



Supplementary Information for

Reaction intermediates during operando electrocatalysis identified from full solvent quantum mechanics molecular dynamics

Tao Cheng, Alessandro Fortunelli and William A. Goddard III*

William A Goddard III
Email: wag@caltech.edu

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Supplementary Information Text

Simulation Details

Quantum Mechanics Molecular Dynamics Simulation

Electronic structure calculations were performed within the density functional framework, as implemented in the Vienna ab initio simulation program (VASP),(1-3) a plane-wave pseudopotential package. The exchange and correlation energies were calculated using the Perdew, Burke, and Ernzerhof (PBE) functional within the generalized gradient approximation (GGA). (4, 5) Spin polarization did not have an appreciable effect on the overall energies. For example, the total energies are different by less than 0.01 eV for adsorbed hydrogen (H*) on Cu(100) surface. The calculations were therefore carried out without spin polarization to reduce computational demands.

We used plane-wave cutoff energy of 400 eV and the First order Methfessel-Paxton scheme with a smearing width of 0.2 eV. Dipole corrections were applied along the z-axis. The PBE-D3 method was employed to correct van der Waals interaction of water-water and water-Cu. (6)

For the vacuum Quantum Mechanics (ν -QM) calculations, we employed a $4\times 4\times 3$ Cu(100) surface slab with the bottom two layers fixed with vacuum layers of at least 15 Å. We investigated 22 reactive intermediates during carbon dioxide reduction reactions (CO₂RR) and carbon monoxide reductions (CORR). The convergence criteria were 1×10^{-5} eV energy differences for solving the electronic wave function. All geometries (atomic coordinates) were converged to within 1×10^{-3} eV/Å. The Hessian matrix and vibrational modes of surface species were computed with finite differences methods as implemented in VASP.

For the explicit solvation calculations, we simulate the water/Cu(100) interface using 48 explicit water molecules (5 layers, 1.21 nm thick) on a 4×4 Cu (100) surface slab (3 layers) with an area of 1.02 nm² with the bottom two layers fixed. The simulation box is 40 Å along the z-axis with a vacuum of 24 Å. The lateral dimensions of the slab were fixed using the 3.61 Å lattice constant.

We calculate the potential of zero charge (PZC) of Cu(100) in contact with explicit water to be 3.61 V, which corresponds to -0.38 V (RHE) ($3.61 - 4.40 + 0.0592\times 7 = -0.38$ V), close to the onset potential [-0.30 V (RHE)] of CO production at pH 6.8. (7) We find that including one extra Na solvated in the solution leads to a work function of 3.40 (± 0.25) eV, which corresponds to -0.59 V (RHE) ($3.40 - 4.40 + 0.0592\times 7 = -0.59$ V), close to the potential [-0.60 V (RHE)] with maximum C₂H₄ production at pH 7.(8)

To equilibrate the interface, we first carried out 2 ns reactive force field (ReaxFF) Molecular Dynamics (MD) simulations at 298K as we did in our previous work. The ReaxFF MD (RMD) simulations were carried out using LAMMPS with a version of 22 Aug 2018. The time step of RMD simulation is 0.25 fs, and the temperature was controlled by coupling a Nose-Hoover thermostat with a temperature damping parameter of 25 fs. From the 2ns RMD generated the interface, we carried out 22 ps QM-MD simulation (2ps for equilibration and 20 ps for production) at 298K with a time step of 1.0 only using the gamma point of the Brillouin zone with no consideration of symmetry. The temperature was controlled by coupling a Nose-Hoover thermostat with a temperature damping parameter of 100 fs. The simulated potential energies of 2ns QM-

MD and 20 ps QM-MD simulation are shown in Figure S1. The potential energies of 20 ps QM-MD production oscillated around the average values indicates an equilibration of interface structure from the simulations that combines 2ns RMD and 2 + 20 ps QM-MD simulation.

2PT analysis

The initial configurations were taken from our previous cases, which has been well equilibrated, and now extended to 30 ps to generate trajectories (saved every step) for two-phase thermodynamic (2PT) model analysis. (9, 10) The analysis results from 2, 5, 10, 20 and 30 ps are shown in Fig. S2.

Free energy calculations

Enhanced sampling methods can increase the time scale of brute force simulations. We calculated the free energies using metadynamics (11, 12) and Constrained Molecular Dynamics (blue moon ensemble). (13) Three parameters are controllable and relevant to the accuracy of a metadynamics simulation: height of a Gaussian hill (h), the width of the Gaussian hill (ω) and frequency to update the bias potential (t_G). In this work, these parameters are $h = 0.08$ eV, $\omega = 0.18$ Å and $t_G = 20$ fs.

From the reactive trajectories, we selected eleven windows for thermodynamic integration calculations. 2.0 ps simulations were carried out at each window to produce the potential of mean force (PMF). Energy profiles were obtained by integrating the PMF.

ν -QM with one to two explicit water molecules and VASPsol implicit solvation

As shown in Fig. S4, interestingly, introducing one explicit water as HB donor to O (in C=O) can significantly increase the prediction as shown in Figure S4 C2. However, if we slightly change the position of water to HB acceptor of OH (in C-OH) as shown in Figure S4 D1, the prediction is even worse than that from ν -QM as shown in Figure S4 D2. These results demonstrate the artificial effects that arise from arbitrary inclusions of a few explicit water molecules, which is a general problem in this kind of explicit-implicit hybrid model.

Increasing the number of explicit water molecules is expected to improve the predictions. Unfortunately, we found that the predictions are worse with two water molecules (one HB acceptor and one HB donor) as shown in Figure S3 E1 and E2. There might be two reasons: first adding more explicit molecules increase the complexity of the potential energy surface, which leads to more local minimums, adding more difficulties in choosing the initial positions of explicit molecules; second, we also suspect the long-range effect, for example, at full solvation conditions water always try to maximize its hydrogen bonds. However, with only two water molecules, neither of the water is saturated, which might lead to too strong interaction with surface species.

Thus, we strongly recommend full solvation calculations for more reliable predictions.

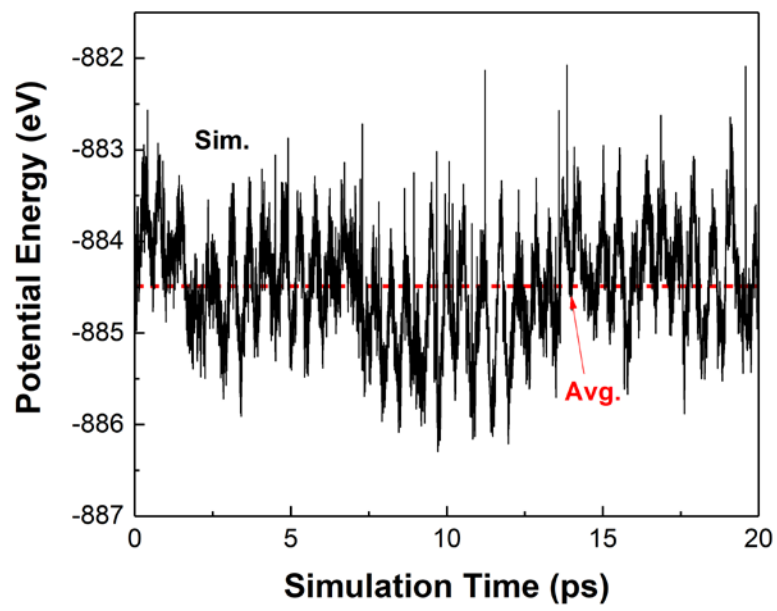


Fig. S1. Potential energies of 20 ps *o*-QM-MD simulation.

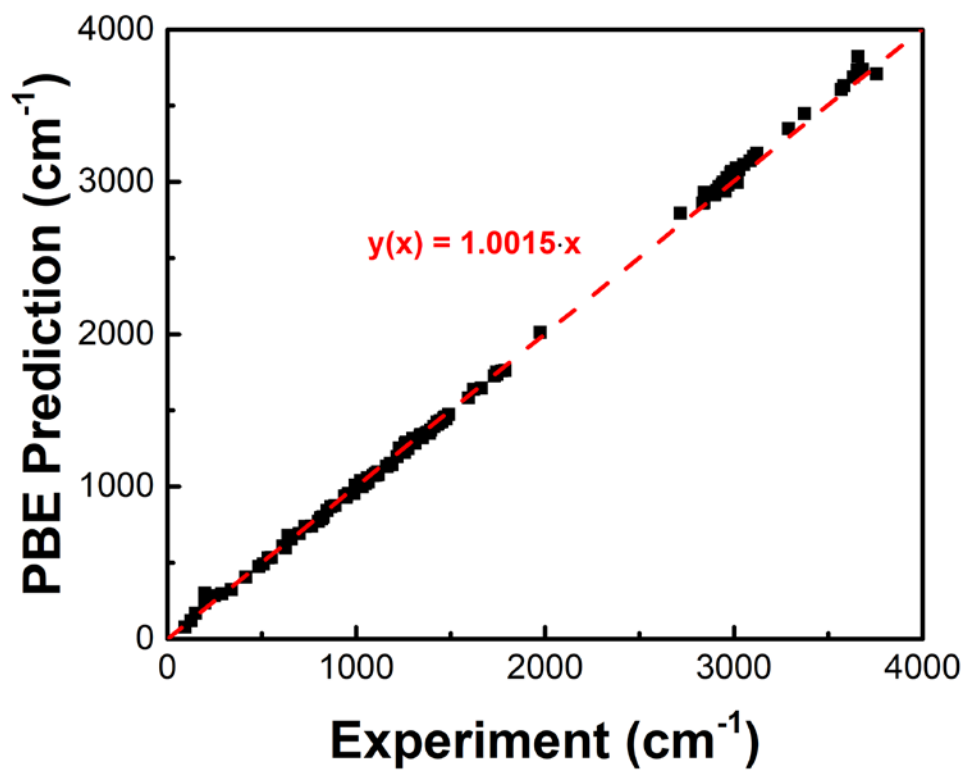


Fig. S2. Comparison of the vibrational frequencies of 14 molecules (CH4, C2H2, C2H4, C2H6, CH2OH-CH2OH, CH3CH2OH, CH3CHO, CH3COOH, CH3OH, CHO-CH2OH, CHO-CHO, H2O, HCOOH, CH2=CHOH) in gas phase between PBE predictions and experiments (from Computational Chemistry Comparison and Benchmark Database, CCCBD). The linear fitting is shown in the red-dashed line.

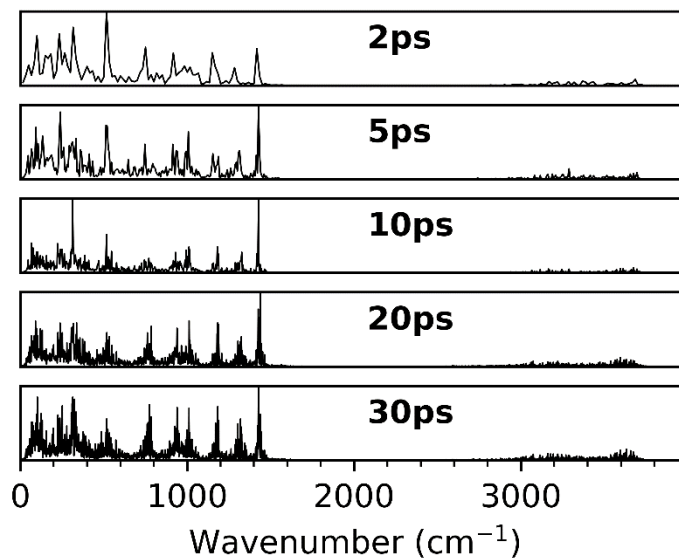


Fig. S3. The DoSs of **HOC-COH* from 2ps, 5ps, 10 ps, 20ps and 30 ps *o*-QMM-MD simulation using 2PT analysis.

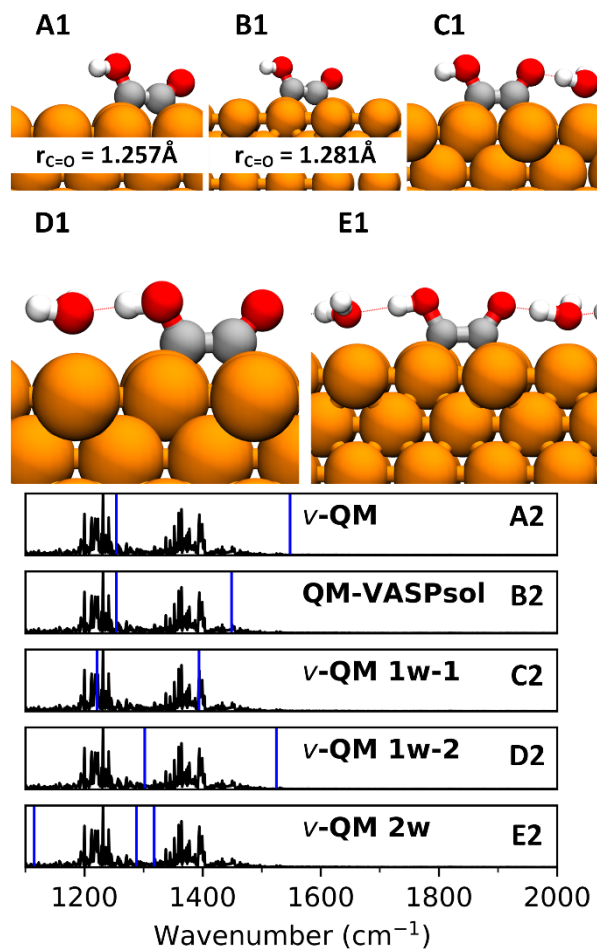


Fig. S4. The optimized atomic structures of $^*COH-CO$ from v-QM (A1), QM+VASPsolv (B1), v-QM + one explicit molecule (as HB donor) (C1) v-QM + one explicit molecule (as HB acceptor) (D1) and v-QM + two explicit molecules (as HB donor) (E1). The predicted vibration frequencies of these models are shown from A2 to E2, respectively.

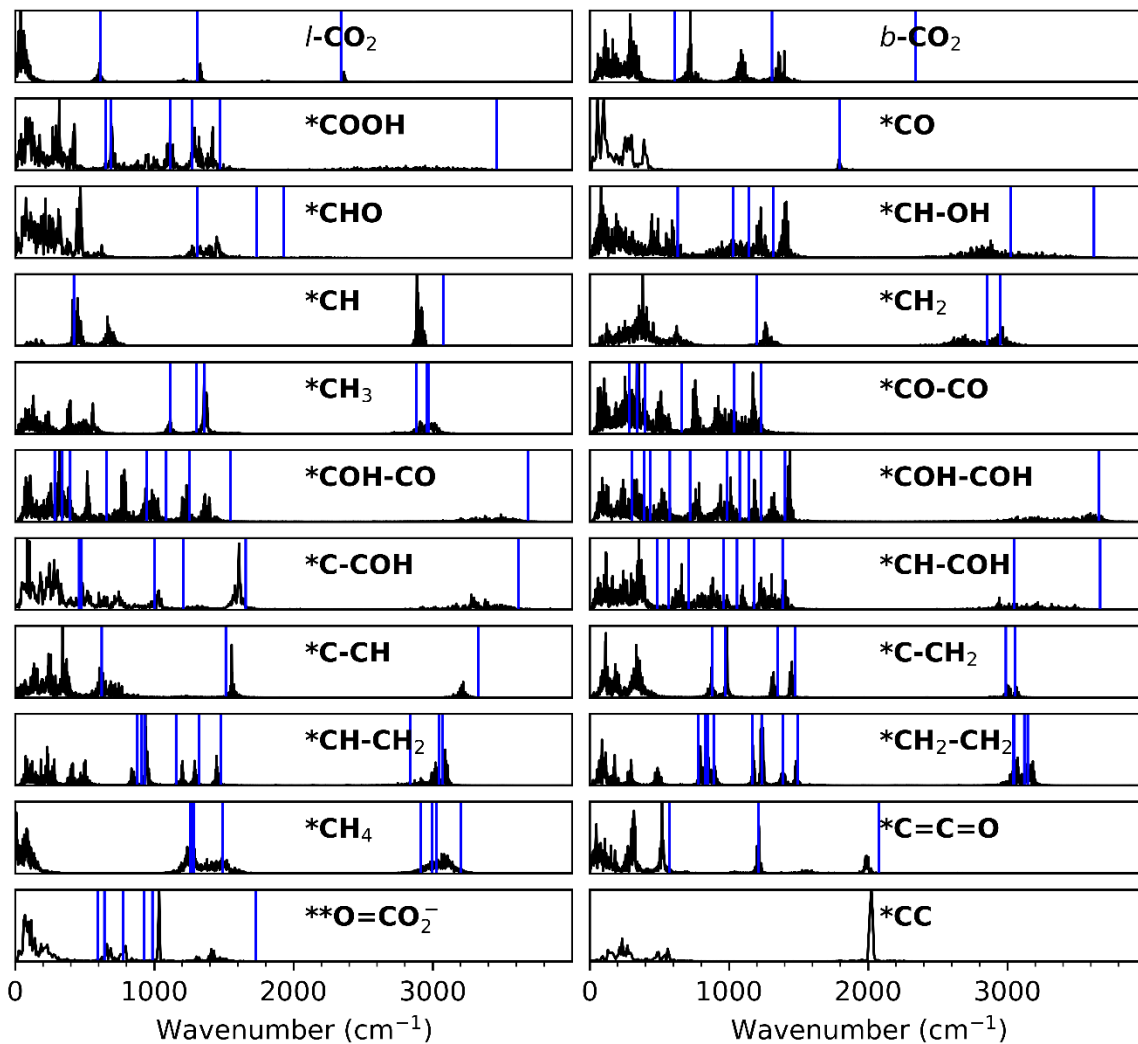


Fig. S5. The DoSs of twenty-two reactive intermediates during CO₂RR and CORR from an *o*-QMM-MD simulation using 2PT analysis (in black). The ν -QM predictions are in blue.

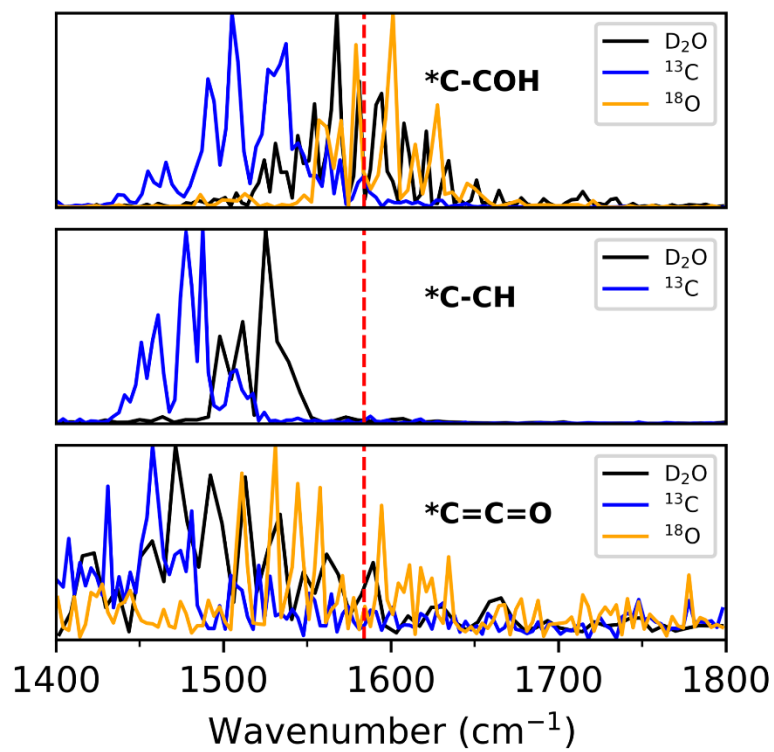


Fig. S6. DoSs of D, ^{13}C and ^{18}O labeled *C-COH, *C-CH and *C=C=O.

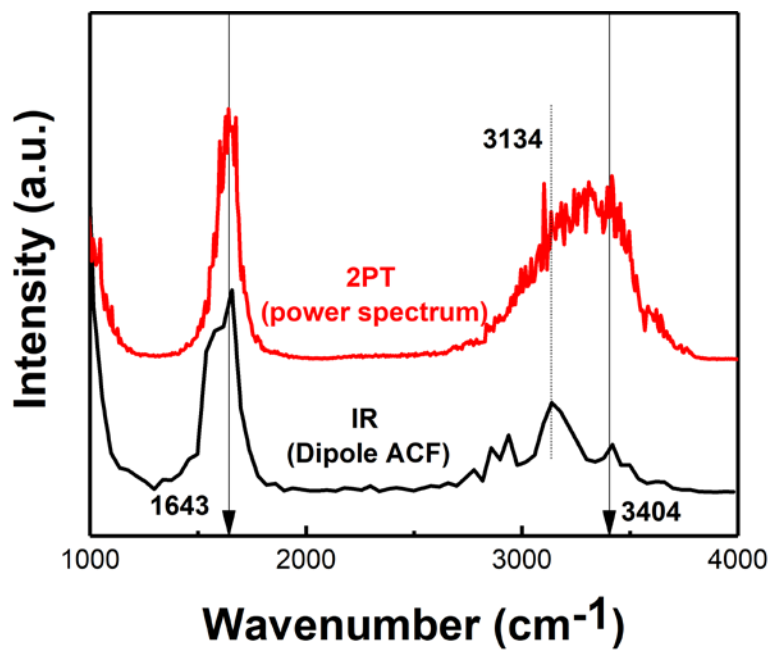


Fig. S7. Comparison of vibrational frequencies of water predicted from 2PT methods (from power spectrum) and IR (from dipole autocorrelation function).

Table S1. The bond length of C-O in surface bonded $^*\text{CO}_3$ in the vacuum (ν -QM), explicit solvation calculation from QM-MD simulation at 298K with an applied potential of -0.33V at pH 13 (o -QM-MD) and CO_3^{2-} anions solvated in 53 water molecules ($\sim 1\text{M}$) of Na_2CO_3 electrolyte at 298K (QM-MD).

	$^*\text{CO}_3$ (ν -QM)	$^*\text{CO}_3$ (o -QM-MD)	$^*\text{Na}_2\text{CO}_3$ (QM-MD)
$R_{\text{C-O1}}(\text{\AA})$	1.214	1.289	1.287
$R_{\text{C-O2}}(\text{\AA})$	1.366	1.311	1.302
$R_{\text{C-O3}}(\text{\AA})$	1.366	1.312	1.326

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