nature portfolio

Peer Review File

Synergistic Cation-Facet Effects Boost Alkaline Hydrogen Evolution Kinetics on Stepped Pt Surfaces

Corresponding Author: Professor Zhiyao Duan

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Attachments originally included by the reviewers as part of their assessment can be found at the end of this file.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The manuscript by Zhang, Sun, Li, and Duan describes a computational study of the hydrogen evolution reaction under alkaline conditions, using constant potential density functional theory and ab initio molecular dynamics. In particular, the effects of alkali metal cations are examined in the double layer, along with step sites, on the kinetics of the reaction. Pt(111) and Pt(311) surfaces were examined to contrast the behaviour between closed-packed, defect-free versus stepped substrates. The Authors show that the undercoordinated step sites present on Pt(311) allow chemisorption of water molecules and additional ion stabilization. The result is a stronger interfacial electric field and a decrease in the water dissociation barrier. As a result of the less pronounced interactions of water with Pt(111), the cations are located farther away from the electrode and thus do not exhibit such a beneficial effect for HER compared to Pt(311). The study is very interesting and the work appears rigorous, thus I believe it may be suitable for publication in Communications Chemistry pending revisions.

The authors are missing some key works in the solvated cation literature from various research groups, including but not limited to:

Monteiro et al. Nat. Catal. 2021, 4, 654–662.
Sakong et al. Phys. Chem. Chem. Phys. 2020, 22, 10431–10437.
Kristoffersen et al. Chem. Commun. 2020, 56, 427–430.
Chen et al. ACS Catal. 2016, 6, 7133–7139.

I believe a more thorough discussion of the literature will help put the Authors' work in context with what has been achieved previously and highlight the impact of their own work.

Reviewer #2

(Remarks to the Author)
see attached file

Reviewer #3

(Remarks to the Author)
Authors employed constant-potential DFT / CP-AIMD with eNEB to elucidate the microscopic mechanism by which alkali-metal cations and step facets cooperate to promote HER in alkaline media: Pt(311) step sites bringing Na^+ closer to the electrode, strengthening the interfacial electric field, and inducing partial O–H dissociation of water, thereby significantly lowering the Volmer-step barrier. I recommend minor revision prior to acceptance, focusing on adding key methodological details, providing additional analyses, and strengthening reproducibility and data support.

1. The manuscript uses –0.7 V vs SHE and adopts an absolute SHE of –4.1 eV. Please justify this choice and provide a sensitivity comparison against commonly used values such as –4.44 eV.

2 “Adjusting the electron count every 5 steps to maintain constant potential”: please specify the target potential tolerance (e.g., ±10–20 mV), the step size/convergence criterion for electron-count adjustment, and how potential consistency is enforced across images (eNEB).
3 AIMD uses a 1 fs timestep and 10 ps sampling. In many cases, water needs ~15 ps to decorrelate from its initial orientation; with only 10 ps, the initial water configuration may bias the conclusions. Please clarify whether this has been considered.
4 Please provide more details about the eNEB setup. I guess a set of sample input for CP-AIMB and eNEB calculations would be good for readers.
5 Please clarify whether ZPE corrections are included.
6. Na^+ position: currently citing ~5 Å (111) vs ~3.6 Å (311). Please provide the z-direction probability distribution P(z_Na), and report mean ± standard deviation/confidence intervals to avoid conclusions based on snapshot configurations.
7.Water orientation stratification: α/β distributions are reported; please provide layer-resolved distributions for the first and second water layers to distinguish contributions from the Stern layer versus the transition to bulk, and clearly define the z-window thresholds used to select interfacial water layers.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The Authors have addressed my comments and I believe their manuscript is ready for publication in Communications Chemistry.

Reviewer #2

(Remarks to the Author)
See attached

Reviewer #3

(Remarks to the Author)
The authors have made a commendable effort to address all the reviewers’ comments. I am pleased to recommend the manuscript for publication.

Version 2:

Reviewer comments:

Reviewer #2

(Remarks to the Author)
[Editorial note: This Reviewer provided no further comments for the authors.]

Response to Reviewer Comments

Ms. ID: COMMSCHEM-25-0545-T

Title: Synergistic Cation-Facet Effects Boost Alkaline Hydrogen Evolution Kinetics on Stepped Pt Surfaces

Reviewer comments in normal type

Author response in italics

Verbatim quotes from the revised text are in boldface

Reviewer: 1

The manuscript by Zhang, Sun, Li, and Duan describes a computational study of the hydrogen evolution reaction under alkaline conditions, using constant potential density functional theory and ab initio molecular dynamics. In particular, the effects of alkali metal cations are examined in the double layer, along with step sites, on the kinetics of the reaction. Pt(111) and Pt(311) surfaces were examined to contrast the behaviour between closed-packed, defect-free versus stepped substrates. The Authors show that the undercoordinated step sites present on Pt(311) allow chemisorption of water molecules and additional ion stabilization. The result is a stronger interfacial electric field and a decrease in the water dissociation barrier. As a result of the less pronounced interactions of water with Pt(111), the cations are located farther away from the electrode and thus do not exhibit such a beneficial effect for HER compared to Pt(311). The study is very interesting and the work appears rigorous, thus I believe it may be suitable for publication in Communications Chemistry pending revisions.

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Kristoffersen et al. Chem. Commun. 2020, 56, 427–430.

Chen et al. ACS Catal. 2016, 6, 7133–7139.

Our response: *We appreciate the reviewer's constructive feedback. In the revised manuscript, we have appropriately included references to key studies on solvated cations from various research groups to ensure that important works are not overlooked.*

Accordingly, we have expanded the discussion in the introduction to reflect these contributions and cited the mentioned literature on page 2: "**In addition to HER, solvated cations have also been demonstrated to play a decisive role in determining activities of other electrocatalytic reactions.[28-30]**"

(28) Monteiro, M. C. O.; Dattila, F.; Hagedoorn, B.; García-Muelas, R.; López, N.; Koper, M. T. M. Absence of Co2 Electroreduction on Copper, Gold and Silver Electrodes without Metal Cations in Solution. *Nature Catalysis* 2021, *4*, 654-662.

(29) Chen, L. D.; Urushihara, M.; Chan, K.; Nørskov, J. K. Electric Field Effects in Electrochemical Co2 Reduction. *ACS Catalysis* 2016, *6*, 7133-7139.

(30) Kristoffersen, H. H.; Chan, K.; Vegge, T.; Hansen, H. A. Energy-Entropy Competition in Cation-Hydroxyl Interactions at the Liquid Water-Pt(111) Interface. *Chem Commun (Camb)* 2020, *56*, 427-430.

We have also further compared our simulation results, especially the orientation of interfacial water molecules, with previous studies.

On Page 10— **"Previous studies of water structures at the Pt(111)/aqueous interface at PZC typically identify a mixture of flat-adsorbed and H-down configurations.[57,59-61] In these studies, the flat-adsorbed water exhibits single-peaked α and β at approximately 60° and 75°, respectively.[61] In contrast, our calculations for the negatively charged Pt(111) surface do not show these flat-adsorbed configurations. The stronger electrostatic interaction with the hydrogen atoms of water favors H-down orientations. Our observed H-down configurations, with α ≈ 140° and β ≈ 90°/160°, are consistent with previous reports.**

Previous work on the electrified Pt(533)/aqueous interface with Na^+ cations has also shown the presence of flat-adsorbed H_2O at step sites and H-down H_2O at terrace sites, both at the PZC and under a mild negative charged density of –26.4 μC/cm², which aligns with our findings. Specifically, a Pt–H_2O–$Na^+(H_2O)_x$ adduct was identified at the stepped sites at this charge density. Furthermore, a similar Pt–OH–$Na^+(H_2O)_x$ species at step sites was previously proposed to contribute to the cation-dependent shift of the H/OH exchange peak on stepped Pt electrodes.[62]"

(57) Xue, S.; Chaudhary, P.; Nouri, M. R.; Gubanova, E.; Garlyyev, B.; Alexandrov, V.; Bandarenka, A. S. Impact of Pt(Hkl) Electrode Surface Structure on the Electrical Double Layer Capacitance. *J Am Chem Soc* 2024, *146*, 3883-3889.

(59) Li, P.; Huang, J.; Hu, Y.; Chen, S. Establishment of the Potential of Zero Charge of Metals in Aqueous Solutions: Different Faces of Water Revealed by Ab Initio Molecular Dynamics

Simulations. ***The Journal of Physical Chemistry C*** **2021,** ***125*****, 3972-3979.**

(60) Le, J.; Iannuzzi, M.; Cuesta, A.; Cheng, J. Determining Potentials of Zero Charge of Metal Electrodes Versus the Standard Hydrogen Electrode from Density-Functional-Theory-Based Molecular Dynamics. ***Phys Rev Lett*** **2017,** ***119*****, 016801.**

(61) Sakong, S.; Gross, A. Water Structures on a Pt(111) Electrode from Ab Initio Molecular Dynamic Simulations for a Variety of Electrochemical Conditions. ***Phys Chem Chem Phys*** **2020,** ***22*****, 10431-10437.**

(62) McCrum, I. T.; Janik, M. J. First Principles Simulations of Cyclic Voltammograms on Stepped Pt(553) and Pt(533) Electrode Surfaces. ***ChemElectroChem*** **2016,** ***3*****, 1609-1617.**

Reviewer: 2

The article describes the formation a Pt-H_2O*-$Na^+(H_2O)_x$ adduct at the step edges of Pt(311). Such an adduct is reminiscent of the Pt-OH*-$Na^+(H_2O)_x$ adducts suggested earlier to play a role in the cation-dependent peak shift of the H/OH exchange peak observed in the CV of stepped Pt [DOI: 10.1002/celc.201600293]. To my knowledge, it is a novel insight that such structures may also occur in the absence of adsorbed OH – as long as adsorbed water molecules exist at the interface. The article further discusses the effect of this adduct on HER.

The article is interesting to read, but there are several points that require attention.

1. I find the model system used rather unrealistic:

   a. Pt(311) does not exist under electrochemical conditions. It reconstructs [DOI: 10.1021/la701566w, DOI: 10.1038/s41929-024-01232-2]

Our response: We *thank the reviewer for raising this point. We agree that under electrochemical conditions the Pt(311) surface undergoes reconstruction, and therefore this model system is not fully realistic. We selected the Pt(311) surface for its well-defined stepped structure and high step density, which enables analysis on the stepped structure while remaining computationally tractable compared to surfaces with lower step-site density, such as the Pt(533) surface.*

In the revised manuscript, we added a note on the reconstruction of the Pt(311) surface and explained why the surface model was chosen.

On Page 5—**"The Pt(311) surface was employed to model a stepped surface at a tractable computational cost, despite being known to undergo a (1×2) missing-row reconstruction under electrochemical conditions.[49,50]"**

(49) Nakahara, A.; Nakamura, M.; Sumitani, K.; Sakata, O.; Hoshi, N. In Situ Surface X-Ray Scattering of Stepped Surface of Platinum: Pt(311). ***Langmuir*** **2007,** ***23*****, 10879-10882.**

(50) Valls Mascaró, F.; Koper, M. T. M.; Rost, M. J. Step Bunching Instability and Its Effects in Electrocatalysis on Platinum Surfaces. ***Nature Catalysis*** **2024,** ***7*****, 1165-1172.**

   b. Under HER conditions, both the step and the terraces will be covered by hydrogen

This brings up the question how relevant the results (in particular the barrier height calculations) are.

Our response: *We agree that the hydrogen coverage on Pt surfaces can be significant, but this should be specific to acidic conditions. The situation is different under alkaline conditions. In alkaline HER, adsorbed hydrogen originates from water dissociation, which requires a significantly higher*

barrier (approximately ~0.6–0.8 eV at 0 V per our calculation) than the proton deposition in acid (~0.2 eV at 0 V). This kinetic limitation results in a low H coverage during alkaline HER. Therefore, we consider that adopting a low hydrogen coverage in our model is a reasonable approximation for alkaline HER conditions.*

This conclusion is also supported by experimental studies. Recently, it has been demonstrated that the hydrogen coverage on Pt remains low under alkaline conditions, as evidenced by the suppressed H_{OPD} (overpotentially deposited hydrogen) peak in the ETS (electrical transport spectroscopy) curves and the markedly reduced integrated charges near the HER onset potential (Fig. 6a,c,d, Nature Catalysis 7, 678–688 (2024)).

2. In Fig. 1d, the potential can be seen to stabilize excessively slowly on the timescales of the simulations used here. Effectively, a potential of -0.7V/SHE is only reached after 8ps. This would leave only 2ps for statistics accumulation, which seems excessively short.

a. Why does the potential stabilize so slowly? After all, the simulations are supposed to be constant potential calculations. According to the methods section, the charges are updated every 5 timesteps. I would thus expect the relaxation time to be on the order of 5fs. To me, it seems that the charge update does not work correctly.

Our response: *The slow charge convergence is found to related to the relatively slow kinetics of the reorganization dynamics of interfacial water molecules. The orientations of interfacial water dipoles (O-down vs. H-down) could significantly influence the surface charge state of the electrode. These electrolyte reorganization processes occur on timescales much slower than that of electronic adjustments, which results in slow convergence of the simulated electrode potential.*

As an illustration to this, in the Pt(111) model, we analyzed the orientation of interfacial water molecules every 2 ps (see Figure R1) and observed a gradual structural evolution that reached a steady state only after ~7 ps. In particular, during the first ~4 ps, two types of water configurations coexisted—one of H-down (large α) and another with O-down (small α). Over time, the O-down configuration progressively converted to the H-down configuration. This demonstrates that the structural relaxation of interfacial water requires longer timescale, leading to slow convergence of electrode potential.

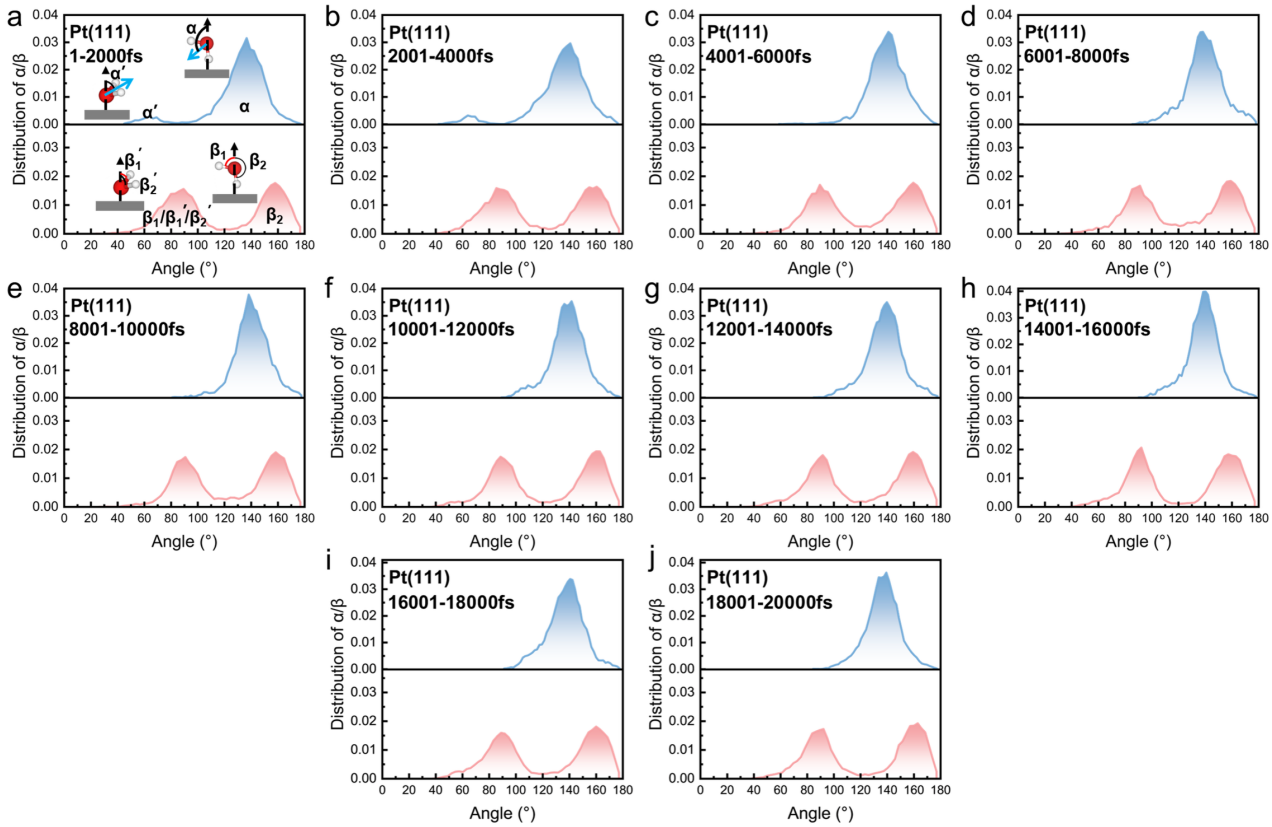

Figure R1. *Distributions of α and β for the orientations of interfacial water molecules at the aqueous Pt(111) interface, sampled every 2 ps.*

b. How did the authors choose the equilibration period?

Our response: *Equilibrium was considered achieved when the surface charge and grand-canonical energy no longer exhibited systematic drift over a sufficiently long period of time. Specifically, the running average of the surface charge density over 100 timesteps fluctuated within 1 μC/cm², and the running average of the energy fluctuated within 1.5 eV at 300 K. In the revision, we extended our CP-AIMD simulations to 20 ps and 30 ps for Pt(111) and Pt(311), respectively. The proper convergence was demonstrated in Figure R2 for pt(111) and R3 Pt(311). The extended CP-AIMD simulations do not alter the main observations and conclusions of our previous manuscript. The Pt–H_2O*–$Na^+(H_2O)_x$ adduct still exists on Pt(311) but not on Pt(111).*

We have updated all related figures and discussions according to the extended CP-AIMD simulations in our revised manuscript:

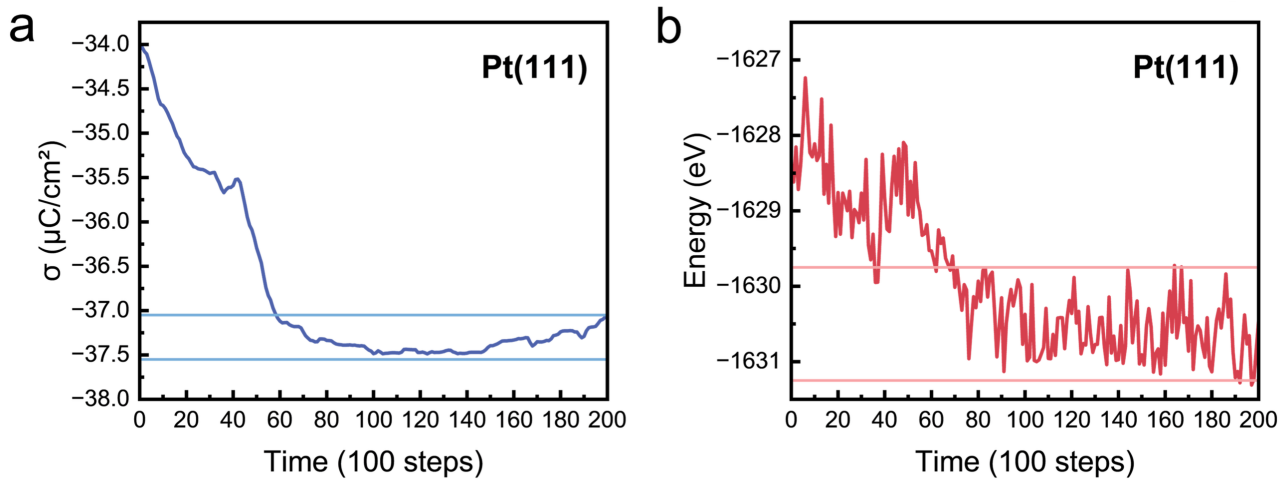

Figure R2. *Time evolution of the average (a) surface charge density and (b) energy for the Pt(111)/aqueous interface during CP-AIMD simulations at* $U_{SHE} = -0.7$ *V and* $T = 300$ *K.*

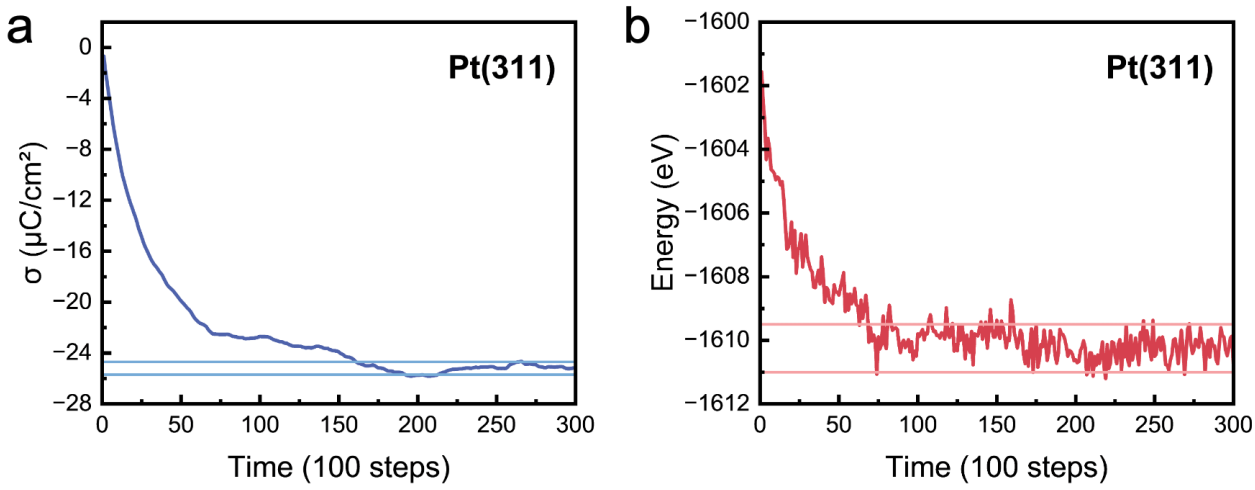

Figure R3. *Time evolution of the average (a) surface charge density and (b) energy for the Pt(311)/aqueous interface during CP-AIMD simulations at* $U_{SHE} = -0.7$ *V and* $T = 300$ *K.*

3. The equation used to determine the surface charge (see figure caption of Figure 1) is incorrect:

a. The surface is not symmetrical. A different amounts of shielding charges is therefore required to bring the metal/implicit solvent interface on the left to the desired potential than will be used for the right interface that we are interested in.

b. Additionally, the equation neglects the charge transferred to the surface from the sodium atom.

Our response: *We thank the reviewer for the careful examination of our work. We fully agree that, as the reviewer points out, the model system is not symmetric and that the equation does not explicitly account for charge transfer from sodium to the electrode. Therefore, the calculated surface charge density cannot be regarded as the exact measure of the surface charge density, but we still considered it is useful such as an convergence indicator and for highlighting relative differences*

across Pt(111) and (311) surfaces.

In the revised manuscript, we put a note on the inaccurate nature of the surface charge density due to asymmetric surface model. We used (q+1)/2S to account for electron from sodium:

On Page 6— **"We note that the calculated σ does not accurately represent the true surface charge density, as the surface model used was asymmetric."**

4. I find it a lost opportunity that this article does not compare to earlier literature. In particular, the presence of adsorbed water on the steps and the resulting angle distribution has been discussed before in literature [DOI: 10.1002/celc.201600293, DOI: 10.1021/jacs.3c11403, DOI: 10.1063/5.0080104].

Our response: *We thank the reviewer for this valuable comment. In the revised manuscript, we have added comparisons with previous studies to make our discussion more comprehensive.*

On Page 10— **"Previous studies of water structures at the Pt(111)/aqueous interface at PZC typically identify a mixture of flat-adsorbed and H-down configurations.[57,59-61] In these studies, the flat-adsorbed water exhibits single-peaked α and β at approximately 60° and 75°, respectively.[61] In contrast, our calculations for the negatively charged Pt(111) surface do not show these flat-adsorbed configurations. The stronger electrostatic interaction with the hydrogen atoms of water favors H-down orientations. Our observed H-down configurations, with α ≈ 140° and β ≈ 90°/160°, are consistent with previous reports.**

Previous work on the electrified Pt(533)/aqueous interface with Na^+ cations has also shown the presence of flat-adsorbed H_2O at step sites and H-down H_2O at terrace sites, both at the PZC and under a mild negative charged density of –26.4 μC/cm², which aligns with our findings. Specifically, a Pt–H_2O–$Na^+(H_2O)_x$ adduct was identified at the stepped sites at this charge density. Furthermore, a similar Pt–OH–$Na^+(H_2O)_x$ species at step sites was previously proposed to contribute to the cation-dependent shift of the H/OH exchange peak on stepped Pt electrodes.[62]"

(57) Xue, S.; Chaudhary, P.; Nouri, M. R.; Gubanova, E.; Garlyyev, B.; Alexandrov, V.; Bandarenka, A. S. Impact of Pt(Hkl) Electrode Surface Structure on the Electrical Double Layer Capacitance. *J Am Chem Soc* 2024, *146*, 3883-3889.

(59) Li, P.; Huang, J.; Hu, Y.; Chen, S. Establishment of the Potential of Zero Charge of Metals in Aqueous Solutions: Different Faces of Water Revealed by Ab Initio Molecular Dynamics Simulations. *The Journal of Physical Chemistry C* 2021, *125*, 3972-3979.

(60) Le, J.; Iannuzzi, M.; Cuesta, A.; Cheng, J. Determining Potentials of Zero Charge of Metal Electrodes Versus the Standard Hydrogen Electrode from Density-Functional-Theory-Based Molecular Dynamics. *Phys Rev Lett* 2017, *119*, 016801.

(61) Sakong, S.; Gross, A. Water Structures on a Pt(111) Electrode from Ab Initio Molecular Dynamic Simulations for a Variety of Electrochemical Conditions. *Phys Chem Chem Phys* 2020, *22*, 10431-10437.

(62) McCrum, I. T.; Janik, M. J. First Principles Simulations of Cyclic Voltammograms on Stepped Pt(553) and Pt(533) Electrode Surfaces. *ChemElectroChem* 2016, *3*, 1609-1617.

5. When discussing the location of the ions, how sure are the authors that this is not an effect of a too short time-scale? The simulations will likely not allow the ions to equilibrate in terms of distance from the surface. It is possible that there is an effect, either due to the chemisorbed water molecules at the step edge of due to tip effects, but I am not convinced that the present simulations can show this. It would be helpful to at least see the ion trajectories. Ideally, several initial conditions should be tested with the ion closer and further from the surface.

Our response: *We thank the reviewer for this important question. To address it, we extended our CP-AIMD simulations to quantitatively compare time evolution of the Na^+-surface distance on Pt(111) and Pt(311).*

The results, shown in Figure R4, reveal a stark contrast. On the Pt(111) surface, the Na^+ ion initially resides at 2.84 Å but is rapidly repelled to a stable position beyond 4.0 Å. This is due to the H-down water layer that forms on the flat Pt(111) surface, which solvates and pushes the ion away. In contrast, on the Pt(311) surface, the Na^+ ion remains much closer, fluctuating between 2.0 and 3.1 Å. This proximity is a consequence of the persistent formation of a Pt–H_2O–$Na^+(H_2O)_x$ adduct at the step edge.*

We added related discussions to the revised manuscript:

On page 7—**"The time-evolution of the Na^+-Pt(111) distance is shown in Figure S6. The Na^+ ion initially resides 2.84 Å above the surface but rapidly moves beyond 4.0 Å as the H-down water layer forms. This spontaneous displacement indicates that the final position of the Na^+ ion is not an artifact of the initial configuration but results from a specific underlying mechanism. Similarly, Figure S6 also shows that the Pt–H_2O*–$Na^+(H_2O)$x adduct is persistently observed during the CP-AIMD simulation."**

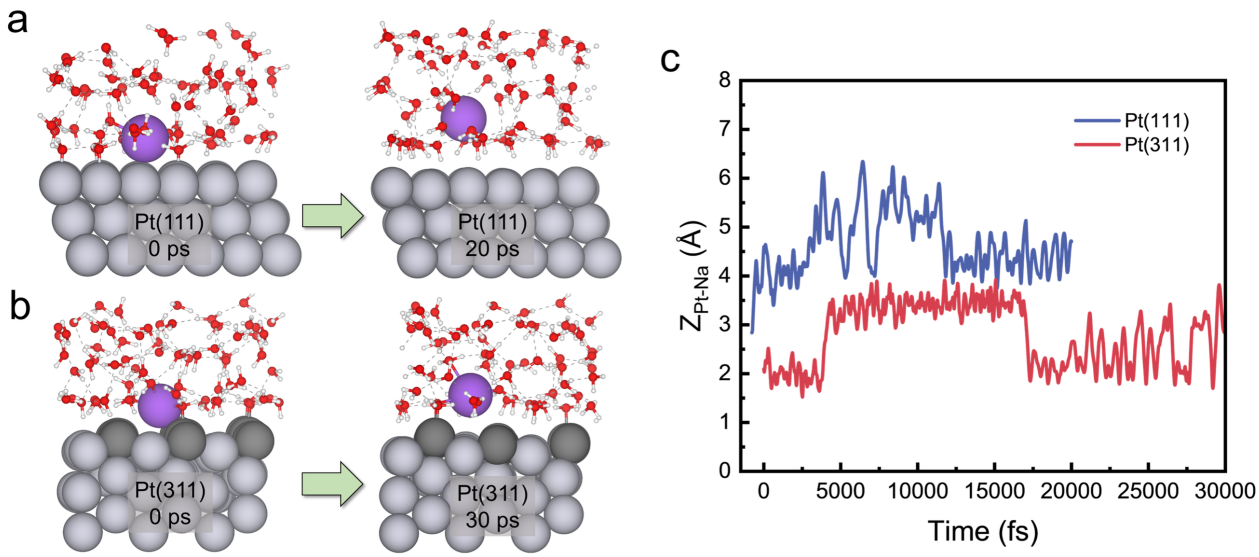

Figure R4. *(a, b) Initial and final structures of CP-AIMD simulations of Pt(111) and Pt(311) surfaces. (c) Time evolution of the Na^+-surface distance during the CP-AIMD simulations for the aqueous Pt(111) and Pt(311) interfaces.*

6. The authors furthermore attribute the smaller ion – surface distance to the presence of undercoordinated sites on Pt. The effect could, however, also be due to tip effects, that should enhance the electric field at the step edges.

Our response: *We thank the reviewer for this important point. As shown in Figure R5, the adsorption of a solvated Na^+ ion (with four water molecules) is consistently stronger on the Pt(311) surface than on Pt(111) across all examined potentials. This is also demonstrated by the equilibrium Na^+-surface distance, which is ~4.3 Å on Pt(111) but only ~3.8 Å on Pt(311). This demonstrates that Na^+ preferentially stabilizes closer to the Pt(311) surface, even without considering the Pt–H_2O*–$Na^+(H_2O)_x$ adduct.*

We attribute this stronger adsorption to the tip effect, as the reviewer suggested. The enhanced electric field at the Pt(311) step edges exerts a stronger electrostatic force on the Na^+ ion, which simultaneously stabilizes Na^+ ion and promotes greater electron transfer to the surface, as evidenced in Figure R5c. This field effect acts in concert with the chemical stabilization provided by the Pt–H_2O–$Na^+(H_2O)_x$ adduct.*

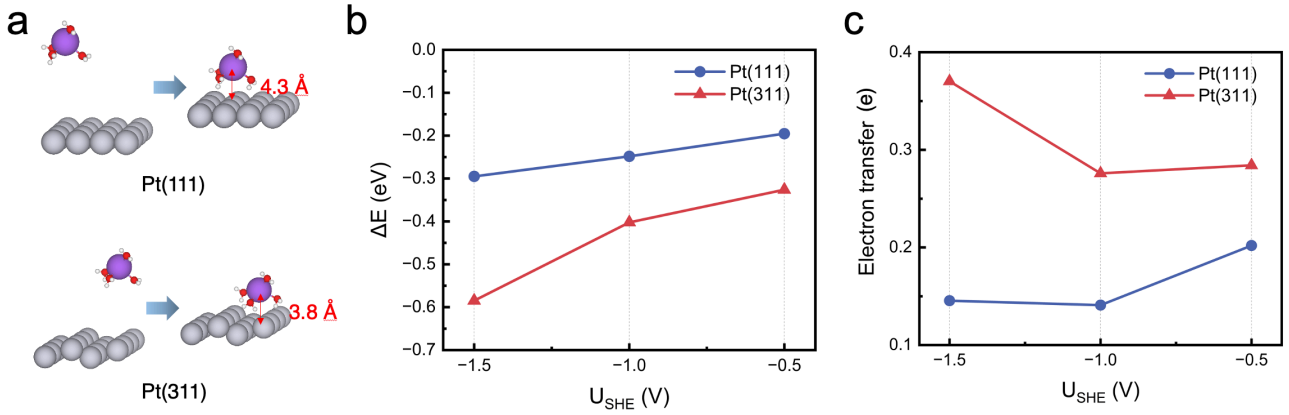

Figure R5. *(a) Atomic structures used for the Na^+ adsorption calculations on Pt(111) and Pt(311) surfaces. (b) Potential-dependent Na^+ adsorption energy. (c) Electron transfer amount upon Na^+ adsorption on Pt(111) and Pt(311) surfaces.*

In the revised manuscript, we have included a discussion of the contribution of tip effects.

On Page 8— **"In addition to the chemical stabilization by the adsorbed water, we propose that the tip effect at step sites also acts in concert to stabilize Na^+ closer to the surface on Pt(311). As shown in Figure S7, the adsorption of a solvated Na^+ ion (with four water molecules) is consistently stronger on the Pt(311) surface than on Pt(111) across all examined potentials. This is further demonstrated by the equilibrium Na^+-surface distance, which is ~4.3 Å on Pt(111) but only ~3.8 Å on Pt(311). We attribute this stronger adsorption to the tip effect: the enhanced electric field at the Pt(311) step edges exerts a stronger electrostatic force on the Na^+ ion, which simultaneously stabilizes the Na^+ ion and promotes greater electron transfer to the surface, as evidenced in Figure S7."**

7. Later on (p8) the authors also explain the stronger Na adsorption to the Pt(311) surface by an enhanced electron transfer to the Na^+ at the stepped surface. However, is this not a hen and egg problem? If the ion comes closer to the surface, it is also more likely to receive more charge from the interface. Additionally, similar effects been discussed earlier by Shengli Chen [DOI: 10.1063/5.0080104], where, however, the authors found a negligible change in Bader charge on the ion upon approach to a stepped Pt(553) surface.

Our response: *We thank the reviewer for this insightful comment. Our adsorption calculations (Figure R5) indicate greater electron transfer to the Pt(311) surface upon the approach of a Na^+ ion. We tentatively attribute this to the stronger electrostatic interaction between the step sites and Na^+, which is likely due to the tip effects discussed in our response to Comment 6. While the paper by Shengli Chen et al. focuses on the Bader charge of Na^+ rather than the surface charge, their reported values of approximately +0.9e are consistent with our calculations.*

8. Throughout the entire paper, Bader charges are used to rationalize several observations. However, Bader charges are only one way to split the charges in a quantum chemical simulation and are by no means a unique charge partitioning and therefore often not meaningful.

a. In particular, Bader charges should not be confused with free charges that define the surface electric field. They may be severely impacted by adsorbates.

   This should be particularly true for adsorbed hydrogen. A change in Bader charge in the presence of adsorbed hydrogen should therefore, in my opinion, not be used to argue anything about electric fields (see page 15).

b. A larger Bader charge at the metal/explicit solvent compared to the metal/implicit solvent interface, to me, also does not necessarily indicate strong electrostatic coupling between surface and water dipoles. It may simply be a question of different charge partitioning in the presence and absence of water close the interface.

   Additionally, it should be noted that (as noted above) a comparison of the charges on the top and the bottom of the slab is illegitimate in the setup used in this paper as the lower surface (Pt(111)/implicit solvent interface) will have a different potential of zero charge compared to the upper surface (Pt(111)/explicit water/implicit water).

c. On page 10, it is discussed that adsorbed water leads to a positive Bader charge. This is possible (see a). However, adsorbed water has earlier been observed to lead to an overall dipole that points away from the surface (i.e, electron transfer occurs on average from the water towards the metal) [DOI: 10.1103/PhysRevLett.119.016801]. This knowledge may impact the authors reasoning.

Our response: *We thank the reviewer for these insights on Bader charge analysis. We now realize the limitations our Bader charge analysis and we revise our manuscript accordingly. Nevertheless, Bader charge analysis remains a meaningful method for comparing the local charge states of Pt atoms on Pt(111) and Pt(311) surfaces. The relevant discussion has been kept but significantly revised based on the reviewer's comments.*

a. We realize that Bader charge analysis is not the appropriate tool for explaining free energy phenomena and related electric fields. We have revised our explanation for the reduced cation effect at the H-adsorbed Pt step sites on the Heyrovsky reaction. Our new analysis indicates that the H adsorbate passivates the Pt step sites, thereby diminishes the local electric field responsible for polarizing the H–O bonds. The manuscript has been updated to reflect this revised interpretation.

On page 16 — **"We attribute this trend to the reduced tip effects on Pt step sites. The**

screening effects of H* diminish the local electric field necessary to polarize the H–O bond of the reacting water molecule."

b. *We thank the reviewer for pointing out the inaccuracies in our discussion regarding the different charge states of implicit and explicit aqueous interfaces. Rather than attributing the charge state difference to a strong electrostatic coupling between Pt and explicit water molecules, we now ascribe it to electron transfer and electron push-back effects from the interfacial water molecules. These effects modify PZCs of the surfaces, leading to distinct charge states between implicitly and explicitly modeled interfaces. The revised discussions are reflected in the revised manuscript.*

On page 11 — **"We attribute this difference to the electron transfer[60] and electron push-back[59] effects of explicit interfacial water molecules. These effects lead to distinct PZCs for the implicit and explicit Pt/aqueous interfaces, resulting in different surface charge states of Pt."**

(59) Li, P.; Huang, J.; Hu, Y.; Chen, S. Establishment of the Potential of Zero Charge of Metals in Aqueous Solutions: Different Faces of Water Revealed by Ab Initio Molecular Dynamics Simulations. The Journal of Physical Chemistry C 2021, 125, 3972-3979.

(60) Le, J.; Iannuzzi, M.; Cuesta, A.; Cheng, J. Determining Potentials of Zero Charge of Metal Electrodes Versus the Standard Hydrogen Electrode from Density-Functional-Theory-Based Molecular Dynamics. Phys Rev Lett 2017, 119, 016801.

c. *We agree with the reviewer that the observed positive Bader charge of step-site Pt may not stem from the oxidation of Pt by H_2O adsorption, but could instead arise from differences in how Bader volumes are partitioned with and without the adsorbate. Furthermore, as the reviewer highlighted and as supported by the literature [DOI: 10.1103/PhysRevLett.119.016801], H_2O* can transfer electrons to the Pt surface. We have therefore revised our statement regarding the positively charged Pt on the Pt(311) surface by highlighting the limitations of the Bader analysis and directing the reader's attention to the literature on electron transfer from adsorbed H_2O to Pt.*

On page 11 — **"The observed positive charge on Pt with water adsorption may not indicate oxidation by H_2O* but could instead reflect a limitation of the Bader charge analysis, where atomic volumes are partitioned differently with and without adsorbates. This interpretation is further supported by evidence that H_2O* can transfer electrons**

to the Pt(111) surface at the PZC.[60] Therefore, the results of the Bader analysis should be interpreted with caution."

(60) Le, J.; Iannuzzi, M.; Cuesta, A.; Cheng, J. Determining Potentials of Zero Charge of Metal Electrodes Versus the Standard Hydrogen Electrode from Density-Functional-Theory-Based Molecular Dynamics. Phys Rev Lett 2017, 119, 016801.

9. On page 6, the authors state that the difference in PZC between the stepped and the flat surface is increased to 0.77V in the presence of Na^+. This statement is not logic to me: A surface with excess cations in the double layer is by definition not at its pzc.

Our response: *We thank the reviewer for identifying this important oversight. The presence of a net ionic charge in the solution shifts the system away from the potential of zero charge (PZC). Consequently, our original statement regarding a "PZC difference of 0.77 V" was incorrect. We have removed this statement and revised Figure S3 accordingly in the updated manuscript.*

10. On page 12 the authors discuss the OH bond lengths shown in Figure 4. They state that the bond lengths on the Pt(311)+Na^+ interface extend to longer distances than on the Pt(311) interface without ion. I cannot follow this statement based on the plots presented. In both panels, e and f, I can see water molecules with bond lengths>1.12A. The main difference is that these water molecules reside higher up in z in the region without Na ion (panel e), but this can be explained by the choice of region, which includes two upper step edges for panel e, but two lower step edges for panel f.

Our response: *We thank the reviewer for raising this point. The issue was indeed due to insufficient simulation time in our original CP-AIMD calculations. Extended simulations show that the previously observed long O-H bond on the Pt(311) surface does not persist. We confirm that the O-H bond length distribution at the Pt(311)+Na^+ interface is indeed longer than at the Pt(311) interface without Na^+ (see Figure 4 in the revised manuscript). Furthermore, we have recalibrated the selection of Region 1 and Region 2 in Figure 4 to ensure both regions contain an equal number of Pt atoms at the upper step edge.*

11. When comparing the barrier heights for the Volmer step with and without Na present, the models chosen seem unfair to me: In the lower panel of Fig. 5c, the reacting water molecule has two neighboring water molecules that act as hydrogen donor, while in the upper panel (no Na), the reacting water molecule only has one hydrogen donor pointing towards it. This difference could significantly affect the barrier without the Na being the "culprit".

Our response: *To eliminate this potential bias, we introduced an additional H_2O molecule into the reaction model for the alkaline Volmer step on Pt(111), both with and without Na^+. This ensures the dissociating H_2O has the same number of neighboring molecules as in the model for the Pt(311) surface. Using this new model, the recalculated reaction barrier (Figure R6) decreases by*

approximately 0.07 eV compared to the model with only one neighboring H_2O. Since this decrease is similar in the presence and absence of Na^+, the overall conclusion that the Volmer reaction barrier remains similar on Pt(111) is unchanged. We also confirmed that the additional hydrogen bonds on the reacting H_2O do not influence its vibrational frequency. These updated results are now included in Figure 5 of the revised manuscript.

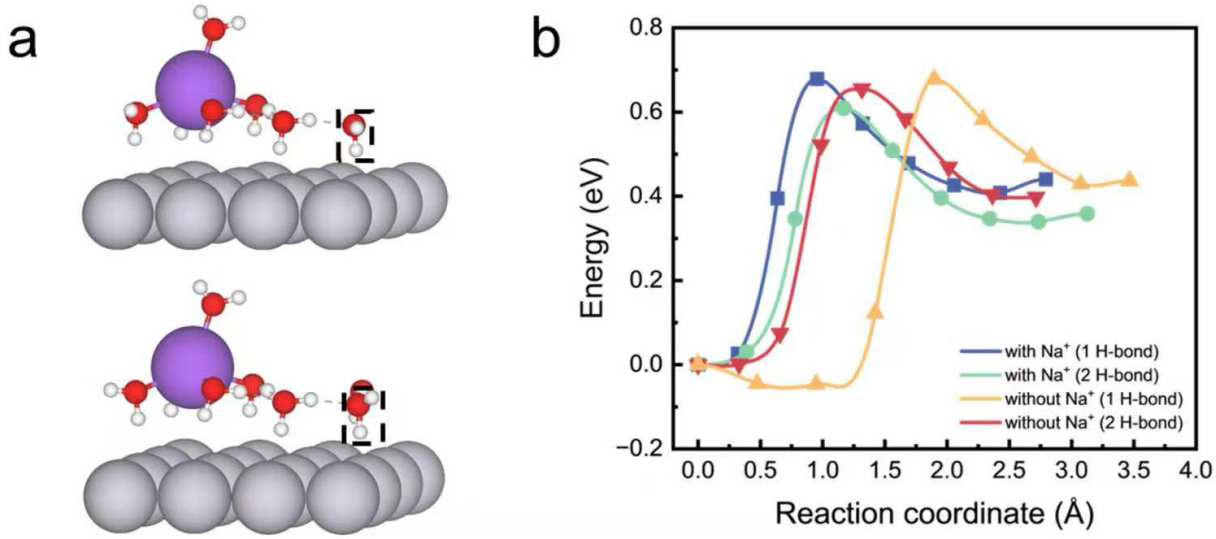

Figure R6. *(a) Initial states of the Volmer reaction on Pt(111) surfaces with Na^+, where the reacting water molecule is stabilized by one or two hydrogen bonds. (b) Corresponding minimum energy paths (MEPs) of the alkaline Volmer reaction on Pt(111) surfaces at U_{SHE} = –0.7 V.*

12. The hydrogen adsorption energies shown in Figure S7 seem incorrect to me: hydrogen adsorption must scale nearly perfectly with applied potential (close to neutral adsorption with small change in surface dipole). However, in Fig 7a red line, the adsorption energy even decreases with decreasing potential and in the blue line the change in adsorption energy is only ~5% if the change in potential. It is not described in the text how this adsorption energy was computed, so I cannot judge what may have gone wrong, but this seems rather strange to me.

Our response: *The hydrogen adsorption energy is calculated as*

$$\Delta\Omega_H = \Omega_{(H^*/slab)} - \Omega_{slab} - \frac{1}{2}E_{H_2}$$

Ω represents the electronically grand-canonical energy. The adsorption energy is slightly modulated by the applied potential due to adsorption-induced changes in excess electrons. In calculating the adsorption energy of H, we do not include the contribution of electron transfer (eU) for the hydrogen deposition reaction. If eU were considered, the hydrogen adsorption energy would decrease monotonically as the applied potential decreases. The calculation method has been updated in the Supporting Information (SI).*

Other notes:

1. On p. 6 the authors argue that the difference in charge must stem from ta difference in PZC. This is not necessarily true (or at least not the only reason): The capacitance could be smaller too. This has actually proposed earlier by Bandarenka [DOI: 10.1021/jacs.3c11403]

Our response: *We realize that the difference in surface charge density may not only originate from variations in the PZC, but could also be closely related to changes in the interfacial capacitance. We have clarified this point in the revised manuscript to provide a more comprehensive and balanced discussion.*

On Page 7— **"However, the σ of Pt(111) (~−37.5 μC/cm²) is significantly more negative than that of Pt(311) (~−25 μC/cm²), suggesting distinct PZCs and double layer capacitances for the two facets.[57, 58]"**

(57) Xue, S.; Chaudhary, P.; Nouri, M. R.; Gubanova, E.; Garlyyev, B.; Alexandrov, V.; Bandarenka, A. S. Impact of Pt(Hkl) Electrode Surface Structure on the Electrical Double Layer Capacitance. J Am Chem Soc 2024, 146, 3883-3889.

(58) Li, P.; Liu, Y.; Chen, S. Microscopic Edl Structures and Charge-Potential Relation on Stepped Platinum Surface: Insights from the Ab Initio Molecular Dynamics Simulations. J Chem Phys 2022, 156, 104701.

2. It is not clear when the 4x4 setup is used and when the 6x6 setup is used.

Our response: *We used a 6×6 supercell in AIMD simulations to reduce finite-size effects. For the eNEB calculations, we extracted representative atomic configurations from the CP-AIMD trajectories and simplified them into a 4×4 supercell, which allows us to reasonably capture the local reaction mechanism while reducing computational cost.*

This clarification has been added to the Computational methods section of the revised manuscript.

On Page 4—**"Pt(111) and Pt(311) surfaces were modeled as 4×4 four-layer slabs with the bottom two layers fixed for eNEB calculations; for CP-AIMD simulations, they were modeled as 6×6 three-layer slabs."**

3. Why use only 2x2 k-points in non-molecular-dynamics simulations?

Our response: *To validate the* choice of the *a 2×2 k-point mesh , we tested the Volmer reaction barrier for the Pt(311) surfaces with Na^+ using 2×2, 4×4, and 6×6 k-point meshes. As shown in*

Figure R7, the obtained barrier heights only differ negligibly, confirming that the 2×2 k-point mesh is sufficient to provide reliable results.

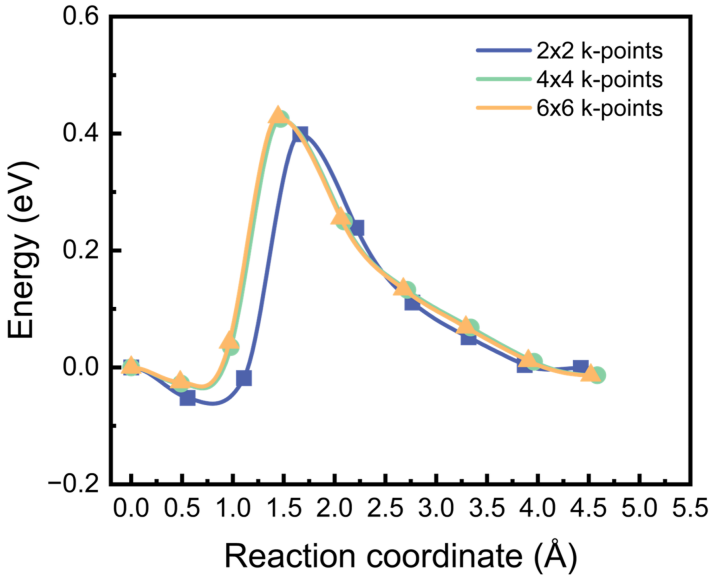

Figure R7. *Minimum energy paths (MEPs) of the alkaline Volmer reaction on Pt(311) surfaces with Na^+ at U_{SHE} = –0.7 V, calculated with different k-point meshes.*

4. Are 3 layers (in combination with a gamma-point-only simulation) not somewhat little for a realistic description of the metal? Does it actually end up being metallic or does it show a band gap?

Our response: *We have checked the density of states (DOS) of this slab and confirmed that the three-layer Pt slab still behaves metallically, without the appearance of a band gap, as shown in Figure R8.*

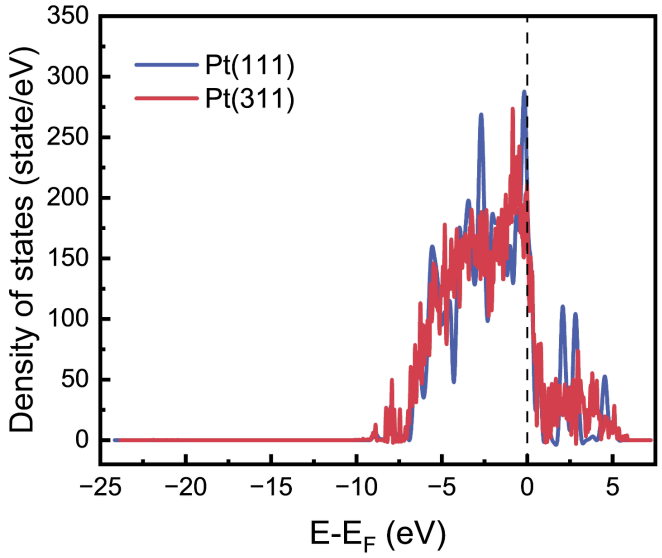

Figure R8. *DOS of the three-layer Pt(111) and Pt(311) slabs.*

5. In the implicit solvation model, what is the density cutoff used?

Our response: *In the implicit solvation model calculations, we used a density cutoff of NC_K = 0.0025 e/Å^3, which is the default for VaspSol for water solvent.*

6. Have the authors checked whether there is leakage of the implicit solvent into the water region (can happen depending on the density cutoff)?

Our response: *Using the default NC_K value, we analyzed the bound charge density (from the RHOB file), shown in Figure R9. The results indicate charge leakage into small cavities within the water solvent and around the Na^+ ion. This artifact is likely caused by the linear PCM framework used in the standard VASPsol implementation. To address this, we plan to employ VASPsol++, which incorporates nonlinear and nonlocal solvent response, in our future studies.*

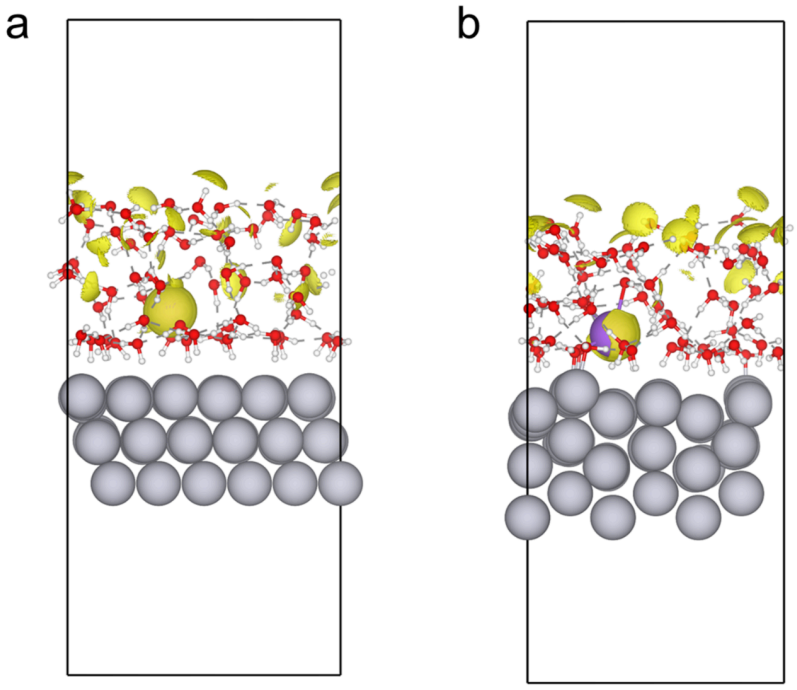

Figure R9. *Isosurface plots of bound charge densities for the Pt(111) and Pt(311)/aqueous models.*

Reviewer: 3

Authors employed constant-potential DFT/CP-AIMD with eNEB to elucidate the microscopic mechanism by which alkali-metal cations and step facets cooperate to promote HER in alkaline media: Pt(311) step sites bringing Na^+ closer to the electrode, strengthening the interfacial electric field, and inducing partial O–H dissociation of water, thereby significantly lowering the Volmer-step barrier. I recommend minor revision prior to acceptance, focusing on adding key methodological details, providing additional analyses, and strengthening reproducibility and data support.

1. The manuscript uses −0.7 V vs SHE and adopts an absolute SHE of 4.1 V. Please justify this choice and provide a sensitivity comparison against commonly used values such as 4.44 V.

Our response: *We obtained the value of the absolute potential of SHE (Φ_{SHE} = 4.1 V) by calibrating it against the experimental Gibbs free energy of the H^+/H_2 reaction.*

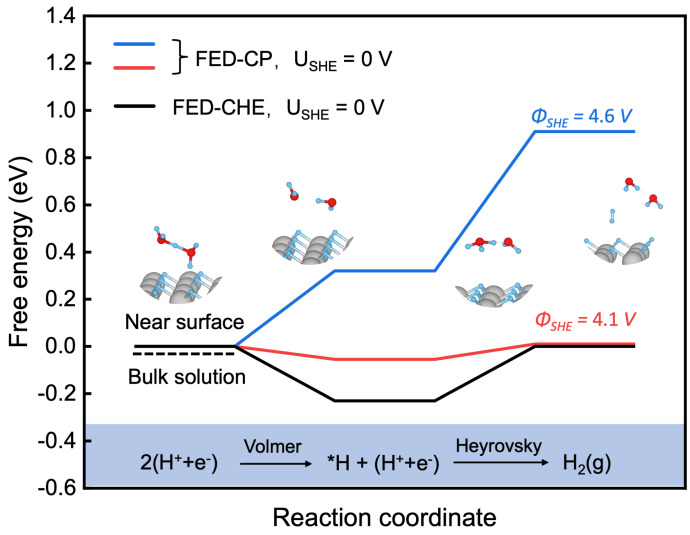

Figure R10. *Calibration of Φ_{SHE}.*

In Figure R10, the free energy diagram (FED) of the HER constructed using the computational hydrogen electrode (CHE) method is thermodynamically accurate and is thus used as free energy references for the initial and final states. At standard conditions (pH = 0 and T = 298.15 K), free energies of the initial and final states are 0 eV at U_{SHE} = 0 V as defined by the reversible reaction $2(H^+ + e^-) \Leftrightarrow H_2$ of the SHE. In addition, we have also constructed the FED of the HER from constant-potential calculations by calculating step-wise reaction free energies of Volmer and Heyrovsky steps. The employed models in the constant-potential calculations are shown in Figure R10. The entropic contribution of gas-phase H_2 to the free energy, $-\Delta TS_{H2}$= –0.41 eV, is added to the final state. First, we adopt the previously used Φ_{SHE} = 4.6 V. The obtained FED using constant-

potential calculations (FED-CP) at U_{SHE} = 0 V is shown in Figure R10. The thermodynamic inconsistency between FED by the CHE method (FED-CHE) and the one constructed with stepwise constant-potential calculations (FED-CP) can be immediately spotted in Figure R10. The final state at U = 0 V is 0.91 eV higher in energy than that of the CHE. To mitigate this energy gap, we thus need to shift Φ_{SHE} to 4.1 V to make FED-CP consistent with FED-CHE at U_{SHE} = 0 V. By using Φ_{SHE} = 4.1 V, we then could ensure consistent kinetics and thermodynamics for the HER.

The calibration procedure is added to the Supporting Information. The manuscript is updated:

On page 5—**"The value was calibrated to reproduce the experimental Gibbs free energy of the H^+/H2 reaction (see Supporting Information for details) ."**

2 "Adjusting the electron count every 5 steps to maintain constant potential": please specify the target potential tolerance (e.g., $\pm 10-20$ mV), the step size/convergence criterion for electron-count adjustment, and how potential consistency is enforced across images (eNEB).

Our response: *We thank the reviewer for letting us clarify details our simulation. Our charge optimization uses a 50 mV tolerance over 5 steps, but the threshold is rarely met. In the CP-AIMD simulations, convergence to the target potential is a prolonged process due to constant atomic fluctuations, particularly from the thermal reorientation of solvent molecules. Hence, the simulated potential constantly fluctuates around the target.*

For the eNEB calculations, the target potential is strictly enforced due to the static nature of the calculations. As shown in Figure R11, for the alkaline Volmer reaction on Pt(311) surfaces, the work function of each image along the reaction coordinate was used to ensure the potential deviation was controlled within 10 mV.

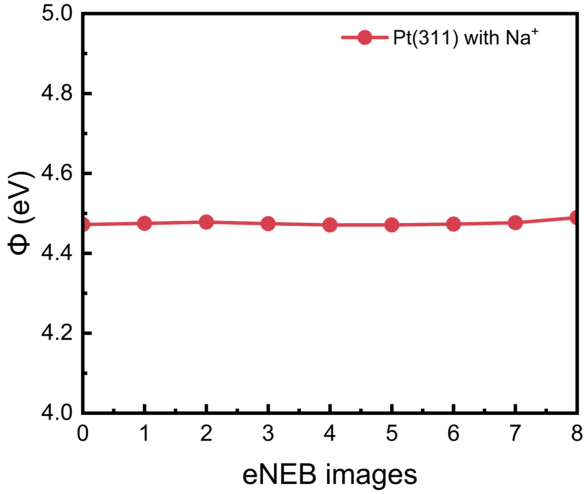

Figure R11. *Work functions the eNEB images for the alkaline Volmer reaction on Pt(311) surfaces*

with Na^+.

3. AIMD uses a 1 fs timestep and 10 ps sampling. In many cases, water needs ~15 ps to decorrelate from its initial orientation; with only 10 ps, the initial water configuration may bias the conclusions. Please clarify whether this has been considered.

Our response: *We thank the reviewer for raising this important comment. To mitigate potential bias from the initial configuration, we have significantly extended our CP-AIMD simulations. The total simulation time is now 20 ps for Pt(111) and 30 ps for Pt(311), which is sufficient to eliminate such bias. All data are updated in the revised manuscript according to extended CP-AIMD simulations. Our original conclusions are not only confirmed but further strengthened by the results from these extended simulations.*

4. Please provide more details about the eNEB setup. I guess a set of sample input for CP-AIMB and eNEB calculations would be good for readers.

Our response: *We have provided python scripts for CP-AIMD and eNEB calculations in the Supporting Information, to facilitate reproducibility of our data.*

5. Please clarify whether ZPE corrections are included.

Our response: *This study focuses on the cation effect in the alkaline HER by comparing reaction barriers with and without Na^+. While ZPE corrections can influence absolute barrier heights, they were omitted because their contributions are expected to be similar in both cases and thus would not affect the comparative analysis.*

6. Na^+ position: currently citing ~5 Å (111) vs ~3.6 Å (311). Please provide the z-direction probability distribution P(z_Na), and report mean ± standard deviation/confidence intervals to avoid conclusions based on snapshot configurations.

Our response: *We thank the reviewer for this constructive comment. We agree that conclusions based solely on snapshot configurations may not be sufficiently robust. To address this point, we extracted the z-direction trajectories of Na^+ from extended AIMD simulations. The corresponding mean values and standard deviations are reported in Figure R12. The results show that the average Na^+–electrode distance is ~4.69 ± 0.57 Å on Pt(111) and ~2.34 ± 0.36 Å on Pt(311). The probability distributions further indicate that Na^+ resides significantly closer to the electrode on Pt(311) with a*

narrower distribution, whereas on Pt(111) the distribution is broader, suggesting a more diffuse and fluctuating interfacial position. Figure R12 is added to the Supporting Information. The manuscript is updated according to the discussion:

On page 8—**"Figure S5 shows the statistical analysis of the Na^+ height on the Pt(111) and Pt(311) surfaces. The Na^+ resides above the closely bounded water layer on Pt(111) surface, staying away from the surface by about 4.69 ± 0.57 Å. On Pt(311) surface, Na^+ locates closer to the surface at about 2.34 ± 0.36 Å due to the formation of a Pt–H_2O*–$Na^+(H_2O)_x$ adduct, with Na^+ tightly coordinated to an adsorbed water molecule. The probability distributions (Figure S5) further indicate that Na^+ resides significantly closer to the electrode on Pt(311) with a narrower distribution, whereas on Pt(111) the distribution is broader, suggesting a more diffuse and fluctuating interfacial position due to weaker bound to the surface."**

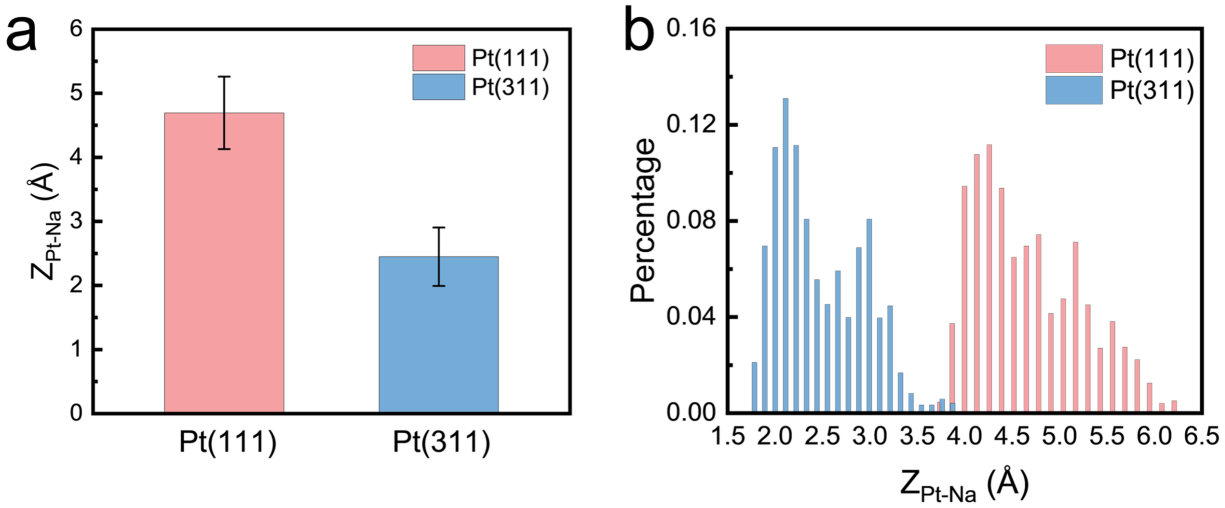

Figure R12. *(a) Average and standard deviations of Na^+–electrode distances and (b) distribution of the distance on Pt(111) and Pt(311) surfaces.*

7. Water orientation stratification: α/β distributions are reported; please provide layer-resolved distributions for the first and second water layers to distinguish contributions from the Stern layer versus the transition to bulk, and clearly define the z-window thresholds used to select interfacial water layers.

Our response: *We thank the Reviewer for this valuable suggestion. We have analyzed the water orientation distribution within the Stern layer (0–3.5 Å) and the transition layer to bulk water (3.5–7.0 Å). The corresponding α/β distributions for these regions are shown in Figures R13 and R14, respectively.*

The results indicate that for both the Pt(111) and Pt(311) interfaces, the water molecules in the

Stern layer exhibit a significantly different orientation than those in the transition layer. The transition layer generally shows broader α/β distributions, which indicates more random molecular orientations.

Figure R14 has been included in the Supporting Information, and a discussion of the transition layer has been added to the revised manuscript:

On page 9—**"The α/β distributions for the solvent layer transitioning to the bulk solvent layer (3.5–7.0 Å) is also analyzed as shown in Figure S8. The results indicate that for both the Pt(111) and Pt(311) interfaces, the transition layer generally shows broader α/β distributions, which indicates more random molecular orientations than that in the Stern layer."**

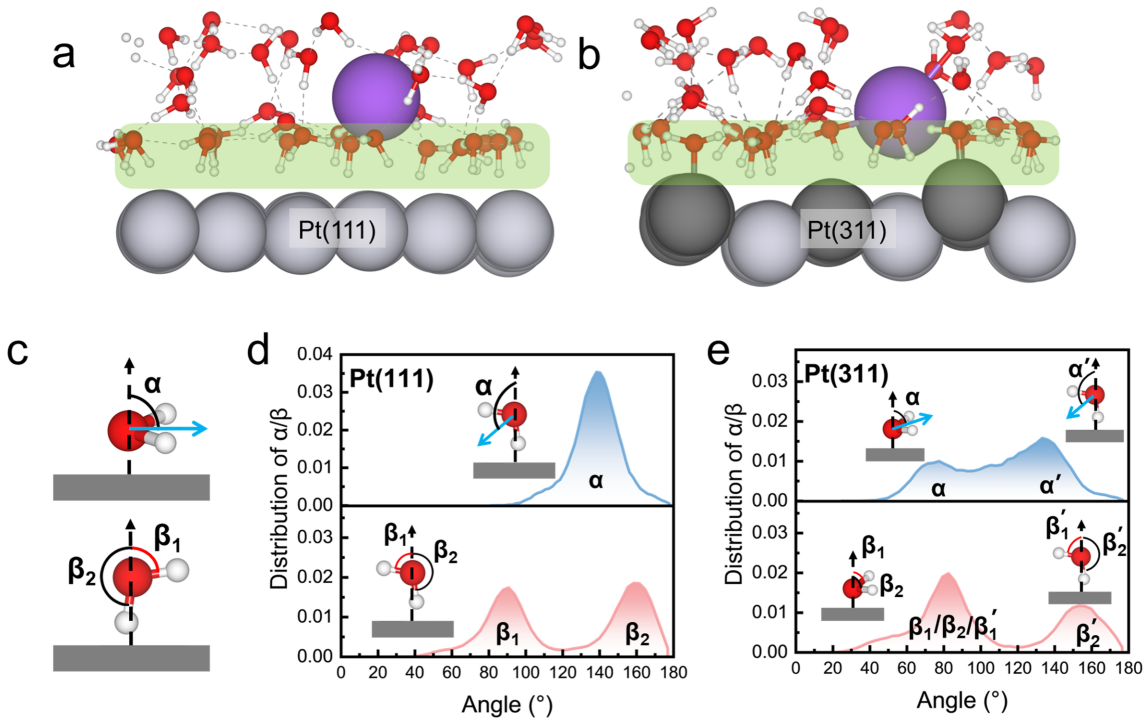

Figure R13. *(a, b) The Stern layer of the electrified aqueous Pt(111) and Pt(311) interfaces. The green shade highlights the interfacial water structures. (c) Illustration of the definition of angles α and β. (d, e) Distributions of α and β for the orientations of interfacial water molecules in the aqueous Pt(111) and Pt(311) interfaces.*

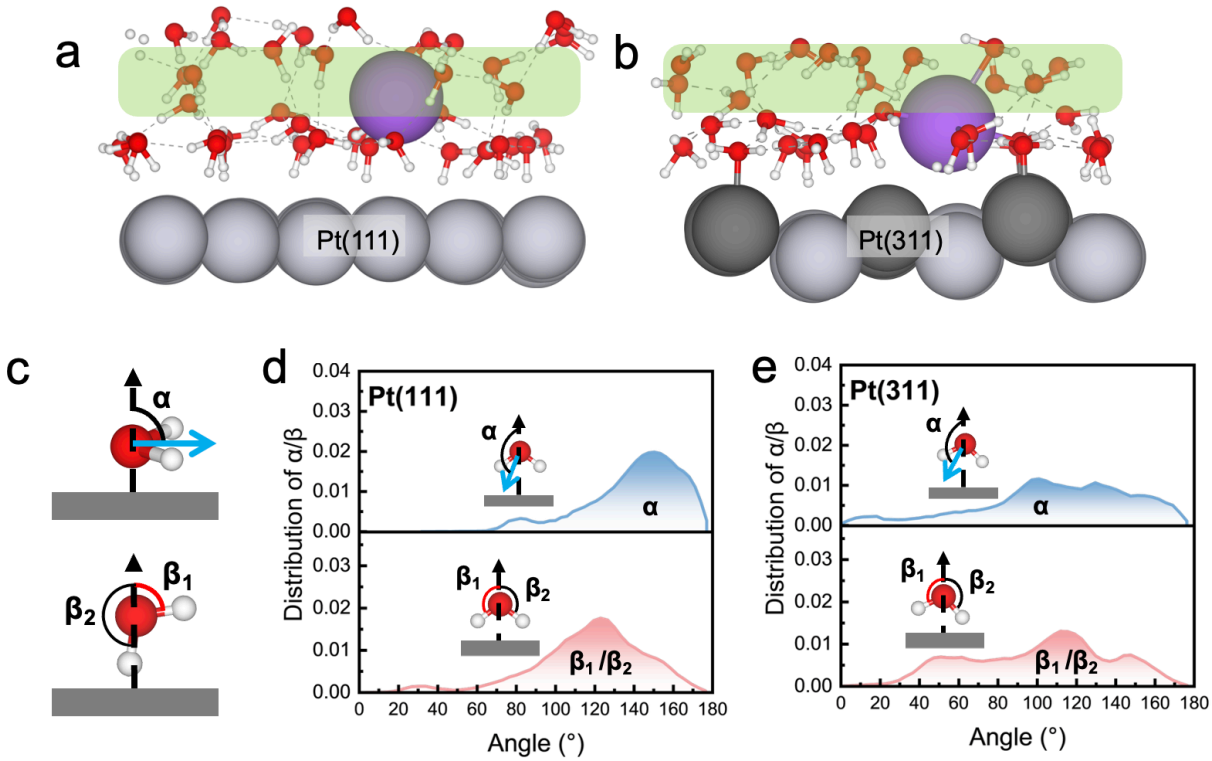

Figure R14. *(a, b) Transition layer of the electrified aqueous Pt(111) and Pt(311) interfaces. The green shade highlights the interfacial water structures. (c) Illustration of the definition of angles α and β. (d, e) Distributions of α and β for the orientations of interfacial water molecules in the aqueous Pt(111) and Pt(311) interfaces.*

Response to Reviewer Comments

Ms. ID: COMMSCHEM-25-0545A

Title: Synergistic Cation-Facet Effects Boost Alkaline Hydrogen Evolution Kinetics on Stepped Pt Surfaces

Reviewer comments in normal type

Author response in italics

Verbatim quotes from the revised text are in boldface

Reviewer: 2

I would like to thank the authors for addressing the reviewer's comments. In particular, I believe that the extension of the trajectories to longer timescales significantly contributes to the credibility of the results. Yet, I have a few more comments/questions that I would ask the authors to address:

1. I have several questions/comments on the free energy profiles.

    a. In figure 5a, not only the barrier heights, but also the reaction energies are visible. The plot clearly shows that the reaction energies depend on the presence of the ion and the surface type. This indicates that the "final state" is actually a reaction intermediate or "pseudo-final state" as the overall reaction energy should be independent of the catalytic interface. The authors may want to discuss this.

Our response: *We thank the reviewer for this valuable comment. We agree that the final states in Figure 5a is not the true thermodynamic final state with OH^- diffused into the bulk solution, but rather a pseudo-final state with OH^- near the interface. To accurately represent the completed Volmer step, we have now explicitly calculated the energy change as the solvated OH^- diffuses away from the surface. This step lowers the energy further due to the relief of repulsion between the OH^- and the negatively charged electrode. The corresponding energy correction has been incorporated into the MEPs and is denoted as "bulk OH^-" in Figure R1. The energy drop for the "bulk OH^-" state is greater on Na^+-Pt(311) than on Pt(311). This likely occurs because Na^+ induces electron enrichments at the nearby Pt edge sites, strengthening their repulsion with interfacial OH^-, as shown in the Bader charge analysis in Figure 3b. The "bulk OH^-" state was not calculated on Pt(111) with Na^+, as it disrupts the Na^+-H_2O coordination in the model, leading to an unreliable energy.*

Importantly, while this correction adjusts the "pseudo-final state" issue, the relative energy differences between catalyst surfaces remain significant. This is expected because the Volmer step is

only the first elementary reaction in the overall alkaline hydrogen evolution reaction (HER). Its reaction energy does not solely determine the overall HER thermodynamics and is inherently influenced by the catalyst surface properties.

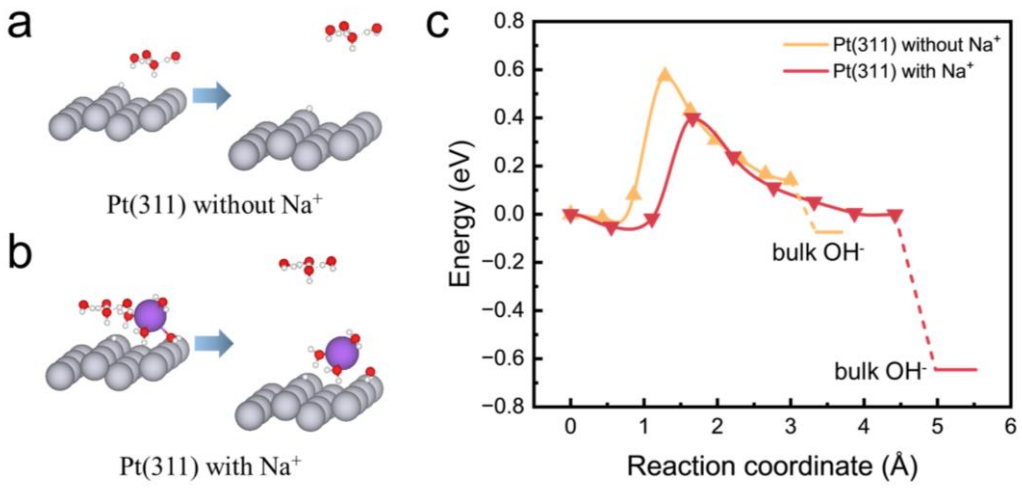

Figure R1. *(a,b) The model used to calculation the energy shift for OH- diffusion to the bulk solution. (c) MEPs for the Volmer step with the "bulk OH-" state.*

However, we believe that manually constructing the "bulk OH^-" state within an implicit solvation model would strongly perturb the interfacial structure. This perturbation could, in turn, lead to a dramatically different surface charge state. Therefore, our current methodology does not adequately address the reviewer's question. Ultimately, modeling the entire Volmer/HER process under constant-potential conditions with explicit solvation will be necessary, which is an objective for our future work.

According to the above discussions, we revised our manuscript:

On Page 15 — **"In the eNEB calculation, the final state does not represent the true product of the Volmer step because the generated OH^- remains near the interface. To model OH^- diffusion into the bulk, we displaced the OH^- ion—along with three solvating water molecules—to a position ~10 Å above the surface. The energy of this "bulk OH^-" state is included in the MEP plots for Pt(311) (Figure 5a), both with and without Na^+. This state was not calculated for Pt(111) with Na^+, as displacing the OH^- disrupts the Na^+-H2O coordination, resulting in an unreliable energy."**

On Page 16 — **"The "bulk OH^-" state further decreases the reaction energies on Pt(311) surfaces, both with and without Na^+, likely due to the relief of repulsion between the negatively charged surface and the adsorbed OH^-. The Pt(311)-Na^+ surface exhibits a greater energy drop for this state. This is probably because Na^+ induces electron enrichment on nearby Pt edge sites, leading to stronger repulsion with the interfacial OH^-, as demonstrated in Figure 3b."**

b. Focusing on the reaction energy, I have several questions that are independent of the above.

The overall reaction energy $\Delta G\circ$ given by the plot for stepped Pt + ion is close to $\Delta G\circ = 0$ eV. At pH=12 (see below on why I use pH=12 rather than 13), $\Delta G\circ = 0$ eV for the reaction $H_2O + e^- + * \rightarrow H^* + OH^-$ should correspond to $\Delta G = +0.7$ eV. Consequently, I would argue that the kinetics of this reaction at -0.7 V vs. SHE (or 0 V vs. RHE) will be determined by the energy of the final (or pseudo-final) state as this seems to be thermodynamically highly unfavorable. In this case, the barrier that needs to be surpassed to reach this state should be less relevant to the overall reaction rate. For Pt(111) with ion, ΔG would even go up to 1.1 eV, suggesting an onset potential for this reaction of around -1.1 V vs. RHE – a result that seems rather inconsistent with experimental results of HER current densities in alkaline media if I am not mistaken. Could the authors please comment on this?

Our response: *We thank the reviewer for this insightful and important comment. To address this question, we constructed complete free energy landscapes for the hydrogen evolution reaction (HER), as shown in Figure R2. Our model for the Heyrovsky step incorporates the energy changes associated with forming "bulk OH^-," in addition to the free energy correction for gas-phase H_2 entropy (ΔTS_{H_2} = 0.41 eV). The resulting profiles indicate that HER on Pt(311) is endothermic by approximately 0.4 eV, while on Na^+-Pt(311) it becomes exothermic by roughly –0.4 eV. Thus, by accounting for both OH^- diffusion to the bulk solution and the free energy of gas-phase H_2, the initial thermodynamic unfavorability is resolved. However, several additional points warrant further clarification: (1) The reaction free energy differs between the two surfaces. We attribute this to the distinct initial states of the reacting interfacial water molecules. As indicated by our structural and vibrational analysis, the O–H bond is more elongated at the Na^+–Pt(311) interface. This implies that interfacial water at the cationic interface has a higher dissociation constant (K_w). In the presented free energy landscapes, both profiles are referenced to zero, corresponding to an assumed equilibrium with bulk water. (2) In our simulations, the initial conditions were set to pH = 12 and $U_{SHE} = -0.7$ V (corresponding to $U_{RHE} \approx 0$ V). However, the pH is not an explicit variable in the computational model and is therefore not controlled during the eNEB simulation. Actually, during the eNEB calculations, the effective pH varies along the reaction coordinate. Thermodynamically, at $U_{RHE} = 0$ V, the hydrogen evolution reaction (HER) should have a neutral free energy change ($\Delta G = 0$). The deviation of our calculated free energy landscape from this constraint stems from the uncontrolled pH in the simulation.*

According to the above discussion, we revised our manuscript:

*On page 17—"***The energy changes associated with "bulk OH^-" formation and the entropic contribution from gas-phase H_2 (ΔTS_{H_2} = 0.41 eV) are also included.***"*

*On page 18—"***Finally, we combine the Volmer and Heyrovsky steps to obtain the complete HER**

free energy landscape at $U_{SHE} = -0.7$ V (Figure S15). The calculated profiles show that HER is endothermic by ~0.4 eV on Pt(311) but becomes exothermic by ~–0.4 eV on Na^+-Pt(311) when the energy for bulk OH^- formation and the entropy of gas-phase H_2 are included. This difference in reaction free energy stems from the distinct initial state of interfacial water. Our structural (Figure 4) and vibrational (Figure 5d) analyses reveal greater O–H bond elongation at the Na^+-Pt(311) interface, implying a higher local water dissociation constant (K_w). This further demonstrates the cationic effect on the stepped Pt(311) surface. It is important to note that while the simulation assumes initial conditions of pH = 12 and $U_{SHE} = -0.7$ V ($U_{RHE} \approx 0$ V), pH is not an explicit controlled variable. The effective pH varies along the eNEB reaction coordinate. Consequently, the calculated free energy profile deviates from the thermodynamic expectation of $\Delta G = 0$ at $U_{RHE} = 0$ V due to the absence of explicit pH control in the simulation.”

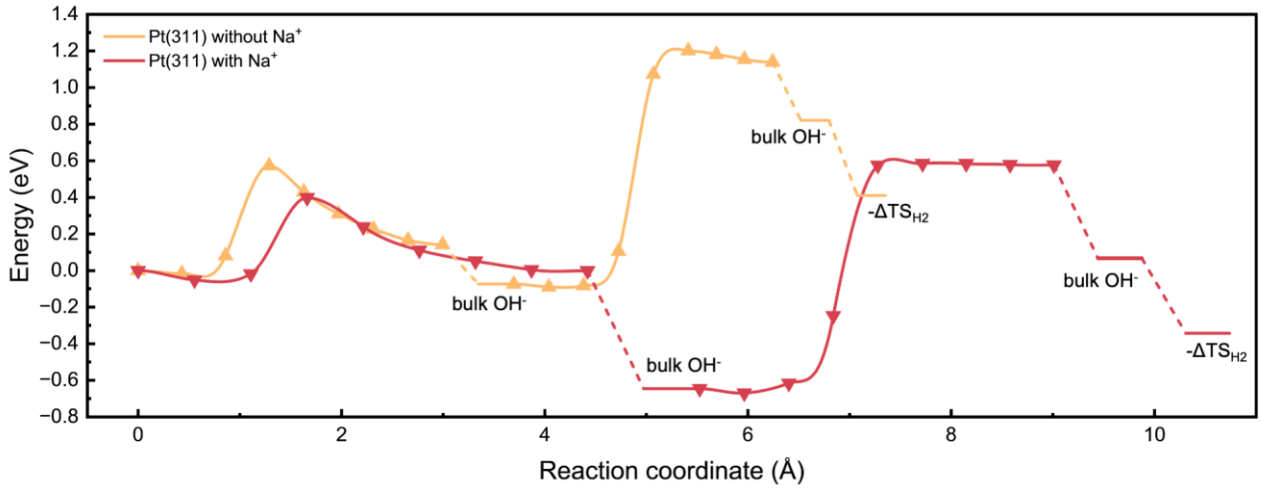

Figure R2. *Full MEPs of HER on Pt(311) with and without interfacial Na^+ at $U_{SHE} = -0.7$ V.*

c. Connected to the above, when assuming the pseudo-final state to be the potential limiting configuration in the reaction, I do not see any noticeable ion effect anymore (at least not when comparing the $\Delta G\circ$ at equal reaction coordinate of $r = 3$ A. Does this impact the conclusions the authors draw.

Our response: *The complete MEPs in Figure R2 reveal a twofold cationic influence on HER thermodynamics and kinetics. First, Na^+ stretches interfacial water molecules, facilitating the Volmer step. Second, the increased energy drop for OH^- diffusion to the bulk solution suggests that Na^+ may also facilitate this step. However, this latter point requires validation in future studies.*

2. I strongly urge the authors to describe the leakage of implicit electrolyte into their explicit water region in the main text (also discussing possible implications). I would consider it bad scientific practice to hide this relevant information in the (possibly unpublished) answer to the referee.

Otherwise, such mistakes (that are quite common in the field) propagate to other papers.

Our response: *We sincerely thank the reviewer for raising this important point and apologize for the oversight. We have now incorporated a description of the leakage of implicit solvation, along with related discussion, into the revised manuscript.*

On Page 5 — **"Analysis of the bound charge density (RHOB file, Figure S2) indicates charge leakage into solvent cavities and around the Na^+ ion. This leakage can induce partial Na^+ desolvation, and may weaken ion-specific interfacial effects. We note this as a known limitation of the linear PCM model used in VASPsol."**

3. The authors provide a value for the PZC of the stepped surface as obtained with the implicit electrolyte. However, the setup shown in the SI does not allow computing the pzc of a non-symmetric slab correctly. (This is obvious when considering that the present approach MUST provide the same value for the work function on the left and the right interface) Hence the pzc reported for the stepped Pt interface is incorrect.

Our response: *The relaxation of only the upper Pt(311) surface resulted in an asymmetric slab model. We have corrected this by relaxing both the top and bottom surfaces while keeping the middle layers fixed. The work function difference between the two surfaces is about 0.42 eV, with Pt(311) having a lower work function than Pt(111). The updated results have been incorporated into the revised manuscript and SI (also shown in Figure R3).*

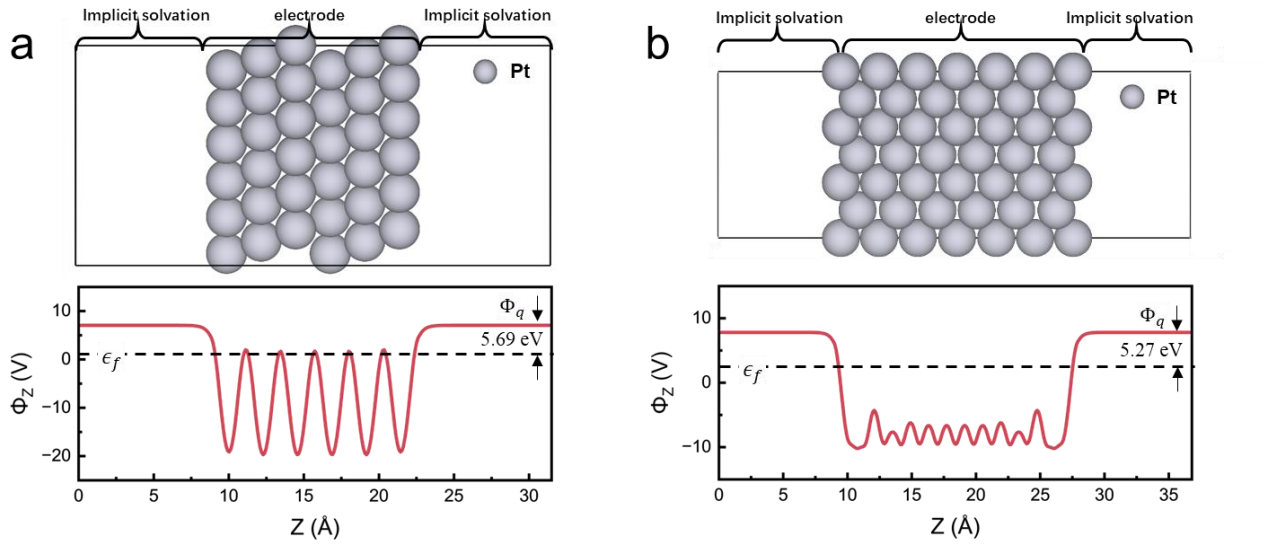

Figure R3. Side view of (a) Pt(111) and (b) Pt(311)/implicit solvation models and plane-averaged electrostatic potential along the z-direction.

4. When the authors discuss the H-bond length, they note an asymmetry and assign it to the interaction with the electric field. However, an asymmetry is already expected due to the anharmonicity of the

O-H bond. Additionally, they state that the ion further enhances the bond length. I assume that this statement is based on the fact that the red-colored region in Fig. 4f extends to larger distances. However,

a. I do not see the same effect in Fig. 4c, while I would expect that water close to the ion should feel a similarly large field – even if the ion resides far from the interface.

b. Fig. 4f also suggests that the overall water density is higher around z=2.7 A in the presence of an ion. The red region extending further to the right could thus also be an artefact of the normalization used. Normalizing the plot by the z- dependent water density (possibly excluding regions with very low water density to avoid dividing by numbers close to 0) would allow for more definite conclusions.

Our response: *We thank the reviewer for this valuable comment. We agree that the intrinsic anharmonicity of the O – H bond naturally leads to a slight asymmetry in the bond-length distribution toward longer distances. However, such anharmonicity should remain essentially comparable across different interfacial environments. The markedly enhanced probability of elongated O–H bonds observed specifically at the Pt(311)+Na^+ interface indicates that the effect cannot be attributed to anharmonicity alone. Instead, it arises from the strengthened interfacial electric field associated with the formation of the Pt–H_2O*–$Na^+(H_2O)_x$ adduct, which further polarizes the interfacial O–H bonds.*

a. *Regarding why the long O–H bond extension observed in Fig. 4f does not appear in Fig. 4c, we clarify the following: under an applied potential of −0.7 V vs. SHE, the Pt surface carries a net negative charge, while Na^+ is positively charged. Therefore, interfacial water molecules located between the Pt surface and the Na^+ ion experience electric fields from both directions, resulting in a stronger polarization effect. In the Pt(311)+Na^+ interface, the specific stepped geometry and the presence of the Pt – H_2O – $Na^+(H_2O)_x$ adduct create a local environment that facilitates such field superposition, which explains why the long-bond tail is more pronounced in this system.*

b. *Regarding the concern that the extended red region toward longer O – H bond lengths in Fig. 4f might arise from the normalization procedure, we clarify the exact normalization steps used in our analysis. In our approach, the z coordinate was divided into uniform grids, so the solvation region is sliced into many xy planes, and the number of O-H bonds during the AIMD simulation in each xy plane was counted. The grid with the global highest count of O-H bonds number was used as the normalization reference, and grid color was obtained by dividing the O-H bond count in the grid by this global maximum. Because this normalization is based on the global highest grid count rather than on the water density at a given z-position, an increase in local water density does not artificially enhance the probability of observing*

longer O – H bonds. Therefore, the rightward extension of the red region in Fig. 4f reflects a genuine difference in the bond-length distribution, rather than an artefact introduced by the normalization method.

Other points (small things that require clarification/correction in the paper):

1. In the main paper, the authors applied a potential of -0.7 V vs. SHE to to reaction, arguing that this is close to 0V vs. RHE at pH=13. In fact, I would argue that at pH=13, this corresponds to 0V vs. RHE at pH=12, rather than 13.

Our response: *We thank the reviewer for this clarification. We agree that, based on*

$$U_{RHE} = U_{SHE} + 0.059 \times pH$$

a potential of −0.7 V vs SHE corresponds to 0 V vs RHE at approximately pH = 12 rather than pH = 13.

In the revised manuscript, we have clarified this point:

On Page 6— the original expression **"−0.7 V vs. SHE (approximately 0 V vs. RHE at pH = 13)"** *has been revised to* **"−0.7 V vs. SHE (approximately 0 V vs. RHE at pH = 12)".**

2. In the methods section, when mentioning the Debye length, it is relevant to mention that the effective Debye length in the simulation will be impacted by the presence of the explicit water region – in particular if the explicit water region is large, as in the AIMD simulations. Consequently, is also not 100% clear whether the charge conditions at - 0.7V in the AIMD cell are equal to those in the cell constructed for the CI-eNEB. The possible difference in surface charge should be discussed.

Our response: *We thank the reviewer for raising this important point. The transferability from an explicit solvation model to a water cluster/implicit model needs to be discussed in more detail, and readers should be reminded of the caveats associated with these differences. As pointed out by the reviewer, a major difference is the presence of an explicit water region can significantly influence the effective Debye length at the interface, thereby modifying how interfacial charges are screened. Therefore, the surface charge conditions differ between explicit and implicit solvation models. To quantify this difference, we computed the surface charge densities (σ) in the CI-eNEB models and obtained σ = −7.6 μC/cm² for Pt(111) and σ = −11.9 μC/cm² for Pt(311) with Na^+ ion. These values differ from those obtained in the AIMD simulations, confirming that distinct solvent environments*

lead to different interfacial charge conditions. However, both models predict enhanced O-H activation of interfacial water at Pt(311), and this agreement serves as the foundation for transferring the explicit solvation model to the implicit model employed in eNEB.

We discussed the difference between the two models to remind readers about the caveat in the revised manuscript:

On Page 14— **"The key difference between the solvation models is that an explicit water region can alter the interfacial Debye length, thereby changing how charges are screened. This results in different surface charge conditions between explicit and implicit models. Quantifying this, we computed surface charge densities (σ) from the eNEB models, finding σ = −7.6 μC/cm² for Pt(111) and σ = −11.9 μC/cm² for Pt(311) with Na^+. These values differ from our AIMD results, confirming that the solvent environment dictates interfacial charge. Crucially, however, both models consistently predict enhanced O-H activation of water at Na^+-Pt(311) interface. This agreement validates the transfer of insights from the explicit solvation model to the implicit model used in the eNEB calculations."**

3. In the methods section, when describing the FF pre-equilibration, it is not clear how the (stepped) surface is then "glued" to the surface, nor is it clear how the ion was introduced into the box. (They cannot have been considered at the FF level as no FF parameters are given for these species).

Our response: *In LAMMPS, we first equilibrated a pure water slab using TIP/3P force field to generate a structurally sound hydrogen-bond network. This water slab was then positioned ~3.7 Å above the Pt surface. A Na^+ ion was introduced into a water network cavity at ~4.5 Å from the metal surface. The combined interface (explicit water, Na^+, and Pt) underwent 10 ps of AIMD equilibration at zero charge to minimize residual forces, producing the starting configuration for CP-AIMD simulations. The LAMMPS input script and detailed procedure for constructing and pre-equilibrating the water layer are updated in the revised manuscript.*

On Page 5—**"The configuration of water solvation was first equilibrated by using classical molecular dynamics simulations employing LAMMPS with TIP/3P force field for 1000 ps to obtain a structurally sound hydrogen-bond network (input script is shown in Supporting Information).[54-56] The relaxed water slab was positioned ~3.7 Å above the Pt surface, and a Na^+ ion was introduced into a water network cavity ~4.5 Å from the metal. This combined interface then underwent 10 ps of AIMD equilibration (1 fs timestep) at 300 K and zero charge, using a Nosé-Hoover thermostat to minimize residual forces and produce the starting configuration for CP-AIMD simulations."**

4. How is the distance from a non-flat surface computed? Could the definition impact the results?

Our response: *For the Pt(311) surface, the metal–ion distance was defined using the average z-coordinate of the step-edge Pt atoms as the reference plane, with the Na^+–surface distance calculated as the vertical separation from this plane. This definition focuses on the step-edge Pt since it is the active site for the HER and is therefore appropriate. Furthermore, this choice of reference plane should not influence key results, such as Pt–H_2O–Na^+ complex formation or O–H bond elongation at the stepped interface. Therefore, this distance definition does not affect the main conclusion.*

5. Is there a particular reason why the authors prefer reporting sigma, rather than the actual surface charge on the surface in question (which can easily be derived from the traces of the implicit solvent?) To me, the latter would be more meaningful as it also allows extracting the capacitance. I do not insist on this. I just ask the authors to reconsider their choice.

The following provides an idea of how to extract the actual surface charges: There should be a region close to the explicit/implicit interface with significant charge: That is the charge "belonging" to the upper surface, and there should be a region with significant charge close to the Pt/implicit water interface (defining the charges on this surface).

Our response: *Thank you for this insightful suggestion. We will carefully examine your proposed scheme for separating surface charges in the asymmetric slab model and perform a more detailed analysis in future work.*

6. When bringing up the unreliability of the charge analysis schemes in my first report, I did not want to imply that the authors should copy my arguments. Instead, I wanted to highlight that their explanation is/was likely incorrect, since adsorbed water usually transfers electrons towards the surface, making their explanation unlikely. While this could be impacted by the charge partitioning, the observation that the step is positive is likely a result from the Smoluchowski effect, which is a well-known electronic spillage effect at rough surfaces. The authors may want to reconsider their text.

Our response: *We thank the reviewer for this important and insightful suggestion. We have learnt a lot from your comments.*

In the revised manuscript, we have clarified this point:

On Page 12 — the original expression "The observed positive charge on Pt with water

adsorption may not indicate oxidation by H_2O but could instead reflect a limitation of the Bader charge analysis, where atomic volumes are partitioned differently with and without adsorbates. This interpretation is further supported by evidence that H_2O* can transfer electrons to the Pt(111) surface at the PZC.[60] Therefore, the results of the Bader analysis should be interpreted with caution." has been revised to* **"However, The positive charge at the Pt(311) step is unlikely to result from oxidation by adsorbed H_2O, as experimental evidence indicates that H_2O acts as an electron donor to Pt sites. Instead, this behavior is more plausibly attributed to the Smoluchowski effect[63]—a well-established electronic spillover phenomenon in which electrons redistribute from high-curvature regions (such as step atoms) toward flatter terrace regions, resulting in an apparent electron deficiency at the step."**

(63) Smoluchowski, R. Anisotropy of the Electronic Work Function of Metals. Physical Review 1941, 60, 661-674.

7. In my eyes, the sentence "We attribute this trend to the reduced tip effects on Pt step sites. The screening effects of H* diminish the local electric field necessary to polarize the H–O bond of the reacting water molecule." is purely speculative and should be removed.

Our response: *We have removed this sentence in the revised manuscript.*

Minor notes (typos, text coherence,…):

1. In the abstract, the authors write "The stark facet dependence arises from fundamental differences in water-cation coordination". However, they never investigate the coordination of the ion with the water in general. They mean the reactant–ion coordination (or otherwise ion–surface coordination).

Our response: *In the revised manuscript, we have clarified this point:*

On Page 1— the original expression "water-cation coordination" has been revised to **"ion-surface coordination"**.

2. The introduction is not ideally structured. For example, the authors first say that there is no atomic-level understanding about ion effects, just to give a literature review on atomistic studies and various proposed mechanisms in the next paragraph – a paragraph that is suddenly interrupted by a statement that cation effects are also known (from experimental studies) to occur in other reactions. This is no severe issue, but it is deterring.

Our response: *We have improved the logical flow of the introduction in the revised manuscript.*

On Page 2— the original expression "Nevertheless, the atomic-level mechanism underlying this cation-surface structure synergy remains unclear, impeding the rational design of catalyst/electrolyte interfaces for improved alkaline HER performance.

Cation effects in electrocatalytic reactions have attracted considerable interest due to their critical role in modulating reaction kinetics and mechanism. Several hypotheses have been proposed to explain how cations enhance HER kinetics, including (i) facilitating reactant adsorption or stabilizing intermediates via electrostatic interaction,[12-21] (ii) modulating hydrogen-bonding networks,[22-24] (iii) altering local pH,[13,25-27] etc. In addition to the HER, solvated cations have also been demonstrated to play a decisive role in determining activities of other electrocatalytic reactions.[28-30]" has been revised to **"Cation effects in electrocatalytic reactions have attracted considerable interest due to their critical role in modulating reaction kinetics and mechanism. Several hypotheses have been proposed to explain how cations enhance HER kinetics, including (i) facilitating reactant adsorption or stabilizing intermediates via electrostatic interaction,[12-21] (ii) modulating hydrogen-bonding networks,[22-24] (iii) altering local pH,[13,25-27] etc. While these studies provide important insights, they do not yet offer a unified atomic-level understanding of cation–surface synergy under realistic interfacial conditions. As a result, the atomic-level mechanism underlying this cation-surface structure synergy remains unclear, impeding the rational design of catalyst/electrolyte interfaces for improved alkaline HER performance. In addition to the HER, solvated cations have also been demonstrated to play a decisive role in determining activities of other electrocatalytic reactions.[28-30]"**.

3. The time step used should go into the methods section rather than the results section.

Our response: *We moved the relevant description from the Results section to the Methods section.*

4. This sentence is unclear to me: "Unlike the Pt/implicit solvation interface at the slab's bottom, this electron enrichment is far more pronounced" Please fix the grammar of this sentence.

Our response: *In the revised manuscript, we revised this sentence:*

On Page 11— the original expression "Unlike the Pt/implicit solvation interface at the slab's bottom, this electron enrichment is far more pronounced." has been revised to **"In contrast to the bottom Pt/implicit-solvent interface, the explicit-solvent interface at the top of the slab exhibits**

much stronger electron enrichment.".

5. Please shorten the paragraph starting with "Previous studies of water structures at the Pt(111)/aqueous interface at PZC". Essentially, all that the authors are saying is that their results for the water orientation match earlier studies performed at the same potential but that clear differences can be seen compared to charge neutral surfaces.

Our response: *In the revised manuscript, we have clarified this point:*

On Page 10— the original passage "Previous studies of water structures at the Pt(111)/aqueous interface at PZC typically identify a mixture of flat-adsorbed and H-down configurations.[57,59-61] In these studies, the flat-adsorbed water exhibits single-peaked α and β at approximately 60° and 75°, respectively.[61] In contrast, our calculations for the negatively charged Pt(111) surface do not show these flat-adsorbed configurations. The stronger electrostatic interaction with the hydrogen atoms of water favors H-down orientations. Our observed H-down configurations, with α ≈ 140° and β ≈ 90°/160°, are consistent with previous reports." has been revised to **"Previous studies of water structures at the Pt(111)/aqueous interface at PZC typically identify a mixture of flat-adsorbed and H-down configurations.[57,59-61] In contrast, our calculations for the negatively charged Pt(111) surface do not show these flat-adsorbed configurations. The stronger electrostatic interaction with the hydrogen atoms of water favors H-down orientations. Our observed H-down configurations, with α ≈ 140° and β ≈ 90°/160°, are consistent with previous reports."**.

6. In the sentence "In contrast to the flat Pt(111) surface, where Na^+ resides closer from the interface", the words "closer" and "further" are switched.

Our response: *On Page 14—the sentence has been revised to* **"In contrast to the flat Pt(111) surface, where Na^+ resides further from the interface"**.

7. The paragraph starting with "Figure 5b depicts the potential dependence of the Volmer step Ea for Pt(111) and Pt(311), both with and without Na+." is confusing: The authors start discussing the slope, but end with the sentence "The stronger cationic effect of Na^+ on Pt(311) is attributed to its closer proximity to the active site, facilitated by the formation of a Pt – H2O – Na+(H2O)x adduct structure.", which, in my eyes, has nothing to do with said slope, but only with the absolute offsets

of the lines.

Our response: *On Page 16—the sentence has been revised to* **"The E_a decreases monotonically with increasingly negative potentials for all systems, and the slopes of the E_a – potential relations are similar, indicating that the potential response of the transition state is not substantially altered by the presence of Na^+. However, the absolute barrier values exhibit clear differences."**

8. In the paragraph starting with "In addition to the chemical stabilization by the adsorbed water", the authors seem to contradict themselves. First,they say that the tip effect acts in addition to a chemical interaction that results from the undercoordinated sites. Then, they say that the tip effect is the main reason. Personally, I believe that there is no way to judge based on the presented data and the authors may want to avoid overinterpreting their data.

Our response: *On Page 8—we rephases the sentence as* **"We propose that the tip effect contributes to this stronger adsorption, …"**

Referee report: COMMSCHEM-25-0545-T
Title: Synergistic Cation-Facet Effects Boost Alkaline Hydrogen 1 Evolution Kinetics on Stepped Pt Surfaces
Authors: Qingqing Zhang, Pengfei Sun, Haobo Li, Zhiyao Duan

The article describes the formation a Pt-H_2O*-$Na^+(H_2O)_x$ adduct at the step edges of Pt(311). Such an adduct is reminiscent of the Pt-OH*-$Na^+(H_2O)_x$ adducts suggested earlier to play a role in the cation-dependent peak shift of the H/OH exchange peak observed in the CV of stepped Pt [DOI: 10.1002/celc.201600293]. To my knowledge, it is a novel insight that such structures may also occur in the absence of adsorbed OH – as long as adsorbed water molecules exist at the interface. The article further discusses the effect of this adduct on HER.
The article is interesting to read, but there are several points that require attention.

1. I find the model system used rather unrealistic:
    a. Pt(311) does not exist under electrochemical conditions. It reconstructs [DOI: 10.1021/la701566w, DOI: 10.1038/s41929-024-01232-2]
    b. Under HER conditions, both the step and the terraces will be covered by hydrogen

    This brings up the question how relevant the results (in particular the barrier height calculations) are.
2. In Fig. 1d, the potential can be seen to stabilize excessively slowly on the timescales of the simulations used here. Effectively, a potential of -0.7V/SHE is only reached after 8ps. This would leave only 2ps for statistics accumulation, which seems excessively short.
    a. Why does the potential stabilize so slowly? After all, the simulations are supposed to be constant potential calculations. According to the methods section, the charges are updated every 5 timesteps. I would thus expect the relaxation time to be on the order of 5fs. To me, it seems that the charge update does not work correctly.
    b. How did the authors choose the equilibration period?
3. The equation used to determine the surface charge (see figure caption of Figure 1) is incorrect:
    a. The surface is not symmetrical. A different amounts of shielding charges is therefore required to bring the metal/implicit solvent interface on the left to the desired potential than will be used for the right interface that we are interested in.

    b. Additionally, the equation neglects the charge transferred to the surface from the sodium atom.
4. I find it a lost opportunity that this article does not compare to earlier literature. In particular, the presence of adsorbed water on the steps and the resulting angle distribution has been discussed before in literature [DOI: 10.1002/celc.201600293, DOI: 10.1021/jacs.3c11403, DOI: 10.1063/5.0080104].
5. When discussing the location of the ions, how sure are the authors that this is not an effect of a too short time-scale? The simulations will likely not allow the ions to equilibrate in terms of distance from the surface. It is possible that there is an effect, either due to the chemisorbed water molecules at the step edge of due to tip effects, but I am not convinced that the present simulations can show this. It would be helpful to at least see the ion trajectories. Ideally, several initial conditions should be tested with the ion closer and further from the surface.
6. The authors furthermore attribute the smaller ion – surface distance to the presence of undercoordinated sites on Pt. The effect could, however, also be due to tip effects, that should enhance the electric field at the step edges.
7. Later on (p8) the authors also explain the stronger Na adsorption to the Pt(311) surface by an enhanced electron transfer to the Na+ at the stepped surface. However, is this not a hen and egg problem? If the ion comes closer to the surface, it is also more likely to receive more charge from the interface.
   Additionally, similar effects been discussed earlier by Shengli Chen [DOI: 10.1063/5.0080104], where, however, the authors found a negligible change in Bader charge on the ion upon approach to a stepped Pt(553) surface.
8. Throughout the entire paper, Bader charges are used to rationalize several observations. However, Bader charges are only one way to split the charges in a quantum chemical simulation and are by no means a unique charge partitioning and therefore often not meaningful.
    a. In particular, Bader charges should not be confused with free charges that define the surface electric field. They may be severely impacted by adsorbates.
       This should be particularly true for adsorbed hydrogen. A change in Bader charge in the presence of adsorbed hydrogen should therefore, in my opinion, not be used to argue anything about electric fields (see page 15)
    b. A larger Bader charge at the metal/explicit solvent compared to the metal/implicit solvent interface, to me, also does not necessarily indicate strong electrostatic coupling between surface and water dipoles. It may simply be a question of different charge partitioning in the presence and absence of water close the interface.

Additionally, it should be noted that (as noted above) a comparison of the charges on the top and the bottom of the slab is illegitimate in the setup used in this paper as the lower surface (Pt(111)/implicit solvent interface) will have a different potential of zero charge compared to the upper surface (Pt(111)/explicit water/implicit water).

c. On page 10, it is discussed that adsorbed water leads to a positive Bader charge. This is possible (see a). However, adsorbed water has earlier been observed to lead to an overall dipole that points away from the surface (i.e, electron transfer occurs on average from the water towards the metal) [DOI: 10.1103/PhysRevLett.119.016801]. This knowledge may impact the authors reasoning.

9. On page 6, the authors state that the difference in PZC between the stepped and the flat surface is increased to 0.77V in the presence of Na^+. This statement is not logic to me: A surface with excess cations in the double layer is by definition not at its pzc.
10. On page 12 the authors discuss the OH bond lengths shown in Figure 4. They state that the bond lengths on the Pt(311)+Na^+ interface extend to longer distances than on the Pt(311) interface without ion. I cannot follow this statement based on the plots presented. In both panels, e and f, I can see water molecules with bond lengths>1.12A. The main difference is that these water molecules reside higher up in z in the region without Na ion (panel e), but this can be explained by the choice of region, which includes two upper step edges for panel e, but two lower step edges for panel f.
11. When comparing the barrier heights for the Volmer step with and without Na present, the models chosen seem unfair to me: In the lower panel of Fig. 5c, the reacting water molecule has two neighboring water molecules that act as hydrogen donor, while in the upper panel (no Na), the reacting water molecule only has one hydrogen donor pointing towards it. This difference could significantly affect the barrier without the Na being the “culprit”.
12. The hydrogen adsorption energies shown in Figure S7 seem incorrect to me: hydrogen adsorption must scale nearly perfectly with applied potential (close to neutral adsorption with small change in surface dipole). However, in Fig 7a red line, the adsorption energy even decreases with decreasing potential and in the blue line the change in adsorption energy is only ~5% if the change in potential. It is not described in the text how this adsorption energy was computed, so I cannot judge what may have gone wrong, but this seems rather strange to me.

Other notes:

1. On p. 6 the authors argue that the difference in charge must stem from ta difference in PZC. This is not necessarily true (or at least not the only reason): The capacitance

could be smaller too. This has actually proposed earlier by Bandarenka [DOI: 10.1021/jacs.3c11403]

2. It is not clear when the 4x4 setup is used and when the 6x6 setup is used.
3. Why use only 2x2 k-points in non-molecular-dynamics simulations?
4. Are 3 layers (in combination with a gamma-point-only simulation) not somewhat little for a realistic description of the metal? Does it actually end up being metallic or does it show a band gap?
5. In the implicit solvation model, what is the density cutoff used?
6. Have the authors checked whether there is leakage of the implicit solvent into the water region (can happen depending on the density cutoff)?

I would like to thank the authors for addressing the reviewer's comments. In particular, I believe that the extension of the trajectories to longer timescales significantly contributes to the credibility of the results. Yet, I have a few more comments/questions that I would ask the authors to address:

1) I have several questions/comments on the free energy profiles.
    a. In figure 5a, not only the barrier heights, but also the reaction energies are visible. The plot clearly shows that the reaction energies depend on the presence of the ion and the surface type. This indicates that the "final state" is actually a reaction intermediate or "pseudo-final state" as the overall reaction energy should be independent of the catalytic interface. The authors may want to discuss this.
    b. Focusing on the reaction energy, I have several questions that are independent of the above.
    The overall reaction energy ΔG° given by the plot for stepped Pt + ion is close to $\Delta G^\circ = 0$ eV. At pH=12 (see below on why I use pH=12 rather than 13), $\Delta G^\circ = 0$ eV for the reaction $H_2O + e^- + * \rightarrow H^* + OH^-$ should correspond to $\Delta G = +0.7$ eV. Consequently, I would argue that the kinetics of this reaction at -0.7 V vs. SHE (or 0 V vs. RHE) will be determined by the energy of the final (or pseudo-final) state as this seems to be thermodynamically highly unfavorable. In this case, the barrier that needs to be surpassed to reach this state should be less relevant to the overall reaction rate. For Pt(111) with ion, ΔG would even go up to 1.1 eV, suggesting an onset potential for this reaction of around -1.1 V vs. RHE – a result that seems rather inconsistent with experimental results of HER current densities in alkaline media if I am not mistaken. Could the authors please comment on this?
    c. Connected to the above, when assuming the pseudo-final state to be the potential limiting configuration in the reaction, I do not see any noticeable ion effect anymore (at least not when comparing the ΔG^0 at equal reaction coordinate of $r = 3$ A. Does this impact the conclusions the authors draw.
2) I strongly urge the authors to describe the leakage of implicit electrolyte into their explicit water region in the main text (also discussing possible implications). I would consider it bad scientific practice to hide this relevant information in the (possibly unpublished) answer to the referee. Otherwise, such mistakes (that are quite common in the field) propagate to other papers.
3) The authors provide a value for the PZC of the stepped surface as obtained with the implicit electrolyte. However, the setup shown in the SI does not allow computing the pzc of a non-symmetric slab correctly. (This is obvious when considering that the present approach MUST provide the same value for the work function on the left and the right interface) Hence the pzc reported for the stepped Pt interface is incorrect.
4) When the authors discuss the H-bond length, they note an asymmetry and assign it to the interaction with the electric field. However, an asymmetry is already expected due to the anharmonicity of the O-H bond. Additionally, they state that the ion further enhances the bond length. I assume that this statement is based on the fact that the red-colored region in Fig. 4f extends to larger distances. However,
    a. I do not see the same effect in Fig. 4c, while I would expect that water close to the ion should feel a similarly large field – even if the ion resides far from the interface.

b. Fig. 4f also suggests that the overall water density is higher around z=2.7 A in the presence of an ion. The red region extending further to the right could thus also be an artefact of the normalization used. Normalizing the plot by the z-dependent water density (possibly excluding regions with very low water density to avoid dividing by numbers close to 0) would allow for more definite conclusions.

Other points (small things that require clarification/correction in the paper):

1) In the main paper, the authors applied a potential of -0.7 V vs. SHE to to reaction, arguing that this is close to 0V vs. RHE at pH=13. In fact, I would argue that at pH=13, this corresponds to 0V vs. RHE at pH=12, rather than 13.
2) In the methods section, when mentioning the Debye length, it is relevant to mention that the effective Debye length in the simulation will be impacted by the presence of the explicit water region – in particular if the explicit water region is large, as in the AIMD simulations. Consequently, is also not 100% clear whether the charge conditions at -0.7V in the AIMD cell are equal to those in the cell constructed for the CI-eNEB. The possible difference in surface charge should be discussed.
3) In the methods section, when describing the FF pre-equilibration, it is not clear how the (stepped) surface is then "glued" to the surface, nor is it clear how the ion was introduced into the box. (They cannot have been considered at the FF level as no FF parameters are given for these species).
4) How is the distance from a non-flat surface computed? Could the definition impact the results?
5) Is there a particular reason why the authors prefer reporting sigma, rather than the actual surface charge on the surface in question (which can easily be derived from the traces of the implicit solvent? To me, the latter would be more meaningful as it also allows extracting the capacitance. I do not insist on this. I just ask the authors to reconsider their choice.
   The following provides an idea of how to extract the actual surface charges: There should be a region close to the explicit/implicit interface with significant charge: That is the charge "belonging" to the upper surface, and there should be a region with significant charge close to the Pt/implicit water interface (defining the charges on this surface).
6) When bringing up the unreliability of the charge analysis schemes in my first report, I did not want to imply that the authors should copy my arguments. Instead, I wanted to highlight that their explanation is/was likely incorrect, since adsorbed water usually transfers electrons towards the surface, making their explanation unlikely. While this could be impacted by the charge partitioning, the observation that the step is positive is likely a result from the Smoluchowski effect, which is a well-known electronic spillage effect at rough surfaces. The authors may want to reconsider their text.
7) In my eyes, the sentence "We attribute this trend to the reduced tip effects on Pt step sites. The screening effects of H* diminish the local electric field necessary to polarize the H–O bond of the reacting water molecule." is purely speculative and should be removed.

Minor notes (typos, text coherence,...):

1) In the abstract, the authors write "The stark facet dependence arises from fundamental differences in water-cation coordination". However, they never investigate the

coordination of the ion with the water in general. They mean the reactant – ion coordination (or otherwise ion – surface coordination).

2) The introduction is not ideally structured. For example, the authors first say that there is no atomic-level understanding about ion effects, just to give a literature review on atomistic studies and various proposed mechanisms in the next paragraph – a paragraph that is suddenly interrupted by a statement that cation effects are also known (from experimental studies) to occur in other reactions. This is no severe issue, but it is deterring.
3) The time step used should go into the methods section rather than the results section.
4) This sentence is unclear to me: "Unlike the Pt/implicit solvation interface at the slab's bottom, this electron enrichment is far more pronounced" Please fix the grammar of this sentence.
5) Please shorten the paragraph starting with "Previous studies of water structures at the Pt(111)/aqueous interface at PZC". Essentially, all that the authors are saying is that their results for the water orientation match earlier studies performed at the same potential but that clear differences can be seen compared to charge neutral surfaces.
6) In the sentence "In contrast to the flat Pt(111) surface, where Na^+ resides closer from the interface", the words "closer" and "further" are switched.
7) The paragraph starting with "Figure 5b depicts the potential dependence of the Volmer step Ea for Pt(111) and Pt(311), both with and without Na+." is confusing: The authors start discussing the slope, but end with the sentence "The stronger cationic effect of Na^+ on Pt(311) is attributed to its closer proximity to the active site, facilitated by the formation of a Pt–H2O–Na+(H2O)x adduct structure.", which, in my eyes, has nothing to do with said slope, but only with the absolute offsets of the lines.
8) In the paragraph starting with "In addition to the chemical stabilization by the adsorbed water", the authors seem to contradict themselves. First,they say that the tip effect acts in addition to a chemical interaction that results from the undercoordinated sites. Then, they say that the tip effect is the main reason. Personally, I believe that there is no way to judge based on the presented data and the authors may want to avoid overinterpreting their data.