PhD Dissertation Defense

Coordination and Reactivity at Dynamic Electrochemical Interfaces

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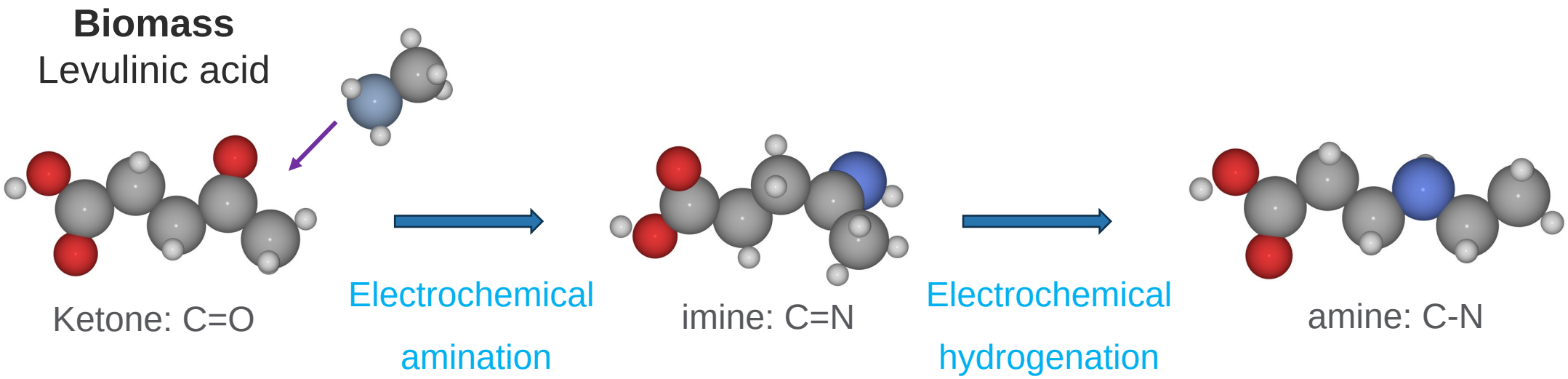
Outline

Intro	**Dynamic interfaces and the amination of acetone** Four observations that the starting electrode cannot explain	Chapter 1
Methods	**Computational methods** AIMD · DFT, CI-NEB, dimer · GC-DFT · COHP, Bader charges, DOS	Chapter 2
Part I	**Change of response** Acetone and methylamine change the double-layer capacitance of Cu	Ch. 3 · ACS AMI 2025
Part II	**Loss of electrode material** Amines pull Cu out of the cathode under reducing potential	Ch. 4 · Chem. Sci. 2024
Part III	**Catalysis by a shuttle** Trace Pb and Bi hydrides carry hydrogen from Ag to the imine	Ch. 5 · Catal. Sci. Technol. 2026; Angew. Chem. 2024, 2026
Part IV	**Catalysis by confinement** Partially desolvated Cs^+ binds CO_2 at a ligand-confined Ag interface	Ch. 6 · Nat. Catal. 2026
Synthesis	**Where the species goes decides the outcome** General discussion, conclusions and outlook	Chapters 7–8

Four systems, one question: where does the species formed at the interface go?

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Electrochemical reductive amination: from biomass to amines



- Renewable energy resource
- Waste management

Serve as fundamental building blocks in

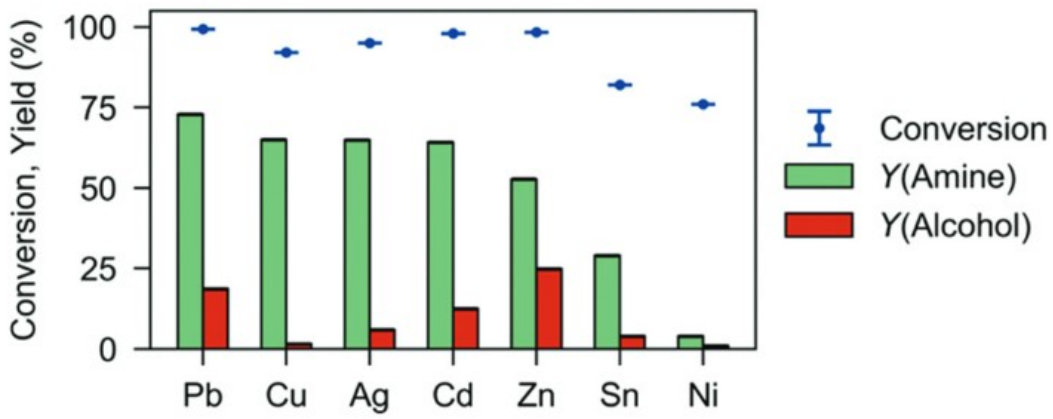
- Pharmaceuticals
- Agriculture
- Chemical Manufacturing

Electrochemistry can turn biomass-derived ketones into amines, with water as the H source.

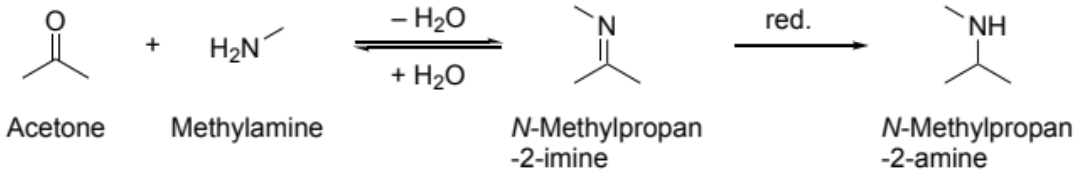
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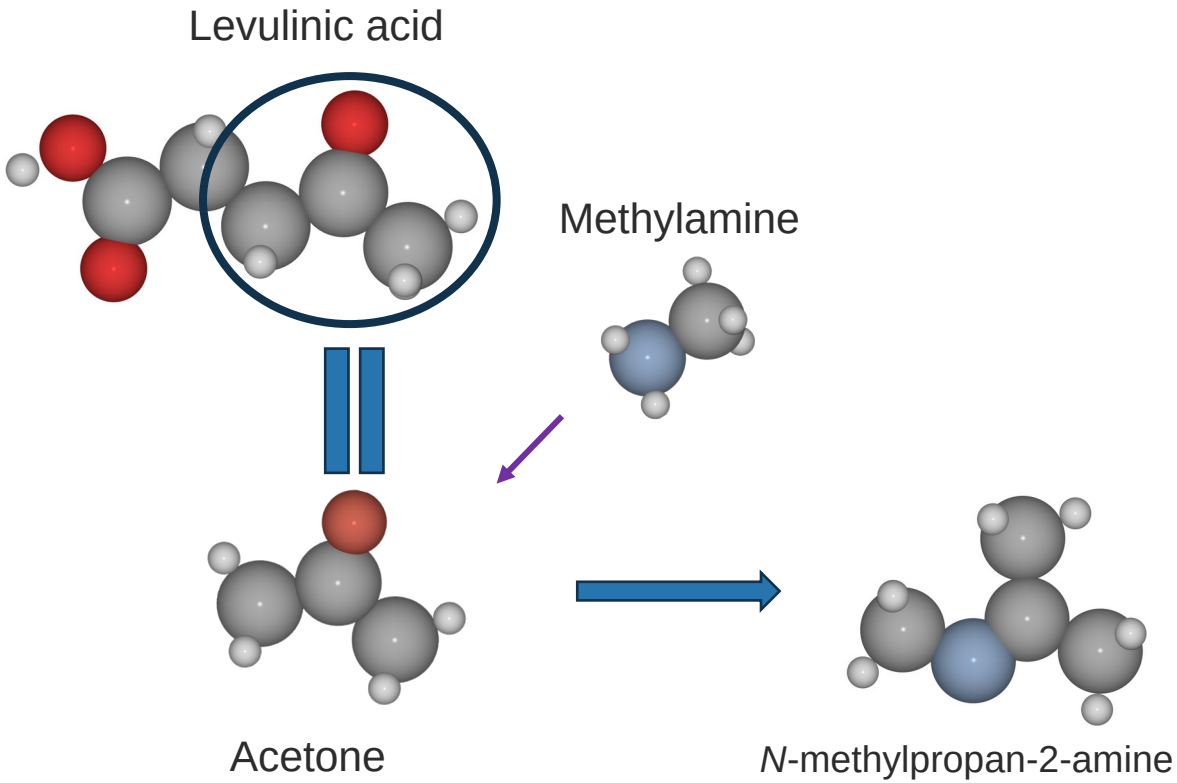
Model reaction: acetone + methylamine on a Cu cathode

Y_{Amine}=65%



Mürtz et al, ***Green Chem.***, 2021,**23**, 8428-8433





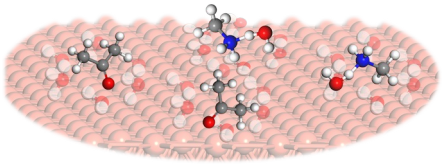
Acetone + methylamine → imine → amine is my model reaction; Cu gives about 65 % amine.

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My argument: where the species goes decides the outcome

Same event in all four systems: an interfacial atom or ion changes its ligands.

Part I



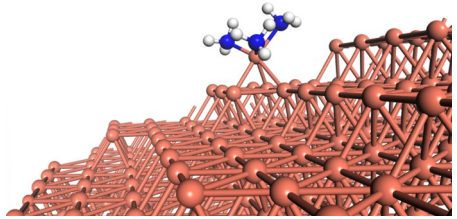
Acetone, methylamine replace interfacial water

Stays, reversible

↓

Change of response

Part II



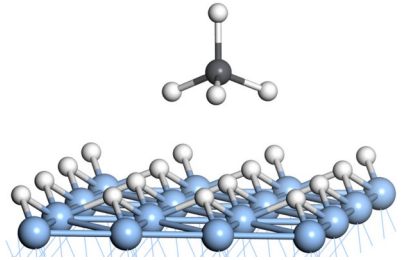
Amines replace the Cu neighbors of a kink atom

Leaves, does not return

↓

Loss of electrode material

Part III



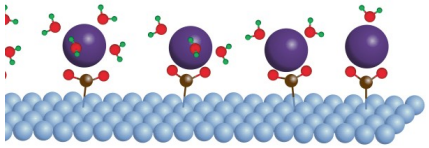
Pb takes H from the Ag electrode: PbH_4

Leaves and returns

↓

Catalysis by a shuttle

Part IV



Cs^+ trades hydration water for CO_2

Stays, held by the ligand layer

↓

Catalysis by confinement

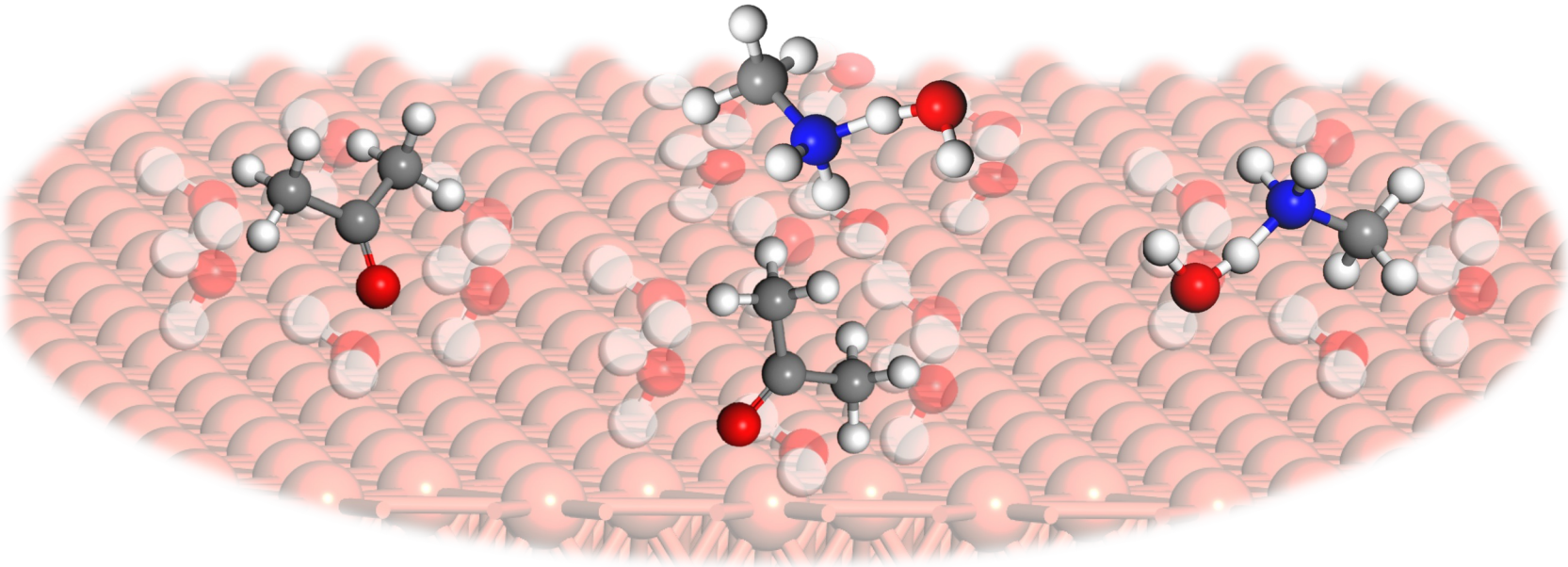
Nothing leaves: response changes · Leaves for good: loss · Returns or stays confined: catalysis

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Why do acetone and methylamine change the capacitance of Cu in opposite directions?

Chapter 3 · Yani Guan et al., **ACS Appl. Mater. Interfaces 17, 4087 (2025)**

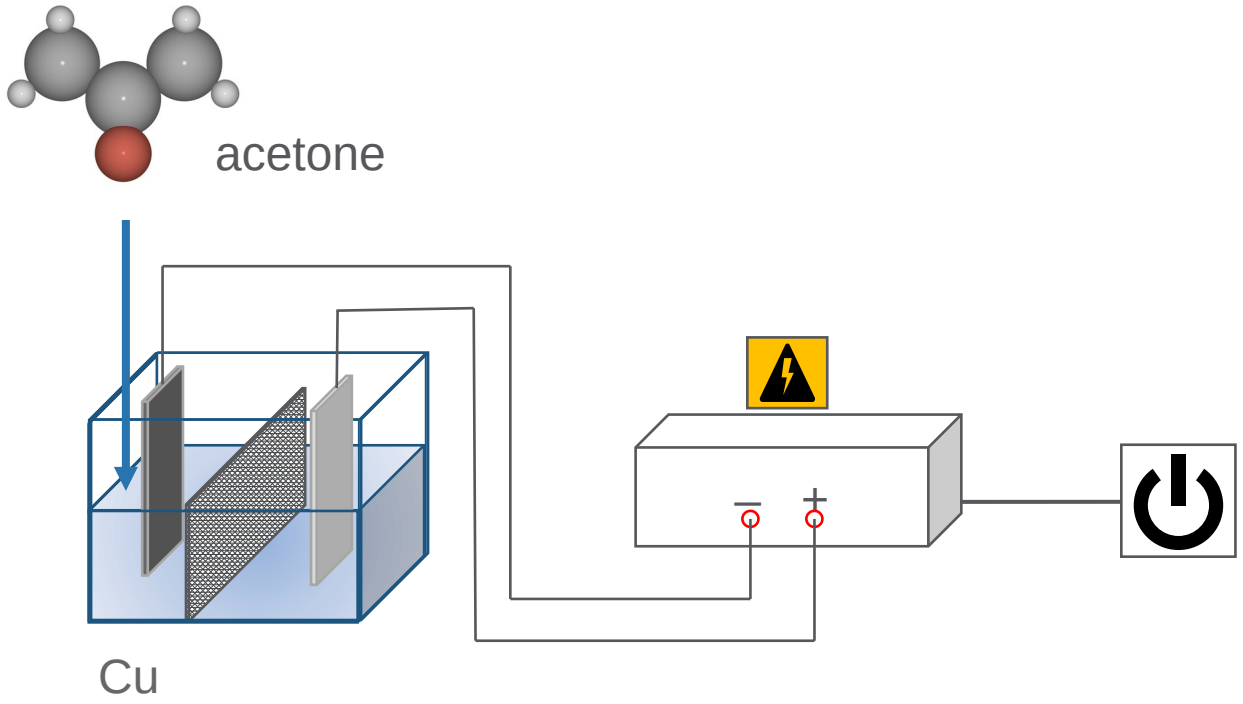
Experiments: Dr. Justus Kümper, Dr. Nick Heiming, Dr. Regina Palkovits and coworkers, RWTH Aachen

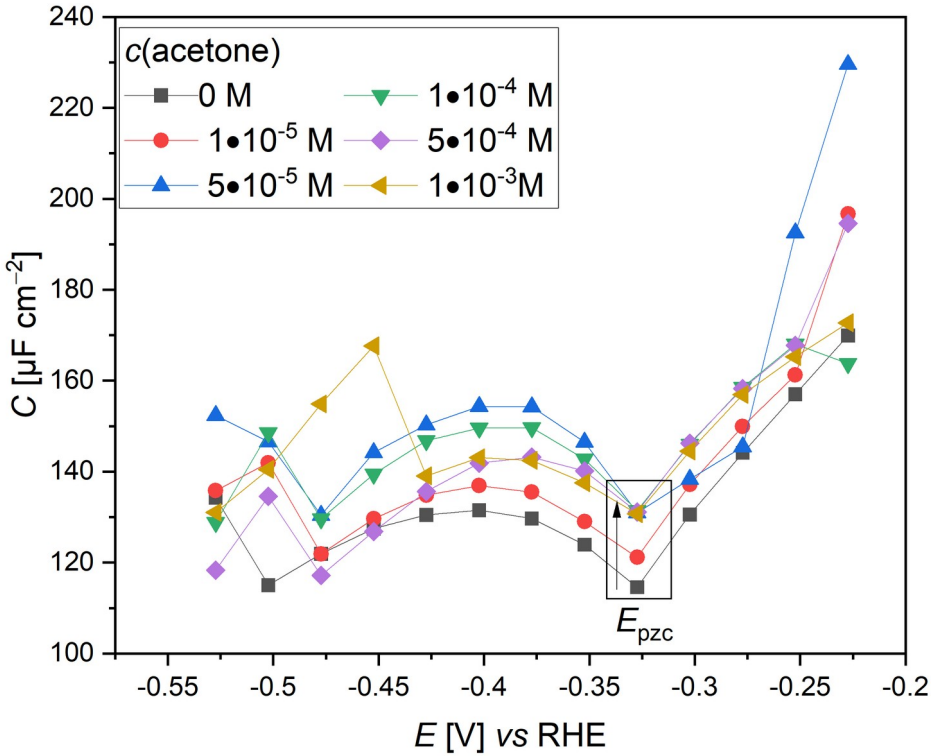


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Acetone raises the Cu capacitance

Impedance on Cu, 0.01 M $NaClO_4$ + KOH, pH 12; E_{pzc} = −0.327 V vs RHE



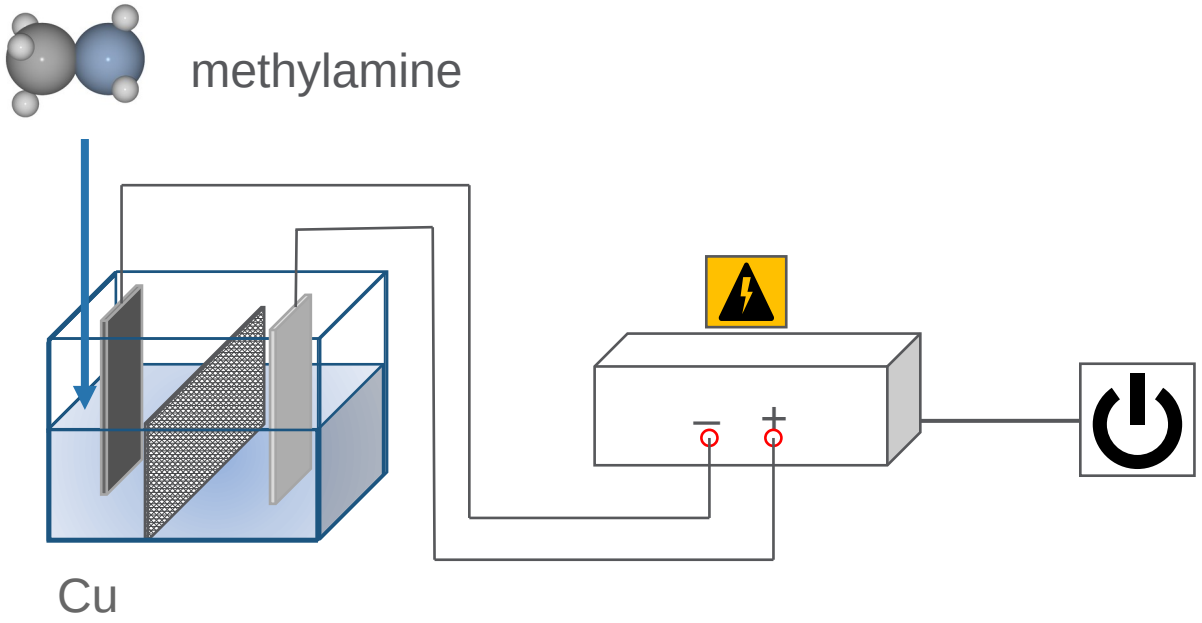


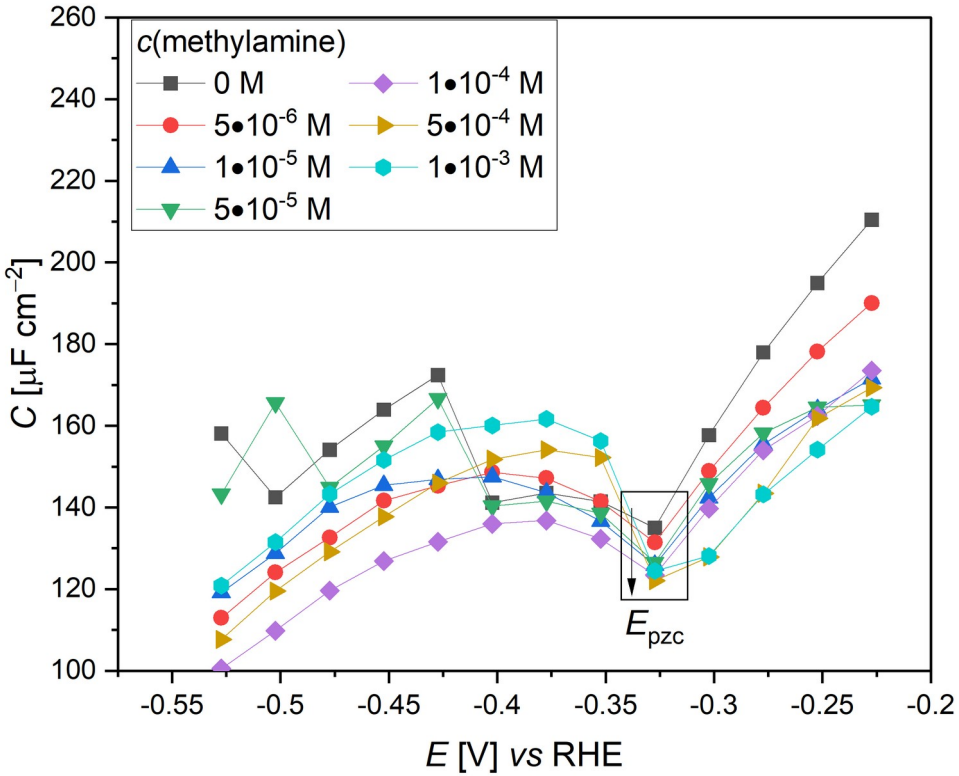
Adding acetone raises the double-layer capacitance of Cu (115 → ~131 μF cm⁻², +14 %).

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Methylamine lowers the Cu capacitance

Impedance on Cu, 0.01 M $NaClO_4$ + KOH, pH 12; E_{pzc} = −0.327 V vs RHE



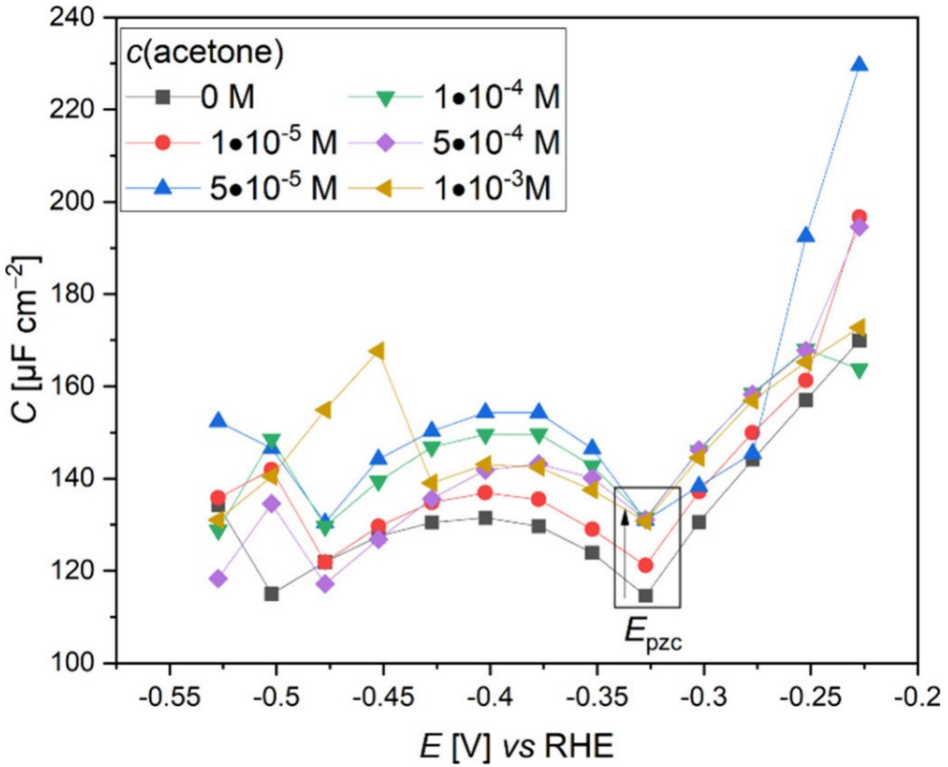


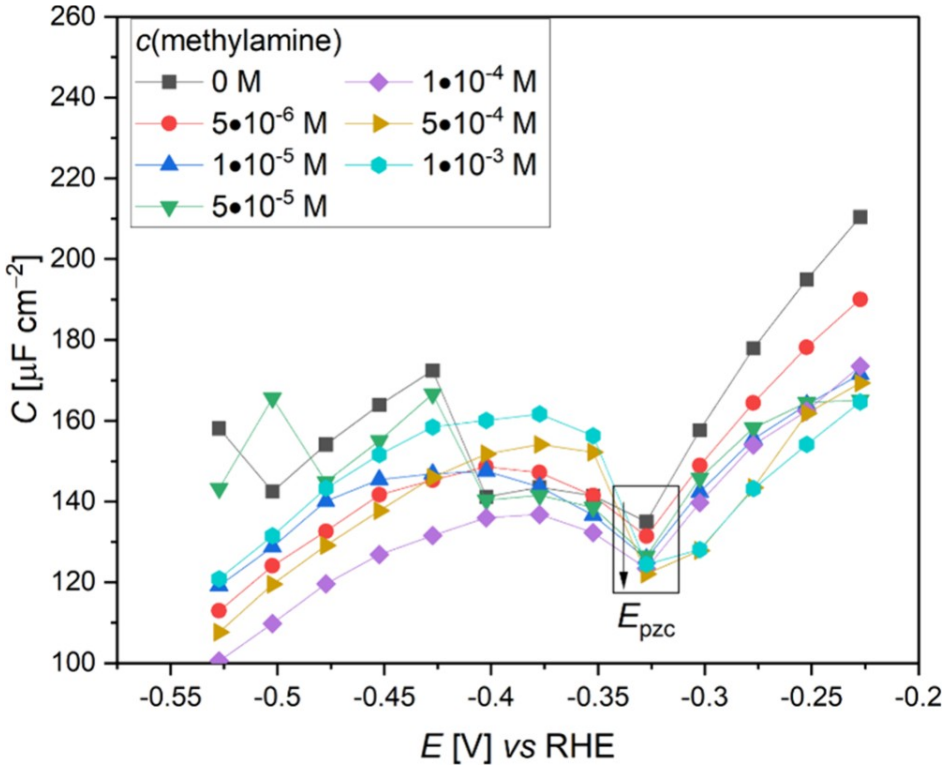
Adding methylamine lowers the double-layer capacitance of Cu (135 → 122–126 μF cm⁻², −10 %).

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Acetone raises and methylamine lowers the Cu capacitance

Impedance on Cu, 0.01 M $NaClO_4$ + KOH, pH 12; E_{pzc} = −0.327 V vs RHE





Acetone: 115 → ~131 µF cm⁻² (+14%)

Methylamine: 135 → 122–126 µF cm⁻² (−10%)

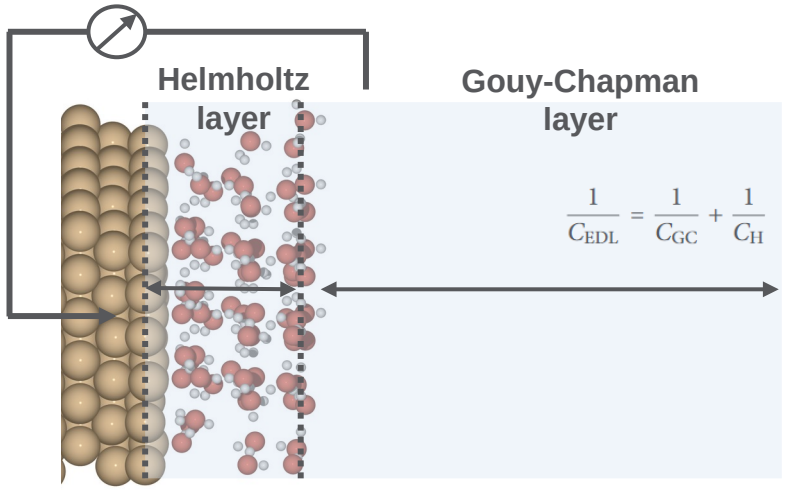
Both molecules are more polarizable than water, yet they change C in opposite directions.

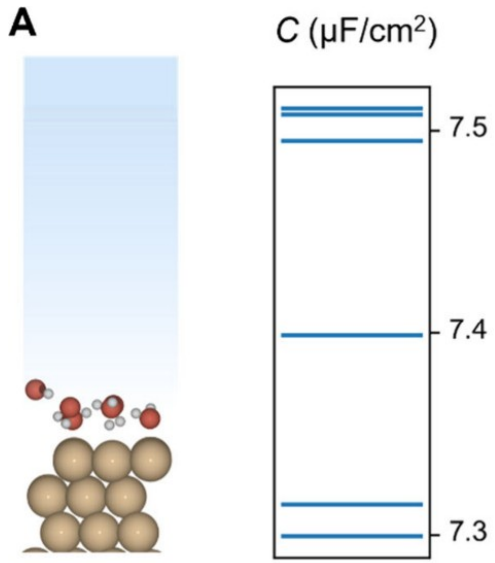
The opposite signs told that the molecules must change the interface itself.

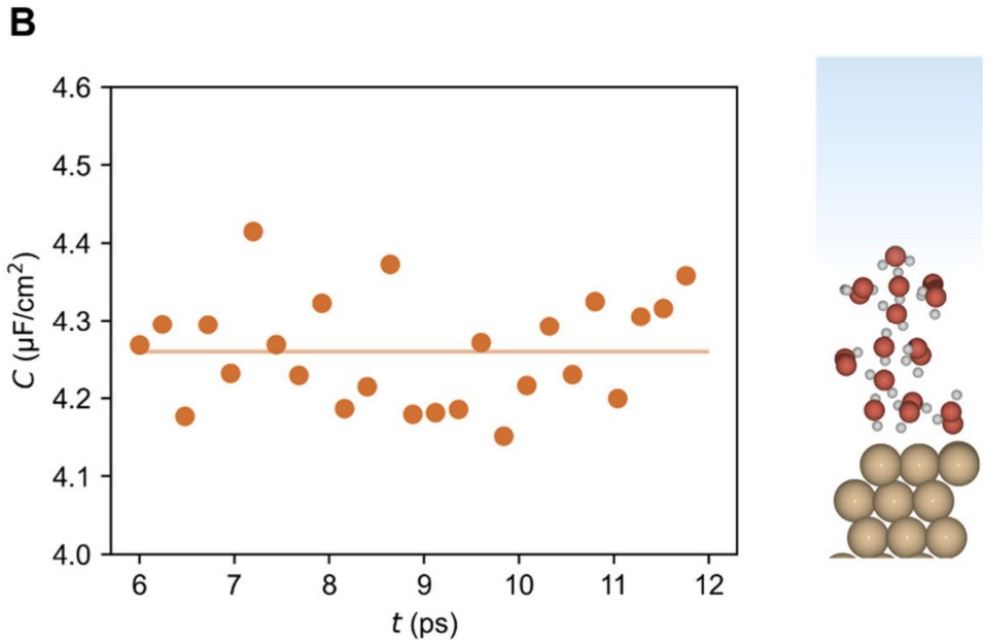
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Guan et al., ACS Appl. Mater. Interfaces 17, 4087 (2025) · measurements: Dr. Justus Kümper, RWTH Aachen

Reference: the calculated C depends on how water is described







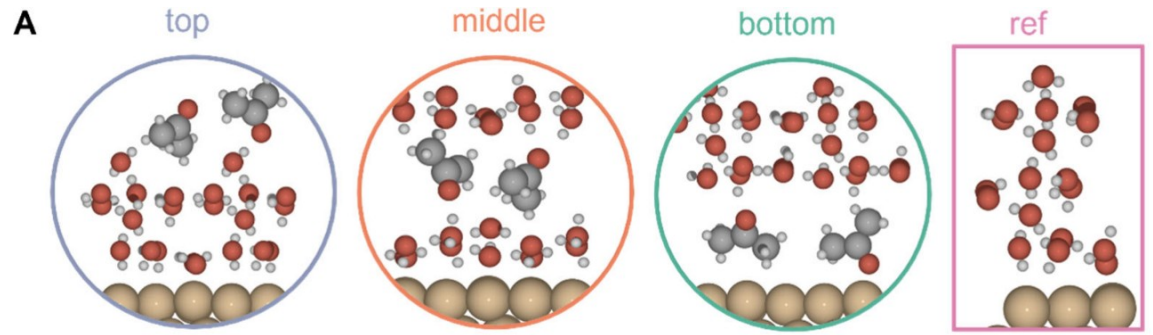
- Continuum only: **13.4** μF cm^{-2}; one explicit water layer: **7.4**; three layers (AIMD snapshots): **~4.2**
- Measured 115–135 μF cm^{-2}: rough polycrystalline electrode, fitted impedance → I compare only **relative changes**

Absolute C depends on how water is modeled, so I compare only relative changes.

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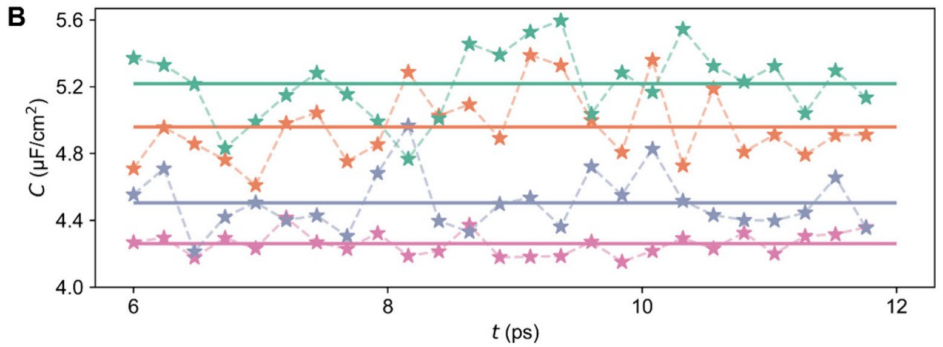
Guan et al., ACS Appl. Mater. Interfaces 17, 4087 (2025)

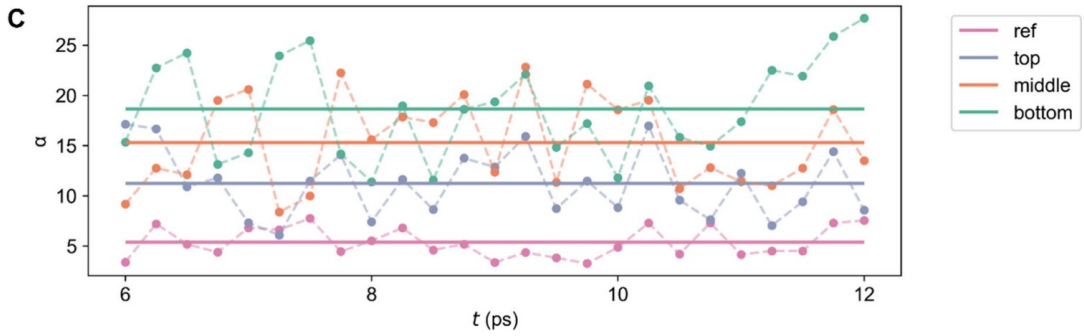
Acetone raises C in every model, most next to Cu



hydrophobic

C +6% **+16%** **+21%** **reference**





Surface charging:

$$\Omega(U) = \Omega(U_0) - \frac{1}{2}\boldsymbol{C}(U - U_0)^2$$

Electric field calculations:

$$E(F) = E(0) + \frac{\partial E}{\partial F}F + \frac{1}{2}\frac{\partial^2 E}{\partial F^2}F^2 + \frac{1}{6}\frac{\partial^3 E}{\partial F^3}F^3 + \dots$$

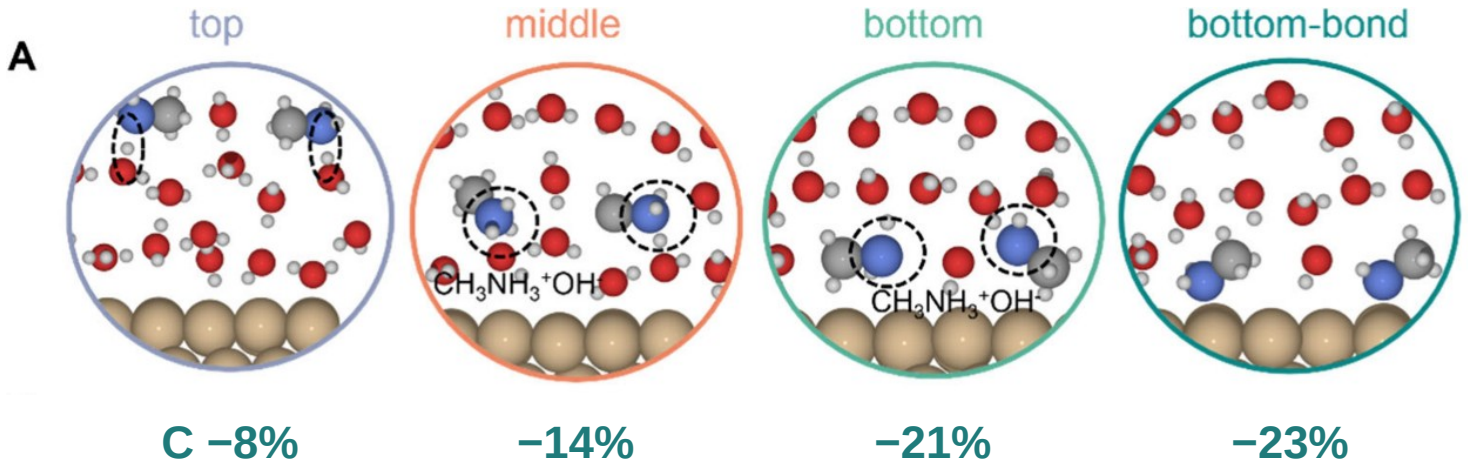
$$= E(0) - \mu_0 F - \tfrac{1}{2}\alpha F^2 - \tfrac{1}{6}\beta F^3 - \dots \qquad \mathrm{E}(F) = E(F_0) - \frac{1}{2}\boldsymbol{a}(\mathrm{F} - F_0)^2$$

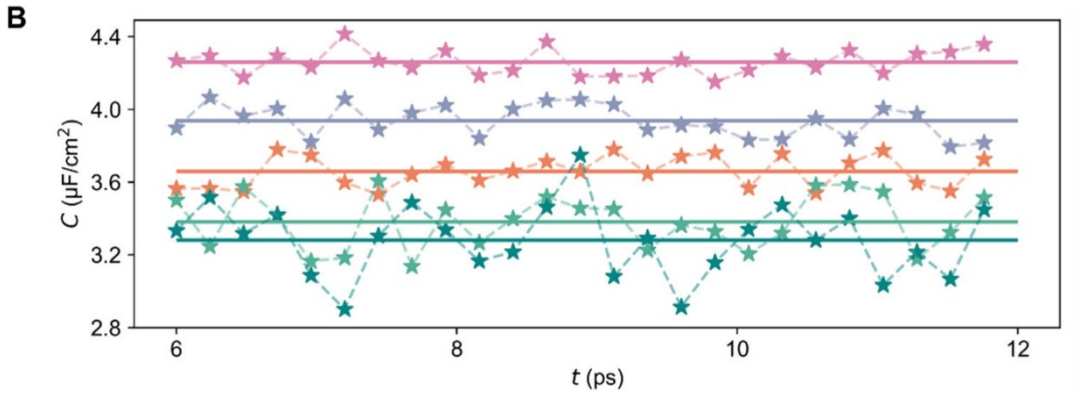
Acetone raises C in every position (+6 to +21 %), bracketing the measured +14 %.

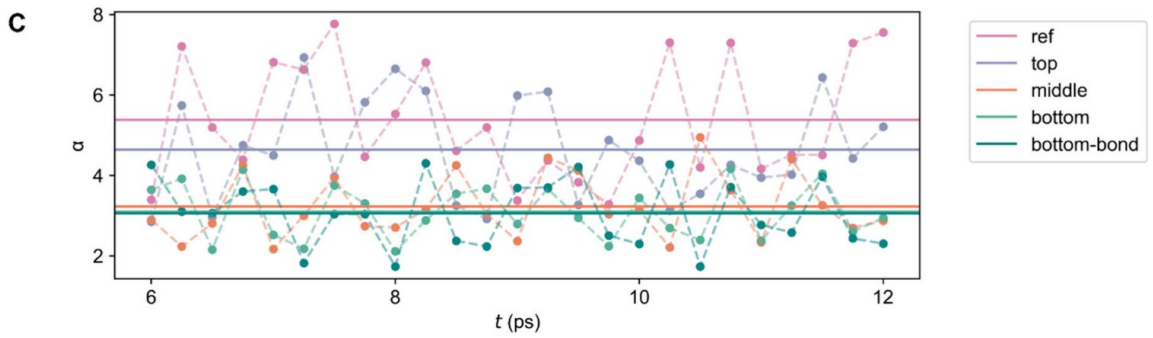
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Guan et al., ACS Appl. Mater. Interfaces 17, 4087 (2025)

Methylamine lowers C in every model, most when bound to Cu





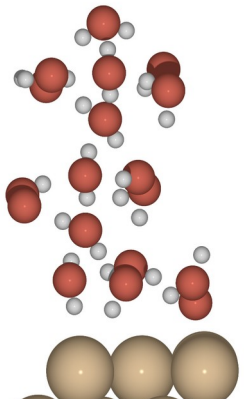


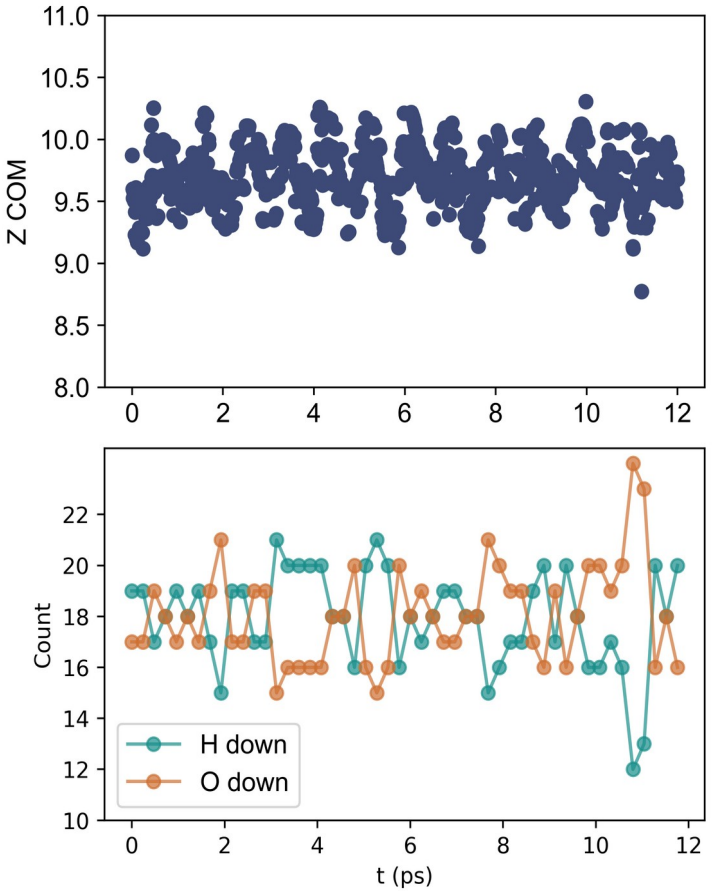
Calculated −8 to −23% vs measured −10%, although methylamine is more polarizable than water.

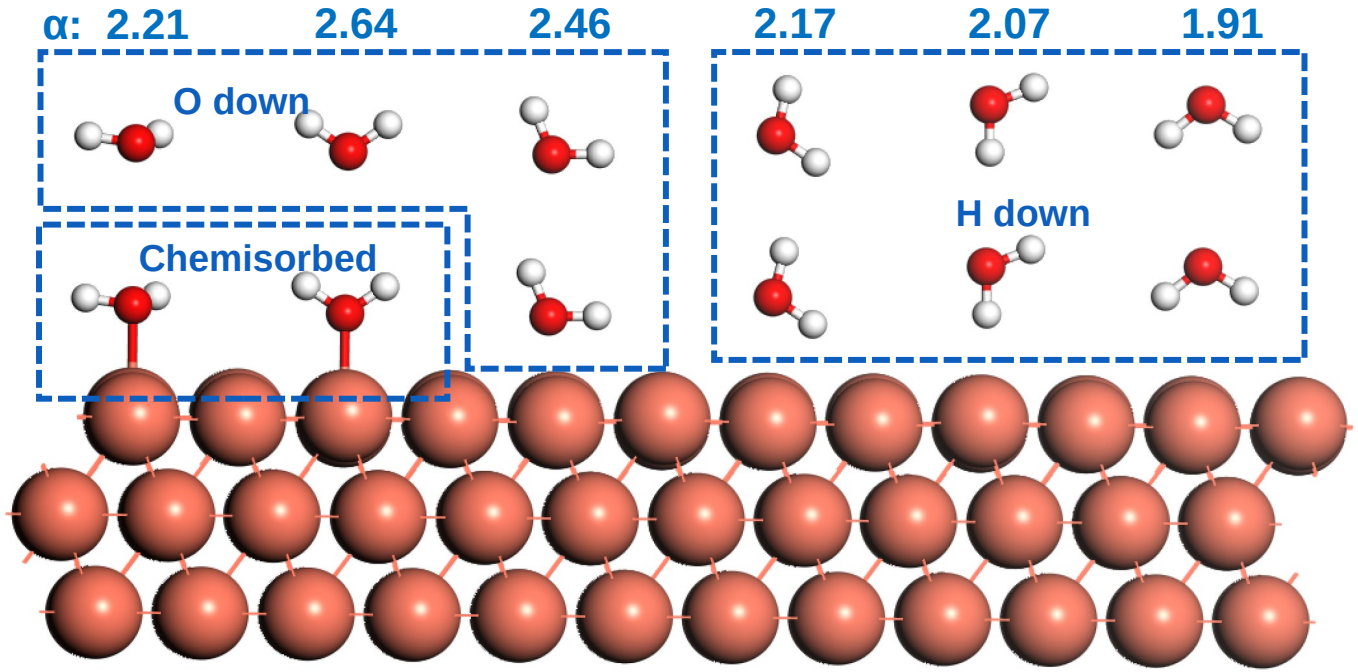
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Guan et al., ACS Appl. Mater. Interfaces 17, 4087 (2025)

Meanwhile what happens to water layers



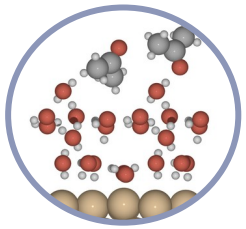


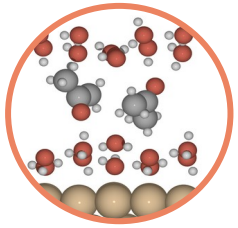


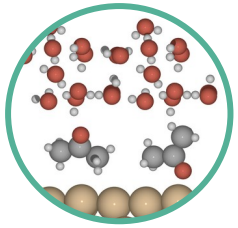
Interfacial water is O-down or H-down; H-down water is 16 % less polarizable (α 2.05 vs 2.44).

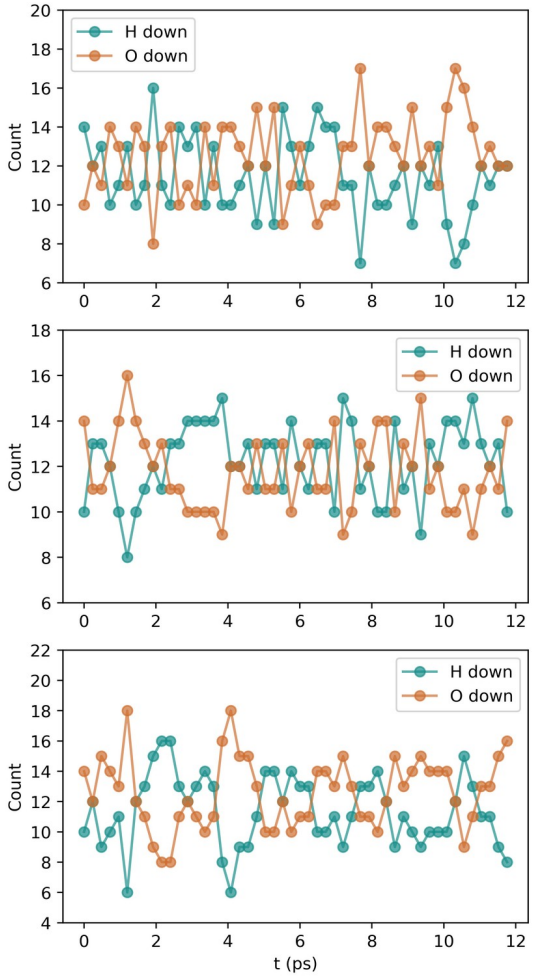
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Acetone doesn’t disturb the balanced water layers





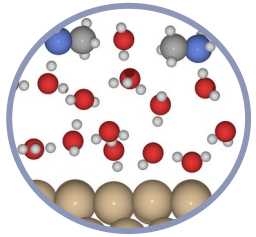


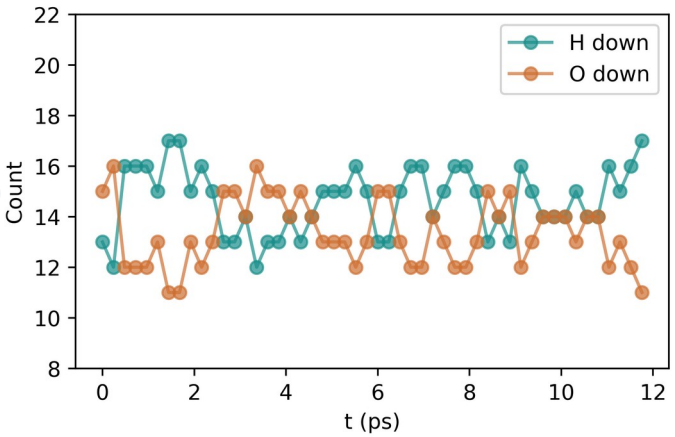


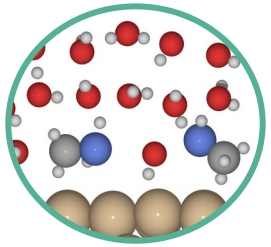
With acetone in any layer, H-down and O-down water stay balanced (about 12 each).

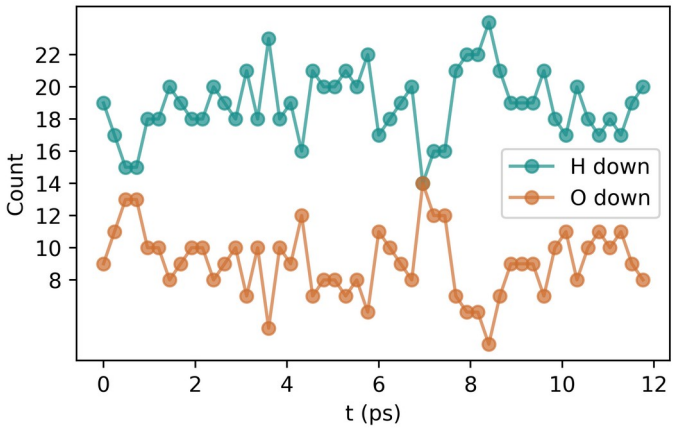
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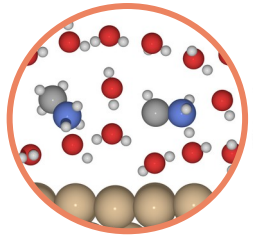
Methylamine turns interfacial water H-down

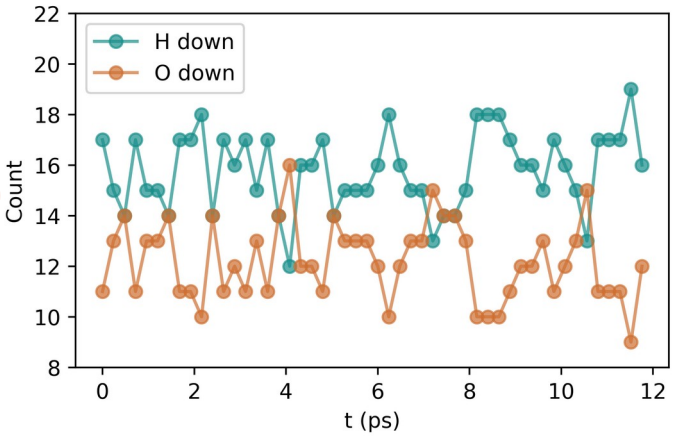


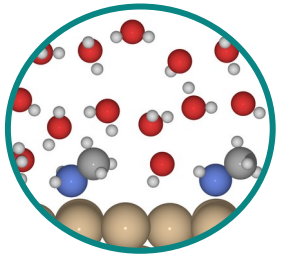


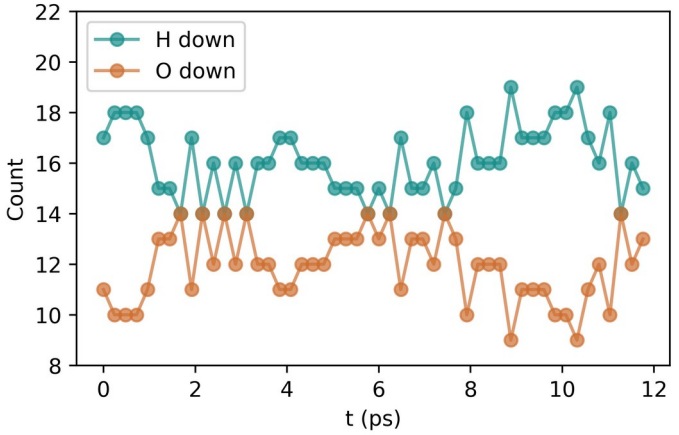












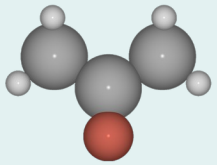
- Acetone: ~12 H-down and ~12 O-down water
- Methylamine, bottom model: **~19 H-down** vs ~9 O-down
- One water layer: H-down is **16% less polarizable** (α 2.05 vs 2.44 e Å^2 V^{-1})

Fewer O-down water molecules → a less polarizable interface → a lower capacitance.

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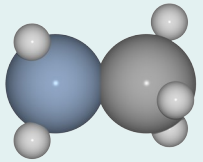
Guan et al., ACS Appl. Mater. Interfaces 17, 4087 (2025), Supporting Information

The assembled interface, not the molecule, sets the response



Acetone

- Partly hydrophobic: forms its own layer
- Keeps the H-down/O-down balance of water
- More polarizable interface → **C ↑** (measured +14%, calc. +6 to +21%)



Methylamine

- H-bond donor and acceptor; $CH_3NH_3^+OH^-$ pairs form near Cu
- Orients water H-down (~19 vs ~9)
- Less polarizable interface → **C ↓** (measured −10%, calc. −8 to −23%)

The reactants change the interface before they react. Nothing leaves: a change of response.

Next: the same N–Cu bond, at a kink atom and with more ligands, pulls Cu out of the electrode → Part II

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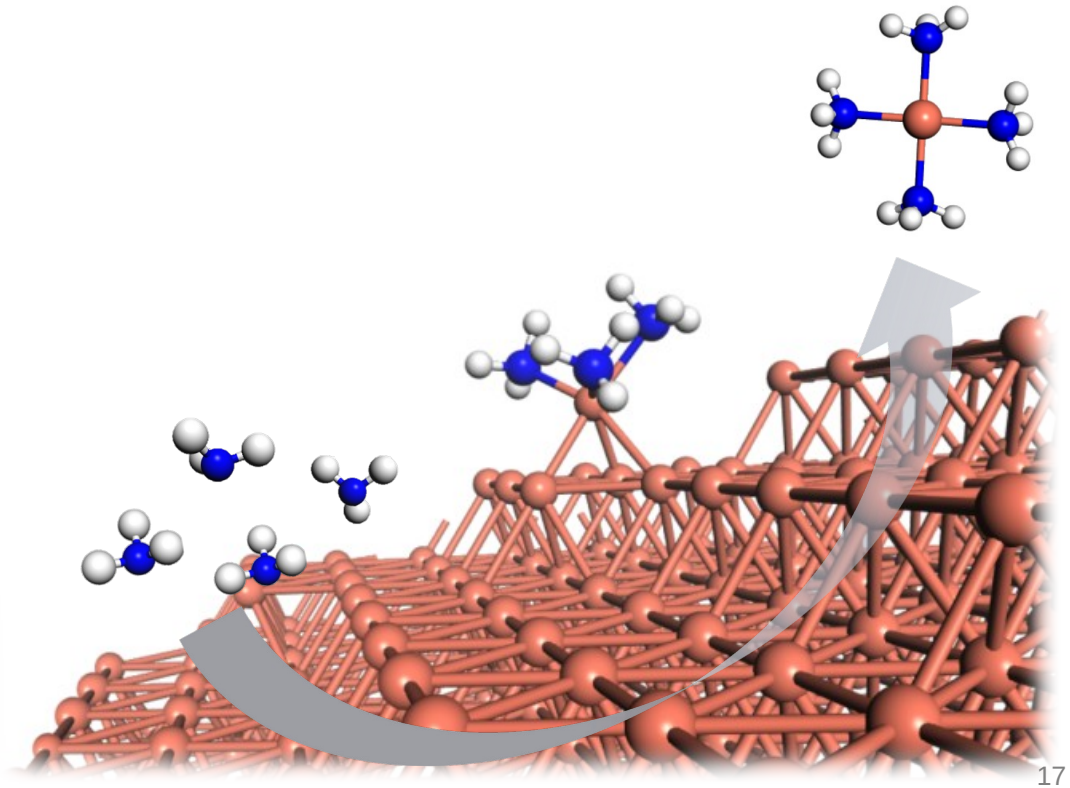
Guan et al., ACS Appl. Mater. Interfaces 17, 4087 (2025)

Part II · Loss of electrode material

Why does a Cu cathode dissolve in amine solutions?

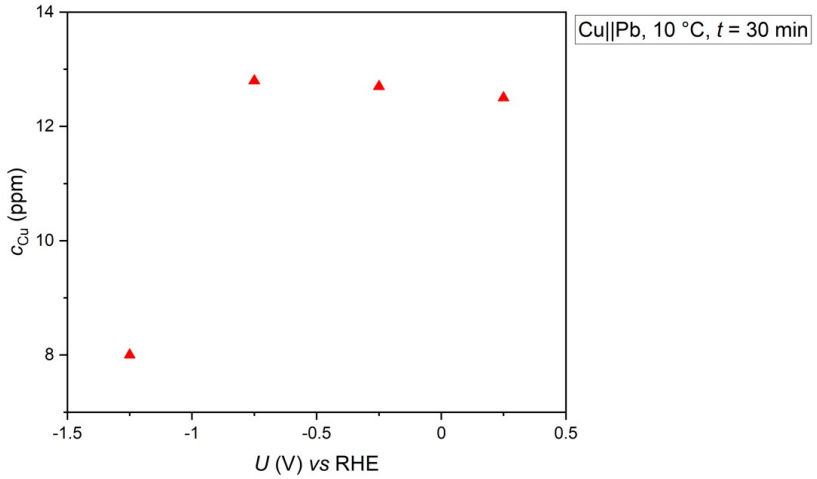
Chapter 4 · Yani Guan et al., **Chem. Sci. 15, 14485 (2024)**

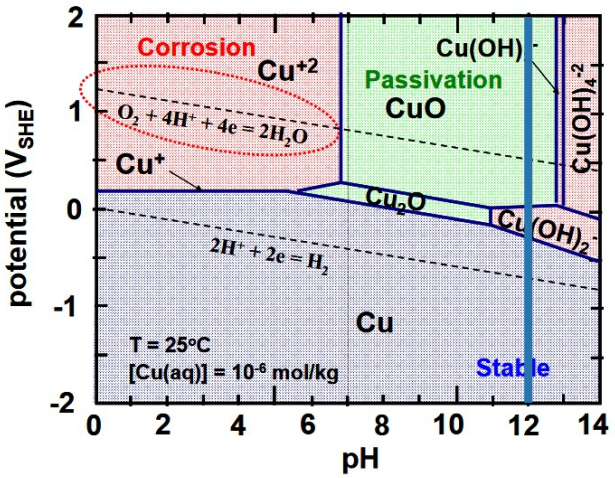
Experiments: Dr. Justus Kümper, Dr. Regina Palkovits, RWTH Aachen



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Cu dissolves at −0.75 V, where bare Cu should be stable





- 30 min at +0.25, −0.25 and −0.75 V: 12.5–12.8 ppm Cu; at −1.25 V: ~8 ppm
- open circuit: 84 ppm in 18 min

- Pourbaix diagram of Cu in water at pH 12: $Cu(OH)_2$ only positive of +0.4 V vs RHE
- **It has no amine ligands in it**

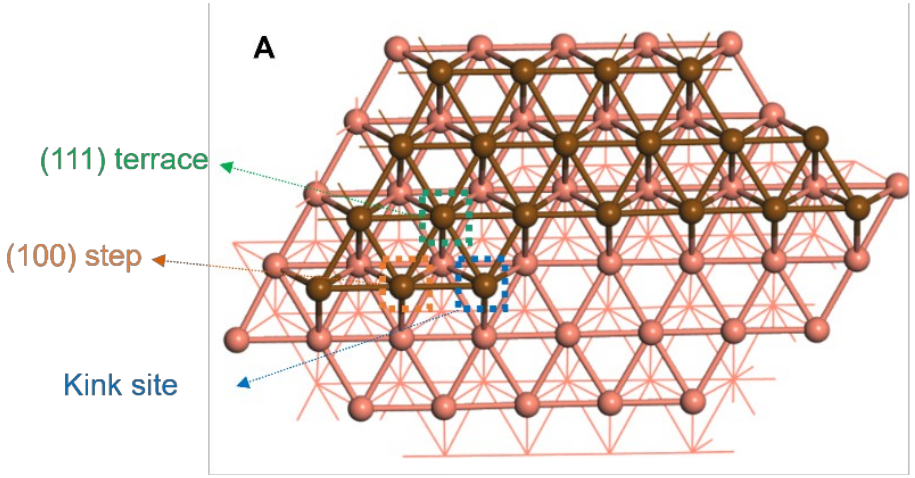
Cu dissolves where bare Cu should be stable: the amine must hold Cu outside the lattice.

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Guan et al., Chem. Sci. 15, 14485 (2024) · measurements: Dr. Justus Kümper

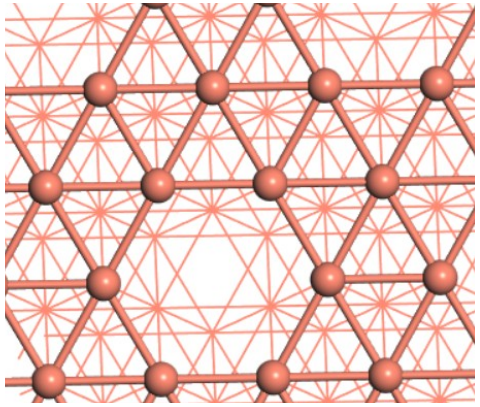
Models: kink and terrace sites, NH_3 as the model amine

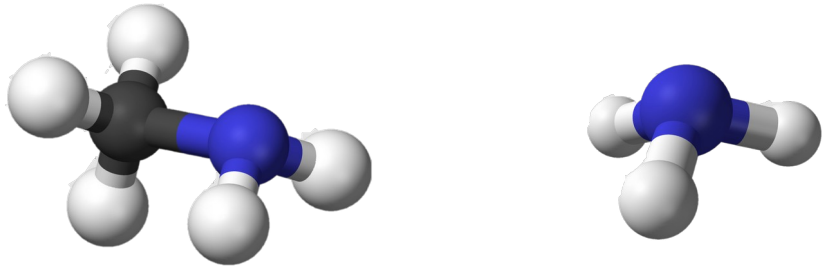
Cu (843)



- Kink atom of Cu(843): 6 Cu neighbors (terrace atom: 9)
- Amines bind ~0.5 eV more strongly at the kink than on the terrace
- NH_3 adsorbs like methylamine → model ligand; four NH_3 in every cell

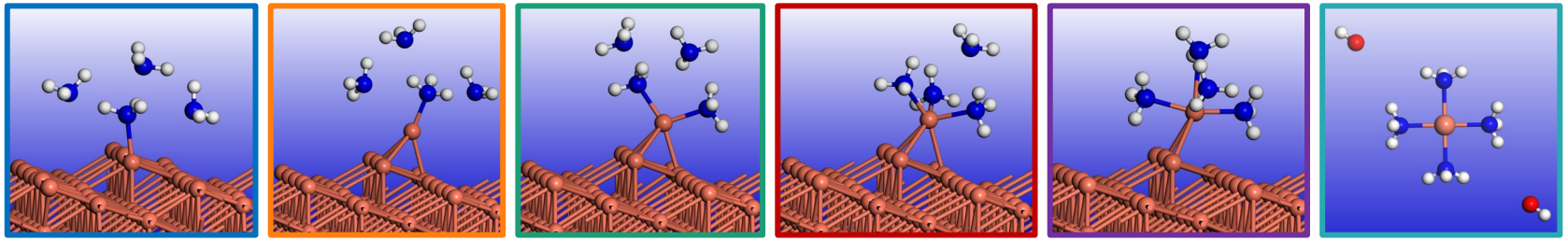
Cu (111)

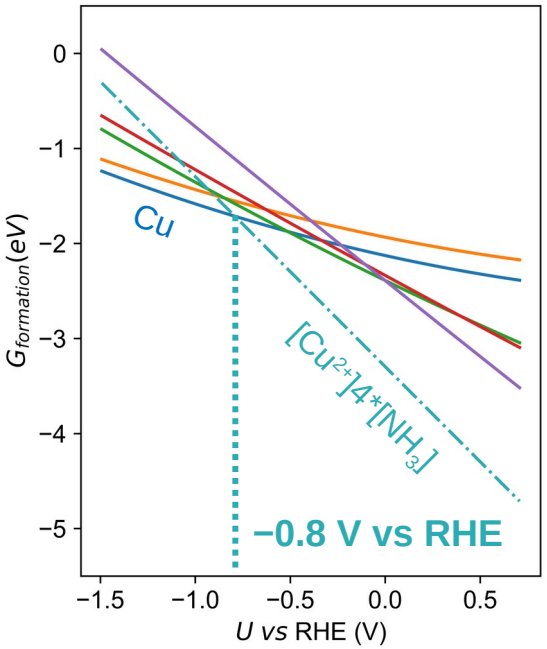


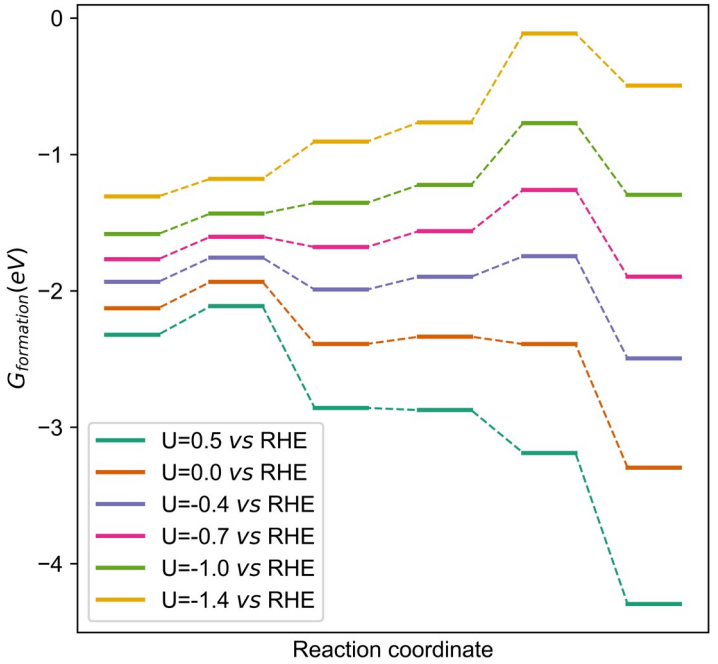


Kink atoms have fewer Cu neighbors and bind amines ~0.5 eV more strongly; NH_3 models the amine.

Kink Cu dissolves as $Cu(NH_3)_4^{2+}$ positive of −0.8 V vs RHE





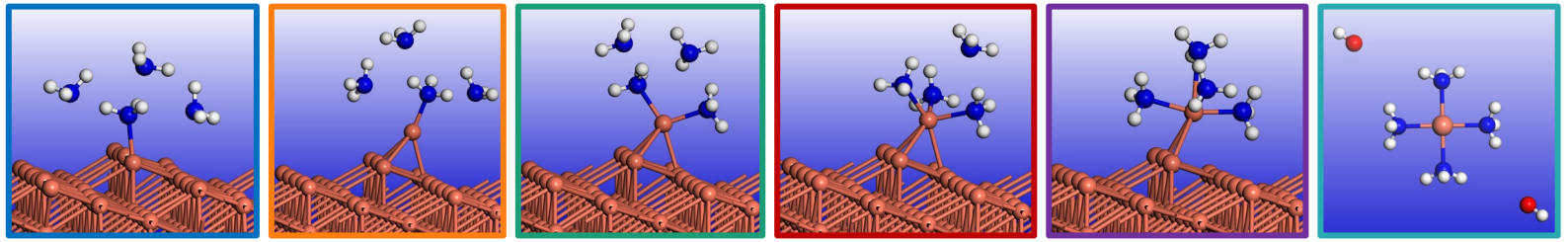


Kink Cu dissolves as $Cu(NH_3)_4^{2+}$ positive of −0.8 V; one NH_3 cuts the extraction to ~0.2 eV.

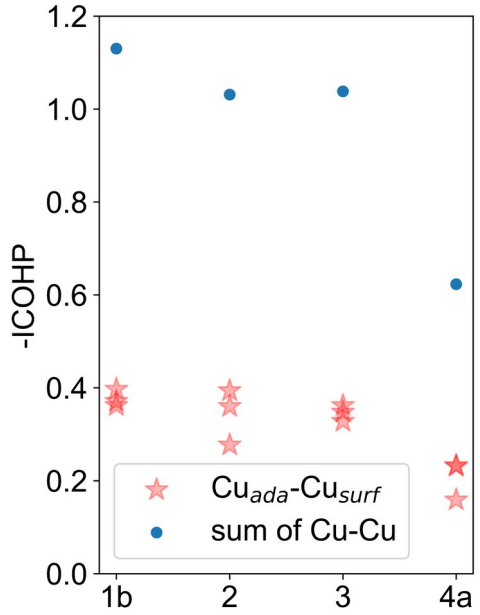
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Guan et al., Chem. Sci. 15, 14485 (2024)

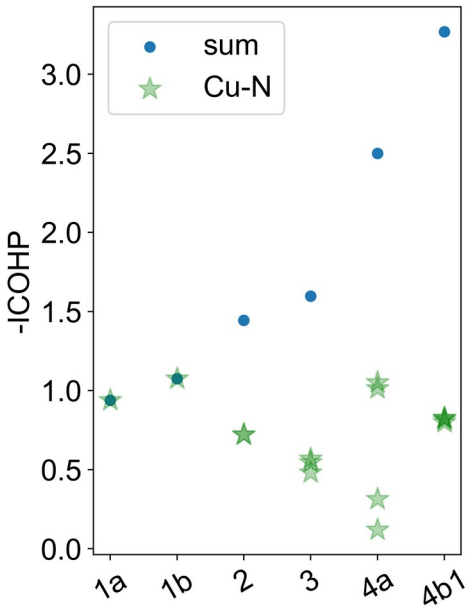
Amine ligands weaken the Cu–Cu bonds that hold the adatom



Chemical bonding between Cu_{adatom} and $Cu_{terrace}$



Chemical bonding between $Cu_{complex}$ and $N_{complex}$

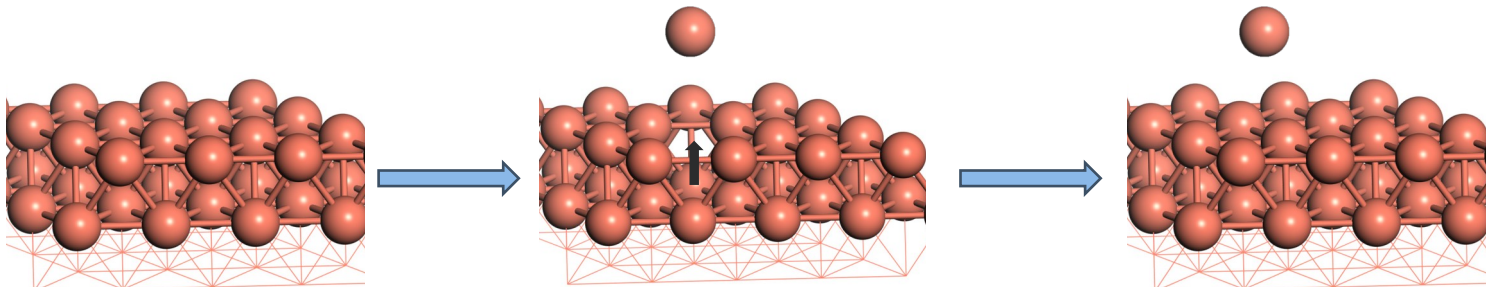


Dissolution is a competition between Cu–Cu and Cu–N bonds at a low-coordinated atom.

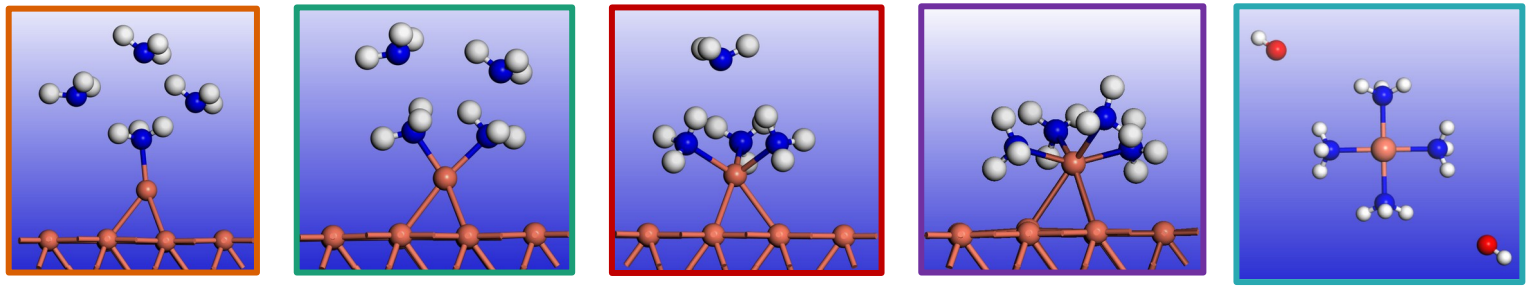
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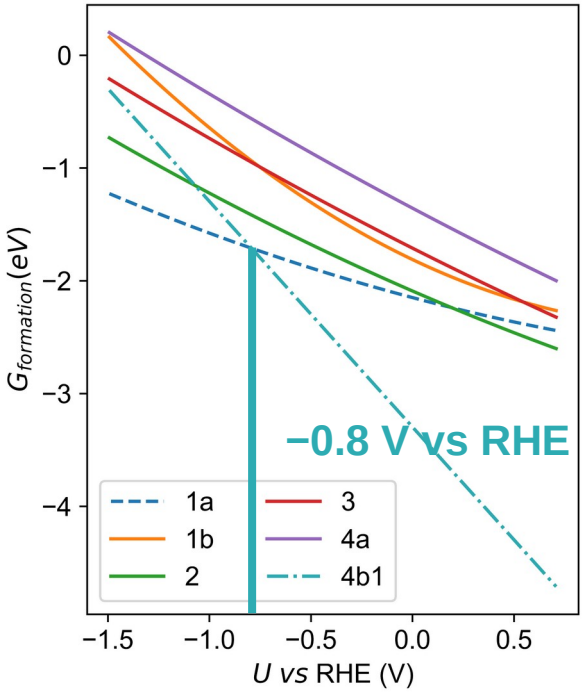
Guan et al., Chem. Sci. 15, 14485 (2024)

Cu(111) with a refilled vacancy: same threshold, higher cost



A bulk Cu reservoir compensates the surface vacancy



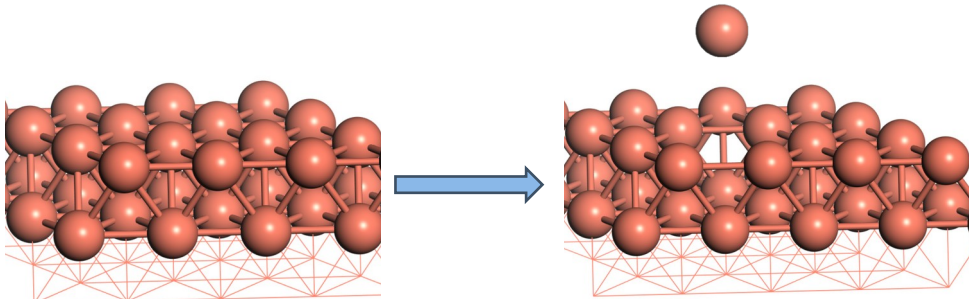


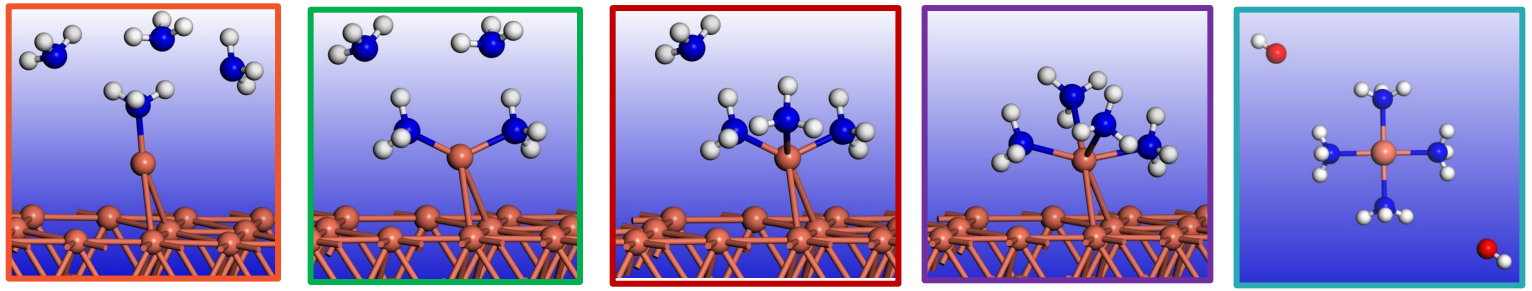
A refilled vacancy behaves like a kink: Cu comes from the bulk, same −0.8 V threshold.

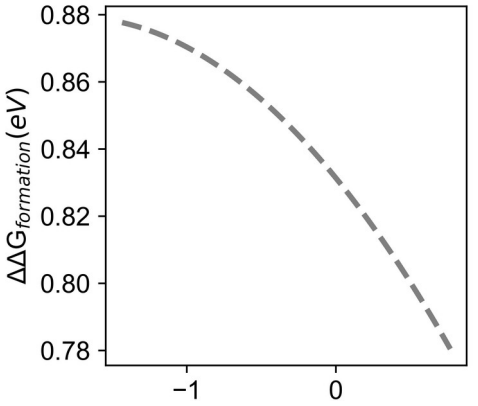
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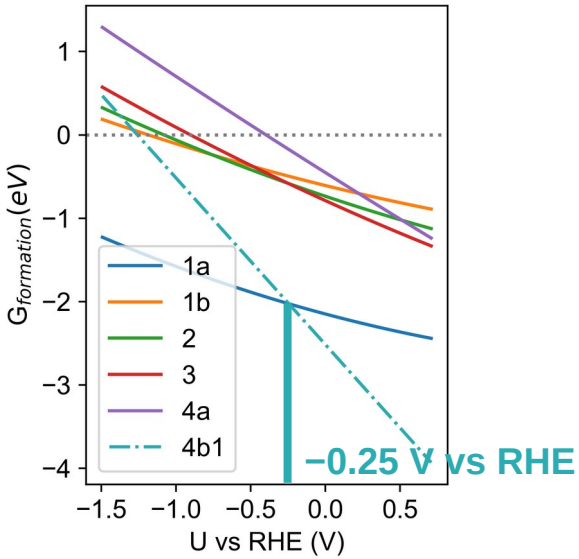
Guan et al., Chem. Sci. 15, 14485 (2024)

An intact terrace does not dissolve: the vacancy costs ≈ 0.8 eV









- Extracting the adatom: **0.8 eV** (~10^{-12} s^{-1} at room temperature)
- All surface complexes lie 1.2–2.5 eV above 1a
- The vacancy moves the $Cu(NH_3)_4^{2+}$ threshold to **−0.25 V**

Keeping the vacancy costs ≈ 0.8 eV: an intact terrace does not dissolve (threshold −0.25 V).

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Guan et al., Chem. Sci. 15, 14485 (2024)

Dissolving Cu comes from low-coordinated sites

Site	Adatom 1a → 1b	Threshold, $Cu(NH_3)_4^{2+}$	My reading
Kink, Cu(843)	0.14–0.21 eV	**−0.8 V**	Removal leaves a new kink
Cu(111), vacancy refilled	0.19–0.42 eV	**−0.8 V**	= an adatom supplied by a kink or step
Cu(111), vacancy kept	1.4–1.55 eV	**−0.25 V**	Intact terrace does not dissolve

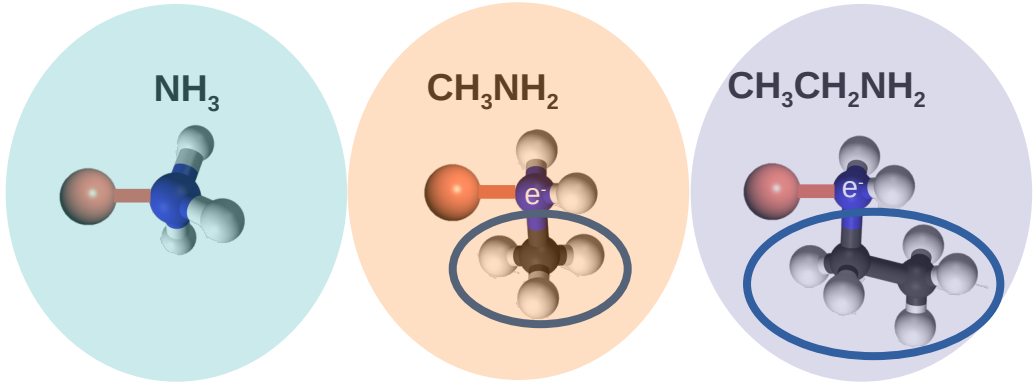
- Kink and refilled terrace share the threshold: in both, the Cu atom comes from the bulk reservoir
- Measured Cu is flat from +0.25 to −0.75 V (12.5–12.8 ppm): once dissolution is allowed, its rate is set by the **number of low-coordinated sites**, not by the driving force

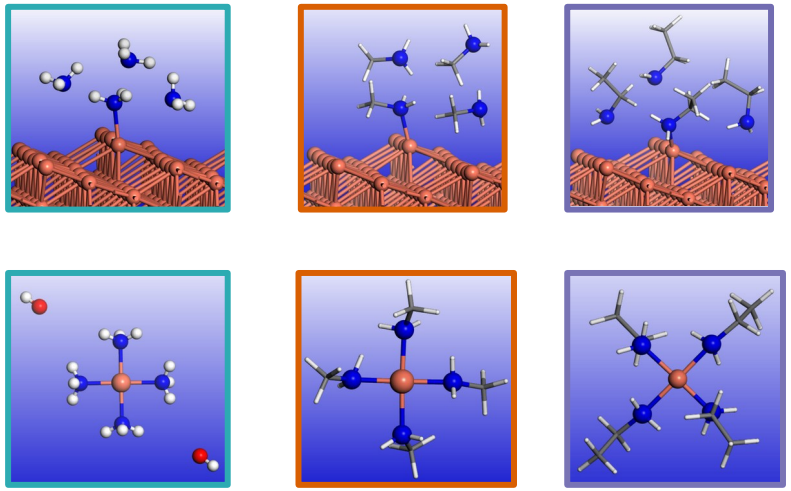
Testable: annealed and roughened Cu electrodes should lose Cu at different rates.

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Guan et al., Chem. Sci. 15, 14485 (2024)

Substituted amines stabilize the complex but slow its formation



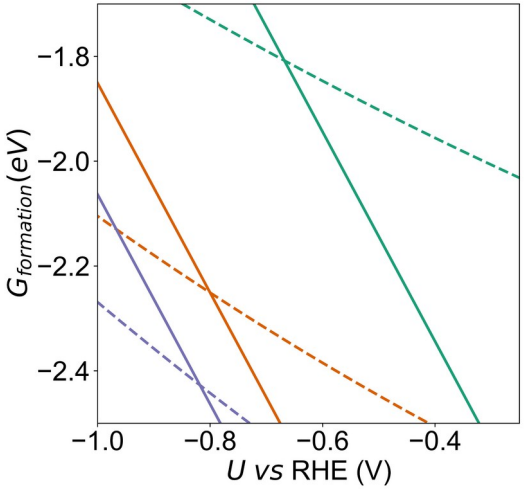


Electron-donating Group

- $-CH_3$, $-CH_2CH_3$
- More electrons on N
- Stronger bonding Cu-N

Extraction of the kink atom (1a → 1b): 0.20 eV (NH_3), 0.39 eV (CH_3NH_2), 0.45 eV ($C_2H_5NH_2$)

Experiment at −0.25 V: less Cu dissolves with methylamine and ethylamine than with NH_3

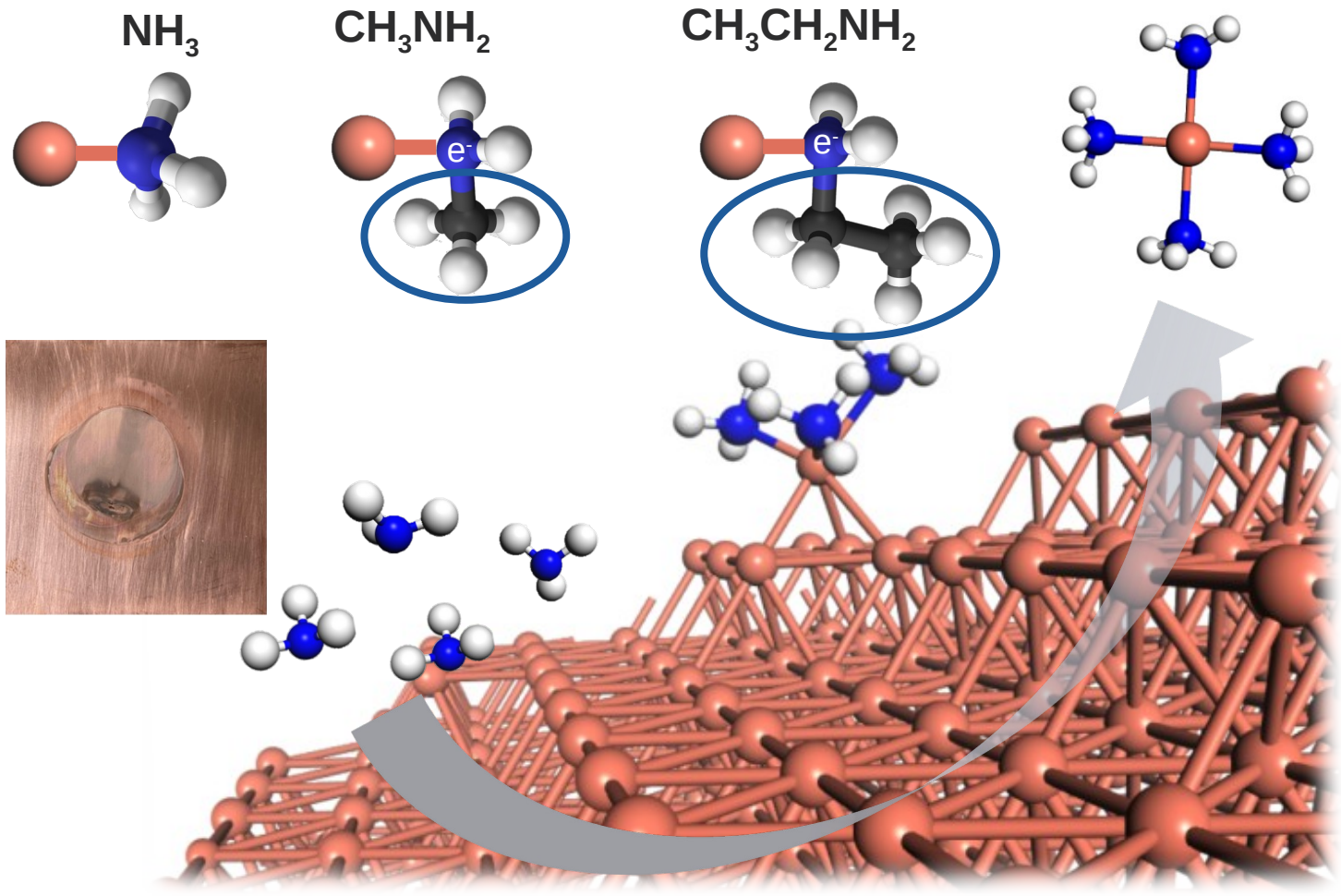


Methyl and ethyl groups stabilize the complex but slow the extraction step (0.20 → 0.45 eV).

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Guan et al., Chem. Sci. 15, 14485 (2024)

Amines turn a Cu cathode into a source of dissolved Cu



- Amines bind low-coordinated Cu and pull it out as an adatom
- Cu–N bonds replace Cu–Cu bonds until $Cu(NH_3)_4^{2+}$ detaches
- Cu cathodes are not stable positive of ≈ −0.8 V vs RHE in amine electrolytes
- Most Cu is lost at open circuit: keep the cathode polarized during start-up and cooling

Next: a metal species that leaves and comes back → Part III

The species leaves and does not return: loss of electrode material.

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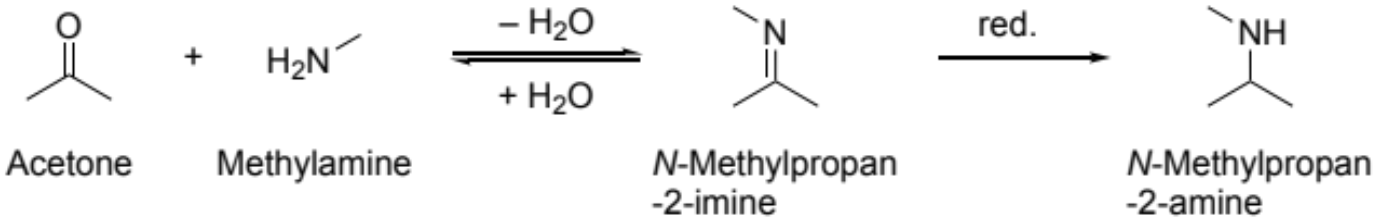
Guan et al., Chem. Sci. 15, 14485 (2024)

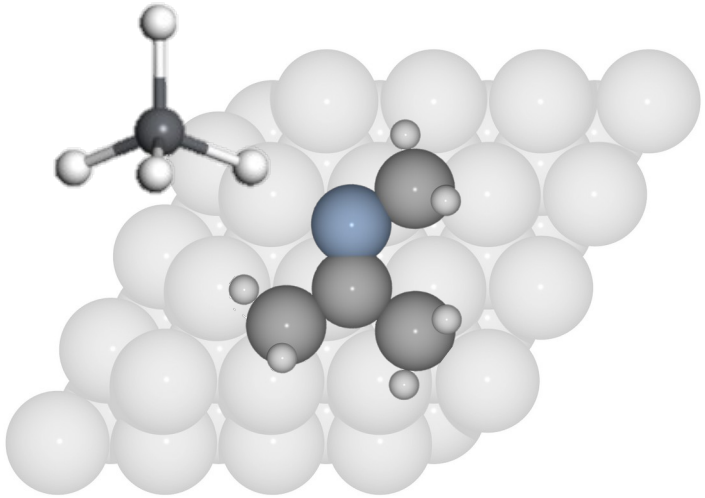
Part III · Catalysis by a shuttle

Why do ppm amounts of Pb make Ag active for the amination?

Chapter 5 · Yani Guan et al., **Catal. Sci. Technol. 16, 4090 (2026)**; Kümper et al., Angew. Chem. 2024, 2026

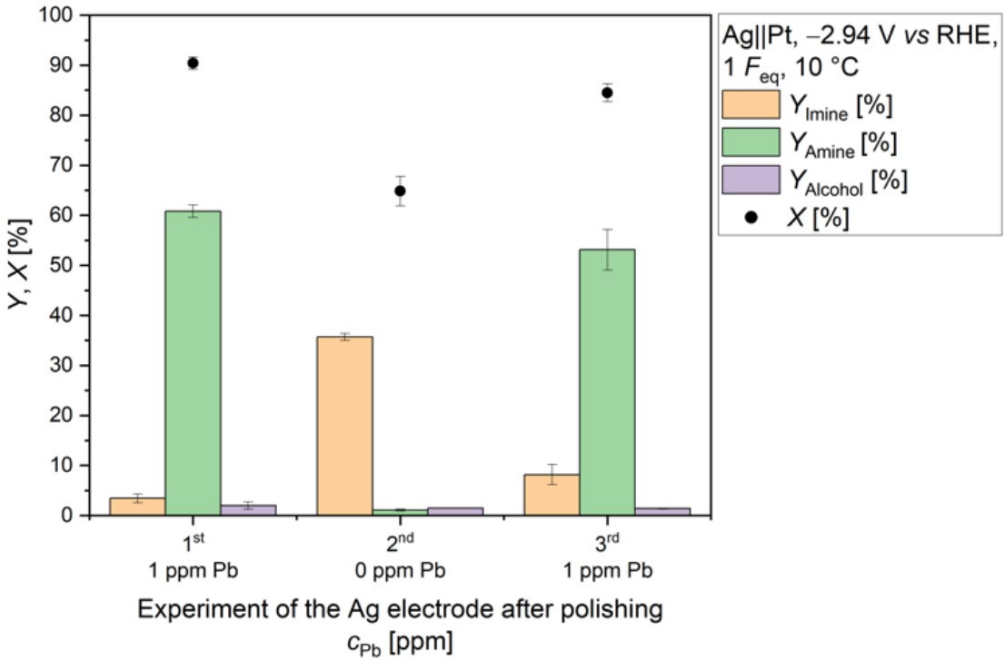
Experiments: Dr. Justus Kümper, Dr. Sonja D. Mürtz, Dr. Regina Palkovits (RWTH Aachen); flow-cell ICP-MS: Dr. Angelina Cuomo, Dr. Pavlo Nikolaienko, Dr. Karl J. J. Mayrhofer

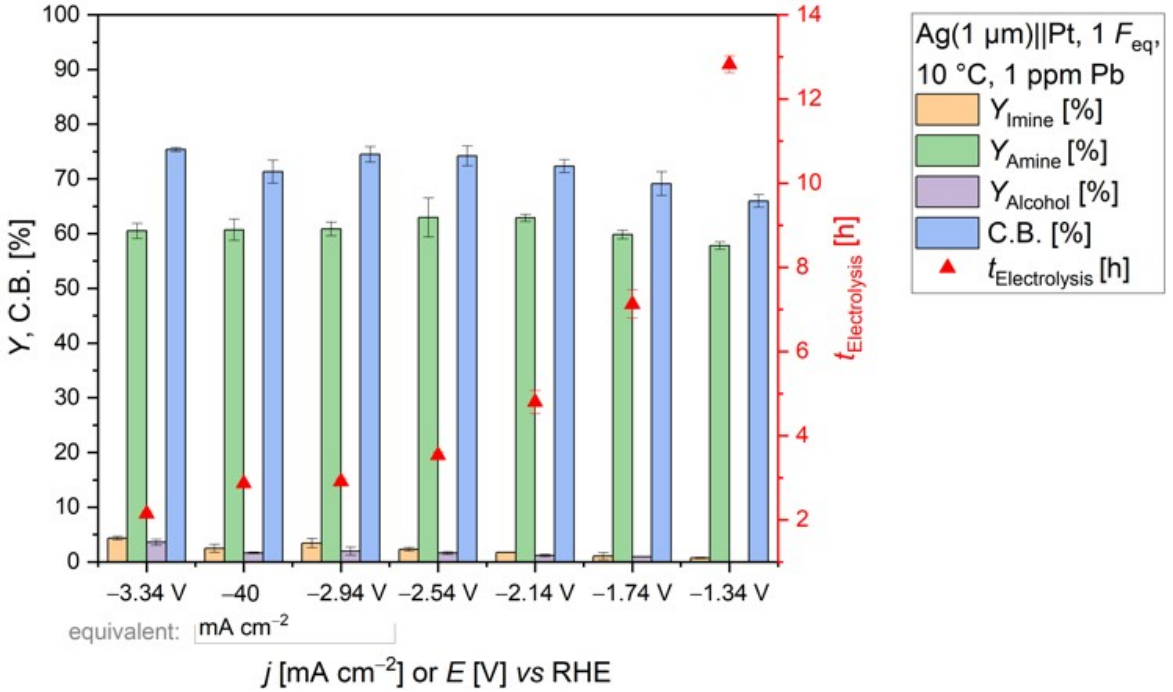




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Pb acts from the solution, not as a modified cathode





Same Ag electrode: 1 ppm Pb → no Pb → 1 ppm Pb

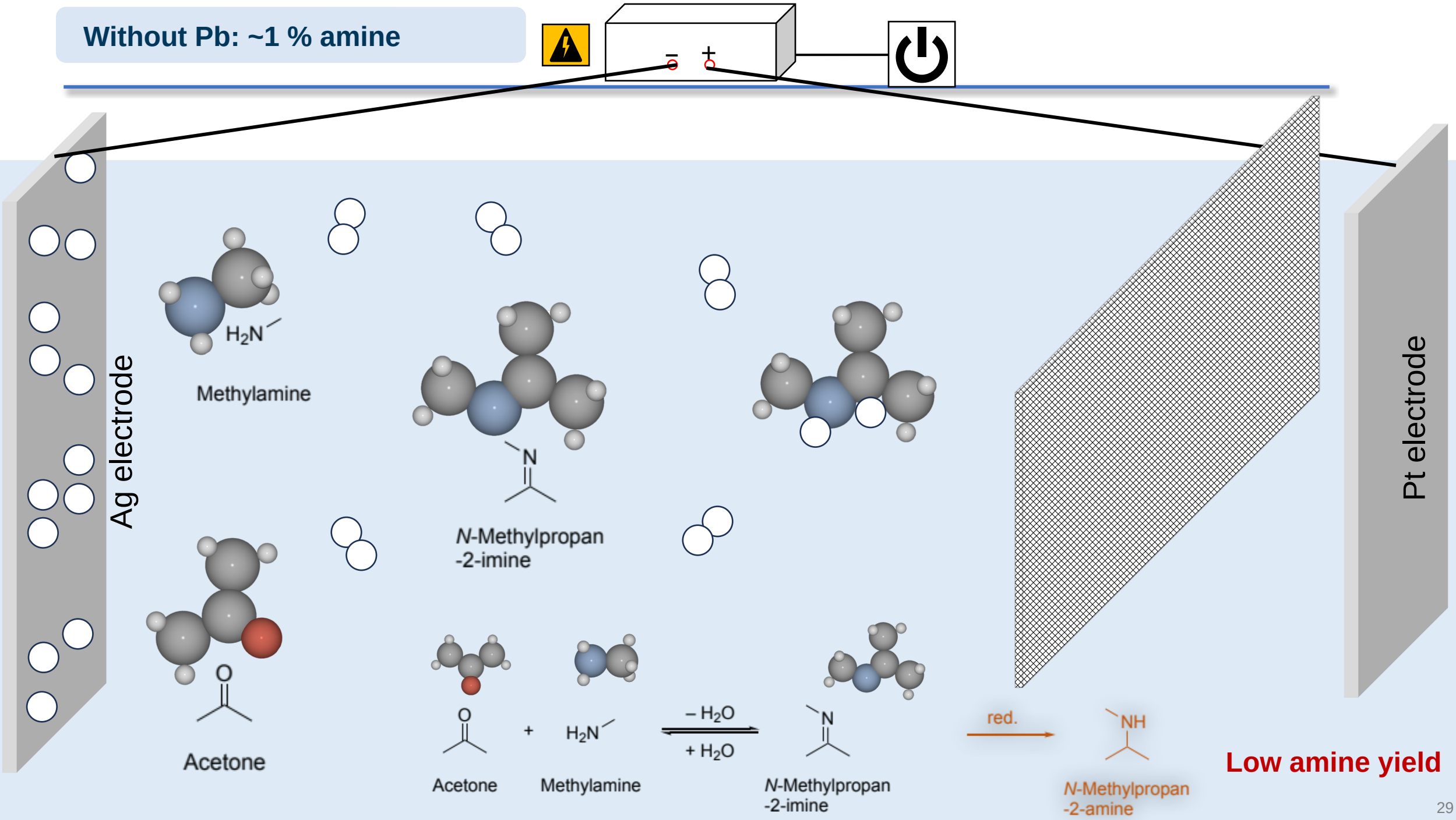
- 1 ppm Pb raises the amine yield on Ag from ~1% to **61%**; the reused electrode without new Pb gives 1.1%
- Pb electrodes disintegrate under HER (from about −0.6 V); dissolved Pb is not redeposited on GC

The active Pb species is in solution; the cathode is needed to make it.

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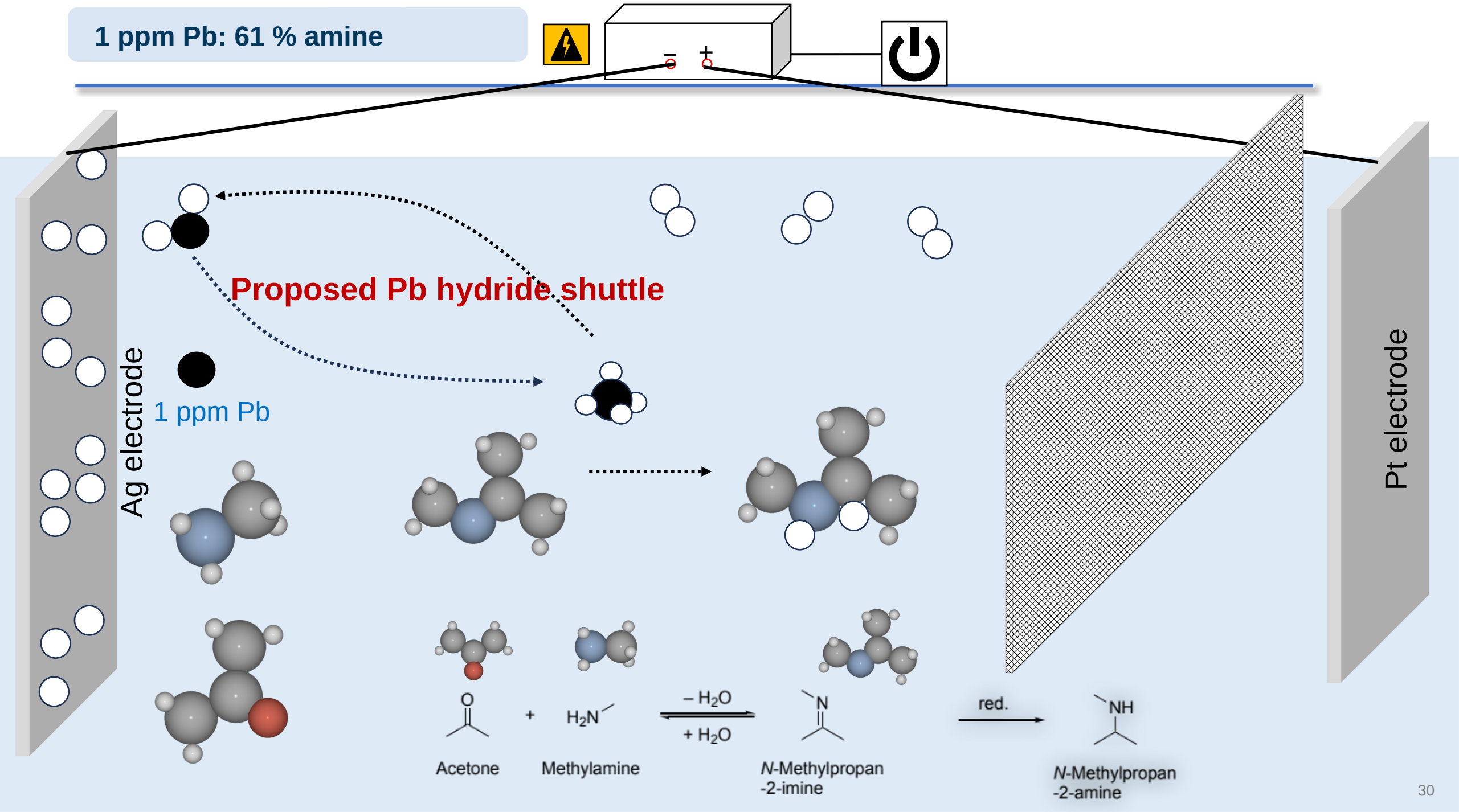
Guan et al., Catal. Sci. Technol. 16, 4090 (2026); Kümper et al., Angew. Chem. Int. Ed. 63, e202411532 (2024)

Without Pb: ~1 % amine

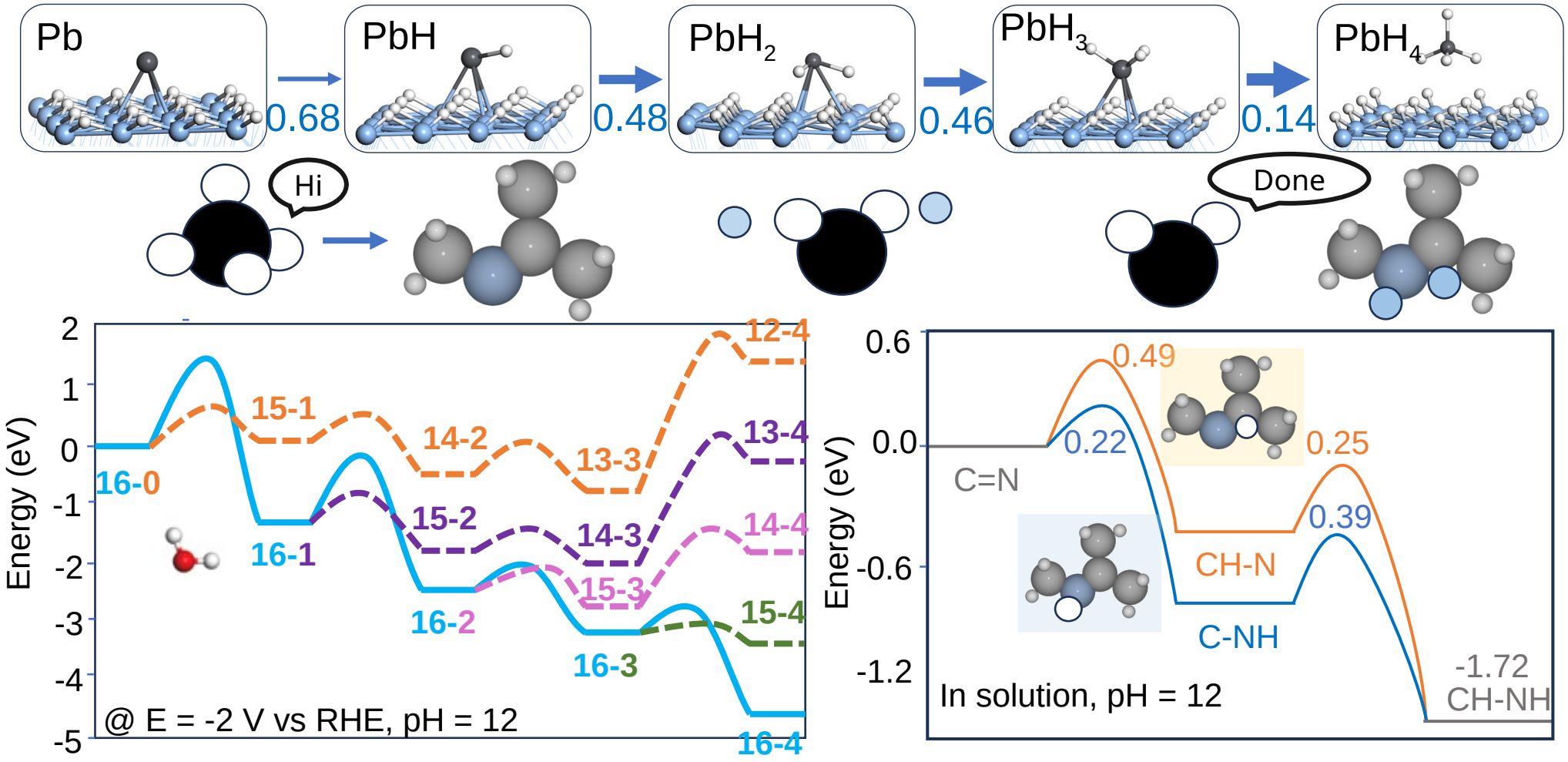


Low amine yield

1 ppm Pb: 61 % amine

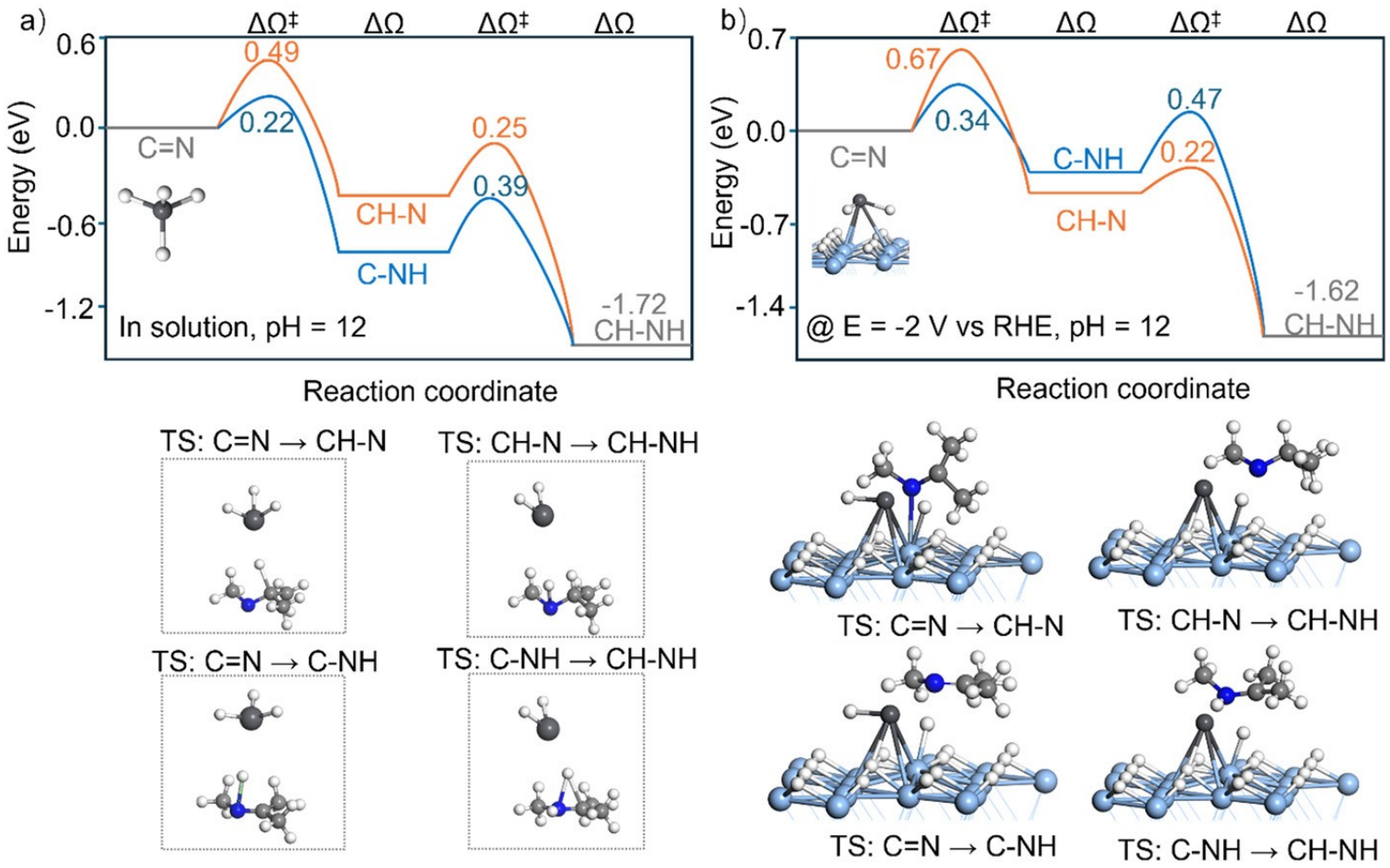


PbH_4 forms on H-covered Ag and reacts in solution



At −2 V, Pb on H-covered Ag becomes PbH_4, which hydrogenates the imine in solution (0.39 eV).

Both Pb hydride routes beat direct H transfer on Ag



PbH_4 in solution

0.39 eV (ΔΩ = −1.72 eV)

PbH_2 on Ag

0.47 eV (ΔΩ = −1.62 eV)

Direct on Ag: > 0.9 eV

I favor the PbH_4 route: its cycle only goes back to PbH_2 (< 0.5 eV), while the surface route must hydrogenate Pb again (0.68 eV)

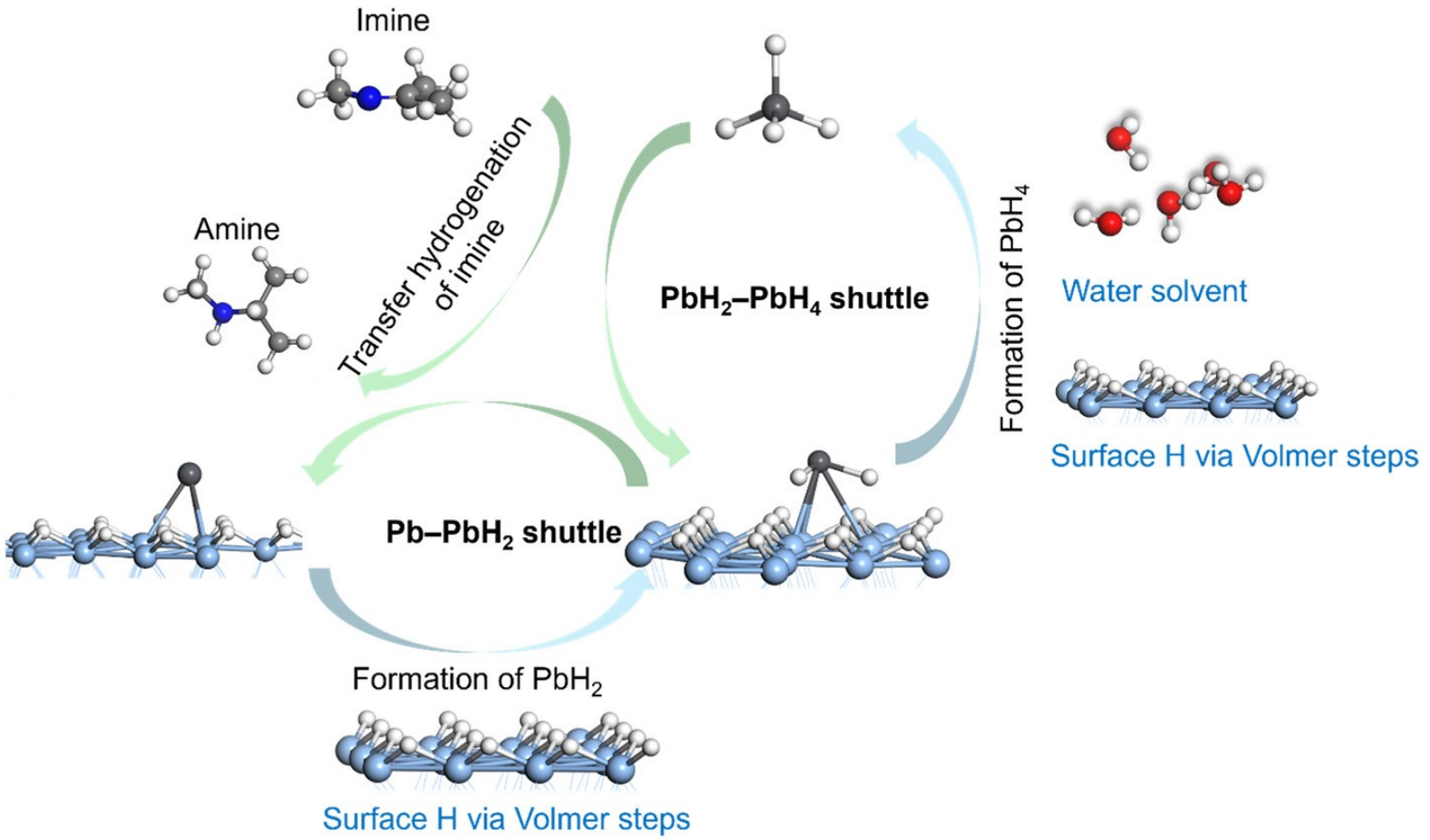
Within DFT accuracy, both remain possible

Both Pb hydride routes (0.39 and 0.47 eV) beat direct H transfer on Ag (> 0.9 eV).

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Guan et al., Catal. Sci. Technol. (2026)

Proposed mechanism: a PbH_4/PbH_2 shuttle



1 · Formation on Ag
Pb → PbH_2 → PbH_4 with H from the surface and from water

2 · Transfer in solution
PbH_4 desorbs and hydrogenates the imine (0.39 eV)

3 · Return
PbH_2 readsorbs and is hydrogenated again

Side reaction: hydrolysis to $Pb(OH)_2$ (0.5–0.8 eV), which is reduced back at the electrode

The yield is flat from −1.34 to −3.34 V: the potential only has to make the hydride.

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Guan et al., Catal. Sci. Technol. (2026)

Part IV · Catalysis by confinement

Does a desolvated Cs^+ bind CO_2 directly?

Chapter 6 · Shan, Jaugstetter, Feijóo, Guan et al., Nat. Catal. 9, 1009 (2026) (first four authors contributed equally)

1 Infrared

When is CO_2 activated, and does Cs^+ lose water?

Experiment

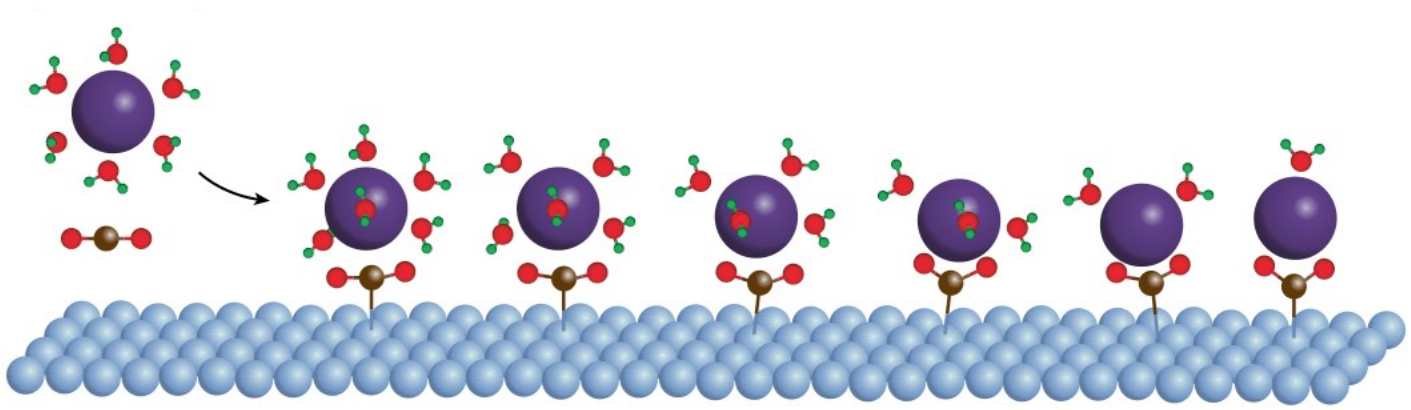
2 My calculations

What is the Cs–O contact, what does it do to CO_2, and when does it form?

DFT · GC-DFT · bonding

Experiments (electrochemistry, in situ IR): Dr. Yu Shan, Dr. Maximilian Jaugstetter, Dr. Julian Feijóo and coworkers; groups of Dr. Peidong Yang and Dr. Miquel B. Salmeron (UC Berkeley, LBNL)

Calculations (DFT, GC-DFT, bonding analysis): my own



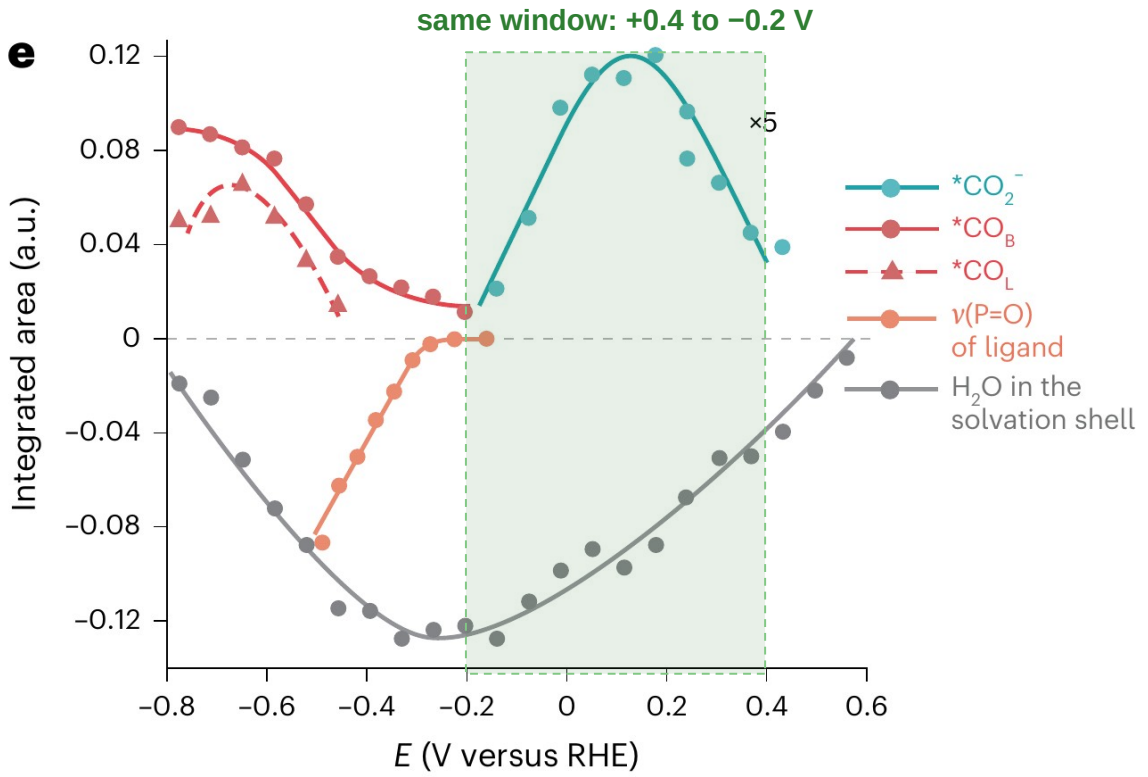
My models: Cs^+ with six to one water molecules next to CO_2 on Ag(111)

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On Ag NOLI, CO_2 is activated from +0.4 V while Cs^+ loses water

EXPERIMENT What happens at the Ag NOLI surface as the potential is made more negative?

In situ IR (SEIRAS)



scan from OCV (+0.6 V, right) to −0.8 V (left)

- **$*CO_2^-$ (1372 cm^{-1})**
  activated, bent CO_2; from +0.4 V, gone by −0.2 V
- **H_2O of the Cs^+ shell**
  removed (negative band) in the same window
- ***CO, then CO gas**
  only below −0.2 V; gas from −0.4 V
- **Ligand P=O**
  ligands move away from Ag

CO_2 is activated ($*CO_2^-$) from +0.4 V, in the same window where Cs^+ loses water.

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Experiments: Dr. Yu Shan, Dr. Maximilian Jaugstetter, Dr. Julian Feijóo · Shan, Jaugstetter, Feijóo, Guan et al., Nat. Catal. 9, 1009 (2026), Fig. 1

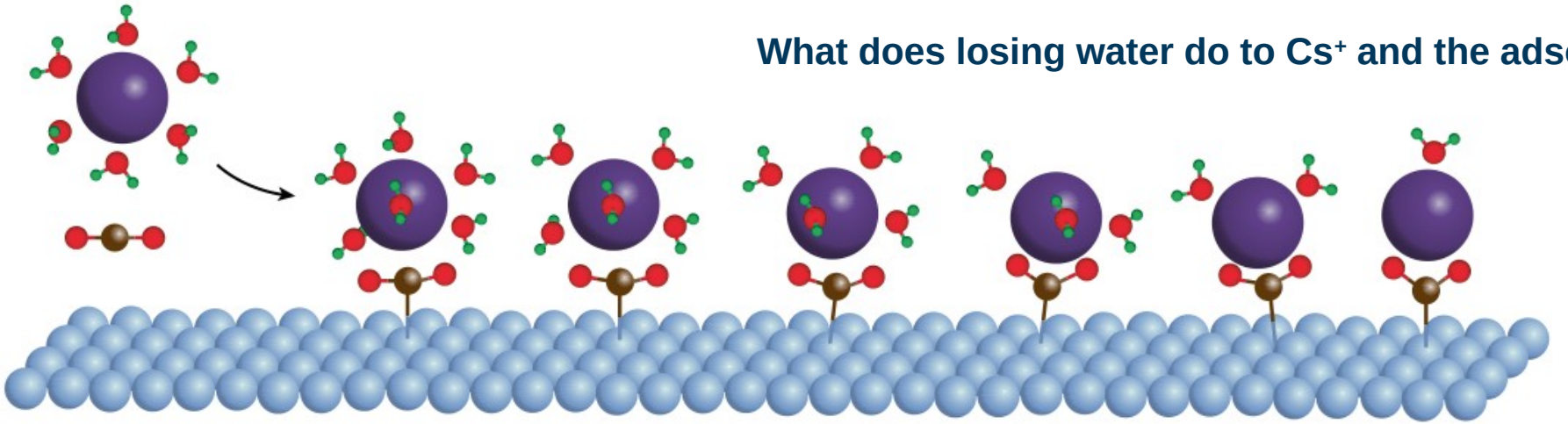
I model desolvation as seven states, from $Cs^+(6H_2O)$ to $Cs^+(1H_2O)$

MY CALCULATION Q1 · What does losing water do to Cs^+ and the adsorbed CO_2?

Reference: $Cs^+(6H_2O)$ away from Ag, CO_2 linear

At the Ag surface, Cs^+ loses water

What does losing water do to Cs^+ and the adsorbed CO_2?



reference 6 H_2O 5 4 3 2 1 H_2O

- Ag(111) (4×4); CO_2 + Cs^+ + n explicit H_2O; implicit electrolyte
- Sampling points along a desolvation coordinate, not a trajectory

- For each state: Cs–O and CO_2–Ag distances, O–C–O angle, −ICOHP(Cs–O), PDOS
- And the grand free energy ΔΩ(U) by GC-DFT

Desolvation becomes a coordinate I can follow. Next: what happens to the contact and to CO_2 along it?

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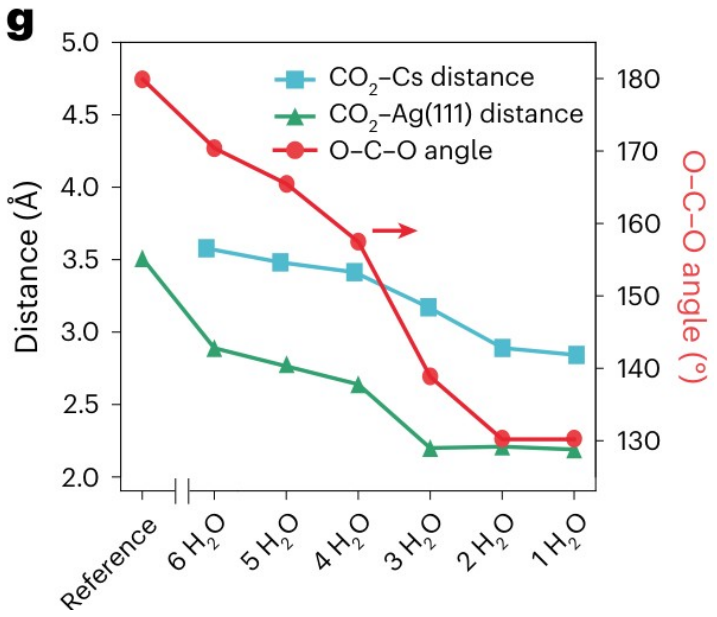
My calculations · Shan, Jaugstetter, Feijóo, Guan et al., Nat. Catal. 9, 1009 (2026), Fig. 4

Losing water brings Cs^+ into contact and bends CO_2 onto Ag

MY CALCULATION

Q1 · What does losing water do to Cs^+ and the adsorbed CO_2?

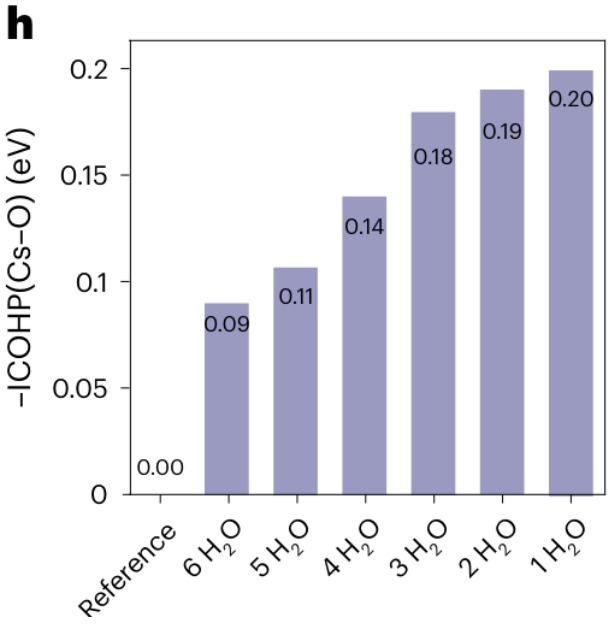
Geometry



5 → 1 H_2O: Cs–O 3.51 → 2.83 Å, CO_2–Ag 2.82 → 2.19 Å

4 → 3 H_2O: 157° → 139°, 2.6 → 2.2 Å: **physisorbed → chemisorbed**

Cs–O bond strength



−ICOHP(Cs–O) **0.09 → 0.20 eV** (6 → 1 H_2O)

With one water: as strong as the short Cs–O contacts in Cs_2CO_3 (0.17 eV)

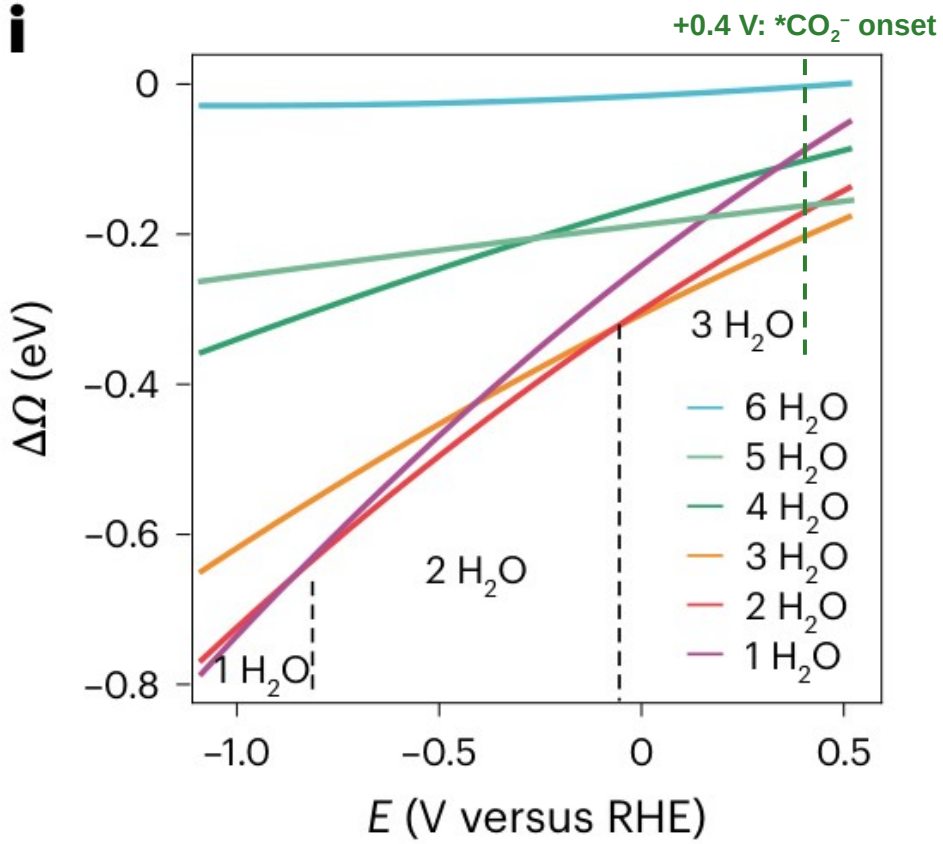
Losing water lets Cs^+ touch CO_2, which bends and binds to Ag, like the $*CO_2^-$ seen in IR.

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My calculations · Shan, Jaugstetter, Feijóo, Guan et al., Nat. Catal. 9, 1009 (2026), Fig. 4

More negative potentials favor more desolvated Cs^+ next to CO_2

MY CALCULATION Q2 · Which hydration state binds CO_2 best at each potential?



$$\Delta\Omega_n(U) = G_{Ag+CO2+Cs+nH2O}(U) - G_{Ag+Cs+nH2O}(U) - G_{CO2}$$

lower ΔΩ = CO_2 binds more strongly next to $Cs^+(nH_2O)$

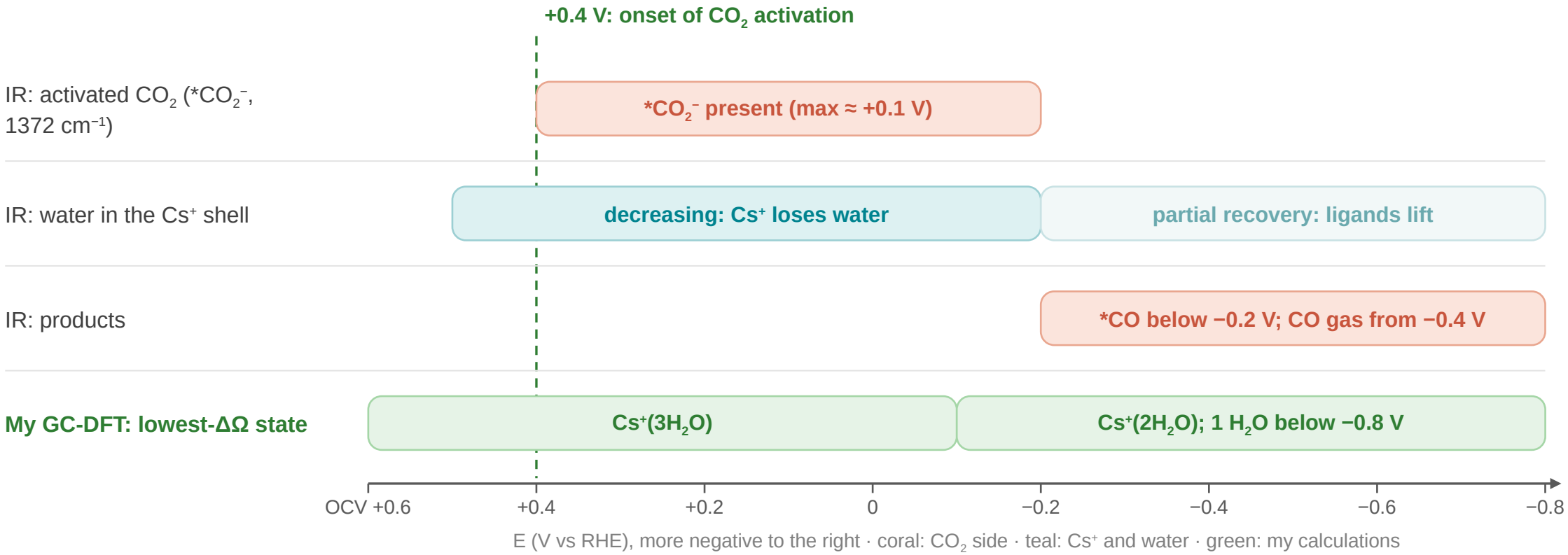
- Lowest ΔΩ: **3 H_2O** positive of −0.1 V, **2 H_2O** from −0.1 to −0.8 V, **1 H_2O** below −0.8 V
- At +0.4 V, where $*CO_2^-$ appears: ΔΩ ≈ −0.2 eV, already favorable; 2, 3 and 5 H_2O lie within 0.05 eV, so no single state
- Same direction as the experiments: Cs^+ loses water as the potential goes negative (IR)

Bias favors desolvated Cs^+ next to $*CO_2$; the ligand layer keeps that Cs^+ at the surface.

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My calculations · Shan, Jaugstetter, Feijóo, Guan et al., Nat. Catal. 9, 1009 (2026), Fig. 4

Confinement makes cation desolvation productive



Most reliable: the structure. The direct contact bends CO_2 and binds it to Ag

Open: the desolvation free energy, and thus how many Cs^+ are in each hydration state

The ligand layer keeps Cs^+ at the surface as it loses water, so it can bend and activate CO_2.

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Shan, Jaugstetter, Feijóo, Guan et al., Nat. Catal. 9, 1009 (2026)

Three outcomes of the same event

System	Does the species leave?	Is the change reversible?	More negative potential	Outcome
Part I Cu with acetone or methylamine	No	Yes, follows the concentration	Not studied (calculations at E_{pzc})	**Change of response**
Part II Cu in amine solutions	Yes, as a Cu–amine complex	No, lost to the solution	Suppresses dissolution, threshold ≈ −0.8 V	**Loss of electrode material**
Part III Ag with trace Pb or Bi	Yes, as PbH_4	Yes, PbH_2 returns and is hydrogenated again	Favors the hydride; yield flat, −1.34 to −3.34 V	**Catalysis by a shuttle**
Part IV Ag NOLI with Cs^+	No, the ligand layer holds it	Yes, water returns below −0.2 V	Favors more desolvated states	**Catalysis by confinement**

The event is the same, a change of ligands; the outcome depends on what happens next.

Parts I and II probe the same N–Cu bond: at a kink atom and with more ligands, it removes Cu.

Conclusions

Part I Acetone makes the Cu/water interface more polarizable and methylamine less: opposite changes of the capacitance

Part II Amines pull low-coordinated Cu out of the surface; dissolution is favored positive of ≈ −0.8 V vs RHE

Part III PbH_4 formed at Ag hydrogenates the imine in solution and returns as PbH_2; Bi can replace Pb

Part IV Partially desolvated Cs^+, held by the ligand layer, binds adsorbed CO_2 directly

Species formed under reaction conditions control the interface: treat them as part of the catalyst.

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Q&A