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

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ABSTRACT

To ENDOR and ESE we have added another advanced EPR technique, VHF-EPR, as a tool with which to observe coal molecular structure, especially organic sulfur. We have constructed a unique VHF EPR instrument operating at the W-band (96 GHz), one of only two such instruments in the world, and the only one studying coal. We are employing this instrument, as well as collaborating with scientists at Cornell University, who have a 250 GHz spectrometer, to develop a clearer understanding of the relationships between the VHF EPR spectra we observe from Illinois coal and the organic sulfur species present in it.

Efforts in this quarter focussed on three areas: recruitment of personnel (especially a new postdoctoral fellow) to join the coal research team, work on improving the W-band spectrometer, and studies of vitrinite, sporinite, and fusinite macerals at G-band (250 GHz). All three areas have shown good progress. This report will discuss in detail the main features of the W-band instrument, stressing its unique engineering features as well as comparing it to the few other instruments in the world operating in the VHF frequency range (90 - 250 GHz). Preliminary analysis of the 250 GHz data on macerals obtained by density gradient centrifugation from an Illinois #6 coal gives the first indication that at the very highest frequencies, there may be a separation of the heteroatom VHF EPR signals into a sulfur and an oxygen-containing component.

GENERAL SUMMARY

This program addresses the need for innovative approaches to characterize the organic sulfur in a variety of coals. With support from the U. S. DOE as well as CRSC, the Petroleum Research Fund (ACS) and the National Institutes of Health, we have developed a very high frequency electron paramagnetic resonance (EPR) spectrometer operating at the W-band of microwave frequencies (96 GHz), one of only 2 such instruments in the world, and the only one in the U.S.A. This instrument has shown unique sensitivity to heteroatoms in coal, and we believe the technique can be successfully applied for the **non-destructive, direct determination of organic sulfur in coal**. 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 approach utilizes the naturally occurring unpaired electrons in coal as "spies" of their environment. Effects of neighboring atoms on the magnetic energy levels of the electron are reflected in changes in the EPR spectrum, and from this data, conclusions about the structure of the coal can be made. In the case of sulfur, the strongest interaction between the unpaired electron and S atoms usually is the spin-orbit (SO) coupling, which changes the value of the external magnetic field needed to 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

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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 1, 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

Figure 1. 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).

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 1(c), is due to heteroatoms, and we have strong evidence that it is largely the result of organic sulfur. The goals of our current work focus on developing a better understanding of the molecular forms of organic sulfur that are responsible for these spectra.

The key to our work plan is the W-band spectrometer. This unique instrument has been built over the last three years, and now incorporates several important technical innovations that make it well-suited for the present research work. A detailed description of the instrument is included in this report.

At the very beginning of VHF EPR work on coal, we were concerned that higher magnetic fields would not produce improved resolution in the spectra, but would simply result in broader lines. The logic behind this concern was that the heterogeneous nature of coal would manifest itself in a range of "g-values" that would produce broader line shapes at higher values of B_0 . This concern proved to be largely

unimportant, as the results in Figure 1 illustrate. Now, in collaboration with Professor Jack Freed at Cornell University, we have begun a VHF EPR study of coal on one of the highest frequency instruments in the world, the Cornell G-band (250 GHz) spectrometer. This further 2.5-fold increase in B_0 produces even better resolution in the spectra, with only modest increases in spectral linewidth. Figure 2 shows a comparison of the W- and G-band spectra from a vitrinite maceral separated by DGC from an Illinois #6 coal. Similar resolution improvements have been obtained at G-band for a sporinite and a fusinite sample.

Figure 2. (a) W-band (96 GHz) spectrum of separated vitrinite. (b) G-band (250 GHz) spectrum of the same sample.

In addition to separated maceral samples, G-band spectra have been observed from perylene cation radicals formed on a silica-alumina catalyst. This system has served us well as a model for the purely hydrocarbon aromatic component in coal, and was used in conjunction with dibenzothiophene (+) to develop a simple, two-compound picture for analyzing W-band spectra from an Illinois #6. Comparison of G-band spectra from vitrinite and perylene (+) reveal a possible third component to the VHF EPR signals from coal, namely contributions from oxygen-containing aromatic compounds. This third component does not interfere with the lower field signal from aromatic sulfur, but does potentially answer the nagging question concerning the missing oxygen heteroatom effect in our earlier, two-compound picture. Thus, G-band experiments give preliminary evidence that VHF EPR spectra can report on sulfur *and* oxygen-containing aromatic compounds in coal, as well as on purely hydrocarbon aromatics. These experiments at 250 GHz will certainly help us to better interpret coal spectra more routinely obtained at 96 GHz, and they point to the opportunity which higher field techniques hold for the study of fossil fuels.

INTRODUCTION AND BACKGROUND

For the past five years, our laboratory has been working on a variety of non-destructive methods for the characterization of organic matter in coal. Our general approach is to use the naturally occurring unpaired electrons in coal as "spies" of their local environment; they report on the number, positions, and types of atoms with which they come in contact or close proximity, and we translate this information into models of coal structure. It has long been known that sulfur has one of the strongest and most

characteristic interactions with unpaired electrons, and with funding from the U. S. Department of Energy, the Center for Research on Sulfur in Coal (IDENR), the Petroleum Research Fund (ACS), and the National Institutes of Health, as well as from an industrial sponsor, we have built a unique, Very High Frequency Electron Paramagnetic Resonance (VHF EPR) spectrometer operating at the W-band of microwave frequencies (ca. 96 GHz) to measure this interaction as a potential avenue to the direct, non-destructive analysis of organic sulfur in coal. This unique instrument is one of only two such devices in the world, and the only one currently operating in the U.S.A.

The fundamental motivation for building a spectrometer to perform the EPR experiment at a magnetic field of 3.4 T. instead of at the usual 0.34 T. is to improve spectral resolution and sensitivity of the technique to sulfur-containing compounds in order to analyze for sulfur in coal. The theory will be discussed in the next quarterly report. Outcome of the theory is that the shift in field, ΔB , of the resonance of our "spy" electrons due to sulfur, is dependent on Δg and ν . The sulfur "g-shift", Δg , is a feature of the coal sample; we cannot change this parameter without changing the chemistry of the sample itself. The experimental frequency, ν , is ours to choose, however, and the higher the better, since the larger ν is, the larger ΔB will be, and the more sensitive our experiment will be to the presence of sulfur. It is for this reason that we have constructed a very high frequency EPR instrument, and with it we have observed the ΔB due to sulfur, which is too small to be seen at lower spectrometer frequencies.

EXPERIMENTAL PROCEDURES

1. W-band experiments.

There are a very few EPR spectrometers in existence which operate at high microwave frequencies. Some of these are discussed in a selective review by Belford et. al. in the book "Electronic Magnetic Resonance of the Solid State," J. A. Weil, ed. (1987). Box's group in Buffalo built a special-purpose high-frequency (V-band, 70 GHz) ENDOR spectrometer² and has produced with it a long series of successful characterizations of radical centers produced by radiation damage in crystalline samples. Clarkson and Nilges in our group have visited that laboratory to examine and use the V-band spectrometer. It uses a TE_{011} cylindrical transmission cavity, a hairpin single-loop rf coil in the cavity for ENDOR, and a conventional ferrous-core electromagnet. There are a few spectrometers which operate at such high frequencies (say, > 80 GHz), that they require superconducting or Bitter magnets to produce the corresponding high fields. D-band (140 GHz) instruments developed by Lebedev and coworkers in a pioneering effort³ exist in Moscow and Novosibirsk. They use a klystron or IMPATT microwave source, a cylindrical side-coupled TE_{011} cavity or Fabry-Perot resonator, and a sweeping superconducting magnet. A 95-GHz (W-band) instrument with ENDOR capability is in Möbius' laboratory in Berlin⁴; Clarkson visited Berlin to evaluate the design of the W-band spectrometer and run samples on it. It uses a klystron or Gunn diode source and a Fabry-Perot resonator with axis perpendicular to the solenoid axis of the sweeping superconducting magnet. At the Naval Research Laboratory in Washington, D.C., Wagner's group does far-infrared magnetic resonance (which they call magneto-optical spectroscopy) on semiconductors with a millimeter-wave rotational-transition gas laser source and simple transmission tube in a large sweeping superconducting magnet. Because we had considered building such a spectrometer, Clarkson, Belford, and Dr. J. C. Cornelius from our laboratory all examined that spectrometer and tried it in experiments on our own samples. Freed's group at Cornell has recently reported a 240-GHz (G-band) EPR transmission system using optical techniques⁵; Clarkson has examined that spectrometer and run collaborative experiments with it. Just last year, Schmidt's group at Leyden described a 95-GHz (W-band) ESE spectrometer⁶, and Griffin's group at the National Magnet Laboratory has constructed a D-band (140-GHz) EPR spectrometer for DNP (dynamic nuclear polarization) experiments⁷. Robert et al. at CNRS in

Grenoble this year announced a magneto-optical (ultra-high-field EPR) spectrometer somewhat like Wagner's instrument; it uses a CO₂ laser (245, 430, or 526 GHz), a simple single-pass teflon transmission cell ($Q=1$), transient magnetic field up to 19T provided by a resistive Bitter coil, and a 1.4°K Ge bolometer detector⁸.

These spectrometers have mostly been constructed by individual groups for specialized purposes; moreover, they are not available to the general scientific public. Therefore, as a research resource laboratory, we have constructed and tested a general-purpose publicly accessible W-band (94GHz, 3mm waves) cw EPR Spectrometer at the Illinois EPR Research Center. With it we have obtained demonstration spectra of various samples, including pure and mixed spin labels in aqueous and nonaqueous solutions, organic radicals in coal macerals and whole coals, metal ions in fuel residues, organometallic chelates (a polycrystalline and a very small single crystal sample), and several melanins under a variety of conditions. Examples of some of these spectra are included in the following discussion.

Methods and Procedures

(i) Overview of IERC W-band development:

(i.1) The Mark I instrument -

Overall design: The block diagram (Fig. 3) shows the basic spectrometer layout, which has been described in our first application paper^{9,10}. The bridge is of a homodyne design. The microwave path (heavy line in Fig. 3) is as follows: Path 1: source (Hughes Gunn or Varian Klystron) --> isolator --> 10 dB directional coupler #1 (through to Path 2; side branch to reference arm) --> variable attenuator --> 3-port circulator --> 15" W-to-Q-to W vertical arm to reentrant resonator assembly in magnet (see below) --> circulator --> directional coupler #2 --> detector. The reference arm has directional coupler #1 --> variable phase-shifter --> 20 dB coupler (#3) (side branch to EPI frequency counter with phase-loop lock option) --> attenuator --> incoming side branch of 10 dB coupler #2. The Varian magnet (4.7 T max. NMR magnet with shim coils and 2"-dia. warm bore) is outfitted with an air-cooled coil insert (maximum sweep, 200 G), with its sweep controlled by an AT computer. Ten- to thirty-second sweeps, repeated a computer-controlled number of times for signal averaging, are typical. The system employs field modulation with phase-sensitive detection. The magnetic field can be monitored with an NMR gaussmeter (Metrolab). The source frequency is stabilized in one of two ways. The first option is to lock to a fixed oscillator reference by a phase-lock loop using the lock option in the EPI frequency counter. The second option is to stabilize on the sample resonator by means of a conventional AFC circuit with source frequency modulation up to 200 kHz and a separate phase-sensitive lock-in amplifier.

Resonator: The initial (Mark I) configuration uses a frequency-tunable cylindrical TE_{01n} cavity. The cavity itself is fabricated from machinable ceramic with a fired-on gold surface. The cavity axis is perpendicular to the solenoid axis of the magnet and therefore to the static field (which is vertical in the laboratory). One end of the cavity is terminated by an end plate with a screw adjustment, allowing us to vary the length of the cavity and thus its characteristic resonant frequency. There is enough adjustment so that one can tune the same cavity to either the TE₀₁₂ or TE₀₁₃ mode. A sample access hole, sufficient to accommodate samples over 1 mm in diameter, is located in the center of the screw tuner.

Coupling: The other end of the cavity is terminated with a thin metal diaphragm. In the diaphragm is an iris, located a quarter-cavity-diameter from the side of the cavity. The diaphragm/iris combination

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FIGURE 3. BLOCK DIAGRAM OF VHF V-BAND (95 GHz) EPR SPECTROMETER -- Mark I at IERC

is replaceable to allow variation in microwave coupling to the waveguide. The other side of the diaphragm forms a segment of the sidewall of W-band waveguide. The waveguide comes from below, passes the cavity, and is terminated by a waveguide stub tuner. To vary the coupling, the stub tuner is adjusted from outside (above) the magnet. This adjustment, together with the provision for different irises, allows close-to-critical matching of the cavity to the waveguide. The unique block design for the cavity assembly (Fig. 4) allows the use of a very thin diaphragm (.004" thick) and provides excellent mechanical stability.

Figure 4. Exploded view of the TE_{01n} W-band resonator.

Sample tubes: Fused-silica sample tubes accommodate typical sample sizes of 0.1-mm to 0.8-mm inner diameter x 2-6 mm long. The corresponding sample volumes range from 16 nanoliters to 3 microliters.

Quality factor and Filling factor: The unloaded Q of the resonator is 4000 (more or less depending on quality and design of the replaceable end plate tuner). The loaded Q of the cavity containing a quartz sample tube filled with water is typically a few hundred. The maximum filling factor, for the largest sample tubes we have used, is 0.078 (7.8%).

Connection of resonator assembly to bridge: Attenuation of microwave power by VHF waveguide is severe. This problem is exacerbated by the fact that the microwave path between circulator and cavity is effectively doubled by the return from the reentrant cavity. In the Mark I spectrometer, we have taken two measures to reduce those losses. First, a section of oversize (Q-band) waveguide (which is much less lossy than W-band guide) with W-to-Q transitions connects the W-band bridge section to the cavity block in the magnet. Second, the circulator-to-cavity path is kept as short as possible by locating the bridge below the magnet. The vertical center of the superconducting solenoid is much closer to the bottom than the top of the warm bore. The total distance from bridge to cavity block is thus kept to 38 cm. The entire bridge is mounted on an elevator platform which is lowers the bridge from the magnet for cavity-sample access.

Magnet: Mark I uses a Varian XL-200 superconducting magnet which Professor Clarkson negotiated as a donation from Varian Associates. This magnet is not ideal, particularly in its poor sweep agility and limited bore, but has served very well for the initial stages of development. Since it was constructed for high-resolution NMR, it has shim coils which we use to improve field homogeneity. The field is homogeneous to ± 50 milligauss over 1.5 cm. We have found that with a separate room-temperature sweep coil, we can observe the entire spectra of most organic free radicals. With a straightforward gas-flow cooling accessory, we have been able to do some low temperature studies, but only down to 200K; the small bore of the magnet, reduced by the room temperature sweep coils, leaves little room for a

cryostat. To acquire spectra of most transition metal ions, we must sweep the magnet in nonpersistent mode. For this magnet, the consumption of liquid helium is very high when the power stick is left in (> 60 liters per day vs 0.17 l/d with the power leads detached!). A magnet replacement, which we expect to be funded by an NIH SIG ("shared instrument grant"), will open up opportunities for a much wider range of important experiments. The magnet would include a wide bore and thermostatted sample temperature control to allow a range of experiments not now possible on any instrument, and it would provide for operation at or below liquid helium temperature, where sensitivity is greatest and spectral lines often sharpest, a capability not available now on any other W-band system in the world.

Computer control: The spectrometer system is interfaced with an IBM PC/AT through an A/D board. The 100GHz frequency meter, a teslameter, and the lock-in amplifier are controlled through an IEEE-488 Bus.

Microwave source: At present we are using a Hughes varactor-tuned GaAs Gunn oscillator with a 35 mW power output. This provides up to 10 mW power at the cavity, which we find to be sufficient for most samples. Varactor-tuned Gunn sources suffer somewhat from phase noise; the Hughes specification for this diode is -80 dBc/Hz. For studies where it is necessary to completely saturate the sample and/or to keep phase noise at a minimum, we have available an alternative source -- a 400mW Varian Klystron with power supply and an optoisolated feedback loop (to inject low-potential voltage offsets into the kilovolt klystron supply) for frequency control. The Klystron offers an FM phase noise specification of -110 dB/Hz. For nonlossy, hard-to-saturate samples this low phase noise and high power are necessary for best sensitivity.

Field modulation: Two coils in a split pair arrangement (dia ca. 0.5 cm) are located in the cavity block and coaxial with the magnet. They produce a maximum modulation field at the sample of 40 G peak-to-peak and are driven at any frequency up to 100 kHz referenced to the signal lock-in amplifier.

Looking ahead: While the system is quite functional now, there is room for considerable refinement. While working on these refinements, we intend to carry out a substantial body of collaborative and demonstration studies and to regularly reevaluate and document performance. Looking to the future, after the basic system is refined and has produced a body of useful results, we expect to incorporate capabilities to explore nonstandard experimental measurements such as light-induced spectra, double resonance (ENDOR and TRIPLE), and pulsed EPR.

(i.2) Performance tests and first results - The Mark I instrument in its present configuration is particularly suited to detection of small g anisotropies and discrimination among multiple radicals. For example, Fig. 5 compares X- and W-band spectra of a dioxane-solution mixture of two nitroxides (TEMPOL and CTPO, 1mM each) with very similar X-band spectra, showing that they are well resolved at the W-band frequency. In this particular case, the two species differ slightly in both hyperfine splitting and isotropic g factor.

Fig. 6 illustrates how W-band spectroscopy can resolve anisotropies and differentiate immobilized species which the usual EPR experiments do not resolve well. This illustration is taken from our currently active study of melanin and melanin-like pigments prepared from a variety of monomers including dopa, dopamine, catechol, and minocycline. We have acquired W-band spectra of several of these poorly understood polymers at several pH points between 1 and 11. Melanins are heterogeneous biopolymers responsible for pigmentation in animals. Like coals, they are difficult to study by most spectroscopic methods, but they contain free radicals detectable by EPR. The radical concentration increases at high pH

FIGURE 5 COMPARISON OF X- AND W-BAND SPECTRA OF A MIXTURE OF TWO NITROXIDES (TEMPOL AND CTPQ) IN DIOXANE SOLUTION, 1 mM EACH. The W-Band microwave frequency is 3.3554 T. Ten 10-second scans were accumulated. Power, - 0.25 mW. Modulation amplitude, 0.7 G. Time constant, 10 ms/scan.

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Figure 6. X-band (left) and W-band (right) spectra of dopa-based melanin (top 3 traces) and a melanin-like pigment formed from minocycline (lower 3 traces). W-band: $\nu = 94.16$ GHz; field range = 0.0140 T centered at 3.3573 T.

FIGURE 6. — Continued. W-Band spectrum of minocycline pigment prepared at pH=4.

Lower curve - experiment at 92.2325 GHz.

Upper curve - Simulation assuming a single rhombic species with g components 2.0477 , 2.00420 , 2.00257 and anisotropic linewidths.

Lower curve - Simulation assuming a mixture of a rhombic species (86%) and a minor axial constituent (14%), with rhombic g components 2.00459 , 2.00423 , 2.00258 and axial g components 2.00485 , 2.00485 , 2.00254 . The lineshapes and linewidths are anisotropic and different.

or in the presence of nonparamagnetic metal ions. These induced (extrinsic) radicals have been identified as chelatable anionic o-semiquinone free radicals, but the nature of the intrinsic radicals, dominant at neutral-to-low pH, is still unknown. Synthetic analogues can be prepared. Their spectra are generally unresolved ill-differentiated at X-band. The beginnings of structure appear at Q-band, but W-band clearly provides dramatic differentiation and resolution. It may be possible to come to definite conclusions regarding the pH-dependent distribution (and equilibria) among coexisting species. We also can now begin to attempt detailed analyses for structural clues through their g -anisotropies (simulation, Fig. 6). These results now have been presented¹¹.

In our first W-band spectrometer tests, we included a representative anisotropic metal complex. In our first attempt with a highly anisotropic powder, we encountered the difficulty that the 200 G range of the sweep coils was not quite sufficient to explore the entire perpendicular (x, y) region of the spectrum in one sweep. Therefore, the spectrum had to be sampled in three separate sweeps with offset superconducting fields and pieced together. The spectrum (Fig. 7) illustrates definitive resolution of rhombic anisotropy in a powder spectrum of a copper(II) chelate (magnetically dilute bis(benzoylacetonato)Cu(II)). Both X- and Q-band data earlier had been acquired and an analysis carried out¹². In the perpendicular region of the spectrum, even at Q-band, the g_x and g_y branches completely interpenetrated and overlapped, reducing our confidence in the spin-Hamiltonian parameters despite a good simulation fit. In Fig. 7, the perpendicular (high-field) part of the W-band spectrum is shown; the lower-field parallel region at W-band was not explored because it is not at all in question and therefore not worth the time, effort, and expense to sweep down the superconducting coil current in order to acquire the parallel features. The spectrum of the perpendicular region was obtained during an early quick survey, and suffers a little from graininess and noise and from having to be patched together from different scans. In short, it is not of publication quality. Nevertheless, it is quite good enough to show rich structure owing to anisotropic Zeeman and hyperfine coupling, and it resolves and almost completely separates the rhombic (g_x, g_y) Zeeman splitting. A full simulation refinement has not been completed, but preliminary simulations show that the W-band features are sensitive to most of the parameters in the spin-Hamiltonian. It appears that W-band spectra of metal centers like this Cu(II) compound will provide the additional information to fix parameters which could not be definitively extracted from lower-frequency spectra. We point out that one immediately anticipates aggravated problems with graining in powder samples at VHF because of the small sample size (hence fewer grains in the sample) exacerbated by the greater $\delta B/\delta \theta$ and $\delta B/\delta \phi$. This problem is expected to be particularly severe for metal-ion systems displaying large anisotropies. We did encounter this problem with the Cu(benzac)₂, but with some effort were able to prepare a sample which displayed only moderate graining. However, we would like routinely to be able to prepare samples exhibiting virtually no graining, even at W-band. In our background experimentation and demonstration projects on very anisotropic immobilized centers, we shall work to find the best ways to achieve satisfactory subdivision of powder samples and glassing of frozen solutions in W-band sample tubes.

Since many EPR samples are of very limited size or spin concentration, it is quite important to be able to maximize signal-to-noise ratio and achieve high sensitivity. In considering spectrometer performance, one recognizes at least eight sample types depending on their degree of dielectric lossiness, ease of saturation, and limitations of sample size and shape¹³. Actually, since every gradation between the eight types is possible, there is an infinite range of sample types. The following Table compares our first measurements of sensitivity, measured as is customary with nonsaturating low-loss samples, with reports from several other spectrometers. We have also made some measurements of sensitivity for the most frequently encountered kind of sample of high dielectric loss -- an aqueous solution. Results from these measurements are described later in this section.

FIGURE 7. W-BAND SPECTRUM: The perpendicular (x,y) region of Cu(II) dilute in Pd(benzac)₂, showing much better separation of x and y features than is seen at lower frequencies. The simulation spectrum uses parameters obtained from a careful Q-band study (T. M. Northern, Ph.D. Thesis, University of Illinois, 1976). It includes a nuclear quadrupole coupling (NQC) of 9.6 MHz and linewidth of 12 MHz. The "x" features are split because of off-axis extrema which are sensitive to both the value of the NQC and the angles of noncoincidence among the electronic Zeeman, hyperfine, and NQC matrices. The simulation analysis has not yet been refined. Because of limited sweep, the experimental is made up from three overlapping sweeps, each with different superconducting magnet persistent field. The parallel features are far outside the currently convenient field range for the IERC Mark I W-band spectrometer, must be very weak, and are perfectly well understood from studies at other frequencies, we have not yet deemed it worthwhile to search for them.

It is unreasonable to rely on these comparative sensitivity values to much better than a factor of 2, especially as they were done with different kinds of samples and instrument conditions. Nevertheless, it is evident that the sensitivity of the IERC W-band spectrometer fits in quite reasonably with those of other high-frequency EPR spectrometers. Early tests of sensitivity are encouraging, but we are not satisfied; we are confident that we can and shall improve it during a continuing campaign of resonator development and attention to all elements of the spectrometer - source, bridge components, detector, electronics system - which may introduce noise or limit signal response. For our TE_{013} cavity with the Gunn source, our first low-power sensitivity measurements were done with two samples, with consistent results - the certified NBS ruby specimen with 1 mW power or a 3 μ l sample of 5 μ M TEMPO in pentane. The TEMPO sample, with 3.6G peak-to-peak linewidth, was run at 4.0G modulation amplitude. On account of the substantial (-80 dB at 100 kHz) phase noise of the Gunn source, the expected square root dependence of sensitivity on power for a nonlossy sample does not hold at high power. The low-power result shown indicates

**Table: Reported sensitivities for EPR spectrometers
at several frequencies for nonlossy, nonsaturating samples**

BAND; INSTRUMENT	SENSITIVITY (N_{min})	SENSITIVITY (C_{min})
X-Band (9.5 GHz); Varian, TE_{102} rectangular resonator, klystron	2×10^{10} spins/G	2×10^{11} spins/G•cm ³
Q-Band (35 GHz), Varian E110, TE_{011} cylindrical resonator at 2.5 mW.	5×10^9 spins/G	1×10^{12} spins/G•cm ³
W-Band (94 GHz); Berlin (Möbius), Fabry-Perot resonator, klystron	1×10^9 spins/G	$\sim 8 \times 10^{11}$ spins/G•cm ³ (estimate)
W-Band (94 GHz); IERC Mark I, TE_{012} cylindrical resonator, Gunn oscillator at low power (2.4 mw)	$\sim 2.0 \times 10^9$ spins/G	$\sim 1.3 \times 10^{12}$ spins/G•cm ³
W-Band (94 GHz); IERC Mark I, TE_{013} cylindrical resonator; Varian klystron, (12 mw)	$\sim 1.8 \times 10^8$ spins/G	$\sim 1.2 \times 10^{11}$ spins/G•cm ³
D-Band (140 GHz); Moscow (Lebedev, Grinberg, et al.) TE_{011} cylindrical resonator, 20 mw klystron	.4 to 1.0×10^8 spins/G	$\sim 2 \times 10^{11}$ spins/G•cm ³
D-Band (140 GHz); Moscow (Lebedev et al.), Fabry-Perot resonator	2×10^9 spins/G	$\sim 3 \times 10^{11}$ spins/G•cm ³
D-Band (140 GHz); MIT (Griffin), solid-state source, folded Fabry-Perot resonator, designed for DNP & EPR (privileged verbal communication)	$\sim 10^{10}$ spins/G	$\sim 1.5 \times 10^{12}$ spins/G•cm ³ (estimate)
G-Band (250 GHz); Cornell (Freed), frequency-multiplied solid-state source, Fabry-Perot resonator	3×10^{11} spins/G	5×10^{12} spin/G•cm ³

$N_{min} \approx 2 \times 10^9$, close to the values which Möbius' and Lebedev's groups cite for their W-band and D-band systems with klystrons and Fabry-Perot resonators. Lebedev quotes a much better sensitivity figure for

the Moscow 140-GHz D-band spectrometer with TE_{011} cavity, measured with a klystron source for lowest noise and a 10 μ M nitroxide solution in a low-viscosity hydrocarbon solvent¹⁴. However, both Möbius and Lebedev inform us that, as a practical matter, they use solid-state sources rather than klystrons for most of their spectroscopy. Nonetheless, we note that the published sensitivity figures for both the Berlin and Moscow spectrometers were obtained with their klystron sources, whereas the solid-state diodes have much more phase noise than klystrons. Therefore, we have extrapolated for comparison to obtain the sensitivity which we expect from the klystron (phase noise, 30 dB better than the Gunn), and then have made noise measurements with the klystron which confirm our predictions. These expected number and concentration sensitivities definitely are in line with the results from the other VHF spectrometers. According to Prisner¹⁵, the 140 GHz spectrometer at the National Magnet Laboratory, with Fabry-Perot resonator, has a rather poor sensitivity of ca. 10^{10} spins/G, roughly power-independent, but is expected to improve after some redesign of the bridge with replacement of certain electronics components to reduce excessive phase noise.

As mentioned previously, it is convenient to divide EPR samples into at least eight classes depending on whether (a) the sample saturates or not, (b) is or is not limited in size, or (c) is or is not lossy. The $C_{\min}$ which applies to samples which are unlimited, non-saturable, and nonlossy is predicted to vary as $(\nu P_0)^{1/2}$ (see, eg., Varian manual or Poole's or Wilmshurst's books). In practice, this square root dependence on frequency may not be seen because of 1) the lower output power of high frequency sources and 2) the higher noise figure expected for detectors. Rather it appears to be roughly independent of frequency, being on the order of 10^{11} to 10^{12} spins/G cc. $N_{\min}$ is most significant for samples which also are limited in size and is inversely proportional to the resonator volume. Thus $N_{\min}$ typically is much better at higher frequencies because of the smaller resonators used. Lebedev et al. attain the best sensitivity because their TE_{011} cavity has a volume of only 12 μ l. Our TE_{013} cavity has a volume of 170 μ l, which we find to be convenient for a variety of samples. We will build a TE_{011} cavity which will have a volume of ca. 60 μ l and should allow us to improve our point sensitivity by about a factor of 3. Such a resonator should be very useful for the study of tiny single crystals.

These measured $C_{\min}$ and $N_{\min}$ figures are applicable only to samples which are nonsaturable and nonlossy. For such samples in our spectrometer, our 400mW klystron, which can deliver over an order of magnitude more power than the Gunn, can improve sensitivity. However, the limited sweep of our magnet now limits us largely to free radicals, which are most often easily saturated. For systems which are saturated at very low power, the klystron is expected to yield little improvement in sensitivity. The Gunn oscillator, which is much more durable and less expensive to replace, is a much more practical option for these samples. The klystron is best reserved for very weak samples which do not readily saturate.

2. G-band experiments.

Samples of an Illinois #6 that had previously been separated by density gradient centrifugation were placed in a teflon cup in the transmission line of the G-band instrument. The sample was continually purged with dry nitrogen during the course of the experiments..

RESULTS AND DISCUSSION

Figure 2 in the General Summary section illustrated the increase in resolution obtained when VHF EPR experiments on Illinois #6 samples are performed at 250 GHz. Figure 3 shows another version of this data, with the two spectra superimposed for comparison. The shaded portion of each spectrum

corresponds to the contribution from sulfur-containing radicals. It is very clear that in the higher field data, not only does the organic sulfur signal move farther downfield, the main peak at higher field also begins to display a partially resolved central feature. In order to better understand how this additional splitting correlates to coal molecular structure, we measured the VHF EPR spectrum of perylene (+) radicals at 250 GHz. Figure 9 shows the perylene (+) spectrum superimposed on that from the vitrinite.

Figure 8. W and G-band spectra of vitrinite from an Illinois #6. Shaded areas correspond to contributions from organic sulfur.

Figure 9. 250 GHz VHF EPR spectra of a vitrinite and perylene (+) radicals.

The downfield movement of the spectral feature related to organic sulfur is expected as we go from 95 GHz to 250 GHz, since this effect is due to spin-orbit coupling of unpaired electrons to sulfur atoms,

as described in the Background section. G-band experiments have helped us to confirm our assignment of this peak to organic sulfur, and we now can proceed with much greater confidence to analyze W-band coal spectra using this model. The broadening and partial splitting of the central resonance feature is less well understood. Based on the comparison made in Figure 9 between vitrinite and perylene (+), a tentative interpretation is that at 250 GHz, we are beginning to resolve g-value differences between purely hydrocarbon aromatics and oxygen-containing aromatics in coal. Such differentiation is vital for a more complete analysis of VHF EPR coal spectra, and really suggests that fields and frequencies above W-band are extremely useful for this work.

CONCLUSIONS AND RECOMMENDATIONS

(1.) Our W-band spectrometer is still under development, but it is already showing excellent resolution and sensitivity, and we expect to continue to improve its performance. (2.) G-band spectra have shown us superb resolution of separated macerals, and much more work needs to be done to understand these data. We plan more experiments in collaboration with the Freed group at Cornell in order to complete this phase of the work, which will allow us to much more accurately interpret our W-band data. The higher field experiments suggest that we would benefit enormously in this work from the availability of an instrument operating between W-band and G-band, and we hope later to construct or invest in a D-band (140 GHz) spectrometer for this work.

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