High-Field EPR Studies of Tryptophan-Based Radicals

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Introduction

A novel tryptophan-based, di-radical intermediate has been captured in preMADH as a result of oxidation by the *bis*-Fe(IV) MauG[1] during catalysis in our previous study using high-field EPR spectroscopy.[2] The di-radical intermediate consists of a cationic tryptophan radical and a cationic 7-hydroxy-Trp radical. The edge-to-edge distance between the two Trp residues is ~3 Å.[3] However, the spatial proximity of the Trp residues does not necessitate strong coupling between these radicals. This project is an attempt to probe the radical properties of the cationic 7-hydroxy-Trp radical with HFEPR spectroscopy. The information obtained from this study will be useful for evaluating how the spectral features and chemical properties of the individual radical species are altered when they are caught in a pair with close proximity.

Experimental

Photochemical methods were used to generate radical species on several model compounds, including Trp and 7-OH-Trp, followed by spectroscopic characterizations. We have used photoexcitation by a laser in conjunction with a photo-catalyst to initiate radical formation on Trp. HFEPR study at the MagLab using the broadband transmission spectrometer and the 15/17 T superconducting magnet followed to resolve the *g*-tensors of several model radicals.

Results and Discussion

Representative spectra of two tryptophan derivatives, 5-methoxy and 5-fluorotryptophan, and spectral simulations are shown in Fig. 1, left and right, respectively. We have been able to generate and measure by HFEPR radicals of 6 different tryptophan based compounds. This has allowed for the determination of the principal *g*-values for some compounds, like 5-methoxytryptophan, Fig. 1, left panel. Unfortunately, we were not able to resolve all of the principal *g*-values for all of the compounds of interest at 14.5 T, as shown in Fig. 1, right panel for 5-flurotryptophan.

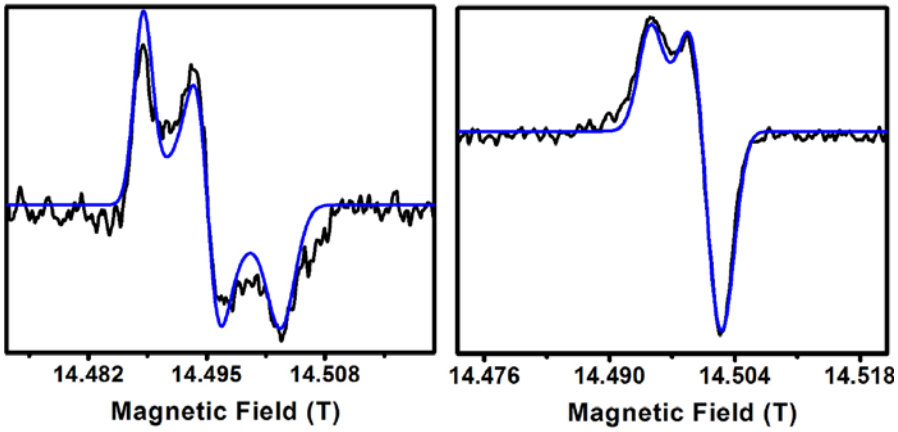

Fig. 1 High-field EPR spectra of Trp analogues. HFEPR spectrum of 5-methoxy-tryptophan (average of 30 scans), left, and 5-fluorotryptophan (average of 20 scans), right, at 406.4 GHz and 5 K. The data is the black trace, and the simulated spectrum is the blue trace.

Conclusions

Preliminary study on the model radicals suggests that HFEPR is a pertinent tool to characterize Trp-derived radicals and the information obtained will be helpful for determining the spin density distributions on the radicals under the influence of electrostatic repulsion.

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