Density Functional Theory Analysis of the Active Site of Class-I Ribonucleotide Reductase Intermediate X: Connecting Structure with Spectroscopy

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Several models for the active site structure of the iron-oxo dimer center in ribonucleotide reductase intermediate X have been compared using broken-symmetry density functional theory calculations. The longer range environment beyond the active site was treated by a conductor like solvation model (COSMO). Calculated properties include optimized geometries, energies, Fe Mössbauer properties, ^{57}Fe, ^{1}H, and ^{17}O hyperfine tensors, and Fe(IV) d-d transition energies for comparison with Mössbauer, ENDOR, and MCD experimental data. Our proposed Fe(III)Fe(IV) structure involves a di-oxo bridge, and therefore differs from previous models proposed from direct analysis of ENDOR and MCD spectra. Also, our calculated geometries for all reasonable models give an Fe-Fe distance significantly longer than the 2.5 Å distance found from EXAFS data analysis. We thank NIH for their financial support of this research (GM43278).