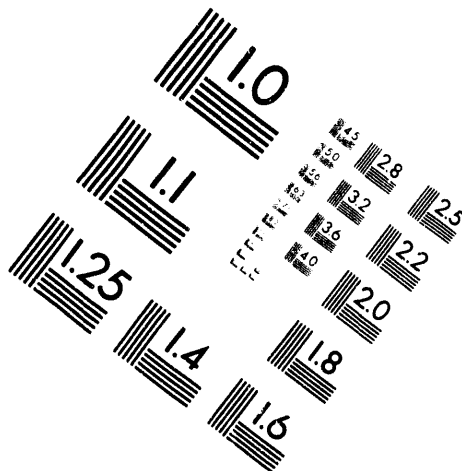
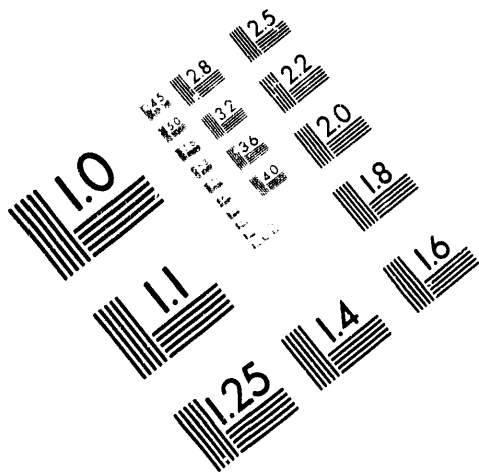




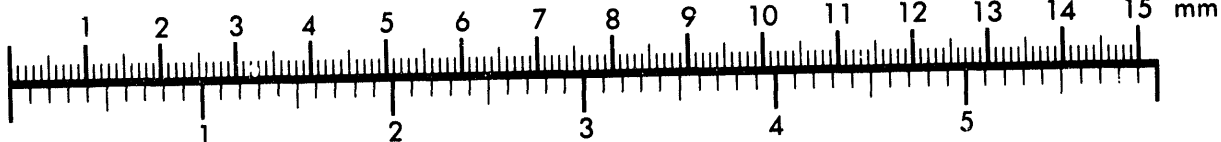
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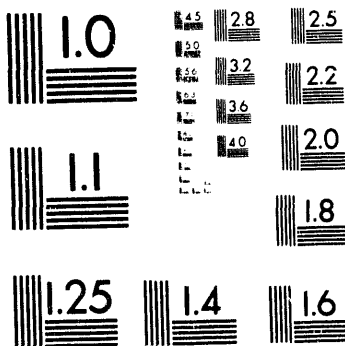
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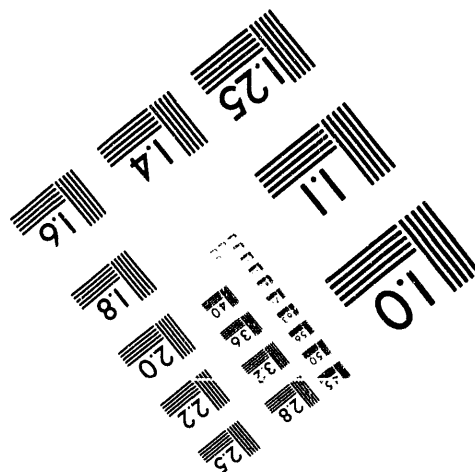
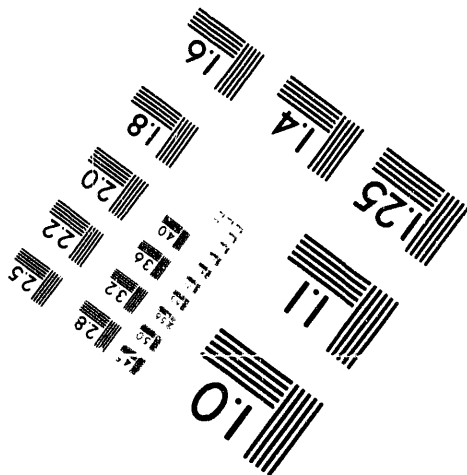
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**1 of 1**

DOE Technical Report No. DOE/PC/88921-1  
First Quarterly Report on Research Grant No. DE-FG22-88PC88921  
Title: SPIN-MAPPING OF COAL STRUCTURES WITH ESE AND ENDOR  
Principal Investigators: R. L. Belford and R. B. Clarkson  
Institution: University of Illinois at Urbana-Champaign  
Date: December 1, 1988  
*US/DOE Patent Clearance is not required prior to publication of this document.*

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## ABSTRACT

Nondestructive chemical and physical characterization of whole Illinois coal and separated macerals, both before and after treatment by various desulfurization techniques is being performed using new electron magnetic resonance methods. The chemical structures of sulfur and non-sulfur containing organic species are being measured by the technique of **HYPERFINE FINGERPRINT SPECTROSCOPY**. Data on hyperfine couplings in a separated vitrinite maceral suggest the presence of small, condensed ring aromatic species, which may be linked by aliphatic bridging groups. Results from multi-frequency EPR experiments performed at X-, Q- and W-bands show slightly anisotropic spectra which have been analyzed by theoretical techniques developed in this laboratory. Analysis of the spectra reveals a nearly axial g-matrix, which agrees well with a model of planar conjugated aromatic species. The W-band data represents the first such experiments performed on coal and separated macerals.

## GENERAL SUMMARY

For the past five years, our laboratory has worked to develop a nondestructive method to determine the molecular structure and distribution of sulfur compounds in whole coal. The technique is based on electron magnetic resonance, and uses the many unpaired electrons which are naturally distributed throughout any coal as spy posts from which to assess local chemical and physical structure. Magnetic resonance is uniquely suited to the study of coal, since it uses radio- or microwave frequencies, to which coal is nearly transparent, thereby overcoming the opacity problem encountered by most optical spectroscopies. Electron paramagnetic resonance (EPR) is an extremely sensitive spectroscopy, allowing the use of very small samples; typically, one can make good observations on maceral samples of 1  $\mu\text{g}$ . This, as we shall see, permits nondestructive analysis of small regions within a whole coal. The combination of excellent sensitivity and ease of application to whole coal samples opens the door to the development of new nondestructive analytical methods.

We use the so-called hyperfine interactions between unpaired electrons and neighboring atoms with nuclear magnetic moments as one probe to investigate local chemical and physical structure. We have developed applications of two new methods to perform this analysis -- Electron-Nuclear Double Resonance (ENDOR) and Electron Spin Echo (ESE) spectroscopy. The basic idea underlying this approach is that the set of hyperfine interactions experienced by one of the spy electrons in coal provides a fingerprint of molecular structures that can be compared to model compounds and analyzed to yield information on atomic and molecular structure. While ENDOR and ESE differ in how they measure this set of interactions, each has as its goal the recording of the hyperfine fingerprint.

In order to effect a simplification of the analysis problem, we have begun a program

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aimed at examining separated maceral components from whole coal. Since about 80 - 90% of maceral material in Illinois #6 is vitrinite, we began by examining this component. ENDOR and ESE experiments successfully measured several hyperfine interactions between unpaired electrons and neighboring protons and carbon atoms. Proton hyperfine data strongly suggests that the unpaired electron is observing the environment of conjugated aromatic hydrocarbon radicals of two, three, four, and perhaps five and six rings. Additional structural evidence was sought to corroborate this first model.

The typical EPR spectrum of a vitrinite measured at a microwave frequency of 9.5 GHz (X-band) and a magnetic field of 3400 G exhibits a single, nearly symmetric absorption line that is too featureless to analyze uniquely. Raising the field and frequency to Q-band (35 GHz and 13,000 G) results in a much more asymmetric EPR lineshape, clearly demonstrating the presence of anisotropy in the g-matrix that characterizes the electronic Zeeman interaction. Our analysis of this Q-band data suggests that the symmetry of the environment of the unpaired electron is axial (i.e. - that there are two axes, one parallel and one perpendicular to the orbital path of the electron, that characterize the system).

In order to confirm this interpretation of the symmetry of the environment of unpaired electrons in vitrinite, we have performed the first EPR experiments ever done on coal at W-band (96 GHz and 34,000 G), at the laboratory of Professor Klaus Möbius at the Free University in West Berlin, Germany. Spectra obtained on Professor Möbius's unique instrument unambiguously revealed the axial character of the system, and allowed us to corroborate the calculations we had made on our data obtained at X- and Q-bands. This result now supports the interpretation of our previous hyperfine measurements as arising from nearly planar species, probably conjugated aromatics. The fact that spectra from other separated macerals are quite different (fusinite EPR shows much less g-anisotropy, for example, suggesting a three-dimensional delocalization of the unpaired electron) leads us to expect more important complementary experimental information from hyperfine spectroscopic methods and multi-frequency EPR.

## OBJECTIVES AND BACKGROUND

The fundamental species that is used to probe coal structure in our non-destructive spectroscopic approach is the unpaired electron. This electronic spin  $1/2$  particle allows us to perform various EPR, ENDOR (electron-nuclear double resonance), and pulsed EPR experiments (electron spin echo or ESE, and 2D-FT EPR) that are designed to measure the atomic and molecular environments of the unpaired electron. ENDOR and pulsed EPR methods focus on measuring electron-nuclear hyperfine interactions, and we have shown that these approaches reveal structural information that is specific to individual maceral components in coal [1, 2]. Because our studies thus far have been directed at elucidating the structure of Illinois #6 coal, we have seen our data dominated by hyperfine information from the vitrinite component that comprises 80 - 90% of all macerals in this coal. We have therefore undertaken a study of separated vitrinite, in order to first develop a structural model of this most maceral component in Illinois #6.

Hyperfine data obtained by ENDOR and ESE experiments on separated vitrinite agrees well with similar data obtained from whole coal, as Table I. illustrates. Table I also includes hyperfine couplings from several conjugated aromatic radicals that are included for purposes of comparison. Based on such comparisons between data from the separated maceral and

model compounds, we believe that a good first model for the molecular structures included in vitrinite are conjugated aromatics of two, three, four, and perhaps five and six rings, connected by aliphatic bridging groups. Such structures, when they are present as stable free radicals, have proton hyperfine couplings that are virtually identical to those measured in the vitrinite. Similar results, based on destructive chemical methods, have been reported by Chung and Goldberg [3].

One prediction from this preliminary model that can be tested involves the symmetry of the environment of the unpaired electron. Indeed, if the unpaired electrons in vitrinite are localized in small conjugated aromatic radicals, then the g-matrix for the system should have decidedly axial character (i.e. one g-value parallel to and one g-value perpendicular to the plane of the aromatic species). On the other hand, if the unpaired electron has three-dimensional delocalization, the g-matrix will not exhibit axial character. To test the model, one needs to obtain EPR spectra from the vitrinite and theoretically model the spectral line.

## EXPERIMENTAL PROCEDURES

Because g-anisotropy is very small in vitrinite, it is very helpful to perform the EPR experiment at the highest magnetic field available in order to achieve the best separation of g-features in the spectrum. We have performed EPR on vitrinite samples at X- (9.5 GHz), Q- (35 GHz), and W-band (96 GHz). The W-band spectrum, recorded on a novel instrument built by Prof. Klaus Mobius at the Free University of Berlin, is the first ever obtained of any coal at this high frequency. We are now completing our own W-band instrument, which should be extremely useful in coal research.

Samples of vitrinite separated from an Illinois #6 coal were obtained from the Illinois Geological Survey, Urbana. The material was powdered to ca. 100 mesh and either evacuated for several days at  $> 10^{-6}$  Torr and then sealed in quartz tubes, or simply sealed in quartz tubes. Little lineshape differences were noted between the two sample treatments.

## RESULTS AND DISCUSSION

Results are shown in Figures 1 (a - c). Evidence of a small but measurable g-anisotropy emerges as spectra are taken at higher fields. Theoretical simulations of these spectra have been calculated using the method of Belford (see, for example, the theoretical approach in Ref [4]). A comparison of calculation and experiment is shown in Figure 2. The important parameters used in the calculation are:  $g_1 = 2.0021$ ,  $g_2 = 2.0024$ ,  $g_3 = 2.0039$ , as shown in Figure 3. The nearly axial character of the spectrum is clearly demonstrated.

These experiments for the first time confirm by EPR that the molecular structures sampled by the unpaired electrons in vitrinite from an Illinois #6 coal are indeed rather planar, as predicted from our hyperfine data. We are now making similar measurements on other separated macerals.

## CONCLUSIONS AND RECOMMENDATIONS

Two major conclusions from this work are: (1) The EPR spectrum from separated vitrinite

is slightly anisotropic, and this effect is much more clearly displayed at higher fields/frequencies. Inherent linewidths remain constant with increases in field, indicating little strain broadening. (2) The g-anisotropy is nearly axial, supporting the evidence obtained from hyperfine data that the environment experienced by the unpaired electrons in this maceral is rather planar, suggesting conjugated aromatic species.

Clearly, high field experiments are most useful for this work, and we are excited that our own W-band EPR spectrometer is nearing completion. When we have our own facility to make these measurements, we will study other macerals and make similar analyses of the data. We already know, for example, that fusinite shows much smaller g-anisotropy, suggesting that the structure of this maceral may be less planar and more a three-dimensional network. Such structural speculation can be tested by other methods in our laboratory, and should help to advance the work that is the goal of this program.

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2. Clarkson, R. B., Cornelius, J., Snetsinger, P. A., Belford, R. L., and Bowman, M. K., FUEL, 66, 925 (1987).
3. Chung, K. E., and Goldberg, I., ICDB/CRSC 4th Annual Contractor's Meeting, Champaign, 1986, pg. 24.
4. Rothenberger, K. S., Nilges, M. J., Altman, T. E., Glab, K., Belford, R. L., Froncisz, W., and Hyde, J. S., Chem. Phys. Lett., 124, 295 (1986).

*(This work also has been reported to the Center for Research on Sulfur in Coal in the State of Illinois, which has provided additional assistance.)*

TABLE I.

## ESE OF ILLINOIS COALS

SAMPLE	A(MHz)	A(Gauss)
Illinois #6 (evacuated)	25	8.9
	22.2	7.9
	18.0	6.4 **
	14.8	5.3
	8.1	2.9
	3.2	1.1 **
		** high g-value
Illinois #6 Vitrinite	22.2	7.9
	20.0	7.1
	19.2	6.9
	8.8	3.1
Synthetic Lignite (R. Winans, ANL)	22.0	7.9
	18.8	6.7
	13.8	4.9
	7.8	2.8
	3.0	1.1
Perylene cation	11.5	4.11
	8.7	3.09
	1.3	0.46
Anthracene cation	18.3	6.5
	8.6	3.06
	3.9	1.38

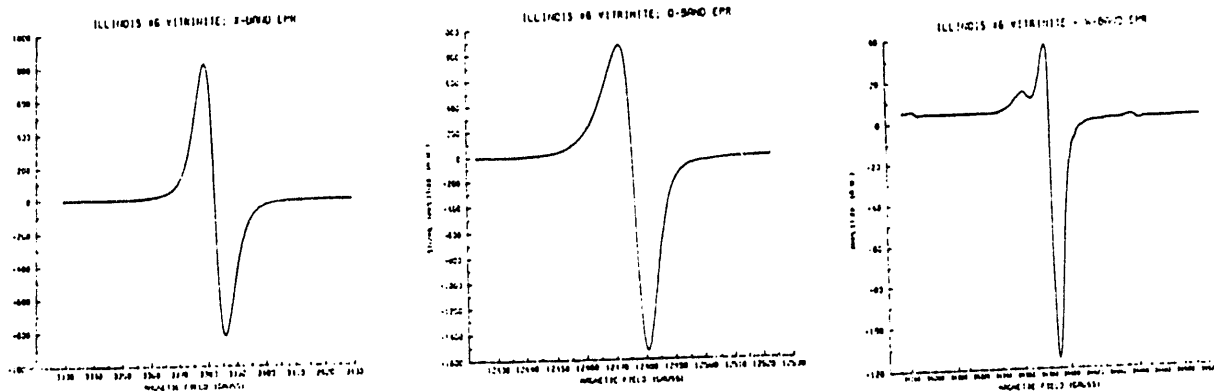


Figure 1. (a) X-band (b) Q-band (c) W-band  
EPR spectra of a vitrinite separated from Illinois #6.

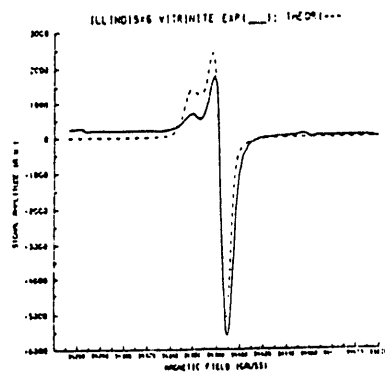


Figure 2. Comparison of experimental and theoretical W-band EPR spectra

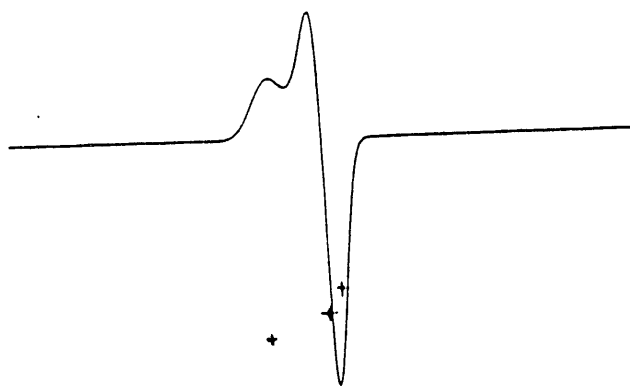


Figure 3. Theoretical W-band spectrum showing the positions of the three principal g-values, which show a nearly axial pattern.



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