

Selection of Species in Divalent Rhodium Hexacyanide Using Pulsed EPR

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The superposition of paramagnetic species in CW EPR spectra usually prevents the measurement of spectral parameters. Separation of superimposed species can be performed in field-swept pulsed EPR by choosing a convenient pulse sequence in such a way that species with different relaxation times can be distinctly affected. Computer subtraction between spectra taken under different conditions may lead to better species identification. For T_2 -based selection, the difference between FID-detected and long τ echo-detected spectra is used. This technique is successfully applied to the $[\text{Rh}(\text{CN})_6]^{4-}$ paramagnetic species created by radiation damage in $[\text{Rh}(\text{CN})_6]^{3-}$ in a KCl host lattice, where spectra corresponding to different positions of a charge-compensating positive-ion vacancy are superimposed. © 1997 Academic Press

SELECTION OF SPECIES

In the EPR spectra of $[\text{Rh}(\text{CN})_6]^{4-}$ paramagnetic species created by radiation damage in $\text{K}_3[\text{Rh}(\text{CN})_6]$ in KCl host lattice, the poorly resolved perpendicular spectra seems to be a seven-line multiplet, leading to the reported g_{\perp} and A_{\perp} measurements (1). Through CW Q-band power variation measurements, Fig. 1, there was observed an intensity variation of the rightmost lines relative to the others in the multiplet, pointing to the existence of superimposed spectra from different species. As the signal linewidth in CW spectroscopy depends on microwave power (2), it is not possible to achieve good signal cancellation when subtracting spectra taken at different microwave powers. In some cases, however, when overlapping spectra have very different saturation factors, it is possible to achieve separation based on phase changes of the modulated signal relative to the CW modulation (3). On the other hand, time-resolved spectroscopy of overlapping radicals, when spin polarization mechanisms are present, can lead to spectral separation (4).

In field-swept pulsed techniques, linewidth does not depend on the time lag chosen for signal measurement. The separation of species by computer subtraction is thus more effective than in CW spectra.

The techniques employed to influence the relative amplitude of a set of paramagnetic species, using pulsed EPR, are based on differences in spin–spin (T_2) and spin–lattice (T_1) relaxation times among species (5, 6). In this work, we used T_2 -based selection. The shorter- T_2 species predominates in a field-swept–FID-detected EPR spectrum, while longer- T_2 species prevail in echo detection using long time intervals between pulses (τ values). The difference between them, suitably weighted, can be used to cancel distinct T_2 species.

X-band measurements reported in this work were carried out on a Bruker ESP-380e pulsed EPR spectrometer using a dielectric cavity. Experiments at Q band were performed on a Bruker ESP-300 CW EPR spectrometer. An Oxford CF-35 helium-flow temperature controller was used for X- and Q-band experiments. All spectra were taken at 7 K.

In the pulsed techniques, two types of pulse sequence

INTRODUCTION

In a previous paper (1), we reported on the $[\text{Rh}(\text{CN})_6]^{4-}$ complex in a KCl host lattice; this complex is produced by X-ray or 2 MeV electron irradiation on KCl single crystals doped with 0.5% $M \text{K}_3\text{Rh}(\text{CN})_6$. The EPR spectra of this $4d^7$, low-spin, D_{4h} symmetry complex reveal a hyperfine interaction between the unpaired electron occupying a d_{z^2} antibonding orbital and the $I = \frac{1}{2}$ rhodium nucleus, besides a superhyperfine interaction with two equivalent nitrogens of the axial cyanides. The fitting of the EPR spectrum obtained with the external magnetic field perpendicular to the principal symmetry axis of this complex is, however, rather poor, indicating the possibility of overlap of slightly different paramagnetic species.

With the advent of a pulsed EPR spectrometer in our laboratory, selection of species can be tried in field-swept EPR experiments, choosing convenient pulse sequences. Species with different relaxation times can be affected differently, resulting in a set of spectra with a suitable variation of relative signal intensity among the species. Computer subtraction between spectra taken under different conditions, conveniently chosen and weighted, may lead to a signal cancellation of selected species, improving species identification and the measurement of spectral parameters.

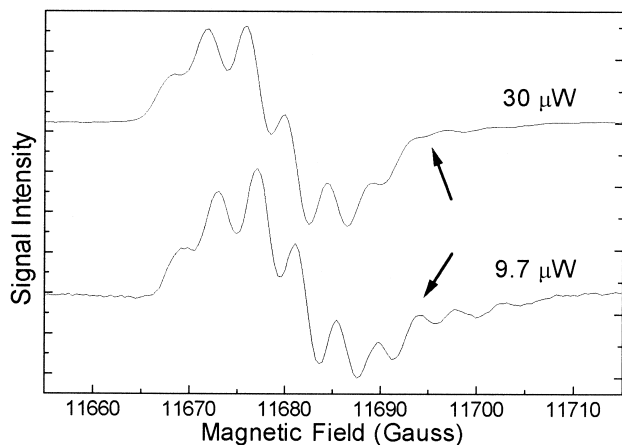


FIG. 1. CW EPR Q-band perpendicular spectra of $[\text{Rh}(\text{CN})_6]^{4-}$ taken at 7 K with 30 and 9.7 μW . The arrows indicate a superimposed species with different relaxation times.

were used. For the FID detection technique, a pulse of 1000 ns was used in each sequence, and the signal intensity was measured at the top of FID, 1264 ns after the beginning of the pulse. For the echo-detection technique, two pulses of 800 ns separated by a τ of 6000 ns were used; the signal intensity was measured at the top of the echo 12400 ns after the beginning of the first pulse.

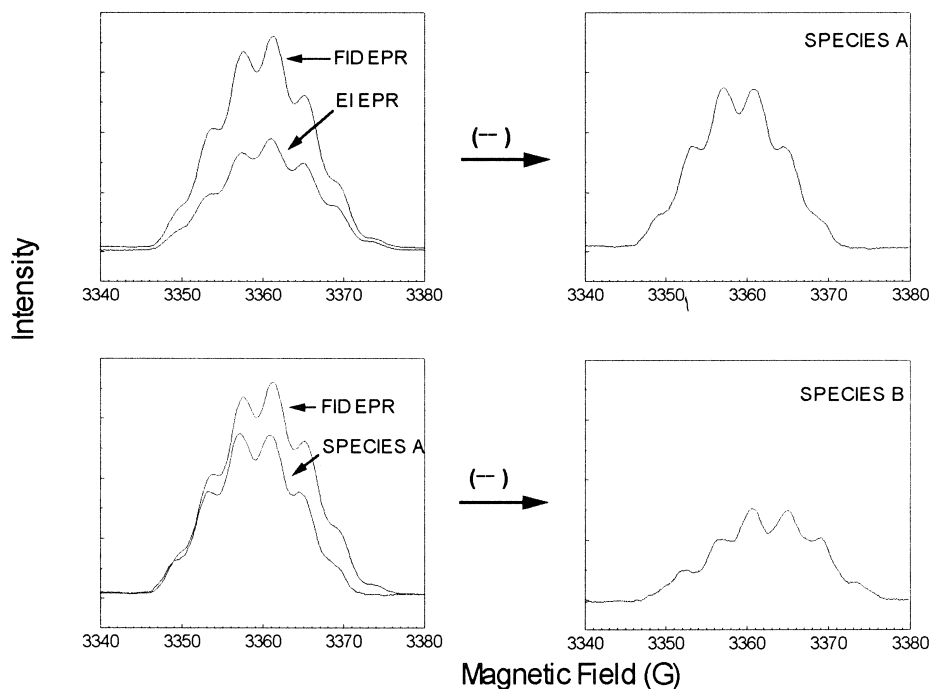


FIG. 2. Steps to the species separation: (1) Weighted subtraction of echo-induced EPR from FID-induced EPR (top left) to get species A (top right); (2) weighted subtraction of species A from FID-induced (bottom left) to get species B (bottom right). The spectra in the figure are not scaled for better visualization.

RESULTS AND DISCUSSION

The T_2 decay measurements were performed using a two-pulse echo sequence with τ variation. The values of 4.2 and 12.5 μs were obtained from fitting with two exponentials. Using the T_2 -based selection technique described above, the perpendicular EPR spectra is decomposed into two six-line multiplets, which we label A and B. The steps of the method are shown in Fig. 2. Each multiplet is fitted independently to a set of spectral parameters. The properly weighted sum is then fitted to the original spectrum. The g values are 2.0825 and 2.0801 for species A and B, respectively. The hyperfine interaction constants A_{\perp}^{N} and A_{\perp}^{Rh} are respectively 3.90 and 4.00 G for species A and 4.20 and 4.50 G for species B. A Gaussian lineshape function was used in the fitting. We also considered inhomogeneous broadening due to unresolved hyperfine splitting with the four equatorial cyanides, A_{equat} . The fitted values of $A_{\text{equat}}^{\text{N}}$ are 0.8 and 0.85 G for species A and B, respectively, using Gaussian lines 0.4 G wide for both species. For simplification, all equatorial nitrogens were considered as magnetically equivalent.

The agreement between experimental and simulated spectra, as shown in Fig. 3, is now very good. The existence of two distinct paramagnetic species is attributed to distinct positions of the charge-compensating positive-ion vacancy.

It must be pointed out that, depending on the way this technique is used, some artifacts may appear. It is well

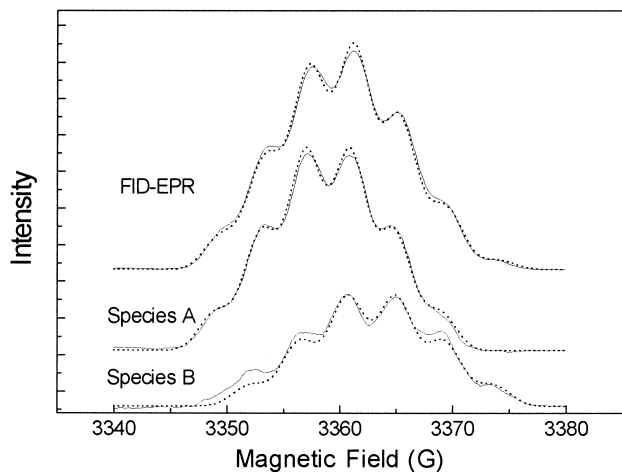


FIG. 3. Fitting to the spectra of separated species A and B (mid and bottom, respectively). Fitting of the FID-induced EPR spectra (top) is a weighted sum of the species A and B fittings. The spectra in the figure are not scaled for better visualization.

known that in FID- and echo-detected field-swept EPR measurements (7), the excitation bandwidth must be kept smaller than the linewidth. This condition can be fulfilled in two ways: using an integrator (5) with a proper integration width (in this case, short- T_2 species can be detected using the spin echo and low τ values) or using soft excitation pulses (in this case, FID detection is necessary to measure short- T_2 species). In the first case, as frequency

band limiting is done during detection, the spectrum energy distribution does not affect the measurement. In the last case, band limiting is done during excitation; if spectral diffusion is effective, a broadening in the spectral energy distribution may happen in the time elapsed until detection, resulting in lineshape distortions and artifacts. In this work, although an integrator was not available and soft pulses were used, artifacts were not observed, very probably because spectral diffusion is negligible due to the low concentration of paramagnetic centers.

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