Exploring the Reaction Mechanism, Electronic, Thermodynamic, and Kinetic Parameters of Electrochemical CO$_2$ Reduction to CO on a Copper Electrocatalyst using First Principles Calculations

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I.   Problem definition and objectives:

Global CO$_2$ emissions increased by 5% and reached 36.3 billion tons, the highest level ever.[1] Reducing CO$_2$ concentration via clean processes such as CO$_2$ electrochemical reduction has attracted great attention to simultaneously solve the two global problems: "energy shortage and air pollution".[2] Cu-based electrocatalysts have a high efficiency in converting CO$_2$ into significant amounts of value-added chemicals, of which CO is a key intermediate.
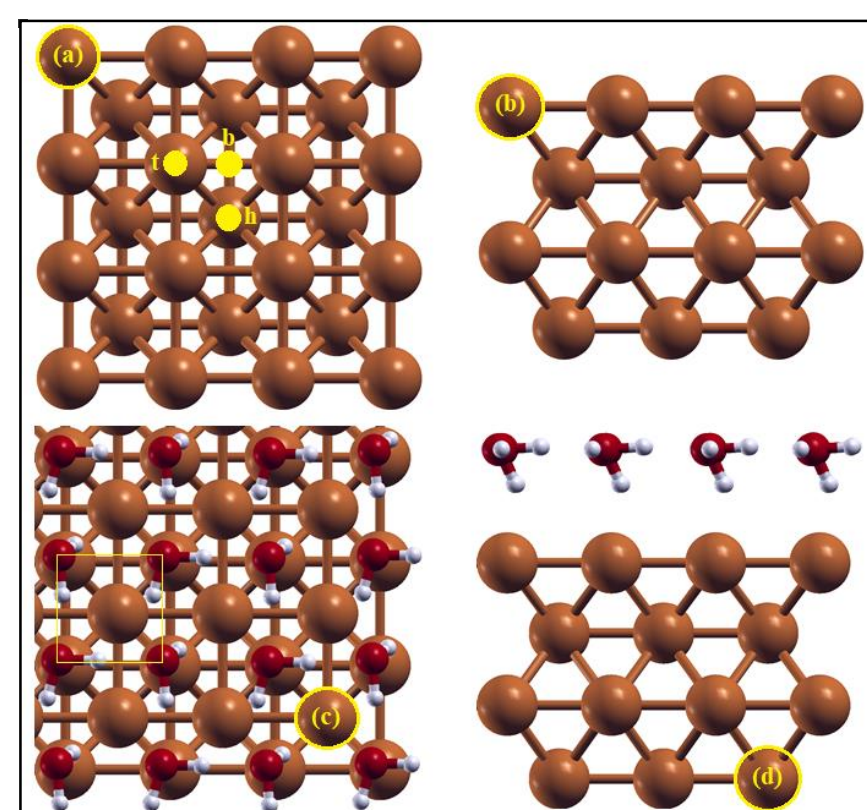

Figure 1. Top and side views of (a, b) Cu(100) catalyst and (c, d) Cu(100) surface with a water monolayer (solvation case).

II.   Strategy, methods, theory:

We map the entire reaction pathways of eCO$_2$RR to CO on a single Cu(100) electrode, including all intermediates and transition states. DFT computations were performed with the plane-wave PWSCF code implemented in Quantum Espresso to analyze the electronic structure of periodic atomic structures.[3,4] To account for the solvent effect, the reaction is studied with and without explicit water molecules. The effects of solvation, pH, and applied potential were investigated.
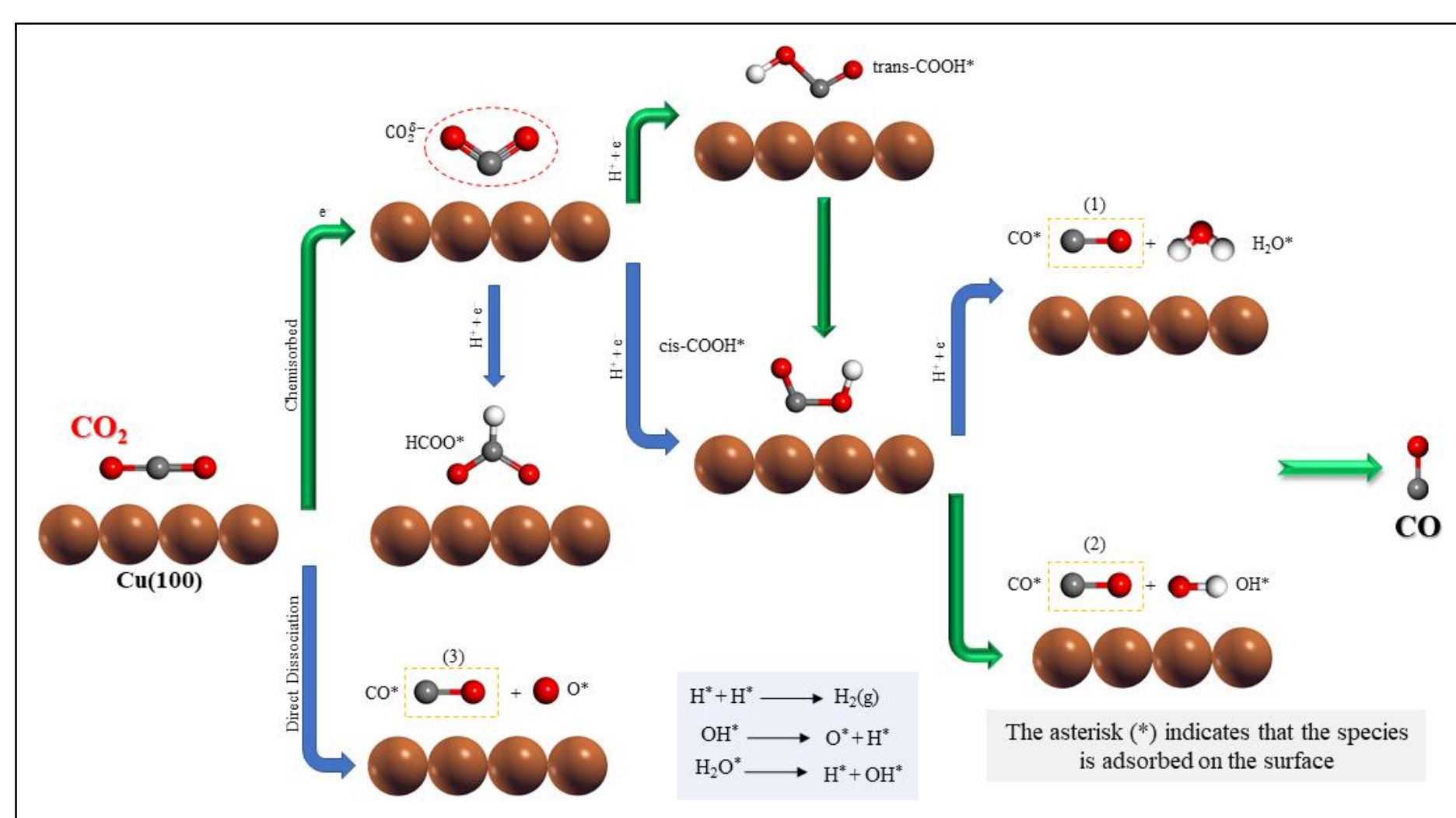

Figure 2. Proposed reaction pathways for the eCO$_2$RR to CO on Cu(100) surface.

III.   Results:

At an applied potential of −0.11 V (−0.52 V SHE) and under neutral pH conditions, all elementary reactions of the CO$_2$RR were thermodynamically favorable, as already shown experimentally. The Gibbs free energies of the reactions in the proposed reaction mechanism were exothermic up to −1.24 V. The dependence of Gibbs free energy on pH and applied potential parameters was investigated. The role of water solvation was investigated by forming a 1.0 ML of water molecules on the Cu(100) surface. While solvation had no effect on the adsorption sites and geometries, detailed analysis revealed significant effects on the stability of the adsorbents and intermediates. In addition, *the activation energies and Gibbs free energies of all elementary reactions were reduced by accounting for solvation*.

Figure 3. TS of all elementary reactions involved in CO$_2$RR to CO in lateral views: (a) CO$_2^*$ + H* ↔ HCOO* (R1), (b) CO$_2^*$ + H* ↔ cis-COOH* (R2), (c) CO$_2^*$ ↔ CO* + O* (R3), (d) cis-COOH* ↔ CO* + OH* (R4), (e) cis-COOH* + H* ↔ CO* + H$_2$O* (R5), (f) $trans$-COOH* ↔ cis-COOH* (R6), (g) CO$_2^*$ + H* ↔ $trans$-COOH* (R7), (h) H$_2$(g) ↔ H* + H* (R8), (i) O* + H* ↔ OH* (R9), (j) OH* + H* ↔ H$_2$O* (R10).

Table 1. Calculated ZPE-corrected forward and backward activation energies and reaction energies of the all considered elementary reactions on the Cu(100) surface (without and with solvation)

Elementary Reactions	Without solvation			With solvation		
	E_a^{fwd}(eV)	ΔE_{ZPE}^{fwd}(eV)	E_a^{bwd}(eV)	E_a^{fwd}(eV)	ΔE_{ZPE}^{fwd}(eV)	E_a^{bwd}(eV)
CO$_2^*$ + H* ↔ HCOO* (R1)	+1.17	+0.29	+0.88	+1.16	−0.26	+1.42
CO$_2^*$ + H* ↔ cis-COOH* (R2)	+1.79	+1.12	+0.67	+1.74	+0.91	+0.83
CO$_2^*$ ↔ CO* + O* (R3)	+1.52	+0.13	+1.39	+1.33	−0.04	+1.37
cis-COOH* ↔ CO* + OH* (R4)	+0.58	−1.33	+1.91	+0.56	−1.23	+1.79
cis-COOH* + H* ↔ CO* + H$_2$O* (R5)	+1.43	−0.08	+1.51	+1.41	−0.16	+1.57
$trans$-COOH* ↔ cis-COOH* (R6)	+0.91	+0.09	+0.82	+0.84	+0.25	+0.59
CO$_2^*$ + H* ↔ $trans$-COOH* (R7)	+0.71	−0.39	+1.10	+0.80	−0.47	+1.27
H$_2$(g) ↔ H* + H* (R8)	+0.50	−0.25	+0.75	+0.47	−0.40	+0.87
O* + H* ↔ OH* (R9)	+0.91	−0.83	+1.74	+0.50	−0.49	+0.99
OH* + H* ↔ H$_2$O* (R10)	+1.79	+0.34	+1.45	+1.77	+0.17	+1.60
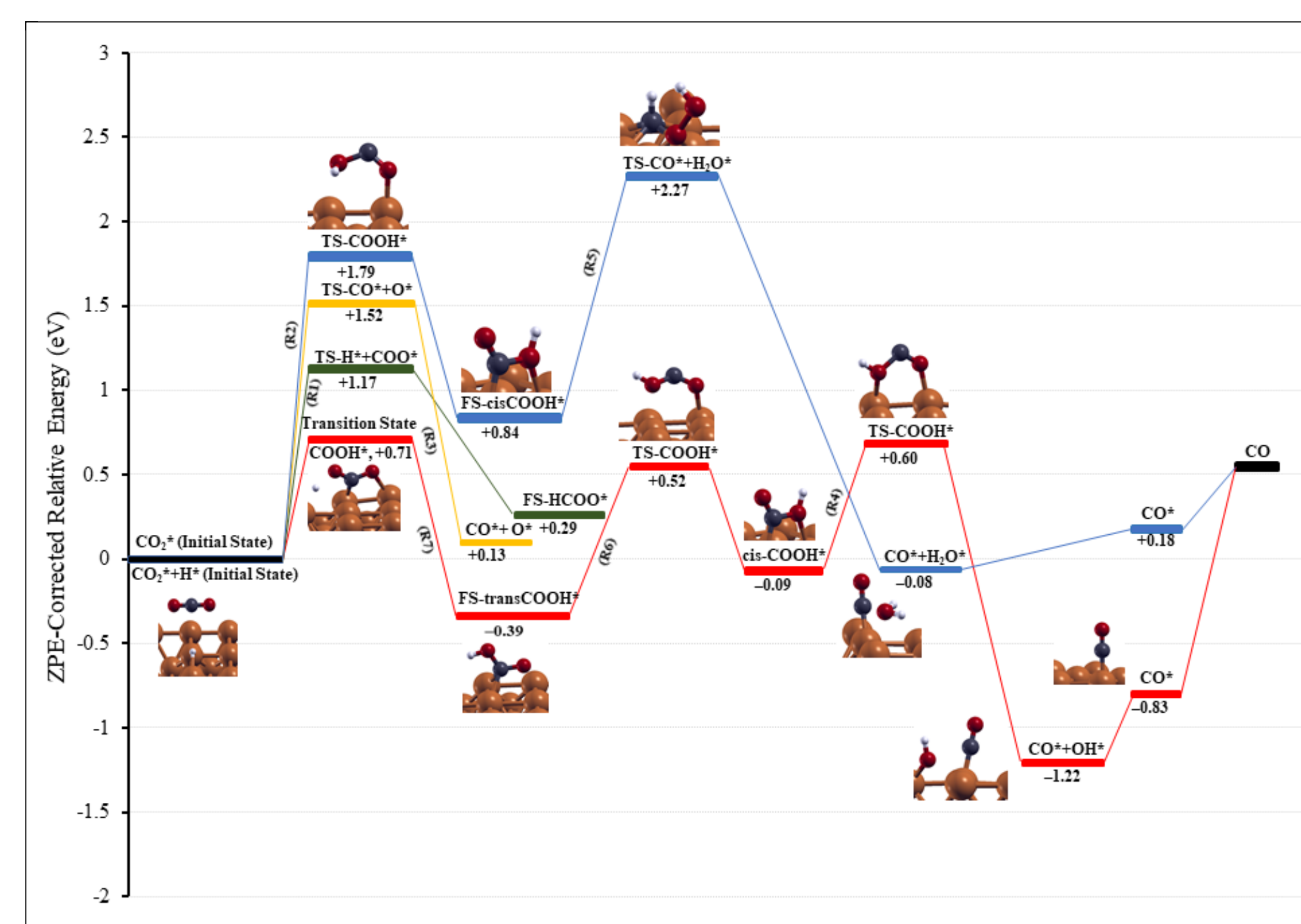
Figure 4. ZPE-corrected relative energy profile of all possible reaction pathways for the CO$_2$ electroreduction to CO on Cu(100) surface.

Table 2. pH effect on the Gibbs free energies (ΔG, eV) of the elementary steps over the Cu(100) surface at 298.15 K and U= −0.11 V in both without and with solvation cases

Elementary Reactions / pH	Without solvation					With solvation				
	0	3	7	10	14	0	3	7	10	14
CO$_2^*$ + H* ↔ HCOO* (R1)	+0.07	−0.10	−0.34	−0.52	−0.75	−1.07	−1.24	−1.48	−1.66	−1.90
CO$_2^*$ + H* ↔ cis-COOH* (R2)	+0.53	+0.35	+0.11	−0.06	−0.30	−0.39	−0.56	−0.80	−0.98	−1.22
CO$_2^*$ ↔ CO* + O* (R3)	+0.28	+0.10	−0.13	−0.31	−0.54	−0.05	−0.22	−0.46	−0.64	−0.87
cis-COOH* ↔ CO* + OH* (R4)	−0.40	−0.57	−0.81	−0.99	−1.22	+0.41	+0.23	−0.01	−0.18	−0.42
cis-COOH* + H* ↔ CO* + H$_2$O* (R5)	+0.10	−0.07	−0.31	−0.49	−0.72	−0.14	−0.31	−0.55	−0.73	−0.97
$trans$-COOH* ↔ cis-COOH* (R6)	+0.14	−0.03	−0.27	−0.45	−0.68	+0.09	−0.08	−0.32	−0.50	−0.74
CO$_2^*$ + H* ↔ $trans$-COOH* (R7)	+0.39	+0.21	−0.02	−0.20	−0.43	−0.72	−0.90	−1.13	−1.31	−1.55
H$_2$(g) ↔ H* + H* (R8)	+0.46	+0.28	+0.04	−0.13	−0.37	+0.27	+0.09	−0.14	−0.32	−0.56
O* + H* ↔ OH* (R9)	−0.44	−0.61	−0.85	−1.03	−1.26	−0.77	−0.94	−1.18	−1.36	−1.60
OH* + H* ↔ H$_2$O* (R10)	+0.51	+0.33	+0.09	−0.08	−0.32	−0.06	−0.23	−0.47	−0.65	−0.89

IV.   Conclusions:

We have shown that it is important to consider the solvation effect and that its omission can lead to qualitatively different results. The reaction mechanisms were proposed, and the carboxyl pathway was found to be predominant route for the production of CO (CO$_2$→$trans$-COOH*→cis-COOH*→CO*+OH*→CO*→CO) while CO$_2$ direct dissociation was not worth mentioning due to its high activation barrier. The adsorption sites of the adsorbates and the reaction mechanism were almost identical when solvation was considered or not. However, we demonstrated that solvation had significant effects on the stability of the adsorbents and intermediates compared to without solvation case.
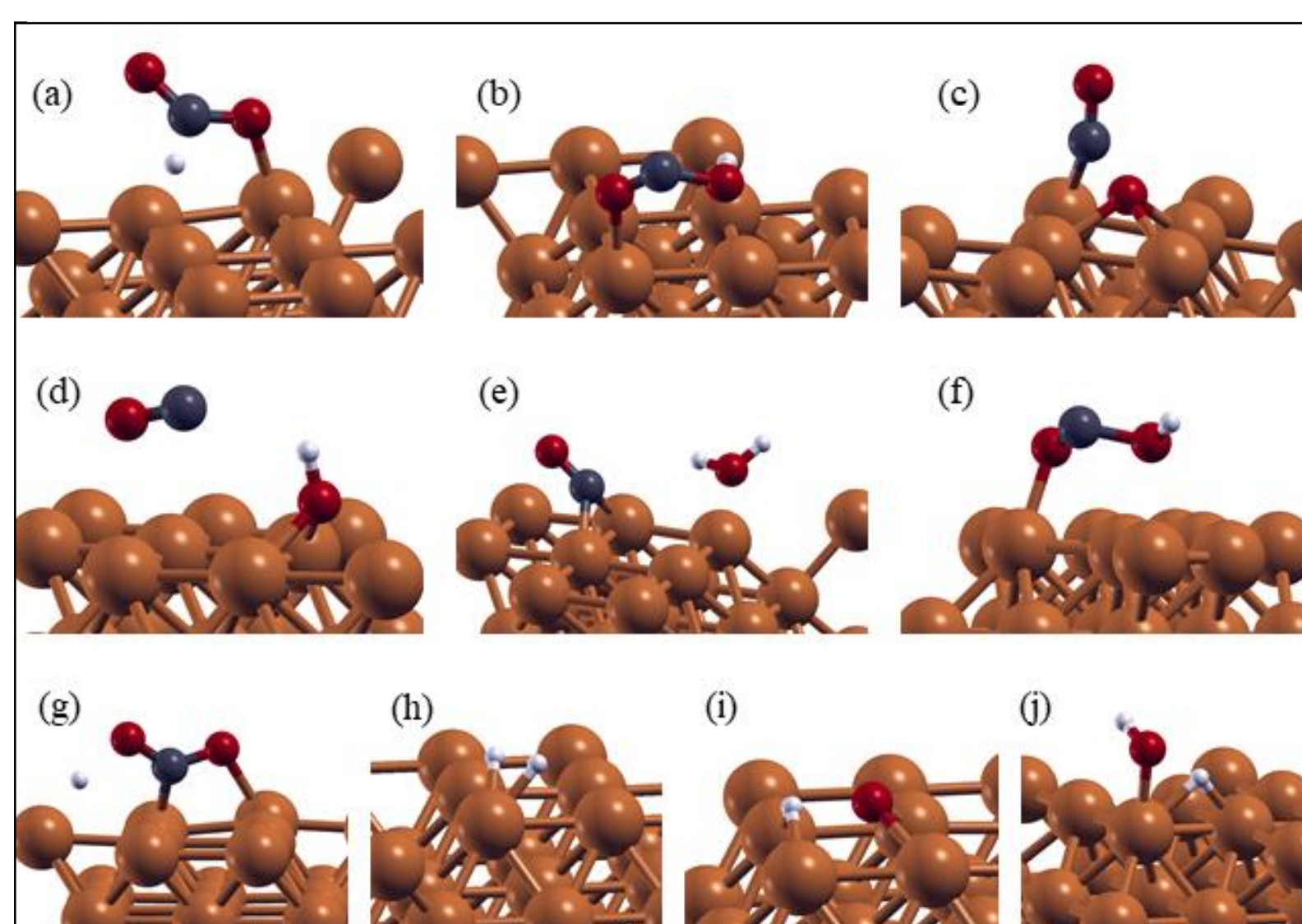
Table.3. Applied potential (in V) effect on the Gibbs free energies (eV) of the elementary steps over the Cu (100) at 298.15 K and pH=7 (with solvation)

Reactions /Appl. Potentials (U)	-2.0	-1.8	-1.6	-1.4	-1.2	-1.0	-0.8	-0.6	-0.4	-0.2	-0.11	0.0	+0.2	+0.4	+0.6	+0.8	+1.0	+1.2	+1.4	+1.6	+1.8	+2.0
CO$_2$* + H* ↔HCOO* (R1)	+0.40	+0.20	0.00	-0.20	-0.40	-0.60	-0.80	-1.00	-1.20	-1.40	-1.49	-1.60	-1.80	-2.00	-2.20	-2.40	-2.60	-2.80	-3.00	-3.20	-3.40	-3.60
CO$_2$* + H* ↔ cis-COOH* (R2)	+1.09	+0.89	+0.69	+0.49	+0.29	+0.09	-0.11	-0.31	-0.51	-0.71	-0.80	-0.91	-1.11	-1.31	-1.51	-1.71	-1.91	-2.11	-2.31	-2.51	-2.71	-2.91
CO$_2$* ↔ CO* + O* (R3)	+3.32	+2.92	+2.52	+2.12	+1.72	+1.32	+0.92	+0.52	+0.12	-0.28	-0.46	-0.68	-1.08	-1.48	-1.88	-2.28	-2.68	-3.08	-3.48	-3.88	-4.28	-4.68
cis-COOH* ↔ CO* + OH* (R4)	+1.89	+1.69	+1.49	+1.29	+1.09	+0.89	+0.69	+0.49	+0.29	+0.09	0.00	-0.11	-0.31	-0.51	-0.71	-0.91	-1.11	-1.31	-1.51	-1.71	-1.91	-2.11
cis-COOH* + H* ↔ CO* + H$_2$O* (R5)	+1.34	+1.14	+0.94	+0.74	+0.54	+0.34	+0.14	-0.06	-0.26	-0.46	-0.55	-0.66	-0.86	-1.06	-1.26	-1.46	-1.66	-1.86	-2.06	-2.26	-2.46	-2.66
$trans$-COOH* ↔ cis-COOH* (R6)	-0.32	-0.32	-0.32	-0.32	-0.32	-0.32	-0.32	-0.32	-0.32	-0.32	-0.32	-0.32	-0.32	-0.32	-0.32	-0.32	-0.32	-0.32	-0.32	-0.32	-0.32	-0.32
CO$_2$* + H* ↔ $trans$-COOH* (R7)	+0.75	+0.55	+0.35	+0.15	-0.05	-0.25	-0.45	-0.65	-0.85	-1.05	-1.14	-1.25	-1.45	-1.65	-1.85	-2.05	-2.25	-2.45	-2.65	-2.85	-3.05	-3.25
H$_2$(g) ↔H* + H* (R8)	+3.64	+3.24	+2.84	+2.44	+2.04	+1.64	+1.24	+0.84	+0.44	+0.04	-0.14	-0.36	-0.76	-1.16	-1.56	-1.96	-2.36	-2.76	-3.16	-3.56	-3.96	-4.36
O* + H* ↔ OH* (R9)	-1.19	-1.19	-1.19	-1.19	-1.19	-1.19	-1.19	-1.19	-1.19	-1.19	-1.19	-1.19	-1.19	-1.19	-1.19	-1.19	-1.19	-1.19	-1.19	-1.19	-1.19	-1.19
OH* + H* ↔ H$_2$O* (R10)	-0.48	-0.48	-0.48	-0.48	-0.48	-0.48	-0.48	-0.48	-0.48	-0.48	-0.48	-0.48	-0.48	-0.48	-0.48	-0.48	-0.48	-0.48	-0.48	-0.48	-0.48	-0.48

V.   References:

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