Substrate Specificity and Active Site Conformations of Ribulose-1,5-bisphosphate

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Poor substrate specificity is a characteristic of the ribulose-1,5-bisphosphate carboxylase/oxygenase (RuBisCO) enzyme, which catalyzes the carbon addition step of the Calvin cycle. Despite its importance to autotrophic life, the enzyme cannot efficiently differentiate between singlet-state CO_2 and triplet-state O_2. Coupling between conformations of the enediol catalytic intermediate[1] and its electronic spin state has been proposed as a mechanism for this lack of specificity[2]. Here, constrained optimizations were performed on 1,2-dihydroxyethylene—a model for the enediol intermediate—and a 2D minimum energy surface for the singlet and triplet electronic states was mapped on the dihedral and pyramidal coordinates (Figure 1). This surface is generated in a series of environments—including gas phase, solvation in water, and complexation with divalent Mg—to model the influence of the enzyme active site on the electronic spin state of the catalytic intermediate.

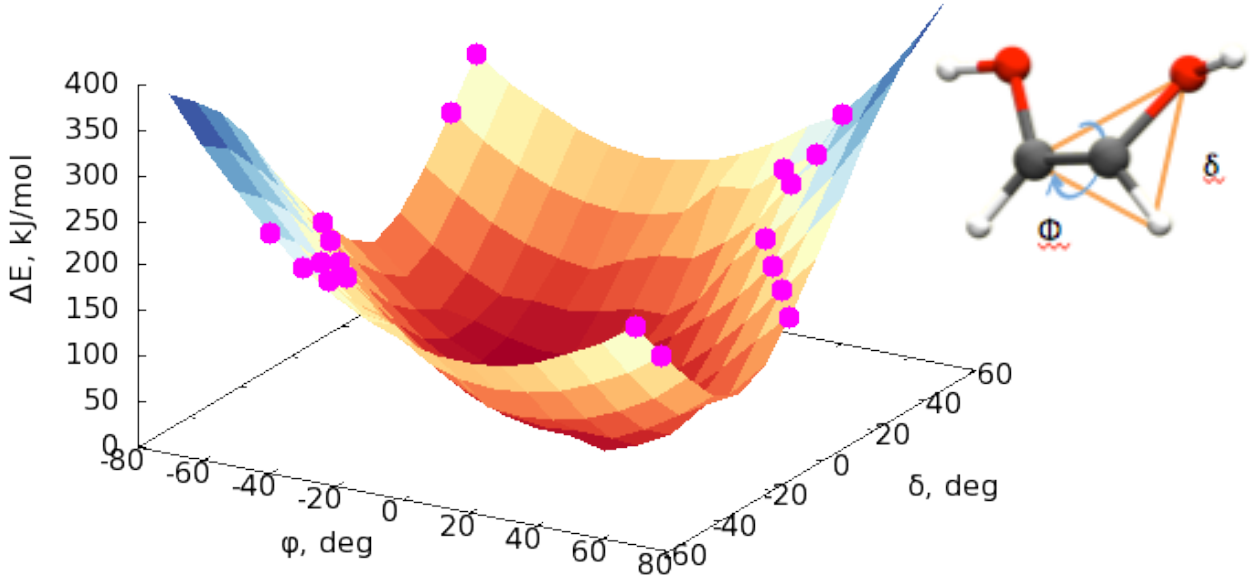

Figure 1. The minimum singlet electronic state of 1,2-dihydroxyethylene on the Φ and δ coordinates as shown on the molecule above. Magenta dots represent intersections with the triplet energy state. Thermal excitation to configurations degenerate with the triplet state must overcome a 200 kJ/mol potential energy barrier. All calculations use the Hartree-Fock method and the 6-31G* basis set.

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