



# DFT MODELING OF Cu-CATALYZED CO to EtOH CONVERSION

Josephine Chen, The Cooper Union, chen20@cooper.edu  
 REU: Earth, Wind, and Fire: Sustainability in the 21st Century, Kansas State University

## INTRODUCTION

Greenhouse gas (GHG) emissions present a growing problem to every facet of everyday life. To combat this, considerable research in the development of renewable, sustainable energy has been conducted. In particular, ethanol, EtOH, has been studied as an alternative fuel source. However, even conventional production of EtOH has its limitations and downfalls. Electrochemical methods of EtOH production present viable alternatives, which are less burdensome on natural resources and tout myriad benefits, such as:

- Path to Energy Independence
- Carbon Offset
- Closed Loop CO<sub>2</sub> to Fuel System
- Reduction of Land and Water Usage

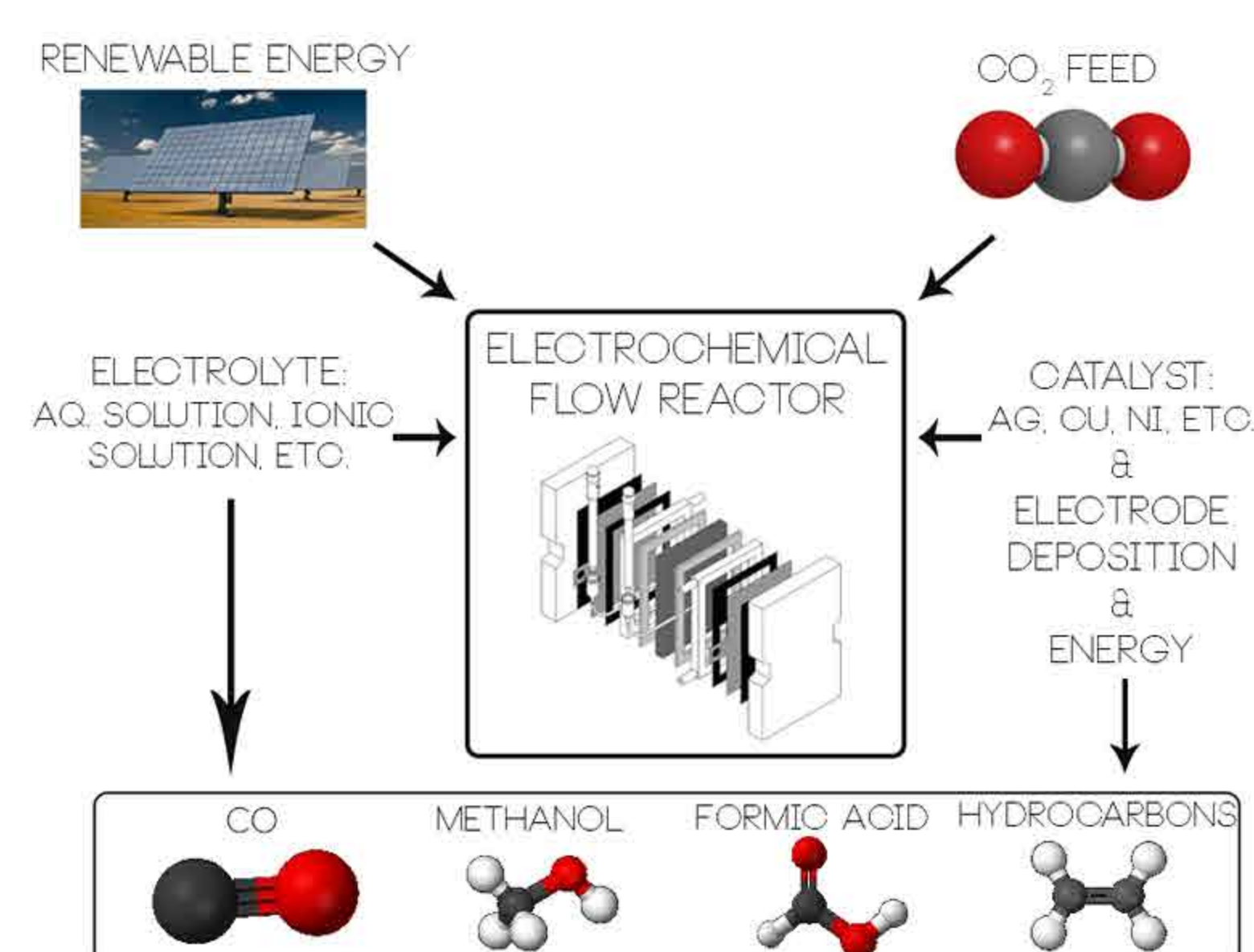


Figure 1. Electrochemical Flow Reactor Schematic

## METHODS

In order to understand the thermodynamics and kinetics of the conversion of CO to EtOH, Cu(211) was chosen as the surface catalyst on which all reactants and intermediates would adsorb. The Cu(211) surface is sufficiently reactive and exhibits high selectivity in the conversion of CO to EtOH.

The Cu(211) surface has three possible adsorption sites: **bridge**, **four-fold**, and **top**. The light pink atoms depict the surface edge.

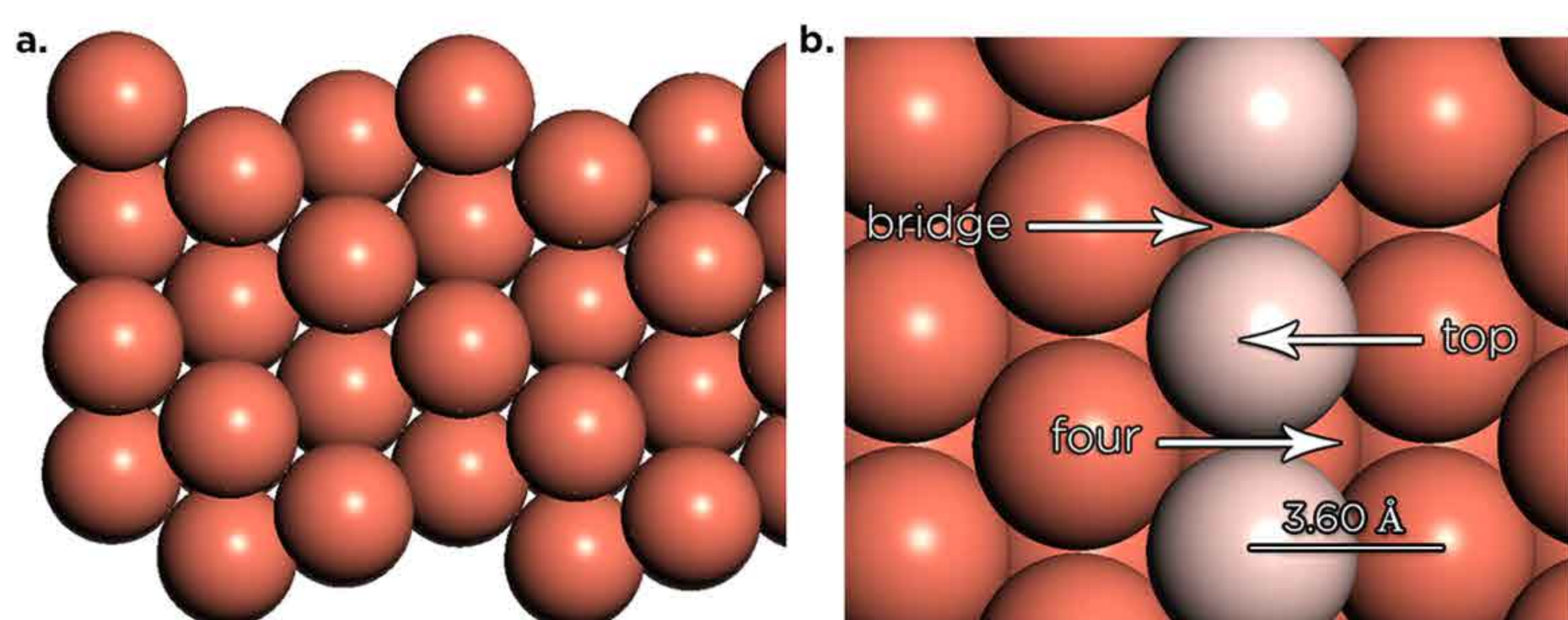


Figure 2a. Side View and b. Top View of Bridge, Four-fold, and Top Sites on Cu(211) Surface.

Optimizations of the initial and final structures of the reaction intermediates outlined in the proposed reaction mechanism, were achieved using the Vienna Ab-initio Simulation Package, or VASP.

## REACTION MECHANISM

The reaction mechanism provides insight into the pathways that lead to the conversion of CO into EtOH. Various configurations of the reaction intermediates were tested to determine the most thermodynamically stable, or lowest-energy, configurations. Figure 3 shows the optimized configurations for the reaction intermediates. The following reaction mechanism was adapted from Calle-Vallejo and Koper.<sup>1</sup>

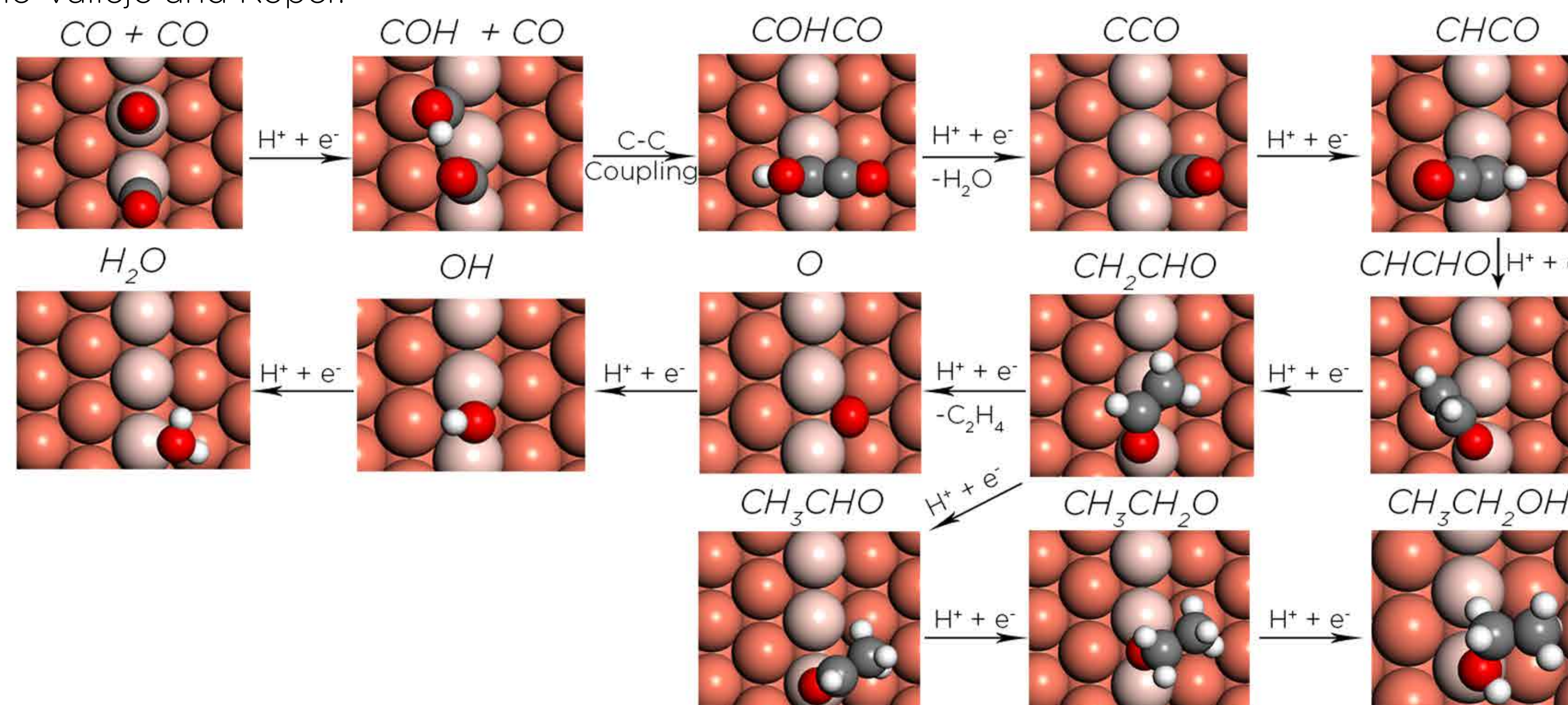


Figure 3. Optimized Reaction Intermediate Structures for Proposed CO to EtOH Conversion.

## RESULTS

A potential energy surface was generated using the total energy values of the optimized reaction intermediates. Figure 4 below shows the potential energy surface for the reaction mechanism and consequently, yields thermodynamic information about the mechanism.

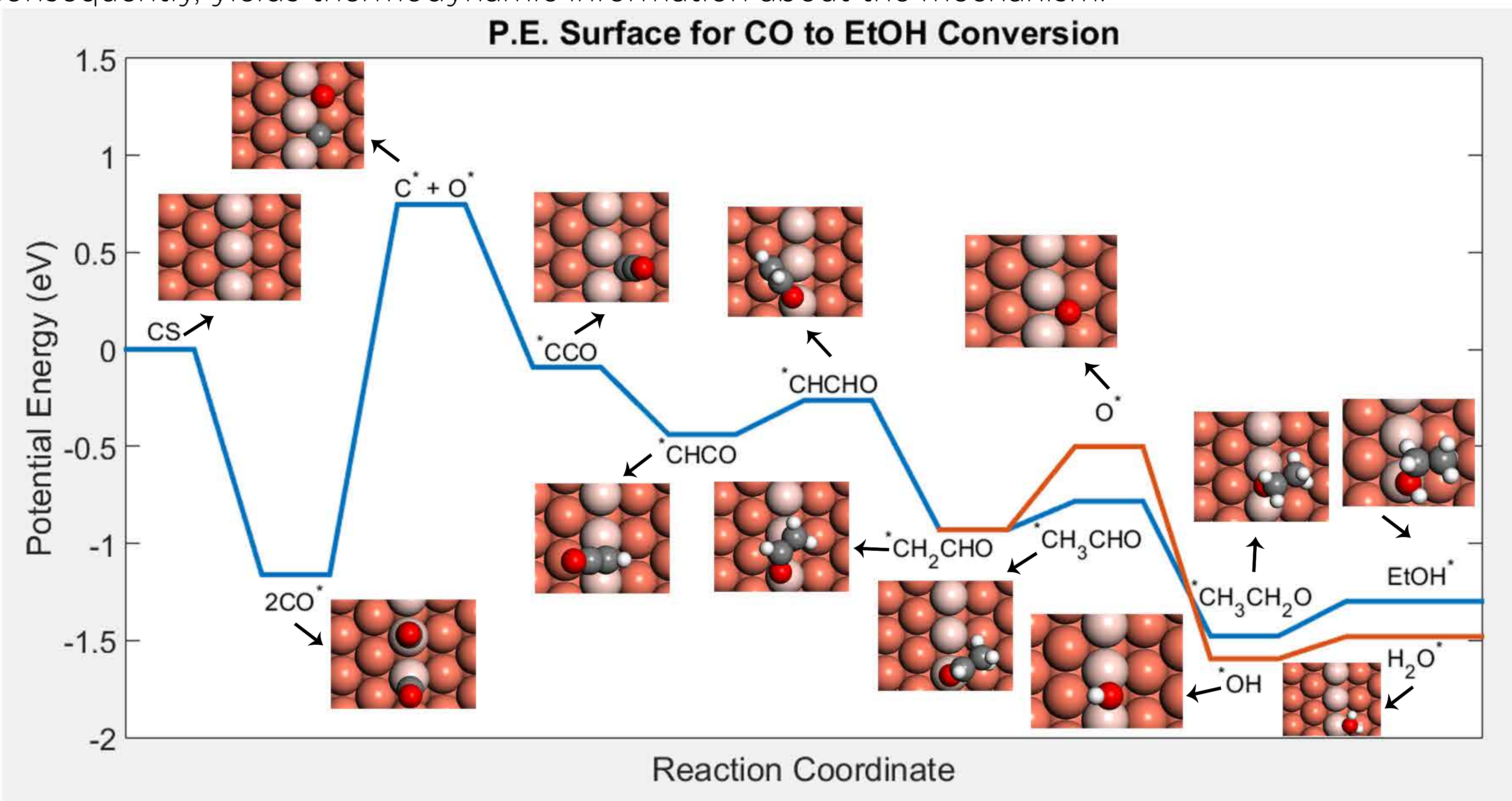


Figure 4. Potential Energy Surface Diagram for CO to EtOH Conversion

## CONCLUSION

In addition to the thermodynamics of the reaction mechanism, the surface geometry is another equally important factor to consider. Using DFT calculations in conjunction with solvation effect, electric potential, ZPE, and entropy of vibrational effect correction factors, the Cu(211) surface was qualitatively compared to the Cu(100) electrode surface used in literature. Generated results attested to the energetic favorability of the reaction. Figure 5 suggests that because the energy generated values (5a) for the Cu(211) surface are lower than those for the Cu(100) surface (5b), the Cu(211) surface is a reactive (as compared to the Cu(100) surface) and thermodynamically stable facilitator of CO to EtOH conversion.

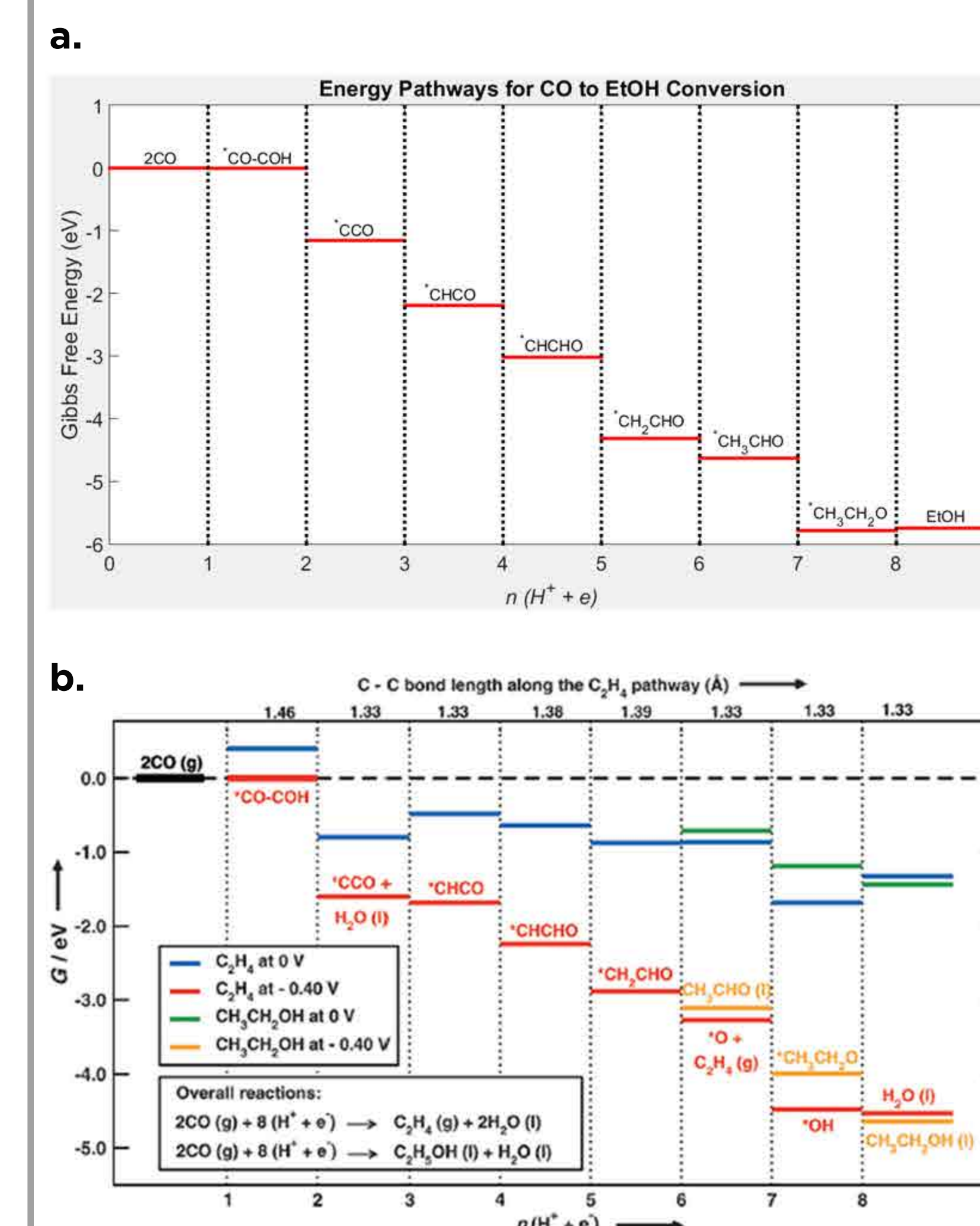


Figure 5a. Generated and b. Lowest energy pathways for the electroreduction of CO to EtOH by F. Calle-Vallejo and M.T.M. Koper.<sup>1</sup>

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## REFERENCES

1. Calle-Vallejo, F.; Koper, M. T. M. Theoretical Considerations on the Electroreduction of CO to C<sub>2</sub> Species on Cu(100) Electrodes. *Angew. Chem. Int. Ed.* 2013, 52, 7282-7285.