Supplementary Material

Theoretical Study on the Mechanism of CO* Electrochemical Reduction on Cu(111) under Constant Potential

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Table S1: The convergence test of the cutoff energy of the plane wave basis set. We take the CHO* forming reaction under the potential of 0.0 V as an example. Geometry optimization and single point energy calculation was done under cutoff energy of 400eV, 440 eV, 480 eV and 520 eV.

(1).Energy results. E(IS) and E(FS) represents the energy of IS and FS respectively, dE represents the reaction energy.

Cut off energy (eV)	E(IS) (eV)	E(FS) (eV)	dE (eV)
400	-158.4396	-157.6473	0.7923
440	-158.3565	-157.5651	0.7913
480	-158.3590	-157.5681	0.7910
520	-158.3783	-157.5873	0.7911

(2).Charge results. Ne(IS) and Ne(FS) represents the electron number of IS and FS respectively, dQ represents the charge difference.

Cutoff energy (eV)	Ne(IS)	Ne(FS)	dQ
400	407.1089	407.0814	-0.0275
440	407.1089	407.0798	-0.0291
480	407.1095	407.0788	-0.0307
520	407.1090	407.0796	-0.0294

It is found that the change in the quantities we are concerned about (such as energy difference, charge) are not significant when the cutoff energy increases. From the above results, we conclude that 400eV gives sufficiently precise results.

Table S2: The imaginary frequencies of the TSs.

(1).The imaginary frequencies of the TS of CHO* path at various potentials.

Potential (V vs SHE)	0.0	-0.4	-0.8	-1.2	-1.6
Frequencies / i (cm^{-1})	-68.98	-49.94	-46.27	-40.29	-38.31

(2).The imaginary frequencies of the TS of COH* path at various potentials.

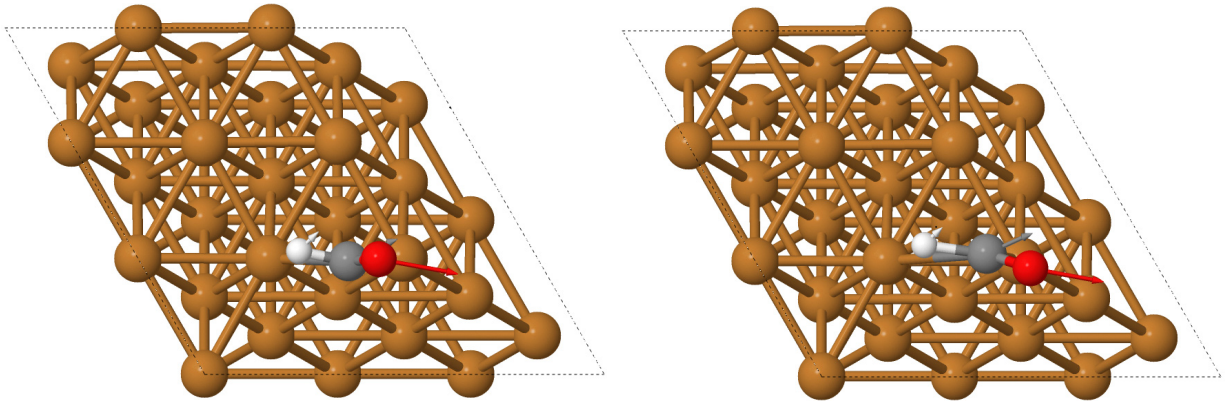
Potential (V vs SHE)	-0.8	-0.9	-1.0
Frequencies / i (cm^{-1})	-199.29	-205.83	-200.01

These imaginary frequencies are quite small because of the gentle potential energy surfaces. In the CHO* path, as the potential increases, the potential energy surface near the transition state becomes more gentle and the corresponding imaginary frequencies becomes smaller.

Figure S1: The vibration mode of the imaginary frequencies.

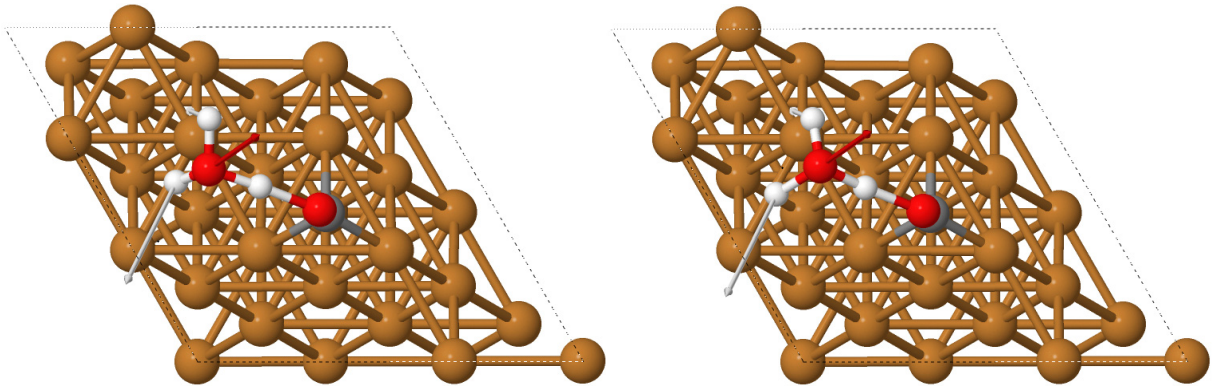
(1).The vibration mode of the imaginary frequencies of the TS of CHO* path. 2 representative images are

taken from the vibration animation.



This vibration mode includes a C-H stretching vibration coupled with a H-C-O bending vibration.

(2).The vibration mode of the imaginary frequencies of the TS of COH* path. 2 representative images are taken from the vibration animation.



This vibration mode is the twisting vibration of water. It shows that the orientation twisting of water molecule is more difficult than the transition of the proton on the COH* path.

Figure S2: Different CO coverage structures. (a) 2/9 coverage. (b) 3/9 coverage. (c) 9/9 coverage.