They then were sealed in the glass. The S-band (2-4 GHz) ESE spectrometer used in the study has been described previously (6).

VI. RESULTS AND DISCUSSION

Very High Frequency (96 and 250 GHz) EPR. Figures 3(a-h) show room temperature W-band spectra of all eight coals from the Argonne Premium Coal Sample Program. The samples show a considerable range of line shapes, in some cases revealing features not seen at lower field strengths. Because of our special interest in high-sulfur Illinois coals, we have begun the analysis of these spectra with APCS ID301 (Illinois #6). Many of the points that have thus far been considered in this analysis should find application in the interpretation of the VHF EPR spectra of other coals.

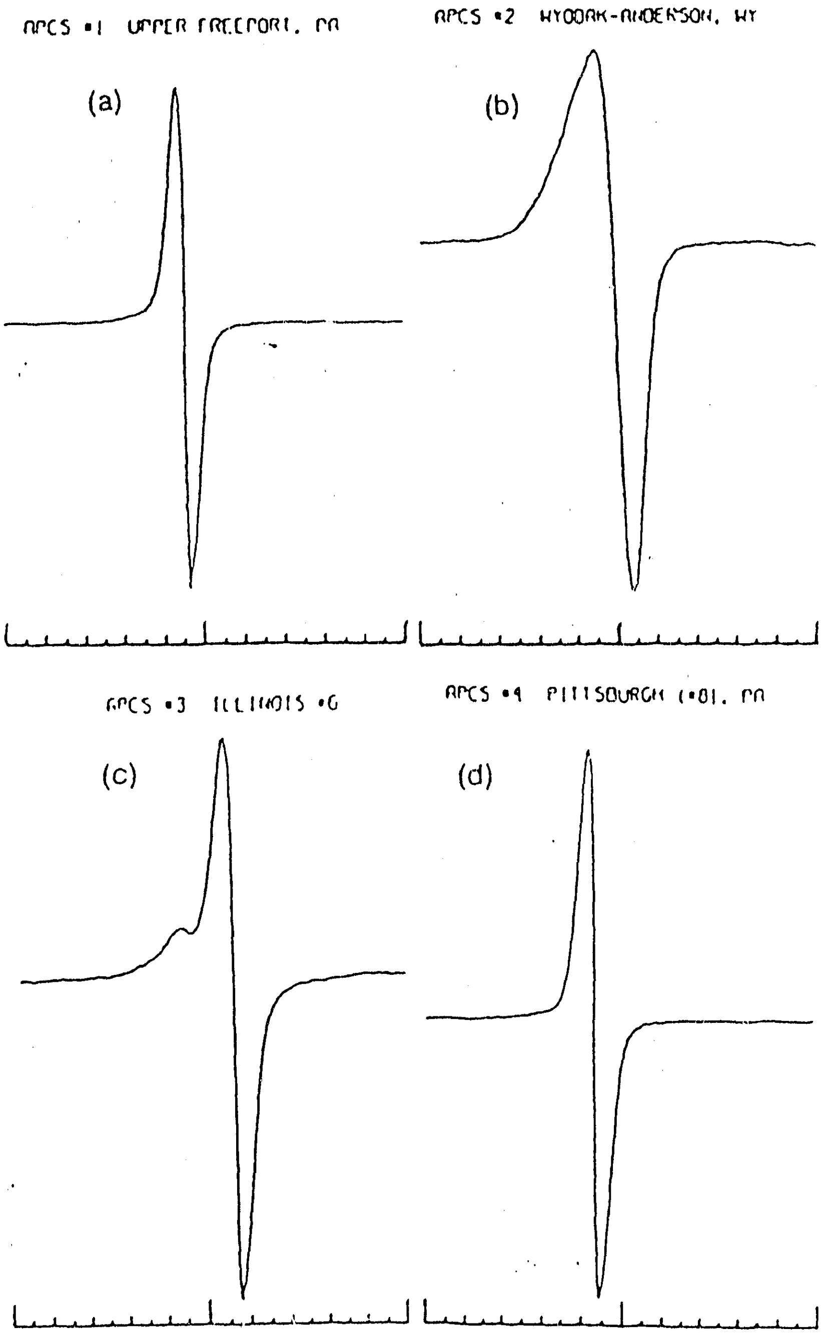

Figure 3 (a-h). W-band EPR Spectra of Eight Argonne Premium Coal Samples. First-derivative presentation. Microwave frequency, ca. 94 GHz. Field span for each spectrum: 200 Gauss centered at 33,600 Gauss = 3.36 Tesla.

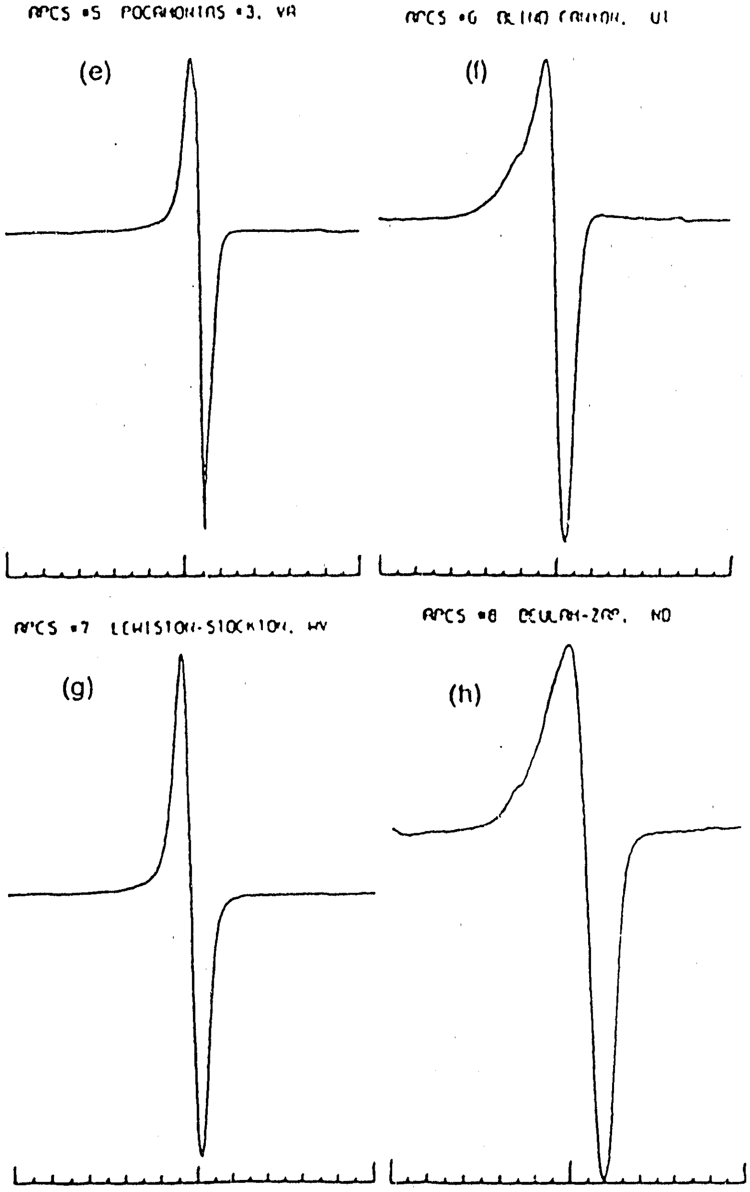

Figure 3 (continued).

The most prominent features of the W-band spectrum of APCS #301, in addition to the largest peak, include a low-field shoulder and a broad, weak, high-field wing. In order to determine whether these features are characteristic of a particular maceral, W-band spectra were taken of vitrinite, sporinite, and fusinite components separated from an analogous Illinois #6 (SIU No. 1822) by the density gradient centrifugation method, together with spectra of the coal after solvent extraction. Spectra of the three separated macerals are shown in Figure 4. These spectra clearly show substantial spectral variation with maceral type, and we will consider each in turn.

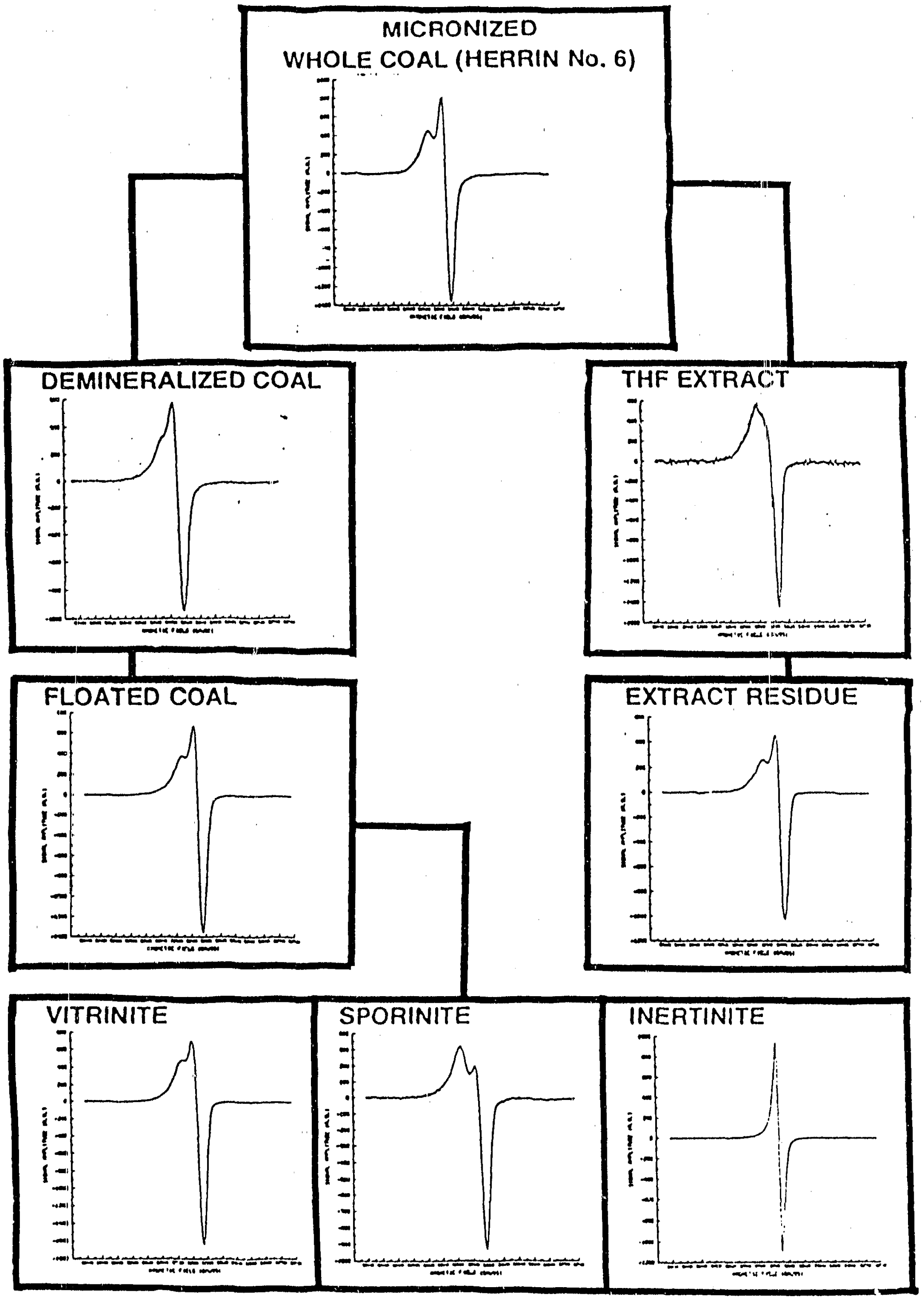

Figure 4. W-band EPR spectra from an Illinois #6 coal (SIU No. 1822). (10).

The fusinite signal in Figure 4 is so different from the other two maceral spectra, it must reflect a dominant interaction that is not as important in the other components. This interaction usually is assumed to be electron spin exchange, resulting in a narrowing of the resonance line (1, 15). We have tested this hypothesis by performing S-band pulsed EPR measurements on the fusinite, and observe only a free induction decay (FID), as shown in Figure 5. The observation of an FID, combined with the absence of echoes, lends strong support for the spin exchange model, particularly since the maceral contains almost as much hydrogen (4.24%) as the vitrinite and sporinite, which give strong spin echoes and proton ESEEM. Fourier transformation of the FID yields a frequency domain spectrum with linewidth nearly identical to that observed in the sample by CW EPR at 3, 9, and 96 GHz, again in agreement with the prediction of a linewidth independent of B_0 for exchange narrowing in the limit $B_e >> B_0$ or $B_e << B_0$, where B_e is exchange field (1).

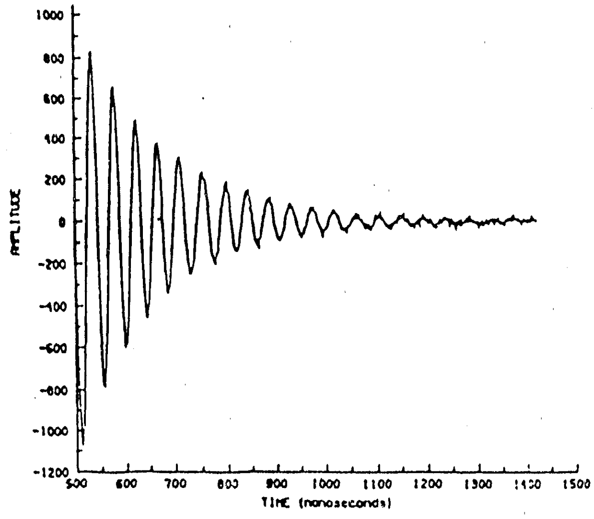

Figure 5. FID at S-band observed in the fusinite from SIU No. 1822, using a single π/2 observing pulse.

The simplest assumption would be to assume that the vitrinite spectrum in Figure 4 is due to a single paramagnetic species and to simulate it with an anisotropic g-matrix and suitable linewidth/line

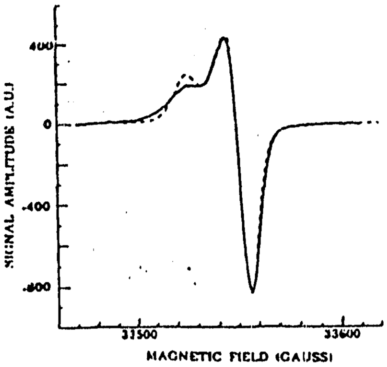

Figure 6. W-band EPR spectrum of separated vitrinite. Experimental (______), Theoretical (---). (10).

shape parameters. This has been done, and the quite reasonable result is shown in Figure 6, for g_1 = 2.0023, g_2 = 2.00274, and g_3 = 2.0042. Other chemical and spectroscopic evidence strongly suggests that this EPR spectrum is the result of contributions from two or more radical species with different heteroatom compositions, so this simulation is useful for identifying the g-values of the main features of the spectrum, but should not be viewed as implying that the single species model is correct. In order to confirm that the low-field peak in this spectrum is a part of an anisotropic lineshape (as opposed to a partially resolved symmetric peak), the separated vitrinite was run at 250 GHz in the laboratory of Professor Jack Freed (Cornell University). Figure 7 shows a comparison of the 96 and 250 GHz spectra and confirms that the low-field peak is, indeed asymmetric and part of one or more overlapping anisotropic spectra.

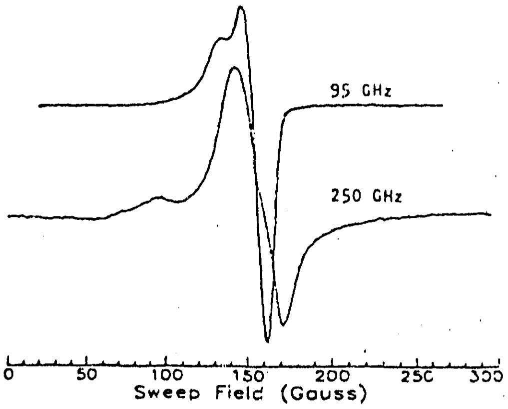

Figure 7. 96 and 250 GHz EPR spectra of a vitrinite maceral separated from Illinois #6 coal. (10).

Comparison of vitrinite and sporinite spectra (see Fig. 4) begin to illustrate the difficulties of the simple model, since features with identical g-values appear with different intensities in the two systems, suggesting the unequal contribution of two or more spectral components. The lower two g-values (g_1 and g_2) of the vitrinite are, in fact, just those observed for many different conjugated aromatic radicals, and predicted theoretically by Stone (16), and it is tempting to see the spectrum as a composite formed from pure hydrocarbon and heteroatomic radical contributions. In all probability, the low-field shoulder in this spectrum is associated with heteroatomic radicals, since spin-orbit (SO) coupling to sulfur (or oxygen) is the most likely mechanism to account for the higher value of g_3. The rather poor low-field fit of the single species simulation then could be a reflection of this composite character. Clearly, this issue of spectral and sample heterogeneity is of utmost importance for the correct interpretation of EPR spectra of fossil fuels, even when well-separated and purified, and we presently are working on several approaches designed to shed more light on the problem.

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

One promising avenue of investigation involves comparing W-band EPR spectra from coal with spectra obtained from model compounds believed to typify organic structures in coal. Figure 8(a) shows a spectrum from perylene cation radicals, together with a preliminary theoretical simulation. The simulation used g_1 = 2.0024, g_2 = 2.0030, and g_3 = 2.0032, proton hyperfine values obtained experimentally by ENDOR (13), and spin packet linewidths determined by electron spin echo measurements. Figure 8(b) shows the perylene(+) spectrum superimposed on a vitrinite W-band spectrum, to illustrate how a portion of the coal resonance line shape might originate from conjugated aromatic hydrocarbon radicals containing no heteroatoms.

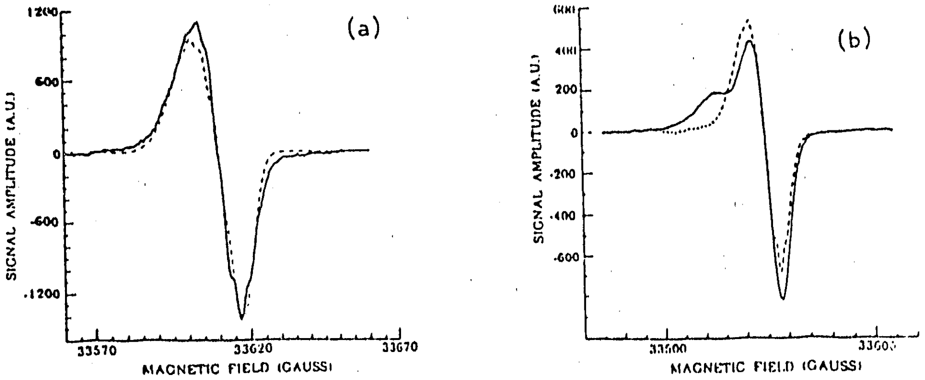

Fig. 8. (a) W-band spectrum of perylene(+) (____) and theoretical simulation (----). (b) Superposition of vitrinite (____) and perylene(+) (----) spectra. (10).

Figure 9(a) shows a W-band spectrum of dibenzothiophene cation radicals, together with a preliminary theoretical simulation (g_1 = 2.0016, g_2 = 2.0054, g_3 = 2.0106). The effect of SO coupling with sulfur is seen in the higher g-values and much more asymmetric line shapes. Attar and Dupuis reported that thiophenes are the most abundant form of organic sulfur in Illinois coals

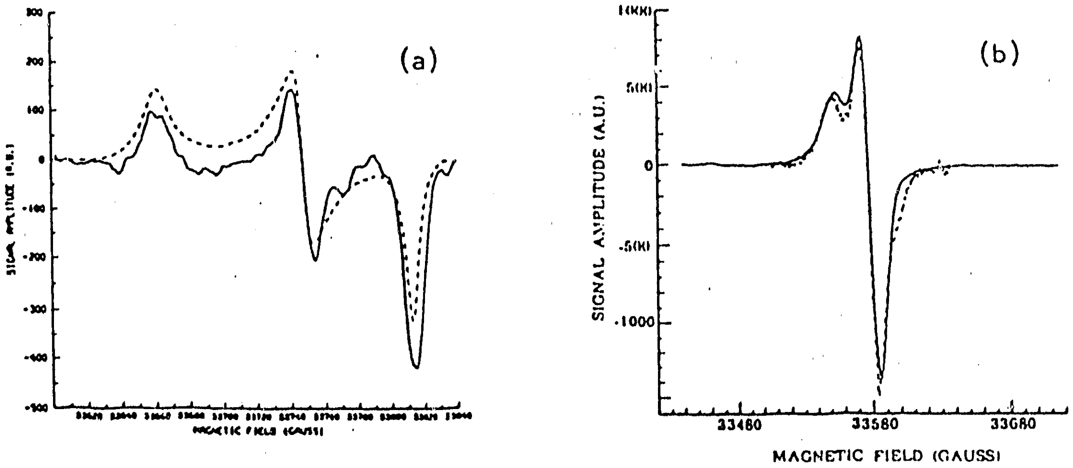

Fig. 9. (a) W-band spectrum of dibenzothiophene(+) (____) and theoretical simulation (----). (b) Vitrinite (____) and composite spectrum of perylene(+) and dibenzothiophene (+) (----). (10).

(thiophenic, 58%; Ar-S-Ar, 20%; R-S-R, 18%; Ar-SH, 15%; R-SH, 7%); thus this model compound should give us an indication of the sulfur-related effects that are to be expected (17).

Because conjugated aromatics are the predominant structural types for organic sulfur in this coal, and because unpaired electrons are expected to be most abundant (and stable) in such chemical environments, it seems likely that EPR spectra from

coal will strongly reflect the delocalization of electrons. This implies that a very small number of sulfur (or oxygen) atoms can exert a large effect on spectral line shapes, making this technique uniquely sensitive to heteroatoms with larger SO coupling constants (7). Since the effect of a sulfur atom on g-values decreases as an electron is delocalized over a larger and larger number of carbon atoms (and the S/C ratio falls), the precise line shapes from sulfur in coal will depend on the size of the aromatic structures, as well as on the type of bonding. This fact represents another opportunity for the nondestructive analysis of high-sulfur coals by W-band EPR, since it may be possible to model the spectra in order to get more detailed chemical information about the forms of organic sulfur that are present. To illustrate this concept, Fig. 9(b) shows a W-band spectrum of vitrinite. Superimposed on it is a composite spectrum constructed by adding the spectrum from perylene(+) and a portion of that from dibenzothiophene(+). While the agreement between data and construct is not perfect, a comparison does suggest that molecular forms like perylene and dibenzothiophene are contributing to the experimental spectrum, although it is very likely that neither of these species, as isolated structures, is a major component in coal. In the future, we hope to use spectral addition methods in a more quantitative way to gain a better understanding of the molecular structure of the organic components of coal, including organic sulfur.

Low-Frequency Pulsed EPR. Pulsed S-band (2 - 4 GHz) EPR was performed on all eight Argonne Coals. By means of a two-pulse ($\theta/2$ - θ) sequence, the phase memory time T_M of the spin echo from each sample was studied at 100K as a function of magnetic field (B_0), pulse duration, and turning angle (θ). Figure 10 shows the two-pulse echo envelope from APCS #101, together with a best fit assuming a single, exponential decay of the form

$$I(2\tau) = I_0 e^{-2\tau/T_M}. \tag{4}$$

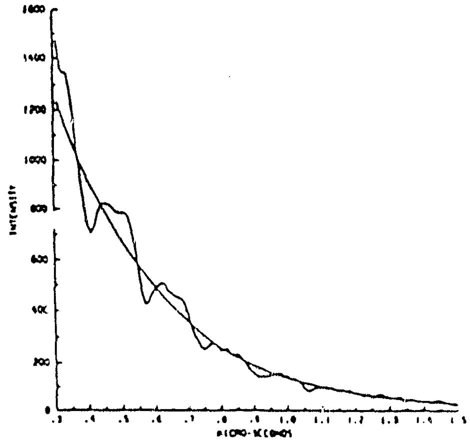

Figure 10. Two-pulse echo envelope (with ESEEM), together with a best fit single exponential curve. T_M = 626 nsec; B_0 = 1436 G; θ = π, 40 nsec.

Generally, there is in these data considerable non-exponential character to the first part of these decay curves, reducing the reliability of exponential fits employing a single time constant T_M. When the microwave pulse power is reduced so that the length of a π-pulse is about 170 nsec, it is observed that the ESEEM effect disappears in two-pulse decay curves, and in most samples an almost perfect exponential decay is obtained, with a time constant that is somewhat longer than the T_M observed for shorter, more powerful pulses, when strong ESEEM is observed. Also, when θ is reduced to values well below π, the apparent T_M values in many samples (and particularly in APCS # 101, 301, 401, 501) increase. This latter effect is much more pronounced when using short, strong pulses.

Recently, Thomann and co-workers published pulsed EPR data taken at X-band (9.5 GHz) on isolated vitrinite macerals from a variety of PSOC coals (18). They point out that T_M in coal can be a function of several contributing mechanisms, including spin-lattice relaxation, hyperfine interactions, and local spin dipole effects (eg instantaneous diffusion). At 9.5 GHz, with the duration of a π pulse set at about 40 nsec (and then reducing θ in successive experiments), they find that instantaneous diffusion makes a very significant contribution to T_M. Our data also demonstrate a θ dependence to T_M, indicating the presence of instantaneous diffusion as a contributing mechanism at lower frequencies in Argonne Premium Coals. It is especially noteworthy to mention that this effect is most pronounced in the highest rank APCS coals, where higher spin densities are found, and local spin dipole effects should be strongest.

Performing pulsed EPR measurements at 3 GHz instead of 9.5 GHz increases the importance of hyperfine interactions relative to electronic Zeeman terms. This was clearly seen in Figure 2, where a comparison was made between ESEEM patterns obtained at 3 and 9.5 GHz. The enhanced probability of double spin flip (electron-nuclear) transitions at 3 GHz causes hyperfine interactions to play a much more significant role as a contributing mechanism for phase coherence decay at this lower field. This is seen in the non-exponential character of initial echo decay curves when short, hard microwave pulses are used, exciting a wide band of branching transitions. Increasing pulse lengths (and reducing microwave power) narrows the bandwidth of the experiment until no double spin flip transitions are excited and ESEEM disappears. Then the echo decay curves are, in most cases, well fitted by single exponential functions. It seems likely that multi-frequency ESE experiments will prove very useful for evaluating hyperfine and local spin dipole fields in whole coals.

One should keep the above-mentioned concerns about the non-exponential character of echo decay curves firmly in mind when examining Table II, which reports T_M values for six of the eight APCS samples, measured at S-band (4 GHz, in this instance). Significant magnetic field (B_0) dependence was observed in many samples, so data at several field points are given for each sample. More complete data on hyperfine interactions and instantaneous diffusion effects in these samples will be published after the current study is completed.

Table II. Electron Spin Echo Decay Times, T_M, for Argonne Premium Coal Samples at 4.0 GHz and Several Magnetic Fields

Argonne Sample	Field (G)	T_M (nsec)
101	1436	626
101	1449	821
101	1434	681
301	1434	534
301	1440	533
401	1440	525
401	1450	665
501	1442	493
501	1452	394
601	1432	378
601	1437	402
601	1442	379
601	1447	352
801	1398	341
801	1416	297
801	1436	281

VII. CONCLUSIONS AND RECOMMENDATIONS

In the next period of this grant, we intend to perform many more VHF EPR experiments on coal and coal-derived materials in order to improve our understanding of the structural factors influencing the spectra. We have received samples from Mobil Research and Development Corporation, Princeton, NJ, that contain from 0.1% to 7% organic sulfur, and we will examine these samples and compare our results with the solid-state NMR data obtained by Mobil, in order to address our goals.

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