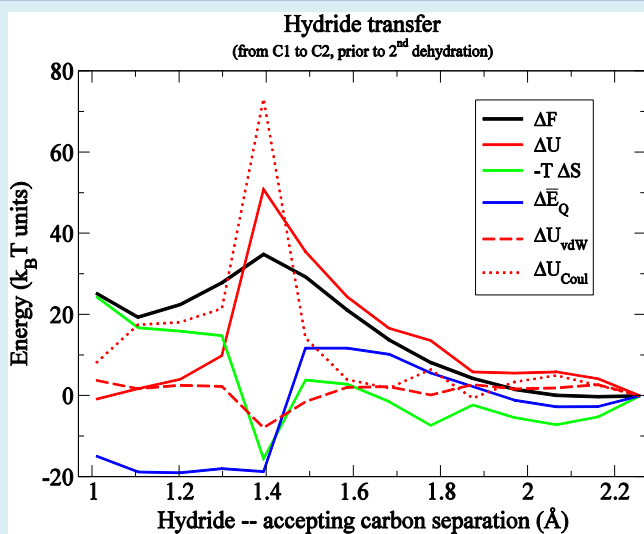


Conversion of Biomass to Fuels and Chemicals – A Theoretical Study of the Dehydration of Fructose to HMF

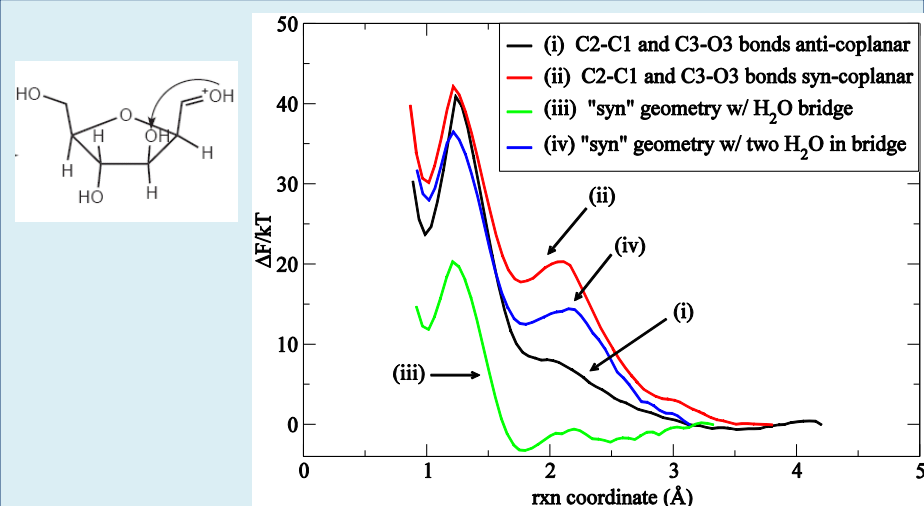
- First-principles catalytic studies usually done in vacuum
- Solvent dynamics too important to neglect: **friction, solvation and concomitant entropic effects, participation in the mechanism**, etc.
- **A new approach to computational catalysis**¹
- We employ for the first time multiscale (QM/MM) MD free energy simulations to study these reactions²
 - Fructose treated quantum mechanically (QM); Solvent treated with Molecular Mechanics force field (MM)
 - Biased sampling to capture rare events
 - We compute **free energy** profiles for all elementary steps

Effects of Solvent Dynamics



Solvent re-organization responsible for the high free energy barrier

Solvent Participates in Reaction



Water-mediated proton transfer lowers the barrier by 14 kcal/mol

Key Findings on Fructose's Dehydration Mechanism

- Considerable energetic cost to remove the first two waters and the rate of re-hydration is substantial
- Reaction proceeds via hydride and proton transfers
- Rate-limiting step is the C5 to C4 hydride transfer prior to the 3rd water loss
- Solvent re-organization responsible for high activation free energy during hydride transfer steps
- Water accelerates proton transfer, but not in all cases