

ENDOR-induced EPR of Disordered Systems: Application to X-irradiated Sucrose and Alanine

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Many research fields benefit from EPR-derived techniques that enable decomposition of multicomponent spectra. In particular, in the field of radiation research of organic molecules, one often encounters spectra with multiple largely overlapping contributions. ENDOR spectroscopy is particularly well suited for these problems, because it offers species discrimination and high HF resolution. For crystalline $S = \frac{1}{2}$, $I = \frac{1}{2}$ systems, recording of the intensity of particular ENDOR lines as a function of the magnetic field, yields absorption-like EPR spectra of corresponding spectral components. These experiments are known as field-swept ENDOR or ENDOR-induced EPR (EIE). The technique compliments echo-detected EPR really well, because it is effective even if relaxation properties of different species are identical. In this contribution, we examine how the applicability of EIE can be extended to disordered systems.

The proposed method is put to a test in the case of the stable spectrum of X-ray irradiated sucrose. In recent years, its radical composition was established by single crystal EPR and ENDOR studies, reliable models have been devised and verified using periodic density functional theory calculations^{1,2}. It is now known that four distinct radical species explain the entire stable spectrum of X-irradiated sucrose and that one of them exhibits a HF interaction that is isolated in the ENDOR spectrum. By exploiting this feature, we successfully extracted the radical's EPR absorption spectrum from a multicomponent powder pattern, demonstrating that EIE can be useful in disordered systems. To discuss the potential limitations of the method, we examine the case of X-ray irradiated alanine, which is inherently challenging for EIE due to peculiar cross relaxation mechanisms.

References.

1. H. De Cooman, J. Keysaby, J. Kusakovskij, A. Van Yperen-De Deyne, M. Waroquier, F. Callens, and H. Vrielinck, *J. Phys. Chem. B* 2013, 117, 7169-7178.
2. J. Kusakovskij, I. Caretti, S. Van Doorslaer, F. Callens, and H. Vrielinck. *PCCP*, 2016, 18, 10983-10991.