

ADVANCED ELECTRON PARAMAGNETIC RESONANCE (EPR) TECHNIQUES FOR THE STUDY OF COAL STRUCTURE

B.G. Silbernagel, M. Bernardo, L.A. Gebhard and H. Thomann
Corporate Research—Exxon Research & Engineering Co
Route 22 East, Annandale, NJ 08801

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INTRODUCTION

Electron Paramagnetic Resonance (EPR) has been extensively applied to the study of coal [1]. In conventional EPR relatively featureless microwave absorptions are observed, from which one extracts the width and position (g -value) of the microwave absorption as well as the density of carbon radicals in the sample. For example, in a conventional EPR study of isolated coal macerals [2], these properties vary with increasing coal rank: g -values fall from values expected for oxidized aromatics to those of aromatic radicals, while radical densities and linewidths generally increase. Microwave saturation techniques (i.e. measuring the intensity of the absorption as a function of applied microwave field) show that high rank coals are much less easily saturated. The relation to the relaxation properties of the carbon radicals is less obvious, since saturation depends on the product of two relaxation parameters of the carbon radicals.

The conventional EPR absorption width results largely from interactions of the unpaired electron spin on the carbon radical with protons in its vicinity, either as a result of direct wave function overlaps (contact interactions) or dipole interactions. Distributions in g -values and dipolar interactions among the carbon radicals themselves will also contribute to the observed width. Identifying and separating these contributions can not be done by conventional EPR alone. The present paper describes two classes of pulsed EPR experiments, analogous to widely-used pulsed NMR techniques: Electron Spin Echo (ESE) determinations of spin-lattice (T_1) and spin-spin (T_2 or T_{m1}) relaxation and double resonance techniques like pulsed ENDOR (Electron Nuclear Double Resonance) [3]. While such techniques can be applied with great effect to relatively homogeneous systems, such as individual compounds or the active sites in enzymes, it is not obvious, *a priori*, that such elaborate schemes will yield useful information in a material as heterogeneous as coal. The present paper will demonstrate the nature of the information that can be obtained and assess its usefulness.

EXPERIMENTAL

The experiments described here have been performed on two series of samples: the isolated coal macerals [2] and a series of "as received" samples of Argonne Premium Coal samples [4]. While there is some concern about the quantitative nature of the data from the "as received" Argonne Premium Coal samples—due to the presence of significant levels of paramagnetic species, the qualitative features are still illustrative. The pulsed EPR experiments were run at microwave frequencies from 9.1–9.4 GHz. The relaxation measurements were performed at room temperature, while the double resonance measurements were done at 100K. For the double resonance experiments, the rf frequency used to excite the protons was swept from 1–30 MHz.

RELAXATION RESULTS

The relaxation properties of the isolated vitrinite macerals as a function of coal rank probe the interactions of radicals in the coal [5]. Instantaneous diffusion contributes to phase memory loss in higher rank coals and can be separated from the asymptotic phase coherence decay rate, T_{m1}^{-1} , which is the EPR analog of T_2 . Values of T_{m1}^{-1} and T_{1e}^{-1} for vitrinites varying in rank from subbituminous C to low volatile bituminous are shown in Fig 1. The T_{1e}^{-1} values are more than an order of magnitude smaller than T_{m1}^{-1} in all cases: spin lattice relaxation is much slower than phase memory loss. The contribution of the dipole coupling to the width of the conventional EPR line can be estimated from the magnitudes of T_{m1}^{-1} , and is much smaller the contributions from hyperfine interactions.

Both T_{1e}^{-1} and T_{m1}^{-1} values are relatively small for low rank coals, with T_{m1}^{-1} beginning to

increase in the vicinity of 78 wt. % carbon, and T_{1e}^{-1} showing a sharp increase near 82 wt. % carbon. The T_{m1}^{-1} values vary nearly linearly with carbon radical density indicating that they result from dipole interactions among the radicals. By contrast, the sharp change in T_{1e}^{-1} does not track radical density and appears related to changes in the local order of the aromatic molecules with increasing coalification.

DOUBLE RESONANCE EXPERIMENTS

Double resonance experiments require that the carbon radicals and the protons be simultaneously excited by microwave and rf pulses. Two of the double resonance schemes, for pulsed ENDOR and EPR detected sublevel coherence, are shown in Fig 2. In each experiment, the electron spin population of the radicals is prepared by the applying microwave pulses and then rf pulses are applied to the protons. At an appropriate time the electron and nuclear spin systems are allowed to mix and the results are detected in the electron spin system. The cavities required to allow simultaneous microwave and rf operations are a challenge to design and construct and remain at the frontiers of the technique development.

Fig 3 shows pulsed ENDOR data on a sample of Pocahontas coal [3]. In one case the ENDOR experiment was performed with the microwave frequency at the absorption center ($g = 2.0026$) and also with the frequency positioned on the low field (i.e. high g -value ≈ 2.0091) portion of the absorption. In each instance, a sharp signal centered at the proton Larmor frequency is seen from "matrix" protons—i.e. those not directly coupled to the radical but interacting with it via dipole interactions. The broader spectrum, which extends at least 15 MHz on either side of the center, comes from "local" protons—i.e. those interacting directly with the moments via some form of wave function overlap. The shape of the local ENDOR signal is nearly identical for all of the high volatile bituminous coal samples observed and has the same shape at 298K and 85K. The ratio of the matrix to local ENDOR signals does vary with rank and temperature, the matrix signals being relatively stronger in the lower rank coals. There is no evidence for major structure in the local ENDOR for any of the samples examined. Fig 3 also shows that the shape of the local ENDOR signal does vary for different positions of the radical-bearing molecules lying at different places in the resonance line—particularly for the heterocyclic molecules which lie at high g -values.

EPR detected sublevel coherence measures proton dynamics on the carbon radicals, an exciting prospect since magnetic broadening usually renders these protons unobservable by NMR techniques. The protons contributing to the matrix ENDOR have faster T_2 relaxation than those in the local ENDOR component of the signal—presumably a result of field inhomogeneities associated with protons close to the radical.

CONCLUSIONS

Advanced EPR techniques provide new, quantitative information about coal chemistry and its variation with rank. The greater information obtained about interactions on the radical itself should further progress in the understanding of coal microscopics.

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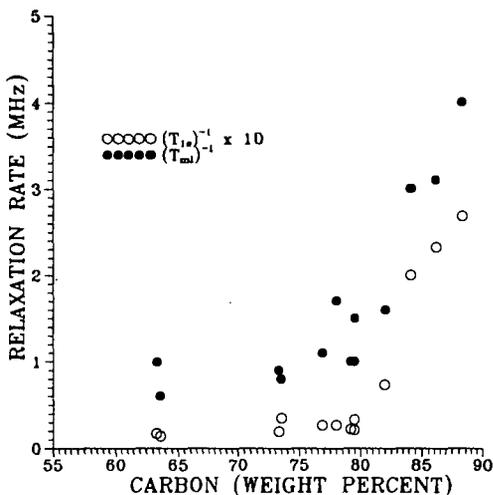


Fig 1 Relaxation rate measurements on isolated vitrinite macerals [5] show significant increases in both T_m^{-1} and T_{1e}^{-1} with increasing coal rank.

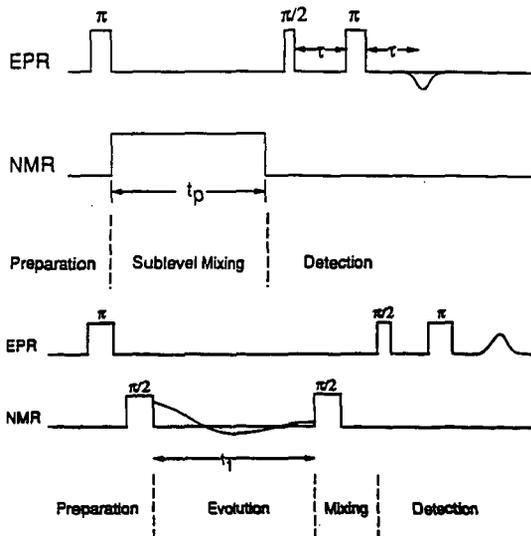


Fig 2 Double resonance schemes for doing pulsed ENDOR (top) and EPR detected sublevel coherence (bottom) experiments.

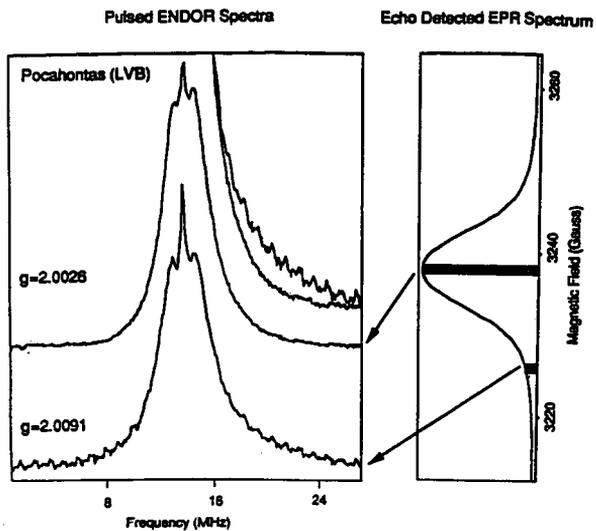


Fig 3 The ENDOR spectra from the center of the resonance ($g = 2.0026$) and the low field end ($g = 2.0091$). Both matrix and local ENDOR signals are observed. The shape of the local ENDOR spectrum is significantly different at high g -value.