TECHNICAL REPORT

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Project Title: **VHF EPR Quantitation and Speciation of Organic Sulfur in Coal**

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ABSTRACT

Over the last few years, we have developed a non-destructive technique called Very High Frequency Electron Paramagnetic Resonance (VHF-EPR) that is proving to be a practical and very sensitive analytical method for the organic sulfur in coal. Already, although still under development, the technique rapidly can quantify organic sulfur, and perhaps provide information on organic oxygen and nitrogen, in typical Illinois coals. At this stage, the precision is not well enough calibrated, and specificity for particular species needs more development. This year's proposal outlined a 12 month work plan designed to improve and extend the utility of VHF-EPR. Two main goals of the work are: (1) refinement and calibration of organic sulfur analysis, in coals of differing rank, over a concentration range from 0.1% to 5%, and (2) better utilization of VHF-EPR coal spectral data for sulfur speciation. Applications of the method for monitoring thermal, chemical, and biological desulfurization also were proposed. This quarter, goal (1) is being pursued; results will be ready to describe in a future report. Meanwhile, work toward goal (2) has produced detailed information about the VHF-EPR spectral behavior of several comparison compounds - sulfur-containing thiophenic fused-ring molecules. So far, dibenzothiophene is best characterized and is reported below. Experimentally, the VHF-EPR spectrum shows high definition and can be related to low-frequency spin echo data. Parameters defining the molecular spectra of the species are extracted cleanly by computerized simulation analysis. A semi-empirical electronic structure computational model that we have devised to provide predictions of EPR parameters for such thiophenic systems has produced values in striking agreement with the experimental spectra.

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EXECUTIVE SUMMARY

Coal represents 85 to 90% of the fossil energy resources in the United States, and the USA has a quarter of the world's proven coal reserves. The full utilization of these resources has been hampered by the high levels of sulfur in many of the major U.S. deposits. The future use of American coal, whether in the near term for electricity production by combustion, or as a feed-stock for the production of liquid fuels and chemicals in the next century, will depend on a better understanding of the structure and chemistry of the sulfur much of it contains. This program addresses the need for better non-destructive analytical methods to analyze organic sulfur in coal, utilizing a new instrumental technique we have begun to develop, which we call Very High Frequency Electron Paramagnetic Resonance (VHF-EPR). The overall goal of our analytical work plan is to quantify more precisely the organic sulfur present in coal, and to identify the chemical forms of organic sulfur.

VHF-EPR is a magnetic resonance method that is capable of analyzing for the organic sulfur in whole coal, separated macerals, and treated and desulfurized coals, as well as in materials produced from coals (e.g. liquefaction and pyrolysis products). With support from agencies particularly including the ICCI and the U. S. Department of Energy (University Coal Research Program), we recently have built instrumentation that takes advantage of new developments in solid-state microwave and digital electronics; these advances have made the VHF-EPR approach possible.

Computer simulation analysis has extracted parameters which define the molecular spectra of the species. The experimental spectra is also showing agreement with a semi-empirical electronic structure computational model that we have devised to provide prediction of EPR parameters for such thiophenic systems. Our approach utilizes the naturally occurring unpaired electrons in coal as "observation posts" from which to analyze surrounding molecular structures. These unpaired electrons have always offered an attractive route to the non-destructive study of coal structure. In a typical Illinois #6 coal, for example, there are about 10^{19} unpaired spins/gram. Because coal is highly aromatic (in the case of Illinois #6, ca. 77% C, it is estimated that 65 - 70% of the carbon is aromatic, with an average aromatic cluster size of 20 - 25 carbon atoms [1]), unpaired electrons delocalize over many carbons. Thus, the unpaired electrons in an Illinois #6 interact directly with 1% of all the carbon, and 2% of the aromatic carbon in the coal. This good coverage of the atoms in coal, together with a reasonably uniform distribution of unpaired electrons throughout all maceral components and the exceptional sensitivity of electron paramagnetic resonance (EPR) spectroscopy, (10^3 times the sensitivity of ^1H NMR),

makes the paramagnetic spins natural observation posts from which to perform non-destructive analysis of coal's molecular structure.

The problem that had prevented the use of EPR as an approach to coal structure analysis was one of resolution. Information about molecular structure and atomic environment was hidden within the EPR spectral lineshape of typical data obtained at 9.5 GHz and 0.34 T. (X-band EPR), and in most cases it could not be deconvoluted. This lack of spectral resolution was especially disturbing in the case of heteroatom (N, O, S) analysis, where indications of the effects of atomic spin-orbit coupling between the unpaired electrons and heteroatoms were even seen in X-band spectra [2], and which higher magnetic field strength experiments were predicted to resolve. In 1990, our laboratory pioneered in the development of a novel 95 GHz, 3.4 T. (W-band) VHF-EPR instrument¹, and demonstrated that this prediction was correct by examining several coals, as well as a vitrinite, sporinite, and inertinite maceral separated from an Illinois #6 coal by density gradient centrifugation [3,4].

Chemical evidence strongly suggests that the complex lineshapes seen in the VHF-EPR spectra of a coal like Illinois #6 (as well as fusinite and sporinite macerals separated from it) is the result of contributions from several molecular populations, some of which contain sulfur. In order to analyze experimental spectra in a quantitative fashion, we have begun work to create a general-purpose computer technique, based on the simplex multi-variable optimization strategy, to simulate experimental data in order to obtain spectral parameters (g-values, linewidths, and composition coefficients) which can be correlated to chemical structure. The first tests of this approach have utilized a model of axial symmetry in which all the contributors to the VHF-EPR spectrum are grouped into two classes -- sulfur and non-sulfur species -- called the two-species model. Theoretical modeling is based on the very successful QPOW algorithm for powder EPR spectral simulation developed by Belford and co-workers [5].

During the first quarter, we had proposed development of standard coal mixtures of samples from the Illinois Basin, with duplicate samples being analyzed using XANES in a collaboration with Professor G. Huffman at the University of Kentucky. The coordination of efforts for this work is proceeding well, and we expect to begin reporting results from it next quarter.

In addition to the application of VHF-EPR to the quantitative analysis of sulfur in coal, we have in this quarter vigorously

¹This is the only spectrometer of its kind in the United States, and one of only two in the world.

pursued a program designed to understand the underlying principles which relate coal spectra and coal structure. This work has made use of model compounds that mimic the organic sulfur in coal, including a series of thiophenes and furans. Extensive quantum-mechanical molecular orbital calculations also have been carried out to better understand the spectral/structural relations in some of the model systems and to provide a basis for predictions. This work is providing the solid scientific basis for interpreting VHF-EPR spectra of coal, and it opens the possibility of using spectral data to characterize the molecular forms of organic sulfur in coal. The data obtained by computer simulation of VHF-EPR spectra contains much more information on sulfur than just the amount present, and work reported in this Quarterly Report focusses on important new developments in this area of the project tasks. Developments which clarify the detailed scientific relationships that exist between VHF-EPR spectra and molecular structure of heteroatomic (S and O) aromatic compounds lead directly to the application of this technique to the speciation of sulfur compounds in coal.

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OBJECTIVES

This project is comprised of two parallel Task Areas of work for the next 12 months, with the following specific goals and objectives:

Task Area 1 - Refine and calibrate VHF-EPR as an analytical method for organic sulfur in coal.

(a) Develop mixtures of IBCSP coals and separated macerals with known organic sulfur concentrations in the range from 0.1% to 5%. Analyze these mixtures by VHF-EPR and calibrate the precision of the method, including error limits, utilizing multiple aliquot for statistical purposes.

(b) Make careful measurements in the presence of known quantities of pyritic sulfur, in order to determine if small, hitherto undetected, effects may be present which could influence analytical results on organic sulfur.

(c) Make VHF-EPR and XANES measurements on duplicate calibrated samples, in collaboration with Prof. G. Huffman, University of Kentucky, in order to establish a clear relationship between the two non-destructive, bulk coal analytical techniques.

(d) Refine the computer analysis of VHF-EPR coal samples by exploring more comprehensive models involving multiple species and symmetries lower than axial. Determine the consequences of model choices on analytical precision.

(e) Make use of even higher frequency VHF-EPR instruments to guide the development of models (Task 1 (d)), through collaboration with Prof. Jack Freed, Cornell University, who has built a 250 GHz spectrometer (the highest continuous field EPR instrument in the world), and who is happy to study this problem with us.

Task Area 2 - Work with model systems to elucidate relationships between coal structure and coal spectra that lead to sulfur speciation by VHF-EPR.

(a) Develop an aromatic organic sulfur model system to explore the effects of electron spin exchange on VHF-EPR spectra. This work will lead to a better understanding of the observed dependence of spectra on coal rank, and will utilize static magnetic susceptibility measurements with a SQUID magnetometer as well as VHF-EPR measurements. It also could provide an important key for utilizing coal spectral parameters for sulfur speciation.

(b) Study mixed heteroatomic aromatic species (S,O and S,N) as well as sulfur and oxygen heterocycles to better evaluate the possible contributions of such structures to the VHF-EPR spectra from coal. Recent work analyzing coals and separated macerals by HRMS, XANES, and XPS has suggested that mixed heteroatomic forms may be quite abundant in some coals [6].

(c) Extend and refine MOPAC semiempirical and *ab initio* calculations of the electronic properties of model systems in

order to further clarify the relationships between chemical structure and VHF-EPR spectra.

(d) Apply theoretical models to analyze VHF-EPR spectra from selected coal and separated maceral samples that have been studied with other methods (e.g. HRMS, XANES), in order to begin the utilization of spectral data for sulfur speciation.

INTRODUCTION AND BACKGROUND

This program is a continuation of the preceding year, which addresses the need for innovative approaches to characterize the organic sulfur in Illinois Basin coals by means of very-high frequency electron paramagnetic resonance (VHF-EPR) spectroscopy operating at W-band microwave frequencies (~96 GHz). VHF-EPR spectra taken using the unique instrument we have designed and built for such purposes show special sensitivity to heteroatoms in coal. The technique then can be applied to the problem of **non-destructive detection, study, and determination of organic oxygen and sulfur aromatic species in coal.** Data from Illinois coals and separated macerals indicate that **it is possible to distinguish extent of conjugation in aromatic portions of the coal.** Through XANES/EXAFS and other techniques can provide information on sulfur, no single technique should be relied upon entirely, and without other methods of corroboration.

It has been difficult in the past to use EPR to identify immobilized organic radicals in the disordered state. This is because when the radicals are immobilized randomly, their spectral linewidths increase and the spectral resolution suffers. Such rigid-limit spectra are very important, since they may yield information such as full matrices or the principal values of g and the hyperfine coupling (A) matrix. Those magnetic parameters, g and A matrices, can be utilized to deduce molecular structure. But if spectral linewidths are greater than either g anisotropies or hyperfine couplings or both, little information can be extracted with certainty from a single EPR spectrum at the conventional frequency of 9.5 GHz (X-band). This is caused not only by the lack of the resolution of g or A matrix at a particular frequency, but also often by the interplay between the g and A matrix which makes the analysis of a powder EPR spectrum much more complicated and the extraction of EPR parameters less certain. In this project, we have as one of our goals the development of a general strategy of: (i) using multiple frequency EPR spectroscopy to determine the principal values of g and A matrix, and (ii) using these magnetic parameters to identify the radical species.

The anisotropic g matrix is one of the most important and fundamental EPR parameters. It is generally viewed as characteristic of the electronic structure of the molecule

that contains one or more unpaired electrons. But for most organic radicals, the elements of the g matrices are very close to the free-electron value ($g_0 = 2.00232$). Experimentally resolving such small differences was difficult using conventional 9.5 GHz EPR, and this greatly limited the usefulness of g matrix as a structure indicator. The development of very high frequency EPR (VHF-EPR) has overcome this problem. From the simple resonance condition one can see easily that the difference in resonance fields for two slightly different g factors is proportional to the product of the microwave frequency and the difference between the two g factors.

$$H_1 - H_2 = \frac{2\pi\hbar\nu}{\beta} \left(\frac{1}{g_2} - \frac{1}{g_1} \right) = -(2\pi\frac{\hbar}{\beta}) \left(\frac{\Delta g}{g_1 g_2} \right) \nu$$

Therefore the g resolution will be enhanced by a factor of 10 on going from X-band (9.5 GHz) to W-band (95 GHz) providing the line does not broaden substantially with microwave frequency.

At a sufficiently high field, the electronic Zeeman interaction could dominate the electron-nuclear hyperfine interaction, and both the electron and nuclear spins will be quantized along the external field. Under favorable conditions, the anisotropic hyperfine coupling matrix, A , can be resolved or partially resolved along the canonical directions of g matrix, yielding additional valuable information about molecular structure and other properties mostly related to the ground electronic state of a molecule. Indeed, we here report the observation of the anisotropic A matrix in the continuous wave VHF-EPR spectrum of dibenzothiophene ionic radical. In addition, an auxiliary experiment using a low frequency pulsed spectrometer at S-band (2-4 GHz) also reveals the anisotropic hyperfine interactions between the electron spin and the ring protons. The multifrequency approach has in this case resulted in a unified set of magnetic parameters (g and A matrices), from which it is possible to identify and characterize the radical species in terms of properties related to its molecular orbital structure.

EXPERIMENTAL PROCEDURES:

a) Status of the standard coal mixtures analysis:

Consistent with the first task (see objectives) described in the initial proposal of 1993-94 "VHF-EPR Quantitation and Speciation of Organic Sulfur in Coal", development of standard coal mixtures of known organic sulfur concentrations has begun. In collaborative work with S. Palmer of the Southern Illinois University Coal Research Laboratory, we have arranged

for the first set of ten samples to be arriving shortly for sulfur content analysis via VHF-EPR. These samples will consist of Illinois coal and Illinois coal which has been desulfurized by thermal and chemical methods. Additional sulfur content analysis by XANES will also be conducted in the laboratory of G. P. Huffman, at the University of Kentucky. Following the initial experiments, meetings with our collaborators will be arranged to discuss this first set of comparative results. Future quarterly reports will discuss the outcome of these efforts.

B) Experiments and computer modeling on comparison compounds:

A 1000:1 mole ratio mixture of powdered boric acid (Alrich) and dibenzothiophene (DBT) or dibenzofuran (DBF) (Alrich) is heated to the melting point of boric acid (190°C). The molten mass is vortexed to maximize the dispersion of DBT or DBF in the molten solution and then allowed to cool to a glass. The glass is crushed into fine powder and loaded into a quartz sample tube. The tube is placed in a Ray-O-Net irradiation unit and subjected to UV irradiation at 254 nm for 20 to 30 minutes. The sample tube is then removed from the UV light and sealed for analysis. Degassing before and after the irradiation shows no effect on the EPR spectra. This method is a convenient way to produce matrix-isolated ionic radicals at room temperature. Their disordered state closely approximates the environment of similar compounds found in coal.

We have used four microwave frequencies, S-band (2-4 GHz), X-band (9.5 GHz), Q-band (35 GHz), and W-band (95 GHz) to study the radicals produced by this method. CW saturation behavior of organic radicals have been obtained. Modulation amplitude profiles of the sample are routinely probed to achieve the best compromise between the S/N and resolution of possible hyperfine structure. Wide magnetic field scans have been performed for the sample at X-band to make sure all signals are accounted for. Low temperature experiments at the liquid nitrogen (77 K) were also performed for the sample at 9.5 GHz, no discernible difference in EPR parameters (g and linewidth) is observed, suggest the radical is part of the rigid structure at room temperature. Care has also been taken to avoid distortion of the signal by RC filters.

X-band and Q-band spectra are obtained from Varian E-line EPR spectrometer outfitted with a tracking Varian NMR gaussmeter and a HP frequency divider with a Fluke frequency counter. W-band EPR is performed using the spectrometer system built in our laboratory. All g-value measurements are based on direct field and frequency measurements. A statistical treatment of the g-matrix measured from seven independently prepared samples of DBT in BAG shows that experimental errors are very

small (max. standard deviation, $\sigma_{n-1}=11 \times 10^{-5}$). S-band ESEEM is done on a locally-built Electron Spin Echo (ESE) spectrometer.

A computer-assisted analysis using an EPR powder spectrum simulation program (Nilges, 1979) and the spectral parameter optimization routine based on the SIMPLEX algorithm are performed to: 1) confirm the direct measurements of principal g values, 2) extract possible hyperfine interaction, and 3) accurately assess the linewidths and lineshapes.

The calculation of principal values of the g matrix is based on Stone's theory (ref Stone) with certain modifications (ref. the other paper). The SCF-MO wave function and orbital energies are obtained from the semi-empirical method PM3 in MOPAC (ref QCPE 455). All calculations employ a IBM R6000 workstation.

Results and Discussion:

The second derivative representation of the EPR spectra of dibenzothiophene radical ions in boric acid glass (DBT/BAG) are shown in Fig. 1, where we see also the importance of choosing instrumental settings - in this case modulation amplitude - carefully to avoid suppressing information. The spectra at higher frequencies (Q- and W-band) show greatly

Figure 1. The modulation amplitude profile of DBT/BAG at W-band.

enhanced g spectral resolution for the powder sample. All canonical points are revealed from the spectrum. They are so well separated in the W-band spectrum that all three principal values of the g matrix can be read directly from the

simplified, almost ideal spectrum of a rhombic g matrix. In contrast, the X-band spectrum only shows a signal with anisotropic hyperfine interactions intertwined with g anisotropy. The g matrix is not resolved at all and the hyperfine interaction is not well resolved either. This has resulted in a very complicated spectrum that is difficult to analyze. However, one should note that there are hyperfine interactions resolved in the W-band spectrum along the high field direction. A five-line pattern of 1:4:6:4:1 intensity proportions, suggests that there is one set of four, or two sets of two very similar, chemically equivalent $I=1/2$ nuclei.

We also obtained an S-band ESEEM (Electron Spin Echo Envelope Modulation) spectrum of DBT/BAG. The analysis of the ESEEM spectrum of DBT yields following possible anisotropic hyperfine coupling constants tabulated in the Table 1. Note that there are two sets of two chemically equivalent protons; but the two protons of a chemically equivalent set are magnetically inequivalent. Assuming that one of the principal axes in which the A matrix is diagonal is along the CH bond, then a simple geometrical model shows that they have different Euler angles α , where the definition of Euler angles conforms with the convention of Rose (Rose, 1957). With the hyperfine

Table 1. Hyperfine Coupling Constants for DBT as Measured by ESEEM, and Initial Assignments of ESEEM Peaks*

INTENSITY (A.U.)	ν_n (MHz)	$A = 2(\nu_0 \pm \nu_n)$ (MHz)	Tentative Assignments
8.6	0.62		^{10}B matrix peak
5.2	0.74	13.0 , 10.2	$A_z(a, a', b, b')$
2.0	1.3	14.3, 9.0	$A_x(b, b')$
1.5	1.6	14.9 , 8.4	$A_y(b, b')$
1.9	2.5	16.6, 6.7	$A_y(a, a')$
1.1	3.3	18.2 , 5.2	$A_x(a, a')$

*Note: $\nu_0 = 5.8$ MHz for the matrix protons. Each hyperfine tensor deduced from the ν_n has two possible solutions (and both solutions are possible), the bold numbers represent our initial guesses and from which the tentative assignment is made.

matrices obtained from the S-band ESEEM peaks, simulation of the W-band EPR spectrum of DBT has been attempted, and the reconstructed EPR spectrum is in good agreement with the experimental spectrum. With the help of the SIMPLEX optimization routine, EPR parameters can be optimized to give

a best fit for the W-band spectrum of DBT. At the high frequency, the goodness of fit between the simulation and experimental spectra is very sensitive to the variation of the g matrix, so the g matrix is best obtained from the high-frequency fitting. With the same g matrix, an X-band EPR spectrum can be also reconstructed and optimized to yield a better A matrix. This set of parameters optimized for X-band is then in turn used for another round of optimization for W-band. After the iteration process converges, a single set of the spin Hamiltonian parameters used in the reconstruction of the best fit spectra at all three frequencies is found (Table 2). The best-fit simulations are shown in Figure 2.

Figure 2. Fit of simulated to experimental W-band spectra of DBT in BAG.

It is interesting to compare the multifrequency EPR spectra of DBT with its oxygen analogue DBF (Fig. 3) from both a chemical and spectroscopic point of view. Although they are thought to be similar structurally, the EPR spectra of these two species are drastically different at each of the corresponding frequencies. Unlike the DBT cation radical, the DBF ionic radical shows little g anisotropy but large hyperfine anisotropy. Therefore, the EPR spectra of these two at the corresponding frequencies are very different. We suggest that the profound differences may prove to be the key to being sure that we are looking at sulfur-containing species in coal rather than oxygen-containing ones, but this point needs considerable exploration. The best fit spin Hamiltonian parameters are listed in the Table 3.

Table 2. The Spin Hamiltonian Parameters of DBT/BAG

	xx	yy	zz	α	β	γ
g tensor	2.01135	2.00630	2.00237			
A tensor of a, a' (MHz)	19.16	3.84	11.88	± 21	0	0
A tensor of b, b' (MHz)	7.87	14.38	10.41	± 141	0	0
linewidths (MHz) @ W-Band	11.94	5.16	3.75			
linewidths (MHz) @ Q-band	6.63	4.10	3.78			
linewidths (MHz) @ X-Band	3.30	3.08	3.20

Figure 3. W-band spectrum of BNT, dibenzofuran, with simulation, for comparison with DBT, Figure 2.

	xx	yy	zz	α	β	γ
g tensor	2.0031 3	2.00210	2.00259			
A tensor of a, a' (MHz)	29.55	6.00	10.00	± 16	0	0
A tensor of b, b' (MHz)	9.44	3.57	3.54	± 74	0	0
linewidths (MHz) @ W-Band	2.59	2.28	2.74			
linewidths (MHz) @ Q-band	1.29	6.02	3.20			
linewidths (MHz) @ X-Band	1.50	1.50	1.50			

If we use $\Delta g = g_1 - g_2$ to measure the g anisotropy and $\Delta A = A_{\max} - A_{\min}$ to measure the hyperfine anisotropy then we can examine the relations between the g and A anisotropy. For DBF at W-band, the g anisotropy is on the same order of magnitude as that of g matrix. In this case, the interplay between the g and hyperfine anisotropy is most strong, resulting in a complicated spectrum. From a spectroscopic point of view, this is similar to the case of DBT at X-band. Therefore, we predict that the spectrum of DBT at a much lower frequency, say at 0.5 GHz, will be similar to that of DBF at X-band. This frequency should be closer to the lower limit of the frequency range of the multifrequency analysis than the X-band frequency that we used experimentally. The anisotropic A matrix would be determined more accurately if the 0.5 GHz frequency data were available. On the other hand, the spectrum of DBF at a much higher frequency, e.g. 1000 GHz, will probably behave similarly to that of DBT at W-band, which means that the g matrix of the DBF would be measured with less uncertainty if 1000 GHz data were available. It is one of the goals of our laboratory to develop this multifrequency capability in order to achieve better results in the characterization of molecular structure in coal and other disordered materials.

CONCLUSION AND RECOMMENDATIONS

1. The proposed development of standard coal mixtures of samples from the Illinois Basin, with duplicate samples being analyzed using XANES in a collaboration with Professor G. Huffman at the University of Kentucky, has started. Recommendation: This multiinstitution development should be pursued vigorously.

2. The experimental and theoretical work with model compounds which are coal constituents has shown remarkable definition and differentiation. Recommendation: Improve the theory, and obtain more experimental data on oxygen-containing aromatic molecules or molecular fragments.

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