

Three-Spin Solid Effect and the Spin Diffusion Barrier in Amorphous Solids

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The solid effect (SE) is a dynamic nuclear polarization (DNP) mechanism that enhances NMR signals via microwave irradiation when the resonance offset matches the nuclear Larmor frequency, $\Omega_S = \pm\omega_{0I}$. This excites weakly allowed e-n transitions and mediates the polarization-transfer mechanism. In 1976 there was a cursory mention by de Boer et al. of the observation of a higher-order SE with an enhancement of ~ 3 at twice the nuclear Larmor frequency ($\Omega_S = \pm 2\omega_{0I}$). [1] Here we report observation of a remarkably high enhancement, $\varepsilon \sim 170$, at the condition $\Omega_S = \pm 2\omega_{0I}$ using trityl dispersed in a glycerol/water glassy matrix at 0.35 T and 80 K. A theoretical analysis and numerical simulations confirm that the effect is attributable to a three-spin system involving an electron and two nuclei, i.e. a three-spin solid effect (TSSE). The theory implies that the enhancement is sensitive to the electron-nuclear distances r , i.e. the transition probability is proportional to r^{-6} . We have thus exploited this feature to probe the polarization transfer pathway from the radical to the bulk nuclei, particularly the size of the spin diffusion barrier. [2] The model of spin diffusion barrier was proposed to account for the phenomenon that the nuclei close to the radical can experience large shift in precession frequencies and fast relaxation rates, thus quenching the spin diffusion to the farther bulk nuclei. We observed that the perdeuterated Finland trityl radical does not exhibit TSSE-DNP enhancement while the enhancement of normal SE ($\Omega_S = \pm\omega_{0I}$) is only 16% lower compared to that for protonated radical. This indicates that the methyl protons on the radical are responsible for mediating the TSSE-DNP transfer in between the radical and the bulk protons. Hence, the methyl protons must be outside the spin diffusion barrier. We have carried out further EPR studies, DFT calculations, and numerical simulations to confirm that the spin diffusion barrier surrounding the trityl radical in the glassy glycerol–water matrix is less than 6 Å, which is the first value reported for an organic radical in an amorphous solids.

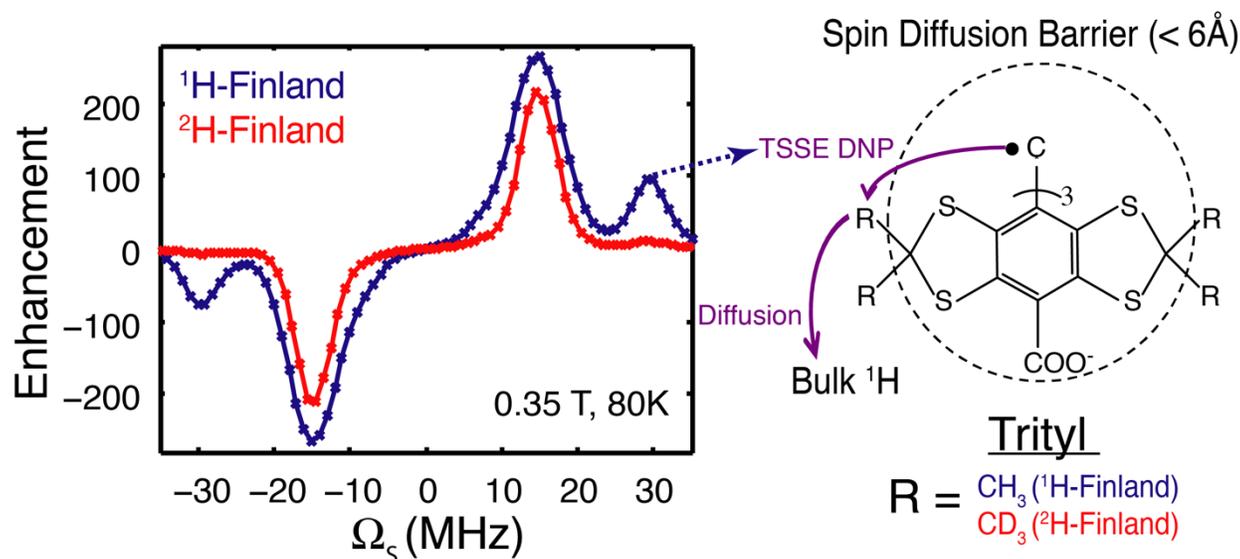


Figure 1. (Left) Field profiles of protonated (blue) and deuterated (red) Finland trityls exhibiting the TSSE DNP, at 0.35 T and 80 K. (Right) Schematic diagram of a spin diffusion barrier surrounding a trityl molecule.

References

- [1] M. Borghini, W. de Boer, and K. Morimoto, Phys. Lett. A **48**, 244 (1974).
- [2] J. P. Wolfe, Phys. Rev. Lett. **31**, 907 (1973).