Inverted Region in Electrochemical Reduction of CO_2 Induced by Potential-dependent Pauli Repulsion

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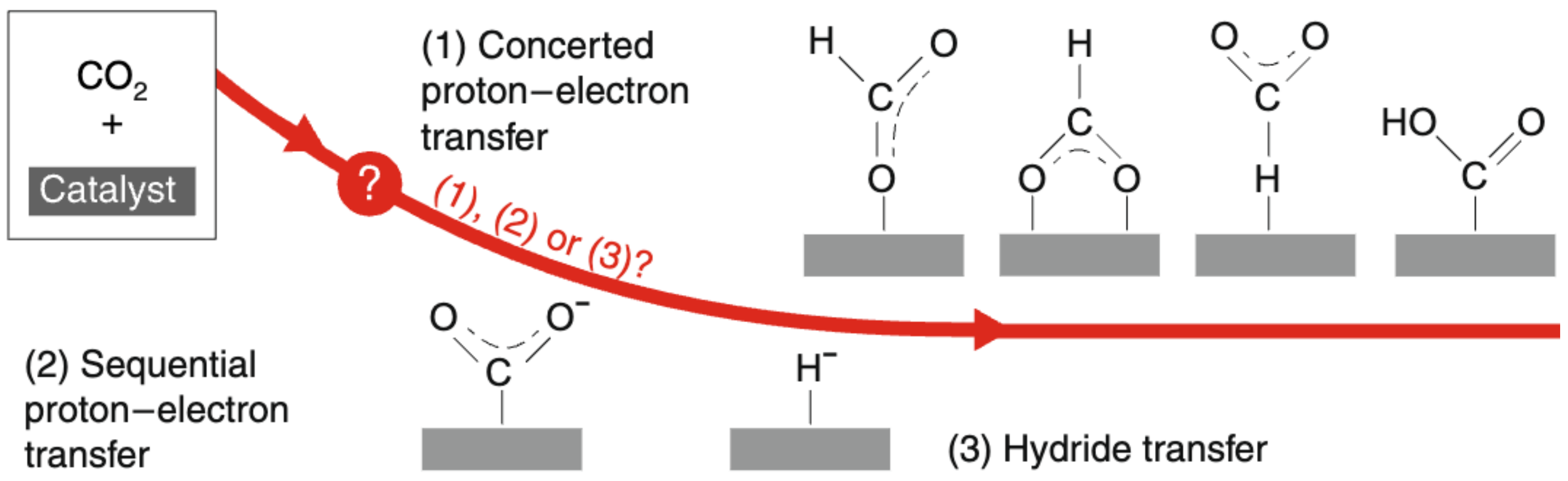
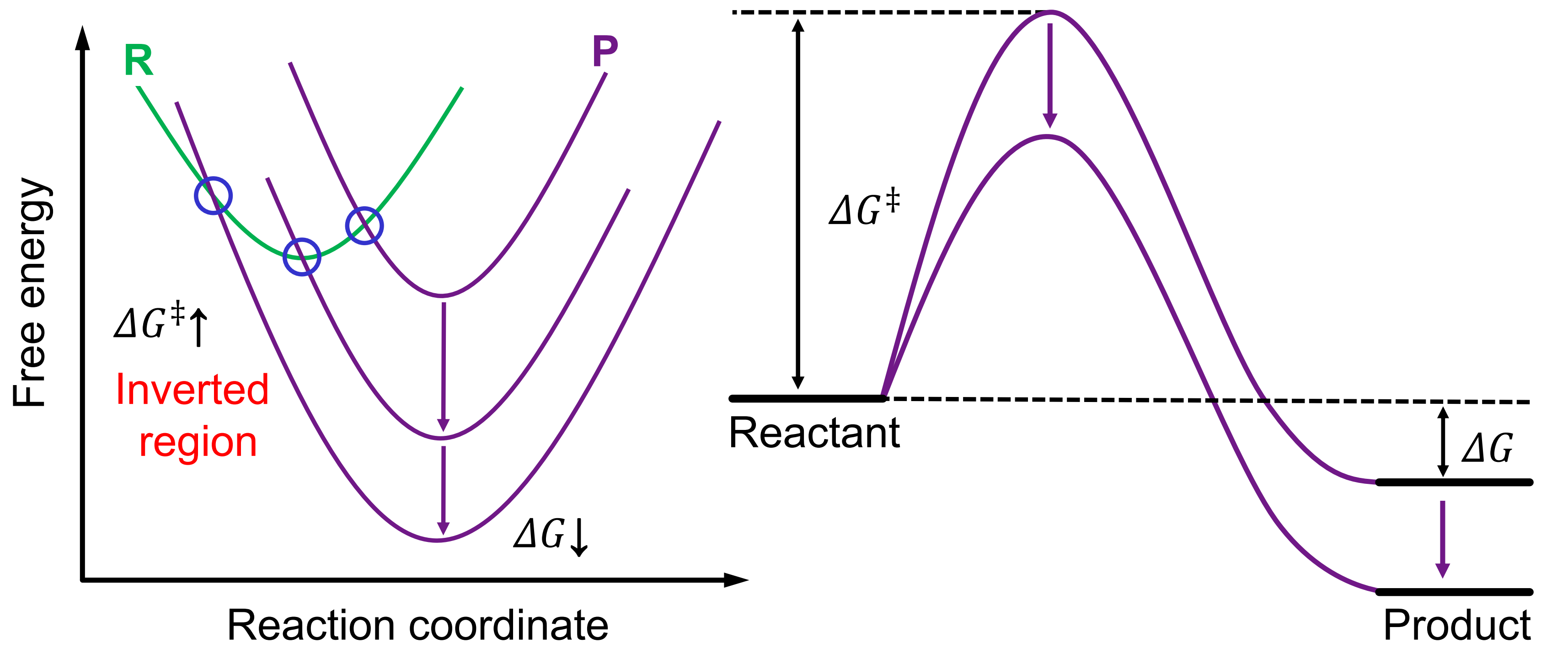
Introduction

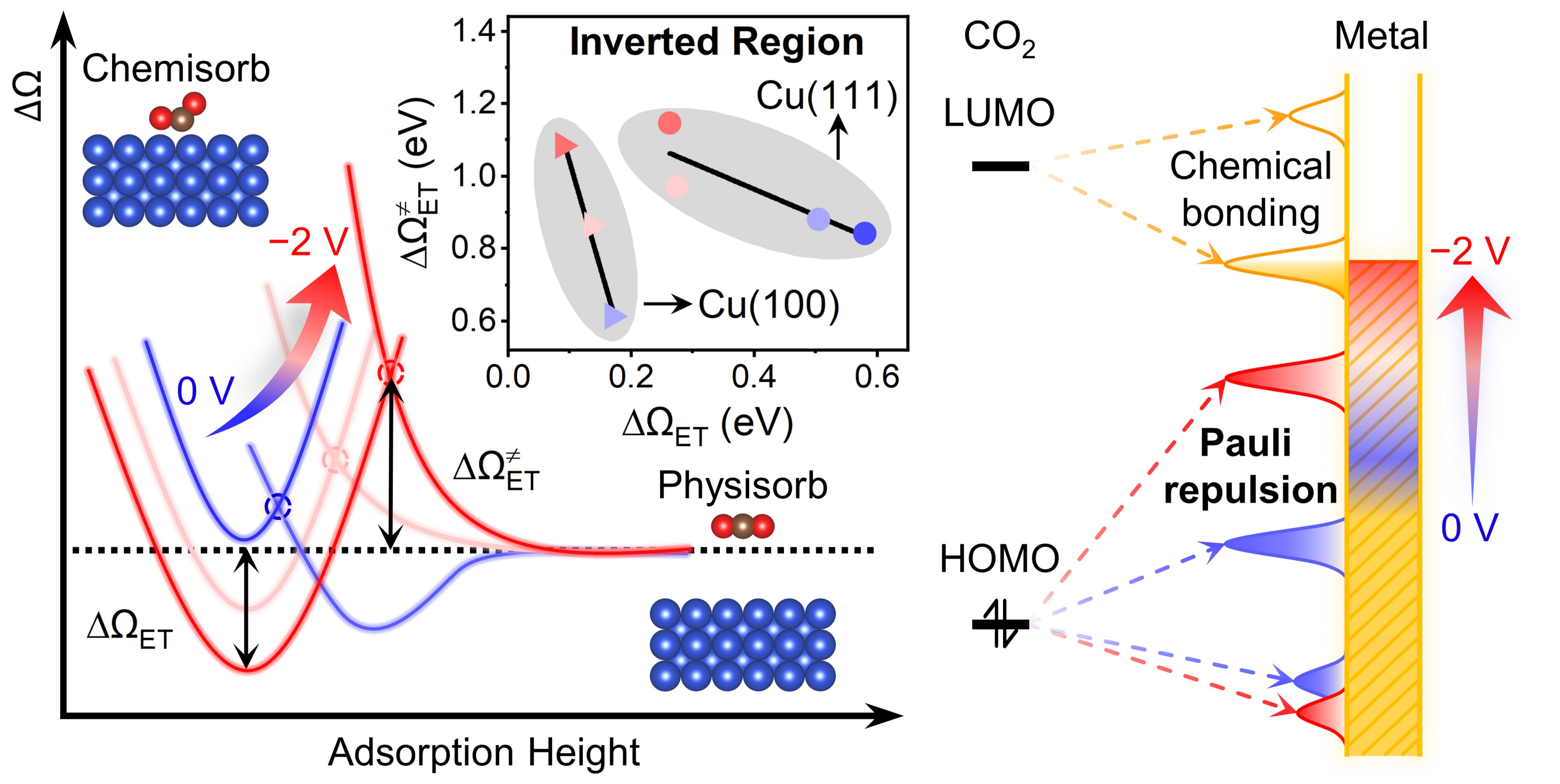
CO_2 activation: SEPT vs. CPET



Electron transfer kinetics: Marcus theory vs. BEP relation



Abstract



- The CO_2 activation mechanism in eCO_2RR varies with *U*
- The barrier of the electron-transfer(ET) step in the SEPT mechanism exhibits an inverted region as *U* decrease

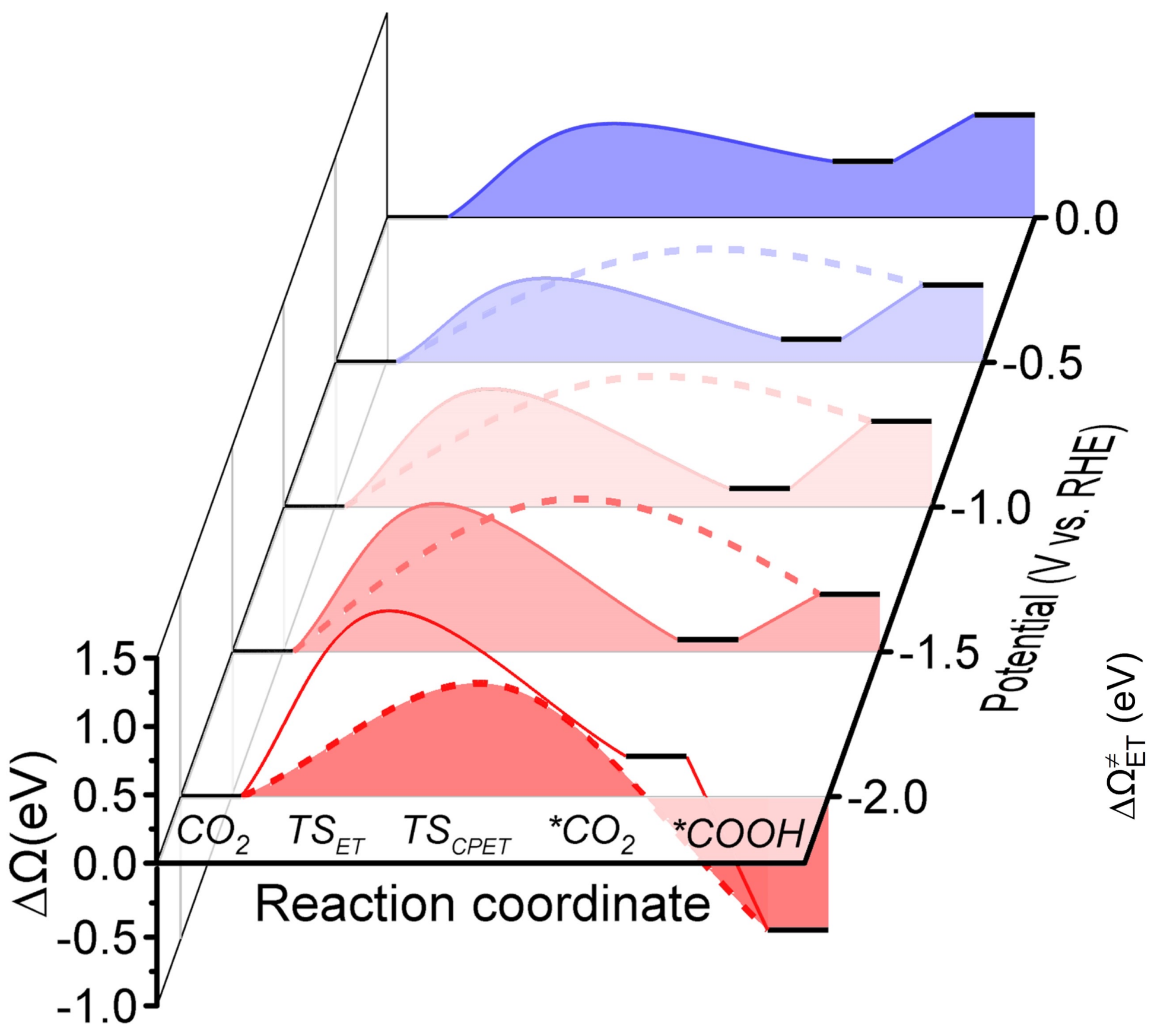
Methods

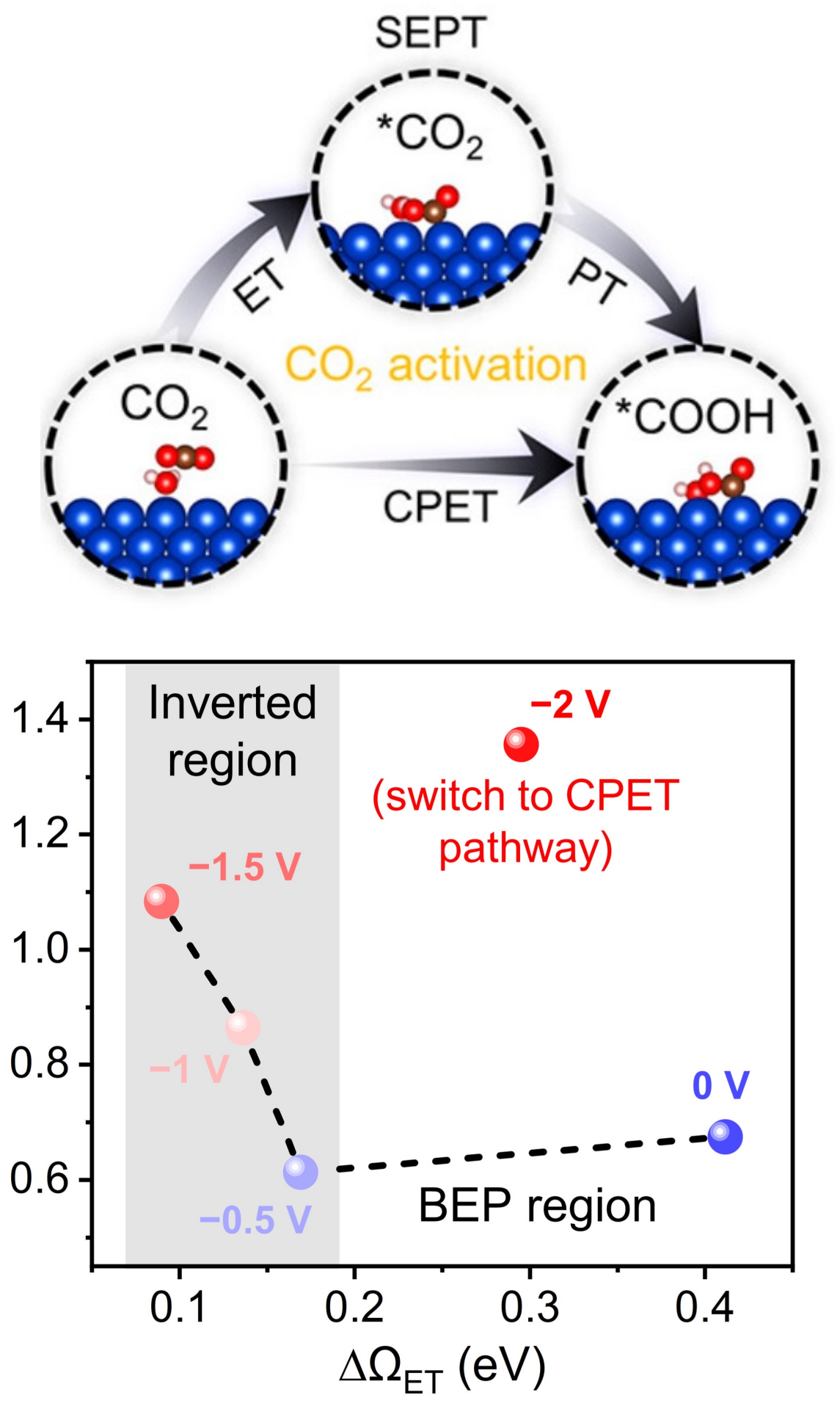
- Grand canonical density functional theory (GC-DFT)

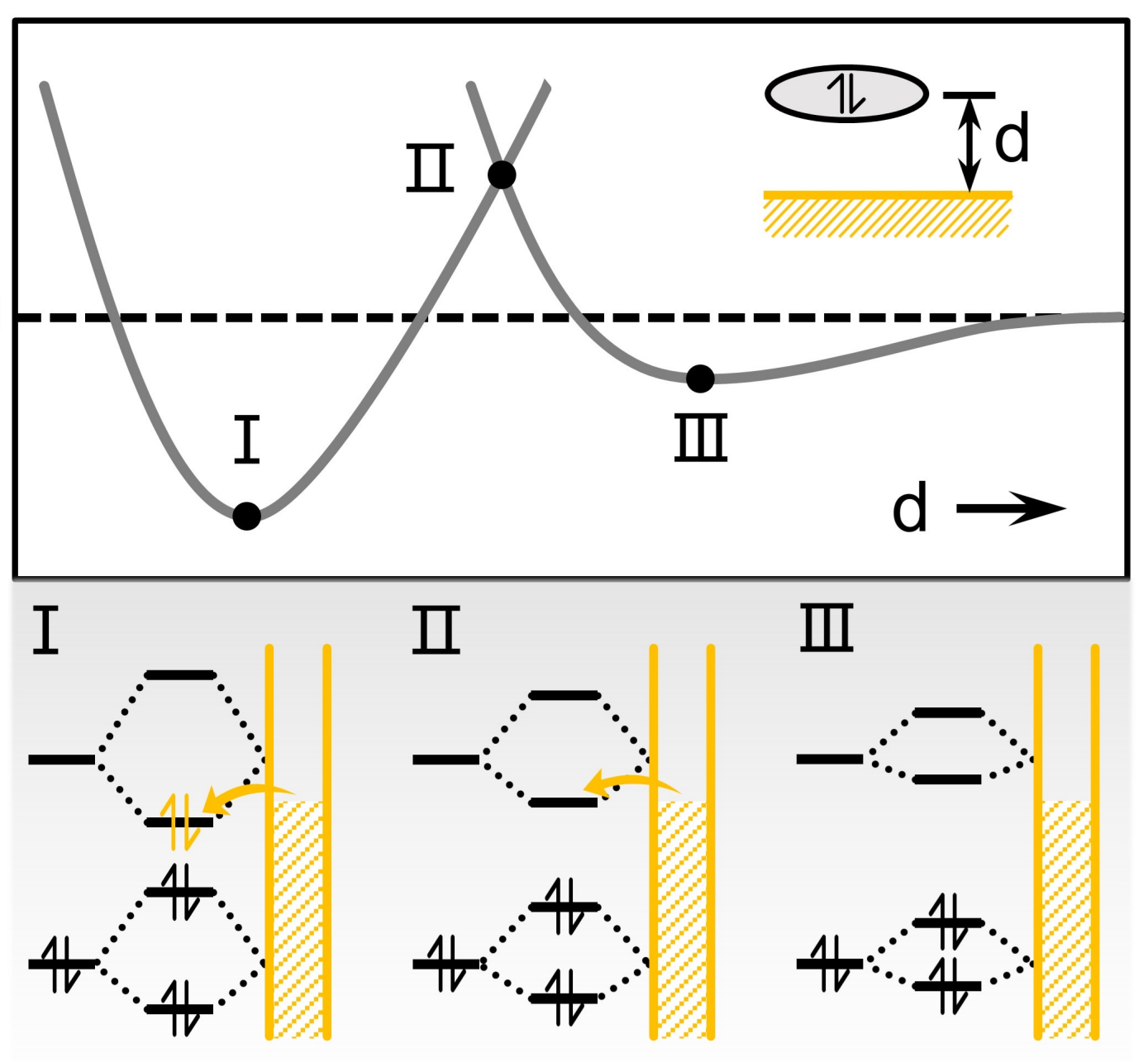
ASE - Atomic Simulation Environment

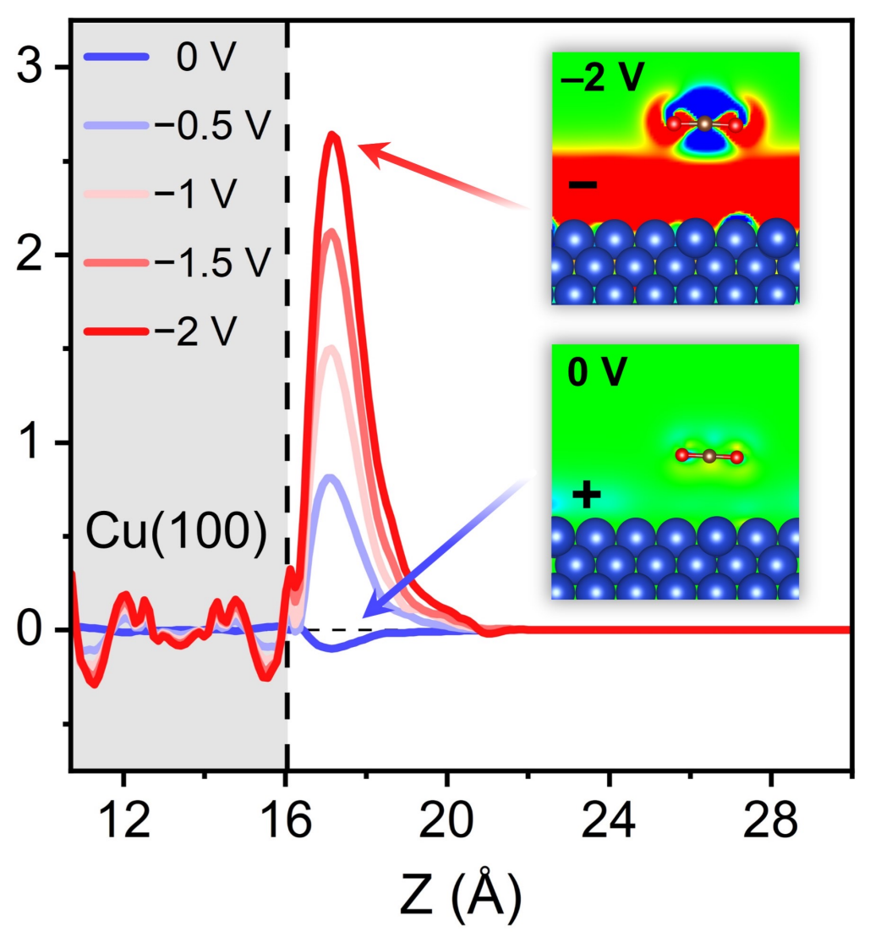
JDFTx - software for constant-potential modeling

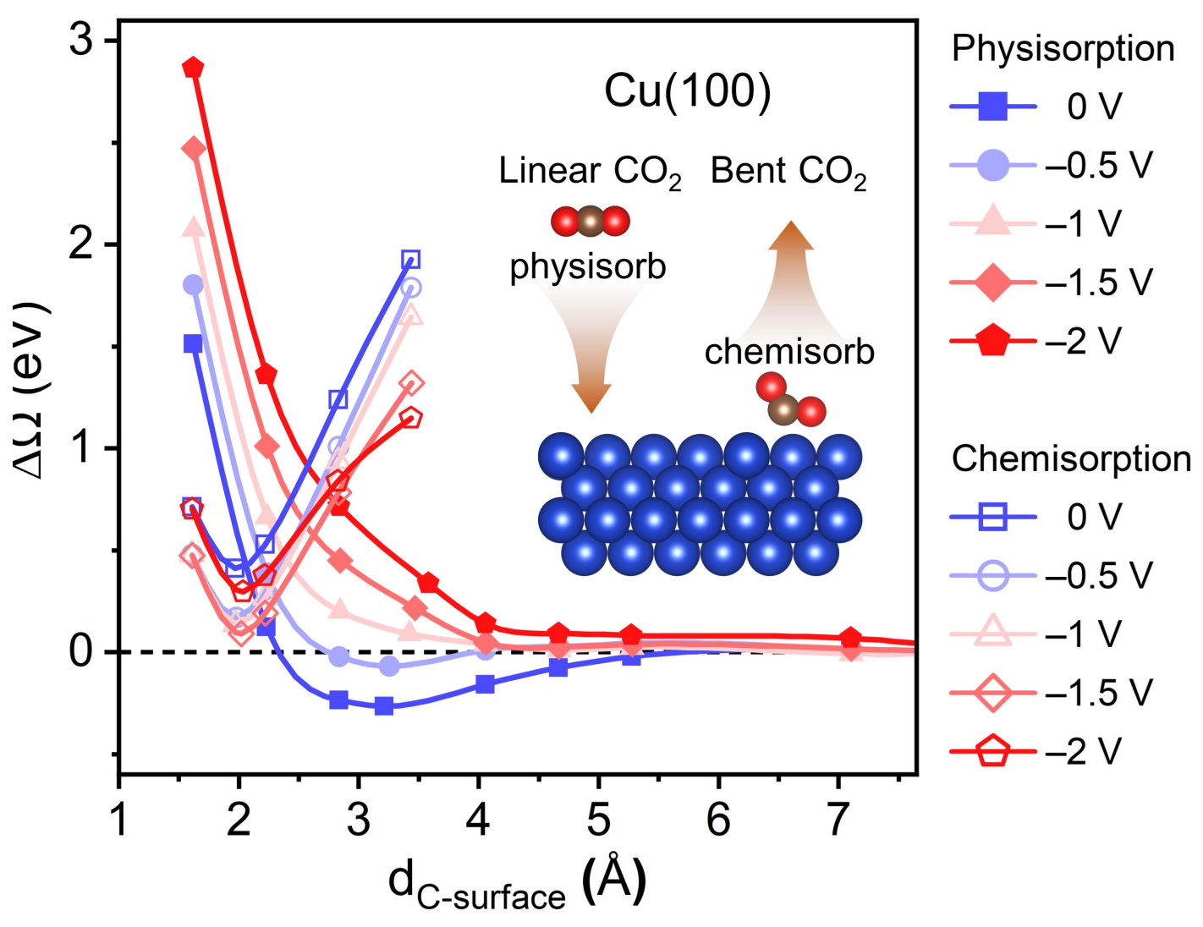
Results & Discussion











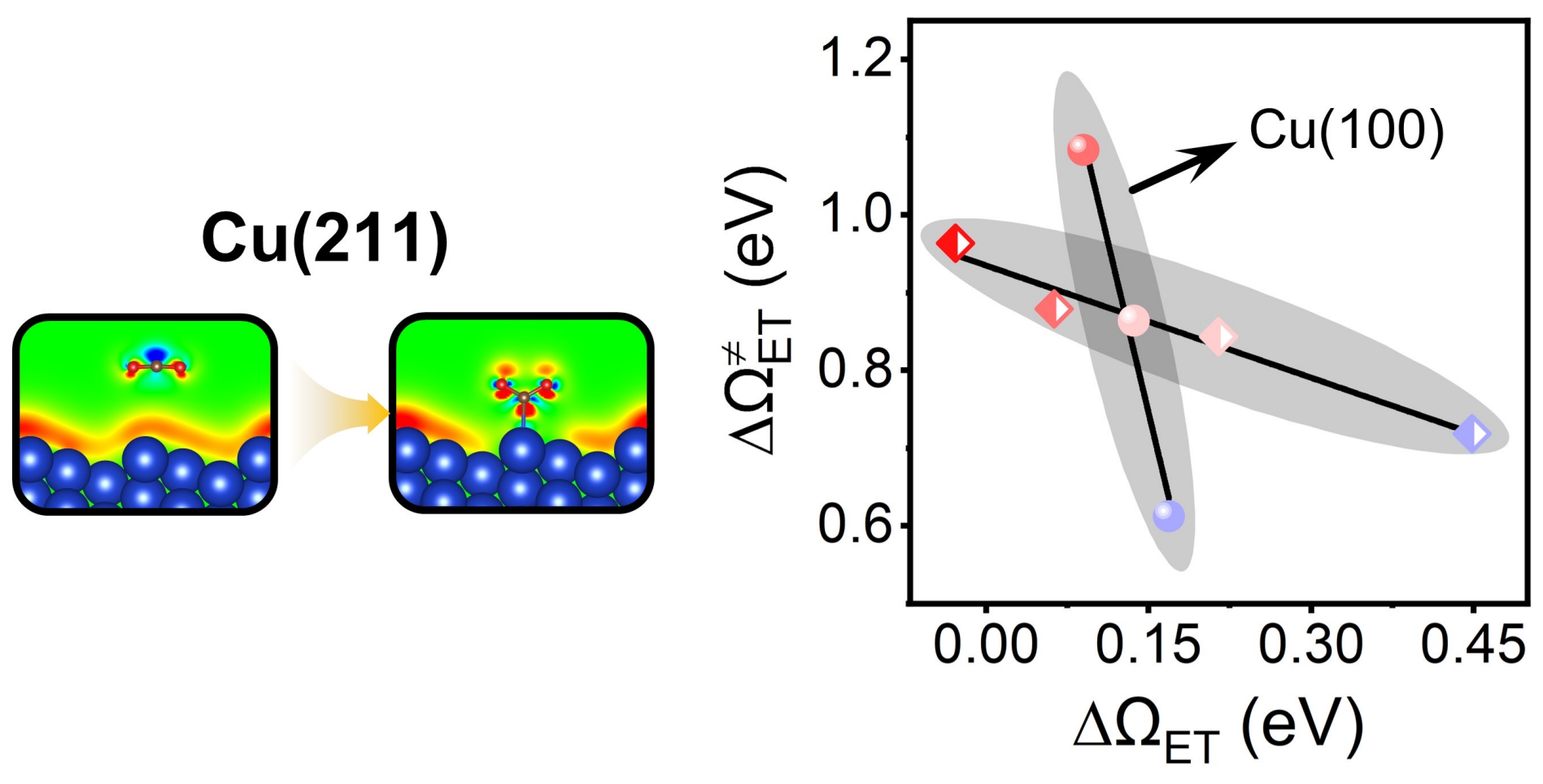
- *U* > −1.5 V, SEPT → CPET
- −0.5 V ~ −1.5 V, a kinetic inverted region of ET step appears in SEPT pathway

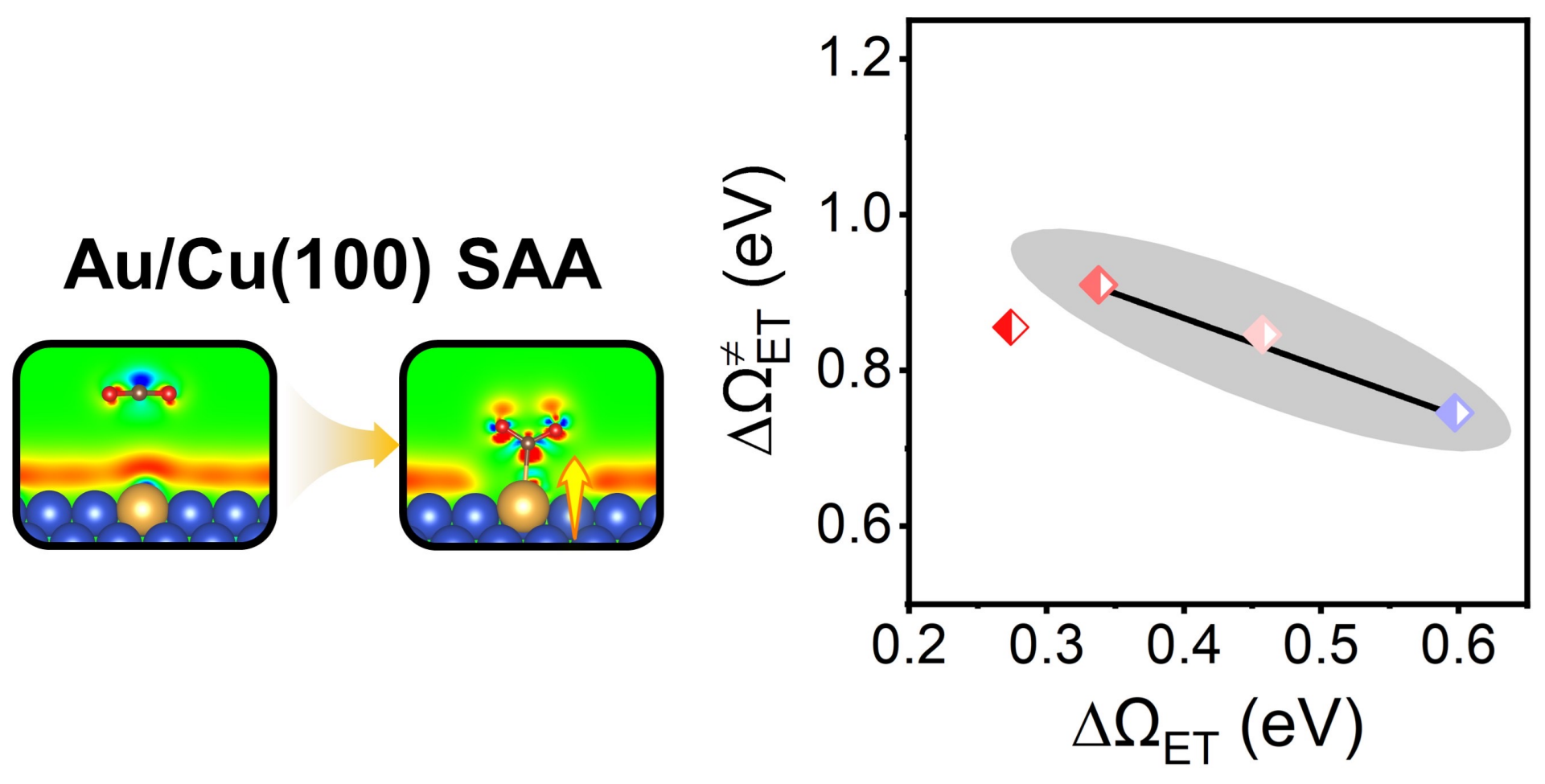
- LUMO-Metal interaction → chemical bonding
- HOMO-Metal interaction → Pauli repulsion

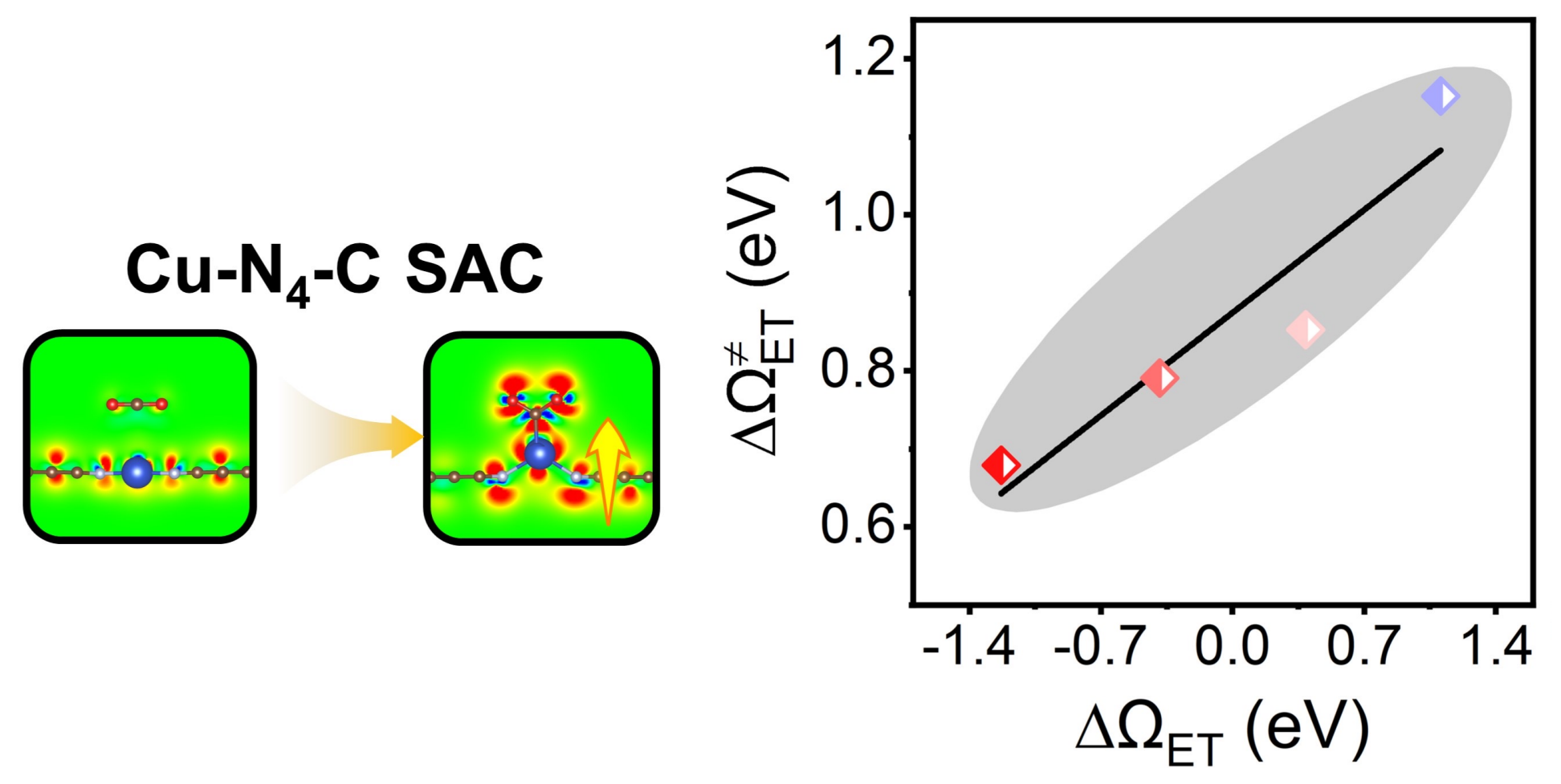
- Accumulating electron density at Cu surface that extends more outward from 0 V to −2 V
- The physisorption PEC rises → the crossing of two PECs, i.e., the barrier for the transition, to rise rapidly as *U* decrease

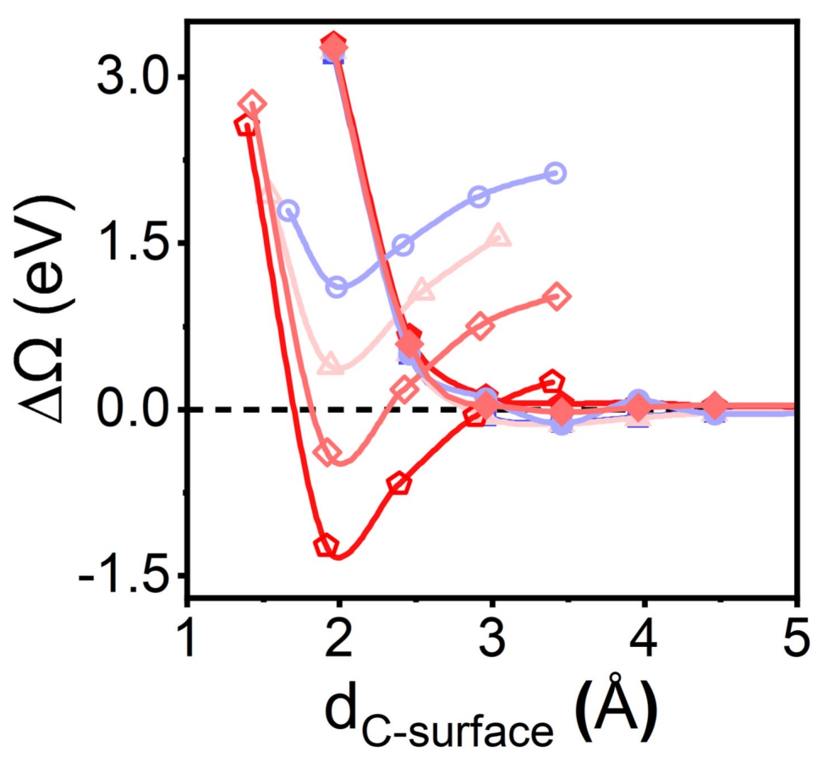
- Catalyst design

1. Increasing surface roughness
2. Increasing the coordination flexibility of the active sites
3. a substrate with less charging









Conclusion

- CO_2 activation mechanism in eCO_2RR: SEPT mechanism at the common working *U* → CPET mechanism at the highly negative *U*.
- The inverted region originates from the rapid rising of Pauli repulsion in the physisorption PEC as *U* decrease.
- Effective designs of electrocatalysts can suppress the adverse effect of Pauli repulsion on the kinetics of CO_2 activation, it is likely to be generally applicable to the electrochemical reduction reactions of other closed-shell molecules including H_2O, CO, and N_2.

1. L. Liu, H. Xiao. *J. Am. Chem. Soc.* **145**, 14267–14275 (2023).
2. M. T. M. Koper et al. *Nat. Energy* **4**, 732–745 (2019)