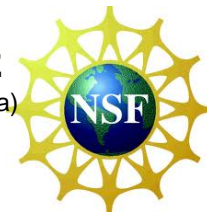




Hydrogen Bonding of Tryptophan Radicals Revealed by EPR at 700 GHz

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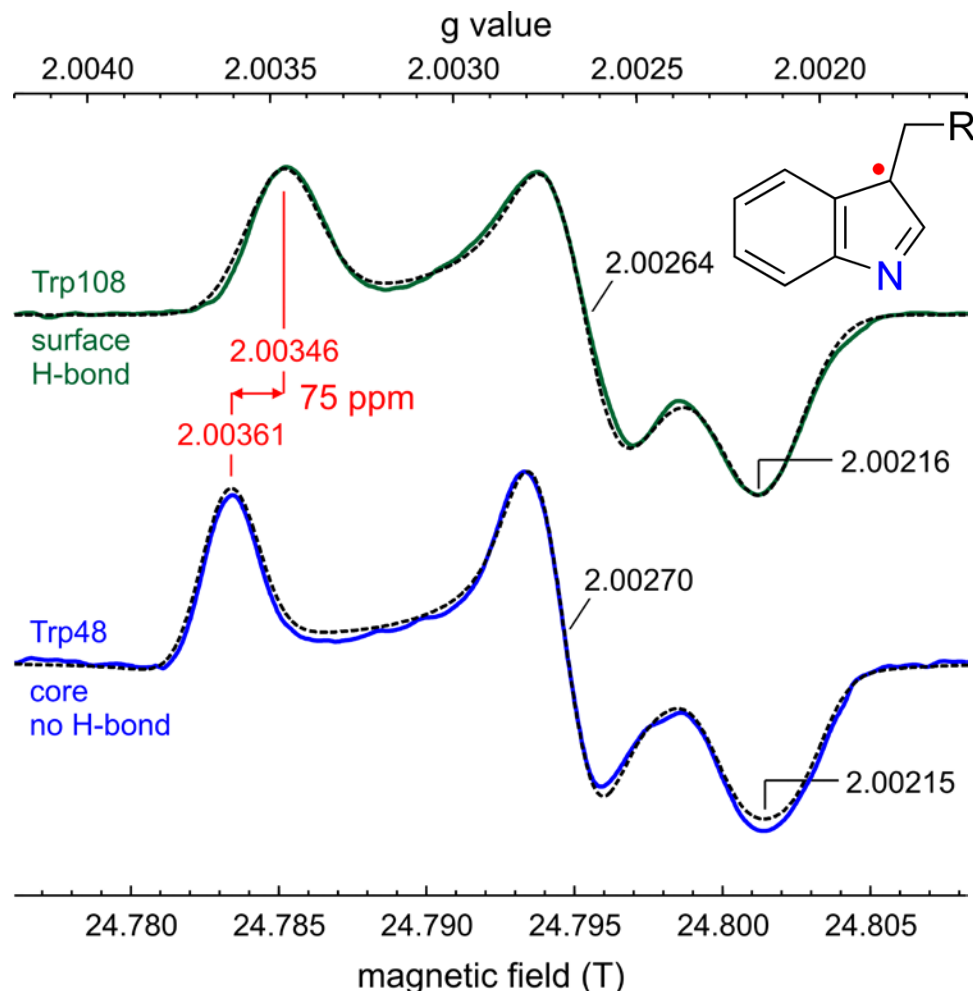
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Proteins catalyze many important biological processes that require the transfer of electrons, among them the enzymatic oxidation and digestion of biomass. These processes are enabled by the protein-bound redox-active amino acid tryptophan (Trp), which is oxidized intermittently. The protein nanoenvironment around Trp tunes its oxidation power but the mechanism is not understood.

The magnetic parameters of oxidized Trp, particularly the g tensor, are sensitive reporters of the protein environment. Using the worldwide unique capabilities of the NHMFL to perform high-resolution EPR at 700 GHz and 25 T, we were able to resolve for the first time the g tensors of two different Trp radicals, one located in the core of the protein azurin, and one on the surface. The g tensors are different and characterize the different nanoenvironments: the surface radical is hydrogen bonded, whereas the core radical is not.

These results advance our understanding of redox-active Trp in proteins, which will support the design of engineered proteins that are more efficient digestors of recalcitrant biomass such as lignin.



Facilities: EMR and DC facility, high-homogeneity 25T Keck magnet.

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