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Indirect Detection of Internuclear Dipolar Couplings in Paramagnetic Solids

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In the solid state, the distance between pairs of nuclei can be determined from the measurement of the internuclear dipolar coupling between pairs of nuclear spins.[1−6] The possibility for geometric structure determination near unpaired electron spins in paramagnetic molecules and solids is more limited. If the classical dipolar coupling is a good description for the anisotropic hyperfine interaction, it is possible to determine the distance from the paramagnetic site to nearby nuclei.[7−9] However, it is not possible to determine distances between ligand atoms within the immediate vicinity of the paramagnetic electron thereby precluding the possibility for 3D structure determination of the coordination structure for a paramagnetic site in the solid state. In this communication, we introduce a new technique, based on the indirect measurement of the internuclear dipolar coupling, for determining the distance between pairs of nuclei near unpaired electrons in solids, thus demonstrating the possibility for 3D structure determination at paramagnetic sites in solids.

The new experiment is a electron−nuclear−nuclear triple frequency magnetic resonance technique. The basic pulse sequence is shown in Figure 1. The first two rf pulses, $\pi/2-\tau_1-\pi$, at frequency ω_1 generate an NMR spin−echo signal at time $2\tau_1$ from nuclei I_1. Suppose that a second nucleus, I_2, is coupled to I_1 by the internuclear dipole interaction. The first rf π pulse applied at frequency ω_2 re-orients the I_2 nuclear moment. This changes the local field at I_1 at time τ_2. Since the ω_1 refocusing π pulse at τ_1 does not affect the I_2 nucleus, the echo intensity at $2\tau_1$ will be reduced by $[1-\cos(\omega_{dd}\tau_2)]$, where ω_{dd} is the dipolar transition frequency of the I_1-I_2 spin pair. This is the NMR SEDOR experiment. To first order in the dipolar coupling, $\omega_{dd}(\theta) = \pm D/2[3\cos^2(\theta) - 1]$, where θ is the angle between the internuclear vector $\mathbf{r}$ and the direction of the external magnetic field. The magnitude of the dipolar interaction is $D = \gamma_1\gamma_2 h/2\pi r^3$. Suppose now that I_1 and I_2 also experience a local magnetic field arising from the hyperfine interactions A_1 and A_2. When the electron spin relaxation times are long compared to the nuclear Larmor frequency, the NMR frequencies (to first order) are $\omega_\pm(i) = |\omega_n(i) \pm A_i/2|$, where $\omega_n(i) = g_n(i)\beta B_0$ and $\pm$ refers to $m_s = \pm^1/_2$. These hyperfine sublevel transition frequencies can be detected indirectly in the Electron Nuclear DOuble Resonance (ENDOR) experiment.

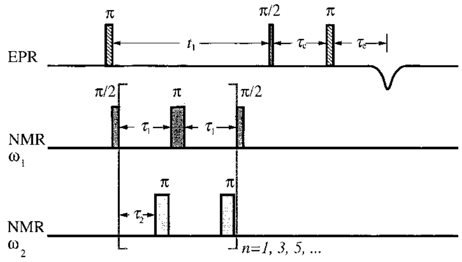

Figure 1. The SEDOR-ENDOR pulse sequence.

For sensitivity enhancement the NMR experiment is preceded by first creating electron−nuclear longitudinal spin order. The most simple pulse sequence to accomplish this is to use a single selective microwave pulse, which is the first microwave pulse in Figure 1. In order to indirectly detect the internuclear dipolar couplings in the presence of large hyperfine interactions, the I_1 coherence is converted to electron−nuclear longitudinal spin order.[11] This is accomplished by placing a $\pi/2$ pulse at frequency ω_1 coincident with the I_1 echo at $2\tau_1$. The electron−nuclear longitudinal spin order is converted to observable electron spin coherence by the second two microwave pulses. The internuclear dipolar coupling is then detected as an oscillation of the intensity of the electron spin−echo signal. These dipolar oscillations are introduced by the two π pulses at frequency ω_2 as indicated in Figure 1.

Since the EPR excitation is selective, a second π pulse must be applied on the ω_2 channel in order to reverse the sublevel polarization transfer created by the first π pulse. This is an important distinction from the usual dipolar dephasing experiments in NMR where the application of rf pulses to observe dipolar oscillations does not coincidentally introduce large frequency shifts. In the present experiments this arises from the hyperfine interactions. Since the preparation and detection periods of the experiment are analogous to the pulsed ENDOR experiment[12,13] while the NMR dipolar dephasing is analogous to the NMR SEDOR experiment,[1,2] we refer to the new experiment as a SEDOR-ENDOR.

The local magnetic field originating from the hyperfine interaction shifts the NMR resonance frequencies of both the I_1 and I_2 nuclei involved so that the SEDOR-ENDOR dipolar dephasing experiment can be applied to both homo- and heteronuclear spin pairs. Additionally, complications from nuclear spin diffusion in the NMR experiments are eliminated in the SEDOR-ENDOR experiment since the nuclei involved are “detuned” from the dipolar reservoir of the bulk nuclei by the large-frequency shifts due to the hyperfine interaction. The hyperfine interaction also mixes the electron and nuclear spin wave functions resulting in a nuclear transition moment which depends on the hyperfine interaction.[10] This is taken into account by measuring the NMR nutation frequencies at each ENDOR transition and adjusting the rf excitation pulses.

We first illustrate some SEDOR-ENDOR experiments on an X-ray irradiated single crystal of malonic acid enriched by 99% ^{13}C in the methylene carbon position. A “nuclear dipole filtered” ENDOR spectrum can be recorded by stepwise incrementing the ω_2 rf pulse on successive pulse sequence iterations in which the coherence for a selected I_1 transition is indirectly observed. This generates a SEDOR edited ENDOR spectrum. A ^{1}H−^{1}H SEDOR edited ENDOR and for comparison a pulsed (Davies) ENDOR spectrum are shown in Figure 2. The ENDOR transitions are assigned to the methylene radical α-proton, carboxyl protons, and protons on neighboring malonic acid molecules in the crystal.[14] The transitions in the edited spectrum originate only from those protons which are in the proximity (as defined by the internuclear dipolar coupling) of the I_1 proton.

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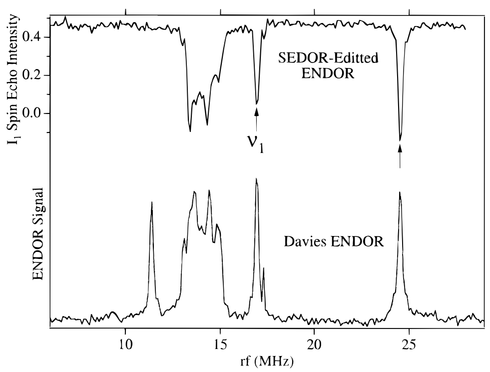

Figure 2. Pulsed (Davies) ENDOR and SEDOR Edited ENDOR of an irradiated crystal of malonic acid, irradiated using a Cu source (40 kV, 30 mA) for 12 h. Experimental parameters: microwave frequency, 9.115 GHz; magnetic field, 3298.7 G; microwave power, 100 W; microwave pulse widths, 0.10, 0.05, 0.10 μs; ω_1 pulse widths, 2.1, 4.2 μs; ω_2 pulse width, 3.5 μs; rf power, 3 kW; $\tau_1 = 75.9$ μs; $\tau_2 = 72.0$ μs; $t_1 = 164.8$ μs. The proton Larmor frequency is 14.052 MHz.

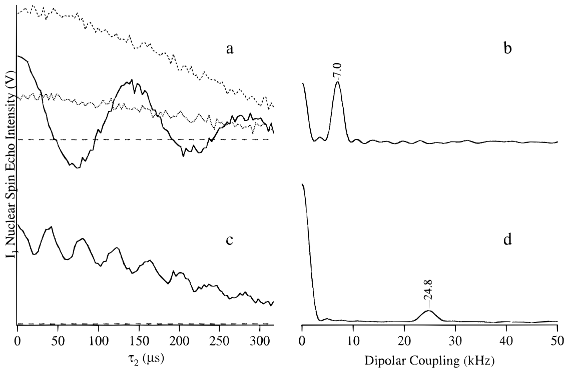

Figure 3. $^1H-^1H$ and $^{13}C-^1H$ SEDOR-ENDOR detected internuclear dipolar dephasing data. The ω_1 and ω_2 frequencies were set as indicated in Figure 2. Other experimental parameters are the same as in Figure 2 except the ω_2 pulse width for (b), which is 6.0 μs. For (a): dashed line, no ω_2 pulses applied; dotted line, one ω_2 pulse applied; solid line, two ω_2 pulses applied. The cosine Fourier transform of the solid line in (a) is shown in (b). Indirectly detected $^1H-^{13}C$ dipolar oscillations observed by SEDOR-ENDOR are shown in (c). The ω_1 and ω_2 frequencies were 16.94 MHz for ^1H and 84.91 MHz for ^{13}C, respectively. The cosine Fourier transform of (c) is shown in (d). The dashed horizontal lines in (a) and (c) indentify the zero levels and provide an indication of the modulation depth.

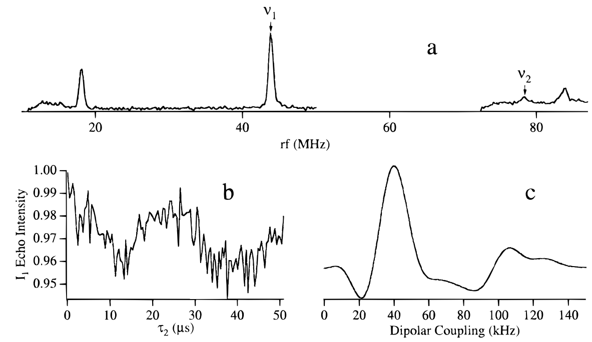

Figure 4. $^{13}C-^1H$ SEDOR-ENDOR detected internuclear dipolar dephasing data for the α-^1H and attached ^{13}C for irradiated malonic acid. The ω_1 and ω_2 frequencies were set to the ^1H and ^{13}C ENDOR transitions as indicated in the ENDOR spectrum in (a). Indirectly detected $^1H-^{13}C$ dipolar oscillations observed by SEDOR-ENDOR are shown in (b) and the cosine Fourier transform of (b) is shown in (c). Experimental parameters are the same as in Figure 2 except for the following: crystal orientation and microwave frequency, 9.120 GHz; magnetic field, 3296.2 G; ω_1 frequency, 43.9 MHz; ω_1 pulse widths, 0.9, 1.8 μs; ω_2 frequency, 78.4 MHz; ω_2 pulse width, 5.2 μs.

$^1H-^1H$ and $^{13}C-^1H$ SEDOR-ENDOR dipolar dephasing data are shown in Figure 3, a and b, respectively. The internuclear dipolar coupling can be indirectly detected by stepwise incrementing on successive pulse sequence iterations the time, τ_2, while keeping all other parameters constant. In order to demonstrate this measurement we show the indirectly detected proton I_1 coherence signal in Figure 3a recorded under three different conditions. When no pulses are applied at ω_2 only the homogeneous dephasing, i.e., the NMR sublevel T_{2n}, of the ENDOR line for the I_1 nucleus is observed.[15] This is illustrated by the dashed line in Figure 3a. The ω_2 ENDOR line is identified by the arrow in Figure 2. When only the first π pulse is applied at ω_2, the sublevel polarization transfer for the I_2 nucleus is indirectly detected. This is analogous to the electron−nuclear−nuclear triple resonance experiment since a signal is only observed when I_2 has a sublevel in common with the I_1 nucleus. This triple-resonance sublevel polarization transfer effect, which is in fact a new pulsed implementation of the General Triple experiment,[16,17] is illustrated by the dotted line in Figure 3a. When the second π pulse is applied at ω_2, the I_1-I_2 dipolar oscillations can be observed as shown by the solid line in Figure 3a. The dipolar couplings between the nuclei can be determined by fitting the time domain data or can be read directly from the spectrum obtained by cosine Fourier transformation.

Bond length determination using the SEDOR-ENDOR experiment is demonstrated in Figure 4. Since the principal values of the anisotropic hyperfine matrix are known for both the α-^1H[17] and attached ^{13}C,[18] the orientation of the crystal can be determined by searching for the Euler angles that correspond to the observed ^1H and ^{13}C ENDOR frequencies.[19] Only the ^1H and ^{13}C ENDOR transitions for the α-^1H and "methylene" ^{13}C are shown in the pulsed ENDOR spectrum of Figure 4a. The lower S/N compared to Figure 3 for the dipolar oscillations in Figure 4b originates from the finite width of the rf pulses. In order to determine an internuclear distance from the measured dipole frequency when the hyperfine interaction is not isotropic, the dipole frequency measured in the laboratory frame of reference must be related to the molecular frame.[20,21] From the measured $^1H-^{13}C$ dipole frequency of 39 kHz, internuclear distances of 1.07 ± 0.02 and 1.14 ± 0.02 Å are calculated. Two possible distances are calculated from the measured dipole frequency because two sets of Euler angles were determined from the measured ^1H and ^{13}C ENDOR frequencies. The uncertainty in the distances mainly arises from the uncertainty in the orientation of the molecular axis determined from the hyperfine splittings. It is also assumed that the principal axes for the ^1H and ^{13}C hyperfine tensors are co-linear.[18,22] Finally, the heteronuclear J_{CH} coupling has been ignored since it is several orders of magnitude smaller than the dipolar coupling.

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