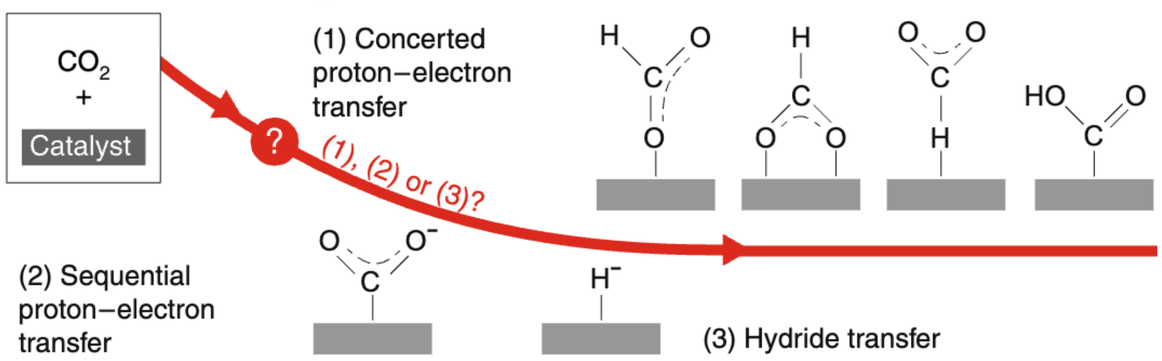
清華大學化学系
Department of Chemistry, Tsinghua University

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

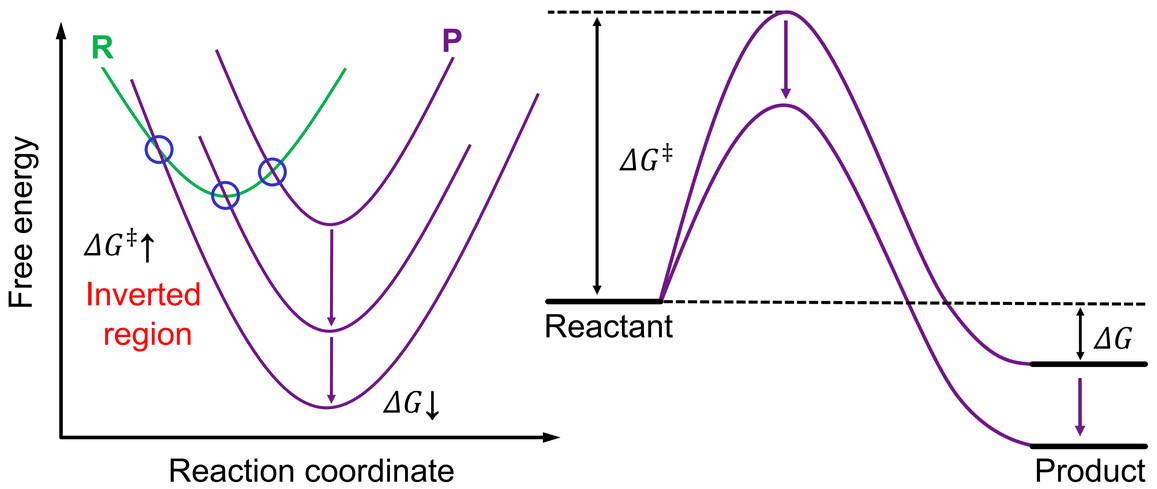
Leyu Liu, Hai Xiao*
Department of Chemistry, Tsinghua University, Beijing 100084 Email:liu-ly19@mails.tsinghua.edu.cn

Introduction

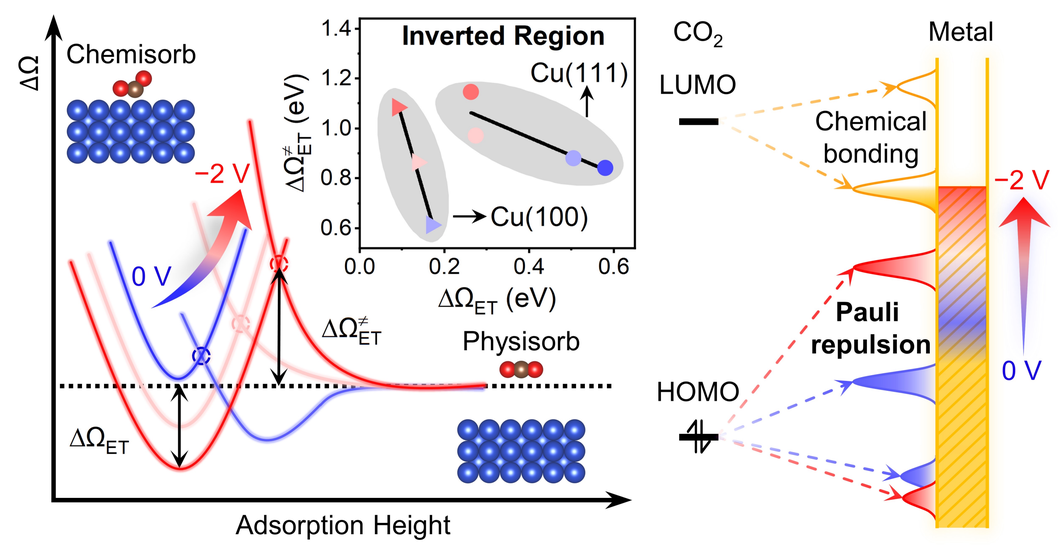
CO_2 activation: SEPT vs. CPET



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 step in the SEPT mechanism exhibits an inverted region as *U* decrease

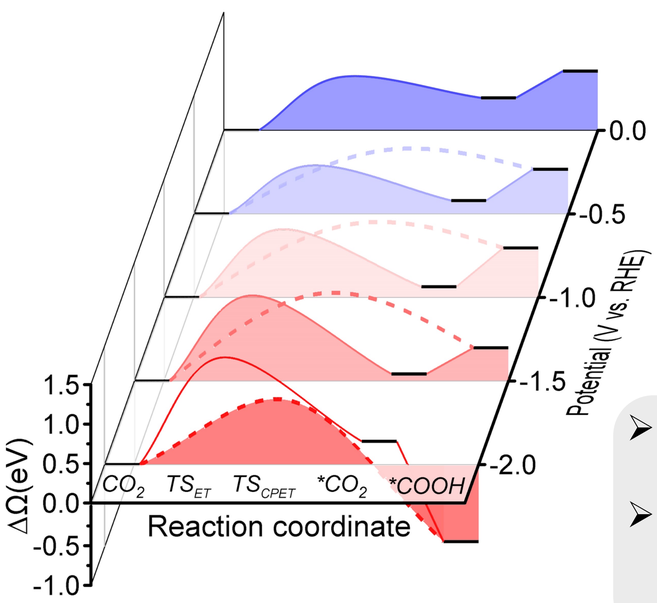
Methods

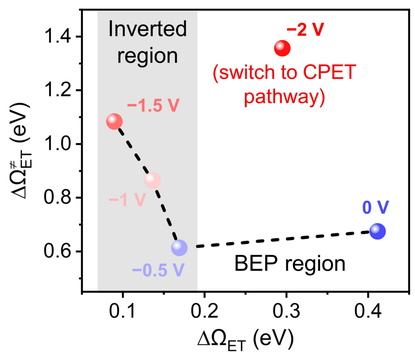
- Grand canonical density functional theory (GC-DFT)

ASE - Atomic Simulation Environment

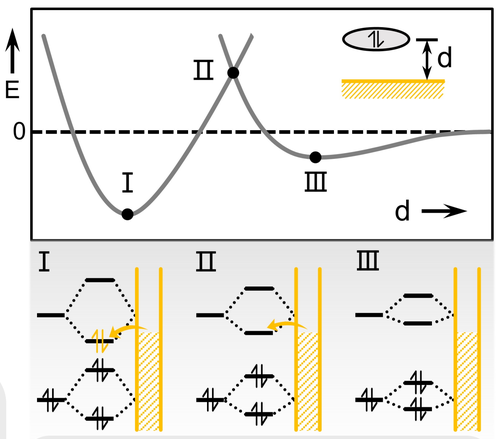
JDFTx - software for joint density-functional theory

Results & Discussion

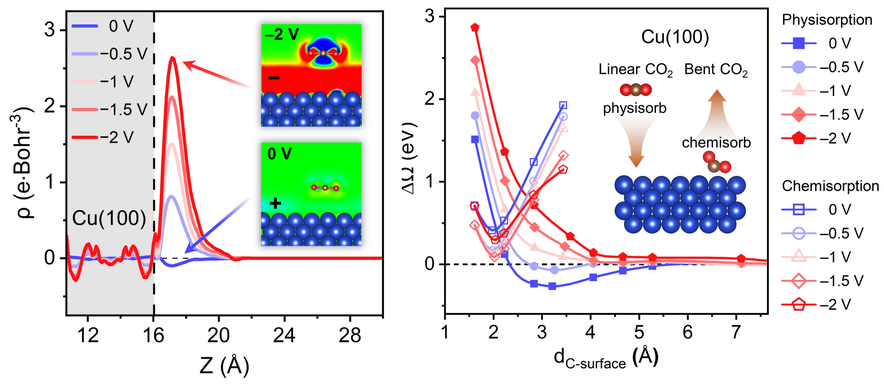




- *U* > −1.5 V, SEPT → CPET
- −0.5 V ~ −1.5 V, an inverted region appears in SEPT pathway



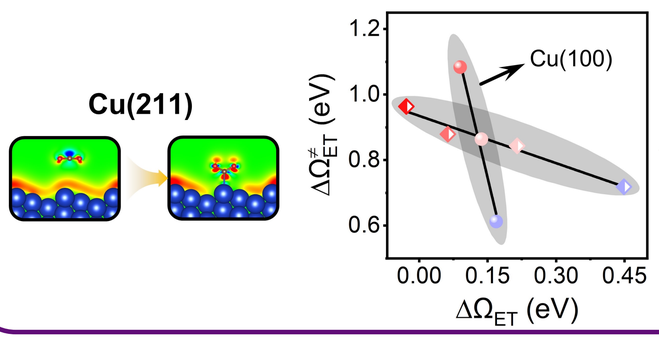
- LUMO-Metal → bonding
- HOMO-Metal → Pauli repulsion



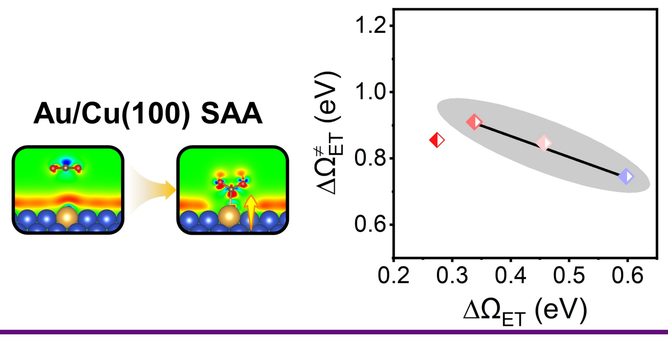
- Accumulating electron density at Cu surface
- The physisorption PEC rises → the crossing of two PECs, i.e., the barrier for the transition, to rise rapidly as *U* decrease

➢ Catalyst design

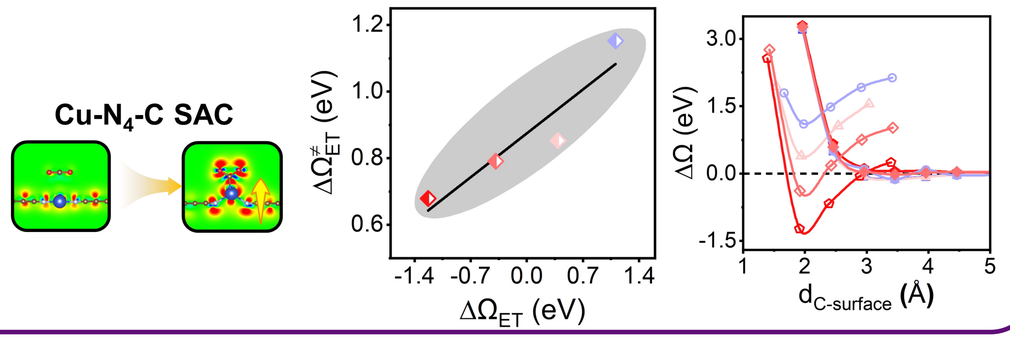
1. Increasing surface roughness



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 in the SEPT mechanism 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 in eCO_2RR

1. L. Liu, H. Xiao, Inverted Region in Electrochemical Reduction of CO_2 Induced by Potential-Dependent Pauli Repulsion. *J. Am. Chem. Soc.* **145**, 14267–14275 (2023).
2. M. T. M. Koper et al. Advances and challenges in understanding the electrocatalytic conversion of carbon dioxide to fuels. *Nat. Energy* **4**, 732–745 (2019)