DOE/PC/88921--7

DE91 004334

DOE Technical Report No. DOE/PC/88921-7
Seventh 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: June 1, 1990
US/DOE Patent Clearance is not required prior to publication of this document.

ABSTRACT

This quarter's report describes an important background activity — the testing of capabilities of newly developed and constructed equipment and of methods by applications to some well-characterized systems. In this case, the new equipment is the world's only S-band ESE spectrometer, the methods are computational and theoretical analysis techniques, and the well-characterized system used for the tests is DPPH, a stable aromatic-based free radical which is a world standard for testing EPR spectrometers.

Experiments employing S-band pulsed electron paramagnetic resonance (EPR) spectroscopy, with the intent of eliciting molecular and electronic structural information in disordered solids, have been emphasized during this period of the grant. In particular, the ability to extract nuclear quadrupole coupling information from S-band electron spin echo envelope modulation (ESEEM) data has been demonstrated. This ability provides a valuable tool for obtaining structural information from systems in which quadrupolar isotopes of sulfur, nitrogen and sodium are present.

Efforts to improve the computational methods used to analyze ESEEM data have also been central to the work done this quarter. Significant improvements to the ESEEM simulation programs have been accomplished. The improvements have eliminated certain simplifying assumptions used previously, which are not always valid.

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GENERAL SUMMARY

Pulsed (time domain) electron paramagnetic resonance (EPR) spectroscopy can be utilized to measure weak electron-nuclear couplings. In electron spin echo envelope modulation (ESEEM) experiments on disordered solids, the modulation of the electron spin echo envelope is a direct result of couplings which take place between the unpaired electrons in the sample and neighboring magnetic nuclei.

In order to make use of the information obtained in an ESEEM experiment, it is most often necessary to reproduce the experimental results via computer simulation. This is no slight task, and previous programs, in order to reduce computation time, have included simplifying assumptions which are not always valid. Computer programs are being developed in this laboratory which do not rely on unnecessary simplifications, while also improving the efficiency of the computations. The simulation problem becomes more complex when quadrupolar nuclei ($I > 1/2$) are coupled to the unpaired electrons and participate in modulating the electron spin echo envelope. Accounting for the effects due to quadrupolar nuclei such as ^{33}S, ^{14}N, and ^{23}Na is relevant to structure problems in native and treated coals. The preliminary results from the simulations for such complex systems have been quite successful.

Other efforts to characterize effects on ESEEM due to quadrupolar nuclei have involved exploiting the microwave frequency range (and hence Zeeman field) available to the S-band pulsed EPR spectrometer. The spectrometer is designed to operate over an octave bandwidth of microwave frequencies, 2-4 GHz. By careful choice of the EPR excitation frequency, it is possible to cause a nuclear Zeeman interaction sufficient to "cancel" the nuclear hyperfine interaction. The resulting nuclear energy levels correspond exclusively to the nuclear quadrupole levels. This makes it possible to observe nuclear quadrupole resonance (NQR) transitions from the ESEEM, allowing direct calculation of quadrupole coupling constants. The quadrupole coupling data lends insight into the electronic environment at the quadrupolar nucleus, thus contributing additional structural information. Results from a model system in which appreciable quadrupole coupling is present have proven to be successful.

OBJECTIVES

The overall goal of this project is the development of nondestructive techniques for studying the molecular structure of coal by probing the chemical environment of naturally occurring unpaired electrons with a variety of electron magnetic resonance spectroscopies. One exceptionally promising method for investigating molecular structure in complex solids possessing unpaired electrons is Electron Spin Echo Envelope Modulation (ESEEM) spectroscopy. Currently the aim of our S-band ESEEM work is to develop better methods for the interpretation of multifrequency ESEEM data. This problem is extremely difficult, especially for modulation resulting from quadrupolar nuclei ($I > 1/2$) such as ^{33}S, ^{14}N, and ^{23}Na. We are pursuing two closely related paths toward this goal. One part of this effort is the development of classification systems which would make ESEEM spectra more amenable to a preliminary interpretation by visual inspection. Since ESEEM is a relatively new technique, a broad foundation of experience with this method must be developed in order to achieve this goal. We have begun this task by examining systems where nitrogen nuclei ($I = 1$) are coupled to the electron spin. The second part of this effort involves the development of improved theoretical models for the quantitative interpretation of ESEEM data. In order to reduce computation time, the most recent theoretical treatments require many assumptions which may not always be valid. We have begun an effort to test the validity of these assumptions when applied to a wide variety of cases.

The objective of the particular application described in this report is the testing of some of the capabilities of our recently constructed ESE spectrometer by carrying out a detailed investigation of a well-characterized molecule which, however, is still interesting in that certain of its characteristics have not been unambiguously determined. The molecule DPPH, diphenylpicrylhydrazyl, is a well-known stable free radical frequently used to test and tune up electron paramagnetic resonance spectrometers, but details of the nitrogen substituents on one of its aromatic rings have been uncertain and, in fact, the focus of a bit of controversy. It therefore made an excellent subject to select for this test. Such tests of performance and capability are particularly important for this new instrument because not only is it new in our laboratory, it is entirely new in science, being the first and only one ever constructed anywhere.

INTRODUCTION AND BACKGROUND

Electron Spin Echo Envelope Modulation (ESEEM) spectroscopy is proving to be an extremely useful tool for studying weak electron-nuclear hyperfine and nuclear quadrupole couplings in disordered paramagnetic solids. The parameters which characterize these interactions contain information about molecular and electronic structure.

In the ESEEM experiment, sequences of microwave pulses excite the electron spin system and cause the electron spins to emit a burst of microwave radiation called a spin echo at a characteristic time following the excitation pulses. In solids, as the time between pulses in the excitation sequence is varied the amplitude of the spin echo oscillates. This oscillation occurs at frequencies determined by the electron-nuclear hyperfine and nuclear quadrupole interactions. The ESEEM pattern recorded as a function of the time between pulses may be analyzed directly in an effort to extract the desired parameters or the pattern may be Fourier transformed for analysis in the frequency domain. However, arriving at a reliable interpretation of experimental data is quite difficult for many systems, particularly when quadrupolar ($I > 1/2$) nuclei are involved. Three such nuclei relevant to structure problems in native and treated coals are ^{33}S, ^{14}N, and ^{23}Na.

EXPERIMENTAL

An improved computer program for the calculation of ESEEM functions from spin Hamiltonian parameters is under development. The program is based on the expressions derived by Mims[1] using the density matrix formalism. A simplified analytical expression for an $S = 1/2$, $I = 1/2$ spin system is given in equation 1. The frequencies, ω_α and ω_β, depend on the orientation of the static applied magnetic field with respect to the molecular coordinates, while the modulation depth parameter, k, depends on the both the orientation of the static field

$$V_{mod}(2\tau) = 1 \quad 2k \sin^2\left(\frac{\omega_\alpha \tau}{2}\right) \sin^2\left(\frac{\omega_\beta \tau}{2}\right) \qquad (1)$$

and the orientation of the microwave magnetic field. In disordered solids, the modulation function calculation must be repeated many times averaging over these orientations. Previous programs performed the averaging over orientation explicitly for the calculation of frequencies but the averaging was performed in an implicit and inexact manner for the calculation of the depth parameter. Also with previous programs, a different program was used for each nuclear spin value (i.e. a program for $I = 1/2$, a program for $I = 1$, etc.) using analytical expressions like equation 1 specific to each case. These simplifications, among others, were necessary to reduce the CPU time required to execute the program. The new program eliminates most of the simplifying assumptions made in previous programs and is general, allowing any value of nuclear spin. The availability of faster computers permits the more extensive calculations to be completed in a reasonable time. Thorough testing of the program is underway.

In an effort to understand the nature of the effects on ESEEM due to quadrupolar nuclei, studies of a test case, a nitrogen-containing paramagnetic species in the disordered solid state have been undertaken. By a judicious choice of the EPR excitation frequency (or equivalently the Zeeman field) employed in the experiment, it is possible to observe nuclear quadrupole resonance (NQR) transitions.[2-4] This occurs for systems in which the electron-nuclear magnetic hyperfine interaction is largely isotropic The energy levels for a quadrupolar nucleus in the presence of a magnetic field due to an unpaired electron (the hyperfine field) while also in the presence of an externally applied field (the Zeeman field) are determined by the mixture of the quadrupole, hyperfine, and Zeeman interactions. If the Zeeman field is chosen such that it "cancels" the effect of the hyperfine field, only the nuclear quadrupole levels remain. By recording ESEEM while this condition is fulfilled, it is possible to observe the NQR transitions. Quadrupole coupling information is valuable for molecular and electronic structural characterization. The S-band pulsed EPR spectrometer used in these experiments is designed to operate over a full octave bandwidth of microwave frequencies (2-4 GHz). This wide span of available excitation frequencies (Zeeman fields) permits observing the NQR for nuclei in various systems, over a range of hyperfine couplings.

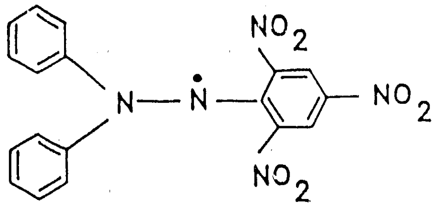
RESULTS AND DISCUSSION

Computation of ESEEM Spectra. Tests of our new program for calculating ESEEM spectra yield the same results when the assumptions used in previous programs are assimilated in this method. This consistency is one important factor in verifying proper operation of the program. The program also predicts some interesting modulation behavior particularly for quadrupolar nuclei. Specifically, the program predicts that the modulation function can take on negative values in some cases. No experimental observation of this behavior has ever been reported.

S-band ESEEM Study of a Nitrogen Containing Free Radical. An S-band ESEEM investigation of the free radical 1,1-diphenyl-2-picrylhydrazyl (DPPH) has been undertaken in an effort to relate experimental results to factors regarding molecular and electronic structure for a system in which coupling takes place between an unpaired electron and nuclei (^{14}N) which possess an appreciable nuclear electric quadrupole moment. The theory for the case in which the nuclear quadrupole coupling is small compared with the nuclear hyperfine coupling has been developed and works reasonably well. However, the case in which the nuclear quadrupole effects are comparable to the hyperfine interaction represents a much more complex situation.

The structure of DPPH is shown in Figure 1. DPPH is an excellent benchmark system, as it has been the subject of numerous magnetic resonance studies.[4-11] The results of these investigations have revealed that the unpaired electron is delocalized over the entire radical. As this is the case, up to 17 electron-nuclear hyperfine couplings (12 protons and 5 nitrogens) may be observed. No single magnetic resonance technique has the ability to resolve all of the possible hyperfine couplings. Even with the best possible resolution, by employing standard EPR techniques, only the hyperfine interactions due to the nitrogens on the central hydrazyl fragment (N_1 and N_2) can be measured to a high degree of certainty.[10] Electron-electron double resonance (ELDOR) measurements confirmed the couplings to the hydrazyl nitrogens as determined by EPR.[7] The couplings to these hydrazyl nitrogens represent by far the strongest of all the electron-nuclear interactions present in the radical, as nearly 90%

of the unpaired electron spin density is localized on these atoms.[12] In attempts to extract reliable couplings for the remaining (weakly coupled) nuclei, techniques such as ESEEM, electron-nuclear double resonance (ENDOR), and NMR have been employed.[4-7,10,11]



1,1-Diphenyl-2-picrylhydrazyl radical

Figure 1. Structure of the DPPH radical.

The various ENDOR and NMR studies have provided reliable hyperfine coupling data for the protons in the radical. The coupling data for the ^{14}N nuclei in the nitro groups on the picryl ring has not yet been well established. This is particularly true for the quadrupole coupling constants associated with these nuclei. By S-band ESEEM spectroscopy, it has been possible to record ^{14}N NQR transitions from the nitro groups. Figure 2 shows the ESEEM pattern and the corresponding frequency spectrum obtained by Fourier transformation for a 10m$\underline{M}$ sample of DPPH in a frozen toluene glass at 100K. The peaks at 0.68 MHz and 0.85 MHz are due to NQR transitions.

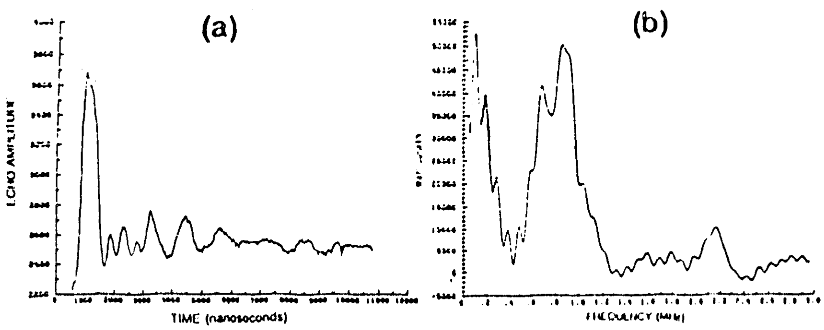


Figure 2. (a) ESEEM pattern from DPPH radical in toluene glass at 100K. (b) Fourier transform of (a).

From these frequencies, values for the quadrupole coupling constant, e^2qQ/h, and the asymmetry parameter, η, can be calculated. It is found that e^2qQ/h = 1.03 MHz and η = 0.33. These values are consistent with those reported for aromatic systems which contain nitro groups, which should have similar electronic-structural characteristics.[13,14]

CONCLUSIONS AND RECOMMENDATIONS

We conclude that our new simulation technique for treating ESEEM data is reliable and can yield valuable structural information, especially for the quadrupolar isotopes of sulfur, nitrogen, and sodium. During the next quarter of this grant, refinements to our computational capabilities will continue. The accurate simulation of ESEEM data is paramount to the success of extracting reliable structural parameters.

We have been successful in obtaining nuclear quadrupole coupling parameters directly from ESEEM data and plan to continue related experiments. The ability to determine the local electronic environment of quadrupolar nuclei adds another dimension to structural characterization.

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(Note: Funding for this work has been augmented by additional funding from the State of Illinois through the Center for Resarch on Sulfur in Coal and by facilities support for the Illinois EPR Research Center, supported by NIH; therefore, results are also being transmitted to those agencies.)

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