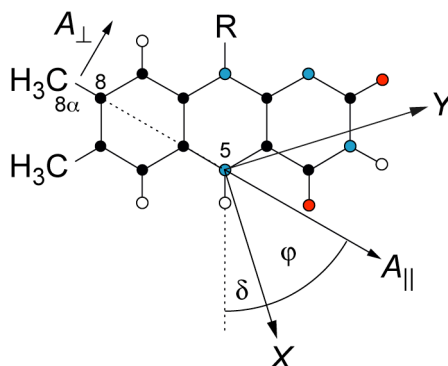


High-Field/High-Frequency EPR and ENDOR Examinations of Photoactive Flavin Radicals

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The \mathbf{g} -matrix and the hyperfine couplings of redox-active proteins carrying a non-covalently bound flavin chromophore in the one-electron reduced semiquinone form have been studied by high-field/high-frequency pulsed and continuous-wave EPR and ENDOR spectroscopies. For the first time, the orientation of the principal axes of \mathbf{g} with respect to the molecular frame of the isoalloxazine moiety of protein-bound flavin has been unambiguously determined (see Figure) using 360-GHz EPR [1] and pulsed W-band ENDOR [2]. Detailed information on the electronic structure of flavin cofactors is furthermore obtained by exploiting site-specific isotope-labeling (^2H , ^{13}C , ^{15}N) in conjunction with multi-frequency ENDOR experiments [3, 4] and density-functional theory calculations [5].



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