

How the Bioinspired Fe₂Mo₆S₈ Chevrel Breaks Electrocatalytic Nitrogen Reduction Scaling Relations

Nicholas R. Singstock and Charles B. Musgrave*

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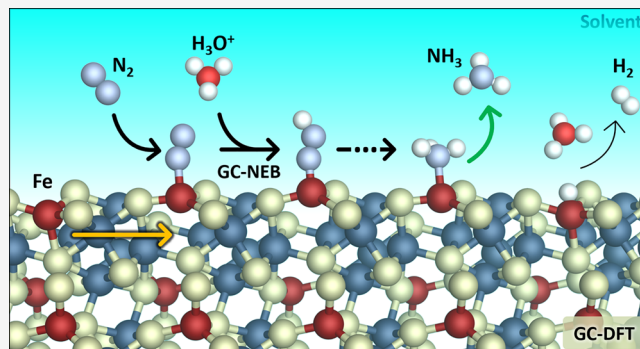


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ABSTRACT: The nitrogen reduction reaction (NRR) is a renewable alternative to the energy- and CO₂-intensive Haber–Bosch NH₃ synthesis process but is severely limited by the low activity and selectivity of studied electrocatalysts. The Chevrel phase Fe₂Mo₆S₈ has a surface Fe–S–Mo coordination environment that mimics the nitrogenase FeMo-cofactor and was recently shown to provide state-of-the-art activity and selectivity for NRR. Here, we elucidate the previously unknown NRR mechanism on Fe₂Mo₆S₈ via grand-canonical density functional theory (GC-DFT) that realistically models solvated and biased surfaces. Fe sites of Fe₂Mo₆S₈ selectively stabilize the key *NNH intermediate via a narrow band of free-atom-like surface *d*-states that selectively hybridize with *p*-states of *NNH, which results in Fe sites breaking NRR scaling relationships. These sharp *d*-states arise from an Fe–S bond dissociation during N₂ adsorption that mimics the mechanism of the nitrogenase FeMo-cofactor. Furthermore, we developed a new GC-DFT-based approach for calculating transition states as a function of bias (GC-NEB) and applied it to produce a microkinetic model for NRR at Fe₂Mo₆S₈ that predicts high activity and selectivity, in close agreement with experiments. Our results suggest new design principles that may identify effective NRR electrocatalysts that minimize the barriers for *N₂ protonation and *NH₃ desorption and that may be broadly applied to the rational discovery of stable, multinary electrocatalysts for other reactions where narrow bands of surface *d*-states can be tuned to selectively stabilize key reaction intermediates and guide selectivity toward a target product. Furthermore, our results highlight the importance of using GC-DFT and GC-NEB to accurately model electrocatalytic reactions.



INTRODUCTION

The synthesis of ammonia from nitrogen is a foundation of modern society due to the critical role it plays in producing ammonia for fertilizers that support feeding nearly half of the global population.^{1,2} Over 90% of the world's 235 Mt/year production of NH₃ is generated via the Haber–Bosch process, which is highly energy intensive and generates ~1.8% of global CO₂ emissions annually.^{3–9} Synthesis of NH₃ via the electrocatalytic nitrogen reduction reaction (NRR) is a promising alternative process because it can be powered by renewable electricity, uses N₂ and H₂O as sustainable inputs, and enables distributed production.^{4,7,8,10,11} Ammonia produced by NRR is also a promising fuel for renewable energy storage and a renewable precursor to other industrial chemicals such as nitric acid.^{2,12} Yet, the development of NRR has been limited by the absence of an active and selective electrocatalyst, with the majority of currently studied materials yielding Faradaic efficiencies (FE) of <1% due to competition with proton reduction via the hydrogen evolution reaction (HER).^{4,6,7,13–20} This results from linear scaling relationships between NRR intermediates that limit NRR activity, where previous work indicated that metals with weaker nitrogen binding are limited by the reductive adsorption of N₂ to form

*NNH and metals with stronger binding are limited by the reductive desorption of *NH₂ to form NH₃ (* denotes adsorbed species).^{4,21}

In nature, NH₃ is synthesized from N₂ by nitrogenase enzymes in conjunction with a catalytic FeMo-cofactor.^{22–24} The impressive activity of the cofactor is enabled by its structure, which is comprised of Fe active sites coupled with Mo through sulfur atoms (Figure 1a). An analogous inorganic structure is the metallic Chevrel phase Fe₂Mo₆S₈, where Fe atoms coordinate to Mo₆ octahedra through sulfur atoms (Figure 1b). The Fe–S–Mo coordination environment of the predominant (101) surface of the P1 Fe₂Mo₆S₈ crystal structure closely resembles that of the Fe active site of the FeMo-cofactor and may therefore also provide favorable energetics for ambient conversion of N₂ to NH₃. Furthermore,

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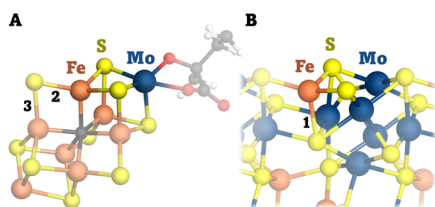


Figure 1. Structural similarities of Fe–S–Mo bonding. Ground-state structures of the nitrogenase FeMo-cofactor (A) and (101) $\text{Fe}_2\text{Mo}_6\text{S}_8$ Chevrel phase surface (B). The similar Fe–S–Mo coordination of the structures is highlighted.

during the preparation of this report, an experimental investigation of $\text{Fe}_2\text{Mo}_6\text{S}_8$ -catalyzed NRR found that it yielded a state-of-the-art FE of 12.5% and a high rate of $70 \mu\text{g NH}_3 \text{ h}^{-1} \text{ mg}_{\text{cat}}^{-1}$ at a low bias of -0.20 V vs RHE, which was stable over 50 h.²⁵ However, the mechanism for NRR on this impressive material has not yet been determined, limiting the understanding necessary to rationally design superior electrocatalysts in this material space.^{26,27}

To probe the NRR reaction mechanism on $\text{Fe}_2\text{Mo}_6\text{S}_8$ under realistic reaction conditions, that is, in solvent under an applied bias, we used grand-canonical density functional theory (GC-DFT, see Section S1 for details)^{28–30} and implemented a new GC-DFT approach to calculate reaction barriers as a function of the applied bias (GC-NEB, see Computational Details). GC-NEB predicts low barriers for both $^*\text{N}_2$ protonation to $^*\text{NNH}$ and $^*\text{NH}_3$ desorption, which we identified to be the two key steps that limit NRR on this material. Consequently, we find that Fe surface sites on $\text{Fe}_2\text{Mo}_6\text{S}_8$ facilitate rapid NRR rates ($>6 \mu\text{g h}^{-1} \text{ cm}^{-2}$) due to the selective stabilization of the key $^*\text{NNH}$ intermediate relative to $^*\text{N}_2$. N_2 adsorption at Fe sites results in a concomitant dissociation of the subsurface Fe–S bond (1 in Figure 1), similar to the N_2 reduction mechanism on the nitrogenase FeMo- and FeV-cofactors where two Fe–S bonds dissociate (2 and 3 in Figure 1) to reveal the Fe active sites.^{17,22,31} On $\text{Fe}_2\text{Mo}_6\text{S}_8$, this yields a Fe active site with narrow bands of free-atom-like d -states that overlap significantly with the nitrogen p -states of $^*\text{NNH}$ but not those of $^*\text{N}_2$ or $^*\text{NH}_3$, which selectively stabilizes $^*\text{NNH}$ to break linear NRR scaling relationships. The elucidation of the NRR mechanism on $\text{Fe}_2\text{Mo}_6\text{S}_8$ provides important insights

that may aid in the rational design of superior electrocatalysts with high NH_3 activity and selectivity.

RESULTS AND DISCUSSION

NRR Mechanism on $\text{Fe}_2\text{Mo}_6\text{S}_8$. NRR involves the transfer of six protons and six electrons to N_2 to yield two NH_3 molecules. In electrocatalytic NRR, the protons and electrons are derived from an anodic oxidation (e.g., oxygen evolution reaction) and are transferred to the $^*\text{N}_x\text{H}_y$ species from the solvent and NRR electrocatalyst, respectively. Three reaction mechanisms have been proposed for NRR: (1) the associative alternating pathway, where the nitrogen atoms of $^*\text{N}_2$ are protonated in parallel to form $^*\text{NH}_2\text{NH}_2$ and then $^*\text{NH}_3$ (Figure 2, opaque), (2) the associative distal pathway, where the nitrogen atoms are protonated in series to form $^*\text{NNH}_3$ and then $^*\text{NH}_3$ (Figure 2, transparent), and (3) the dissociative pathway, where N_2 dissociatively adsorbs into two $^*\text{N}$ atoms at separate sites, which are subsequently protonated.^{4,17,18} The dissociative pathway is not considered further due to its large change in grand free energy ($\Delta\Phi$) on $\text{Fe}_2\text{Mo}_6\text{S}_8$, which ranges from 2.81 to 2.44 eV at 0.0 V and -0.5 V , respectively (see Figure S1). In addition to these three NRR mechanisms, we also examined a hydride-based mechanism, analogous to the Lowe–Thorneley mechanism of biological N_2 reduction by the FeMo-cofactor of nitrogenase (Section S2);^{17,32} however, we found that this mechanism has a negligible contribution to NRR on $\text{Fe}_2\text{Mo}_6\text{S}_8$.

Chevrel phase $\text{Fe}_2\text{Mo}_6\text{S}_8$ is a multisite catalyst with Mo, Fe, and S surface sites that bind nitrogen and hydrogen. Here, we consider the (101) surface of the triclinic $P\bar{1}$ $\text{Fe}_2\text{Mo}_6\text{S}_8$ crystal structure (Table S1-1), which we previously showed by powder X-ray diffraction to be the predominant surface and crystal structure of $\text{Fe}_2\text{Mo}_6\text{S}_8$ at ambient conditions.³³ Figure 2a,b shows the GC-DFT-computed energies for the associative NRR pathways on Mo and Fe surface sites, respectively, in H_2O solvent and under an applied bias of 0.0 to -0.5 V , which spans the range of commonly studied reducing biases.^{6,15,25} Nitrogen and hydrogen binding is not favorable at S sites (Figure S2), while at Mo sites, NRR proceeds via either the associative alternating or associative distal pathways (Figure 2a). However, the final reaction step of both pathways is $^*\text{NH}_3$ desorption, which requires a large grand free energy ($\Delta\Phi_2$) of 1.16–1.32 eV at the considered biases. Consequently, the rate

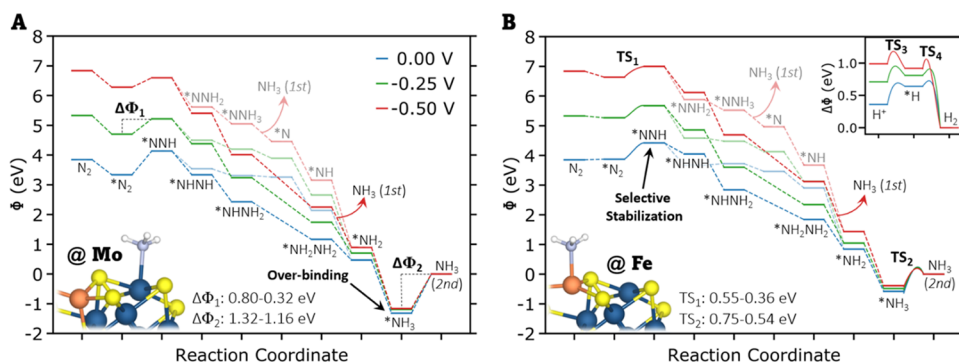


Figure 2. NRR Mechanism on $\text{Fe}_2\text{Mo}_6\text{S}_8$. The associative alternating (opaque) and associative distal (transparent) NRR pathways at Mo (A) and Fe (B) surface sites, at applied biases of 0.0, -0.25 , and -0.5 V vs RHE (red, green, and blue, respectively) in H_2O solvent at pH 7. The Volmer–Heyrovsky HER pathway on Fe sites is shown in the inset. Transition states are included for $^*\text{N}_2$ protonation (TS_1), $^*\text{NH}_3$ desorption (TS_2), H^+ adsorption (TS_3), and $^*\text{H}$ protonation (TS_4) on Fe sites. $\text{NH}_3(\text{aq})$ is set as the grand free energy (Φ) reference, which results in the bias dependence of the initial state. The energies for each pathway and bias are provided in Table S1.

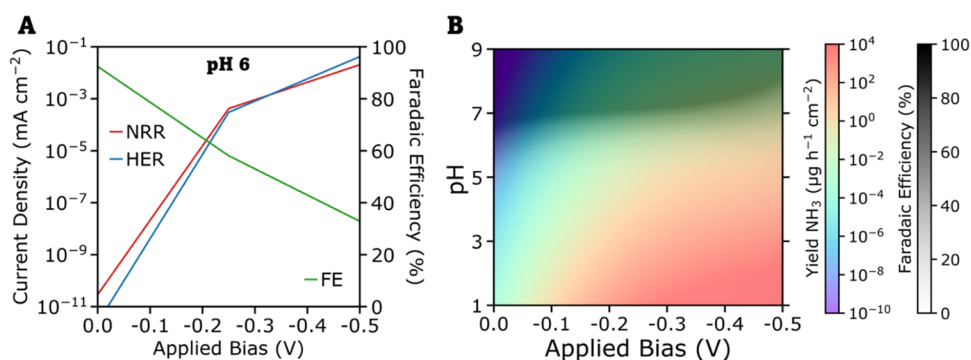


Figure 3. NRR microkinetic model. Current densities for NRR and HER, and NRR Faradaic efficiency (A) were calculated at biases of 0.0, -0.25, and -0.5 V at pH 6 using an NRR microkinetic model based on reaction barriers computed by GC-NEB. (B) Heatmap of NH₃ yield (color) and NRR FE (black & white shading) as pH and applied bias are varied in the NRR microkinetic model for Fe₂Mo₆S₈. Both Fe and Mo sites are considered in the microkinetic model.

of NH₃ production (r_{NH_3}) from Mo sites between 0.0 and -0.5 V is negligibly low, with $r_{\text{NH}_3} < 4.4 \times 10^{-5} \mu\text{g NH}_3 \text{ h}^{-1} \text{ cm}^{-2}$ (i.e., $4.2 \times 10^{-7} \text{ mA cm}^{-2}$) and a $^*\text{NH}_3$ coverage $> 99.999\%$ if no additional activation barriers exist that would further lower NRR activity (i.e., $\text{TS}_2 \geq \Delta\Phi_2$). Consequently, our calculations predict that Mo sites are poisoned by over-binding of $^*\text{NH}_3$, which results in negligible NRR and HER activity at these sites at biases between 0.0 and -0.5 V (Figure S3).

NRR at Fe sites may also proceed through either associative pathway (Figure 2b), which both involve the same key reaction steps: $^*\text{N}_2$ protonation to form $^*\text{NNH}$ and $^*\text{NH}_3$ desorption. Relative to binding at Mo sites, N₂ and NH₃ binding energies are shifted by +0.53 and +0.66 eV at 0 V, respectively. This suggests that Fe sites bind NRR intermediates more weakly than Mo sites. However, the binding energy of $^*\text{NNH}$ is -0.03 eV lower on Fe sites than on Mo sites, indicating that Fe sites selectively stabilize the $^*\text{NNH}$ intermediate relative to $^*\text{N}_2$, which lowers the grand free energy of $^*\text{N}_2$ protonation ($\Delta\Phi_1$). Consequently, $\Delta\Phi_1$ and $\Delta\Phi_2$ are both lower on Fe sites than on Mo sites. The $\Delta\Phi$ for these steps on Fe sites is not affected by $^*\text{NH}_3$ adsorption at neighboring Mo sites (Figure S4). The selective stabilization of $^*\text{NNH}$ on Fe surface sites results in Fe₂Mo₆S₈ favorably breaking linear NRR scaling relationships.

Grand Canonical Microkinetic Modeling. To compute the kinetics of Fe₂Mo₆S₈-catalyzed NRR, we developed and applied a grand canonical implementation of the nudged elastic band method (GC-NEB, see Computational Details) to calculate the activation energies (Φ_a) for four key transition states (TSs) on Fe sites: (1) $^*\text{N}_2$ protonation by H_3O^+ to form $^*\text{NNH}$ and H_2O (TS₁), (2) $^*\text{NH}_3$ desorption (TS₂), (3) proton adsorption from H_3O^+ to form H^* and H_2O (HER, Volmer step, TS₃), and (4) H^* protonation by H_3O^+ to form H_2 and H_2O (HER, Heyrovsky step, TS₄). The TS grand free energies are shown in Figure 2b as a function of bias. TS₁ has a low Φ_a at all three biases, decreasing from 0.55 to 0.36 eV as the bias decreases from 0.0 to -0.5 V, resulting in a large rate constant (k) of $> 1.9 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. $^*\text{NH}_3$ desorbs reductively, requiring ~ 0.40 electrons to be transferred to the desorbing NH₃. Consequently, TS₂ is bias-dependent, with a Φ_a that decreases from 0.75 eV at 0.0 V to 0.54 eV at -0.5 V. This results in an increase in k from 8.1 to $2.9 \times 10^4 \text{ s}^{-1}$. Thus, NRR at the Fe sites of Fe₂Mo₆S₈ proceeds via low Φ_a s for both TS₁ and TS₂ due to the selective stabilization of $^*\text{NNH}$ and the moderate binding energy of $^*\text{NH}_3$. The RDS between 0.0 and -0.5 V is TS₂. Non-GC approaches, such as the computational

hydrogen electrode (CHE), fail to capture the bias dependence of the RDS because it is not a proton-coupled electron transfer. GC-NEB was also used to compute the Φ_a s of the Volmer–Heyrovsky mechanism for HER at Fe sites to determine the activity of this reaction and the resultant selectivity toward NRR. At 0.0 V, both the Volmer ($\text{H}^+ \rightarrow \text{H}^*$) and Heyrovsky ($\text{H}^+ + \text{H}^* \rightarrow \text{H}_2$) steps have low Φ_a s of 0.34 and 0.09 eV, respectively, with the Volmer step being rate limiting. At more reducing biases, the Volmer barrier decreases and the Heyrovsky barrier slightly increases, shifting to 0.23 and 0.11 eV, respectively, at -0.5 V.

We developed a microkinetic model for NRR and HER on Fe₂Mo₆S₈ using the computed thermodynamics and Φ_a s of each reaction step (see Section S3). Mo sites have a negligible contribution to the current densities of NRR and HER (Figure S3). The low Φ_a s for both $^*\text{N}_2$ protonation and $^*\text{NH}_3$ desorption at Fe sites result in high selectivity toward NRR, with a FE of 81–99% at pH 7 and 33–92% at pH 6 (Figure 3a). However, at pH 6–7, the activity of NRR is low due to the low $[\text{H}^+]$, with a current density of 2.1×10^{-2} to $2.1 \times 10^{-3} \text{ mA cm}^{-2}$, respectively, at -0.5 V. Decreasing the solvent pH increases NRR activity; however, it also increases HER activity at a greater rate, resulting in a decrease of FE as pH decreases. This effect is evident in Figure 3b, where the NH₃ yield is maximized at lower pH and more reducing biases, but the FE is maximized at higher pH and less reducing biases. Figure 3b further demonstrates the challenge of identifying superior NRR electrocatalysts with desirable metrics for both activity and selectivity, which are maximized under different conditions. Despite this limitation, a pH of 5.5 combined with a bias of -0.5 V balances a high FE (17%) and a high NH₃ yield ($6.9 \mu\text{g h}^{-1} \text{ cm}^{-2}$), which is superior to most NRR electrocatalysts studied to date.^{6,11,13} These results are in close agreement with recent experimental metrics of 12.5% FE and $3.9 \mu\text{g NH}_3 \text{ h}^{-1} \text{ cm}^{-2}$ at pH 4.5 and -0.2 V.²⁵ Our model predicts 14.6% FE and $1.8 \times 10^{-2} \mu\text{g NH}_3 \text{ h}^{-1} \text{ cm}^{-2}$ at pH 4.5 and -0.2 V, despite the exponential sensitivity of NRR activity and selectivity on reaction conditions. The difference between the calculated and experimental activity values indicates an absolute error of only 0.14 eV for the RDS Φ_a , highlighting the accuracy of GC-NEB to reproduce macroscopic NRR metrics and validating the proposed NRR mechanism and calculated energetics for Fe₂Mo₆S₈.

We also developed a simplified microkinetic model based on energies calculated with the CHE approximation²⁹ (Figure

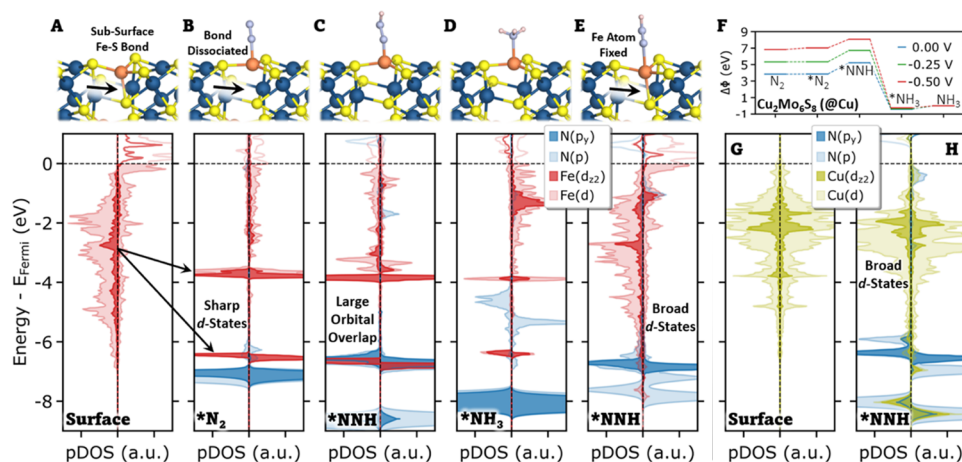


Figure 4. Selective $^*\text{NNH}$ stabilization. Structure and projected density of states (pDOS) for the clean $\text{Fe}_2\text{Mo}_6\text{S}_8$ surface (A), the $\text{Fe}_2\text{Mo}_6\text{S}_8$ surface with $^*\text{N}_2$ (B), $^*\text{NNH}$ (C), $^*\text{NH}_3$ (D), and $^*\text{NNH}$ with the Fe surface atom fixed at its position on the clean surface (E). The abbreviated NRR mechanism on $\text{Cu}_2\text{Mo}_6\text{S}_8$ (F) is included for comparison alongside the pDOS of the clean (G) and $^*\text{NNH}$ covered (H) $\text{Cu}_2\text{Mo}_6\text{S}_8$ surfaces. The pDOS for these structures is shown for the surface Fe/Cu atom and adsorbed $^*\text{N}$ atom at 0.0 V.

SS), which deviates considerably from experiment (i.e., 1.8% FE and $6 \times 10^{-4} \mu\text{g NH}_3 \text{ h}^{-1} \text{ cm}^{-2}$ at pH 4.5 and -0.20 V) and underscores the need for GC-DFT and GC-NEB to accurately model electrochemical NRR.

How Fe Sites Break Linear Scaling. The impressive activity and selectivity of the Fe surface sites of $\text{Fe}_2\text{Mo}_6\text{S}_8$ are a consequence of their selective stabilization of $^*\text{NNH}$ relative to $^*\text{N}_2$ and $^*\text{NH}_3$. This is consistent with the reactivity of the biological FeMo-cofactor, where Fe has been demonstrated as the active site for nitrogen reduction.¹⁷ During N_2 adsorption on Fe sites of $\text{Fe}_2\text{Mo}_6\text{S}_8$, a concurrent dissociation of the subsurface Fe–S bond occurs to stabilize the Fe–N bond (see Figure 4a,b), enabling an $\text{S}_\text{N}2$ reaction for this step to activate the N_2 triple bond. This is similar to the N_2 reduction mechanism of the nitrogenase FeMo- and FeV-cofactors where two Fe–S bonds (2 and 3 in Figure 1) dissociate to produce the trigonal pyramidal Fe active sites.^{17,22,31} Fe–S subsurface bond dissociation on $\text{Fe}_2\text{Mo}_6\text{S}_8$ also yields a trigonal pyramidal active site (tetrahedral with $^*\text{N}_2\text{H}_y$). This mechanism supports the biomimetic properties of $\text{Fe}_2\text{Mo}_6\text{S}_8$. The Fe–S subsurface bond remains broken until $^*\text{NH}_3$ desorbs (Figure 4d), whereas it remains intact upon proton adsorption at Fe sites.

An intriguing consequence of the subsurface Fe–S bond dissociation and the reorganization of the Fe site geometry is the narrowing of the d_z^2 band of the surface Fe atom into free-atom-like states at -6.5 and -3.8 eV below the Fermi level. Narrow d -state bands in single-atom catalysts have been shown to influence selectivity via hybridization with the molecular orbitals of adsorbing molecules of a similar energy, which selectively stabilizes the adsorbates.³⁴ The bonding d_z^2 state at -6.5 eV exhibits significant overlap with the p_y state of the bound N of $^*\text{NNH}$ (Figure 4c); however, minimal overlap exists between these states in $^*\text{N}_2$ and $^*\text{NH}_3$ (Figure 4b,d). The large and selective overlap between the Fe d_z^2 and $^*\text{NNH}$ p_y states indicates a selective stabilization of $^*\text{NNH}$ relative to $^*\text{N}_2$ or $^*\text{NH}_3$, consistent with the calculated binding energies of these adsorbates. Additionally, we fixed the Fe surface atom in our model to its position on the clean surface and then adsorbed $^*\text{N}_2$, $^*\text{NNH}$, and $^*\text{NH}_3$ to the fixed Fe atom to determine the importance of the Fe–S bond dissociation on the binding energies of these adsorbates. This prevents the Fe–S bond from dissociating and the band of surface d -states

from narrowing (Figure 4e). Consequently, no selective stabilization of $^*\text{NNH}$ is calculated when the Fe surface atom is fixed, and the $\Delta\Phi$ for $^*\text{N}_2$ protonation to $^*\text{NNH}$ is 1.19 eV at -0.5 V , vs 0.36 eV when the surface Fe atom is free to dissociate from the subsurface S atom. The Mo surface sites of $\text{Fe}_2\text{Mo}_6\text{S}_8$ possess a broad band of surface d -states that overlap similarly with the nitrogen p -states of $^*\text{N}_2$, $^*\text{NNH}$, and $^*\text{NH}_3$ (Figure S6), which thus results in no selective stabilization of $^*\text{NNH}$ (Figure 2a). Sharp nitrogen p -states exist at approximately -6.5 eV below the Fermi level for $^*\text{NNH}$ at both Fe and Mo sites (Figure S6).

In contrast to $\text{Fe}_2\text{Mo}_6\text{S}_8$, the measured FE and activity of NRR catalyzed by the $\text{Cu}_2\text{Mo}_6\text{S}_8$ Chevrel phase are an order of magnitude lower than that of $\text{Fe}_2\text{Mo}_6\text{S}_8$,²⁵ despite its similar structure, composition, and bulk electronic properties.^{33,35} The Cu surface sites of the predominant (101) $\text{Cu}_2\text{Mo}_6\text{S}_8$ surface (see ref 33) bind more weakly to $^*\text{N}_2$ and $^*\text{NH}_3$ (see Figure 4f) and do not selectively stabilize $^*\text{NNH}$. This significantly increases the $\Delta\Phi$ of $^*\text{N}_2$ protonation to 1.06 – 1.36 eV between 0.0 and -0.5 V vs 0.36 – 0.55 eV on $\text{Fe}_2\text{Mo}_6\text{S}_8$, which dramatically decreases the calculated NRR activity of Cu sites to $<1.0 \times 10^{-8} \mu\text{g h}^{-1} \text{ cm}^{-2}$ at all conditions (Figure S7). Analogous to $\text{Fe}_2\text{Mo}_6\text{S}_8$, $^*\text{NNH}$ binding at Cu surface sites of $\text{Cu}_2\text{Mo}_6\text{S}_8$ causes a concomitant dissociation of the subsurface Cu–S bond. However, the Cu atom only shifts $0.54 \text{ \AA}$ in the z -direction vs a $0.76 \text{ \AA}$ shift of Fe in $\text{Fe}_2\text{Mo}_6\text{S}_8$. Furthermore, the band of d_z^2 states of the surface Cu atom does not narrow, and this broad band of d -states overlaps minimally with the N p_y states of $^*\text{NNH}$ (Figure 4g,h). Thus, the negligible overlap of surface Cu d_z^2 states with the $^*\text{NNH}$ p_y states at Cu sites produces conventional scaling limitations of NRR intermediates on $\text{Cu}_2\text{Mo}_6\text{S}_8$ and ultimately low NRR activity and selectivity (Figure S7).

Our results demonstrate that superior NRR activity and selectivity may be achieved by materials that selectively stabilize $^*\text{NNH}$ relative to $^*\text{N}_2$ and bind $^*\text{NH}_3$ weakly (e.g., $\text{Fe}_2\text{Mo}_6\text{S}_8$). This suggests that new materials may be rapidly screened by their $\Delta\Phi$ for $^*\text{N}_2$ protonation and $^*\text{NH}_3$ desorption to identify promising candidates that minimize the Φ_a barriers of both of these key reaction steps. We note that these proposed NRR screening criteria differ from the previously suggested NRR scaling relations of $\text{N}_2 \rightarrow ^*\text{NNH}$ vs

$^*\text{NH}_2 \rightarrow \text{NH}_3$.²¹ The multinary Chevrel phases may provide an ideal platform for designing superior NRR electrocatalysts due to the similarity of their active sites to the nitrogenase cofactors and their tunable compositions that allow a range of chalcogenide stoichiometries and transition-metal intercalants.^{36–38} Expanding the set of NRR electrocatalysts that break scaling relations via GC-DFT studies may elucidate the importance of narrow bands of surface *d*-states near -6.5 eV below the Fermi level, concomitant N_2 adsorption and subsurface bond dissociation, and the trigonal pyramidal active site geometry (tetrahedral with $^*\text{N}_x\text{H}_y$).

CONCLUSIONS

$\text{Fe}_2\text{Mo}_6\text{S}_8$ achieves state-of-the-art activity and selectivity for NRR via the selective stabilization of $^*\text{NNH}$ relative to $^*\text{N}_2$ that results in low Φ_a s for the key NRR reaction steps of $^*\text{N}_2$ protonation and $^*\text{NH}_3$ desorption. This selective stabilization results from the narrow band of free-atom-like *d*-states that arise via a biomimetic Fe–S bond dissociation during NRR. This suggests that a rational electrocatalyst design platform may be developed by compositionally tuning the Chevrel phases and that new materials may also be screened by their $\Delta\Phi$ s of $^*\text{N}_2$ protonation and $^*\text{NH}_3$ desorption to identify promising NRR electrocatalysts that break scaling relations, analogous to $\text{Fe}_2\text{Mo}_6\text{S}_8$.

Our results also highlight the need for a grand canonical approach for modeling electrocatalytic systems, which was necessary to illuminate the bias dependence of the RDS at Fe surface sites and to accurately predict NRR activity and selectivity. We anticipate that grand canonical modeling, including GC-NEB, will enable the development of realistic and accurate mechanisms and microkinetic models for other electrochemical reactions. Furthermore, the mechanism discovered here provides new insights that may guide the design of stable, multinary electrocatalysts for other reactions, where the energy levels of narrow bands of surface *d*-states may be tuned to selectively hybridize with key reaction intermediates, resulting in improved activity and/or selectivity toward a target product.

COMPUTATIONAL DETAILS

GC-DFT. GC-DFT calculations were performed using the JDFTx software.^{39,40} All calculations were performed using the PBE functional,⁴¹ with the D2 van der Waals correction.⁴² General calculation parameters included a 20 Hartree electronic energy cutoff, spin polarization, no symmetry constraints, a Γ -centered *k*-point grid with a density of $1000/\text{N}_{\text{atoms}}$, and an energy convergence threshold of 1 meV. Calculations of surfaces and adsorbate systems were performed using the CANDLER linear PCM solvation model for H_2O , with 0.5 M Na^+ and F^- ions.^{28,43} A more complete description of the methods used to calculate and generate reaction pathways (Figure 2) is provided in Section S1.

All reaction pathways were shifted so that the final state, 2NH_3 or H_2 , was defined as having a grand free energy of 0 eV. This shifts the initial state, N_2 and six protons for NRR, two protons for HER, as the bias becomes more reducing due to the relative destabilization (stabilization) of protons (electrons) in the solvent (bulk electrode). This represents the system more accurately than setting the initial state of the reaction pathway as the reference, which implies that the neutral product molecules NH_3 and H_2 are stabilized by a

more reducing bias. Additional discussion of reference states is available in Section S1.

Orbital projected density of states (pDOS) were calculated for specific surface and adsorbate systems using JDFTx. Calculated pDOS were plotted with the Gaussian smearing of 0.1 eV using Pymatgen⁴⁴ and centered to the Fermi level.

Grand Canonical Nudged Elastic Band Approach. We implemented the GC-NEB approach to calculate TS pathways as a function of bias while allowing the fractional transfer of electrons between the surface and adsorbate throughout the TS pathway. GC-NEB is only the second implementation of a fully grand-canonical approach for relaxing TS pathways in equilibrium with an applied bias.⁴⁵ We improved the base JDFTx calculator in the pythonic atomic simulation environment (ASE),⁴⁶ to enable its use with the ASE implementation of the NEB method.^{47,48} This allowed each NEB image to be calculated with JDFTx at the corresponding bias with an independent charge density and solvent response. GC-NEB calculation parameters are readily switched between a variety of different solvent models, biases, NEB optimizers, TS images, DFT functionals, etc., and this code can be readily applied to any surface and adsorbate calculations. The GC-NEB code is available at <https://github.com/Nick-Singstock/GC-NEB> and contains a detailed description and tutorials to set up and run GC-DFT and GC-NEB calculations.

In this work, we used five NEB images (not including the initial and final states) to calculate the TS pathways and Φ_a . Φ_a is calculated as the difference between the maximum energy along the converged TS path and the energy of the initial state. For protonation reactions, an H_3O^+ molecule was placed above the atom being protonated, with a hydrogen atom pointing in the *z*-direction toward the surface, separated from the atom being protonated by 1.8 Å. The final state included both the protonated adsorbate and the remaining H_2O molecule above the surface.

Microkinetic Model. A microkinetic model was developed that includes NRR and HER steps to calculate the coverage of different adsorbates, the reaction rates of the elementary steps, the current density for NRR and HER, the mass yield of NH_3 and H_2 , and the FE of NRR. Detailed descriptions of the calculations of elementary step rate constants, steady-state adsorbate coverages, and microkinetic model outputs are included in Section S3.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.2c03661>.

Calculation details, microkinetic model parameters, and additional figures for dissociative N_2 dissociation, adsorption at sulfur sites, NRR activity and selectivity diagrams, and reaction energetics (PDF)

AUTHOR INFORMATION

Corresponding Author

Charles B. Musgrave – Department of Chemical and Biological Engineering, University of Colorado Boulder, Boulder, Colorado 80303, United States; Materials Science and Engineering Program and Renewable and Sustainable Energy Institute, University of Colorado Boulder, Boulder, Colorado 80303, United States; orcid.org/0000-0002-5732-3180; Email: charles.musgrave@colorado.edu

Author

Nicholas R. Singstock – Department of Chemical and Biological Engineering, University of Colorado Boulder, Boulder, Colorado 80303, United States; orcid.org/0000-0003-2093-0216

Complete contact information is available at:
<https://pubs.acs.org/10.1021/jacs.2c03661>

Author Contributions

N.R.S. and C.B.M. contributed equally to this manuscript.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

NRR	nitrogen reduction reaction
HER	hydrogen evolution reaction
FE	Faradaic efficiency
GC-DFT	grand-canonical density functional theory
GC-NEB	grand-canonical nudged elastic band method
RDS	rate-determining step
TS	transition state
CHE	computational hydrogen electrode method

REFERENCES

- (1) Erisman, J. W.; Sutton, M. A.; Galloway, J.; Klimont, Z.; Winiwarter, W. How a Century of Ammonia Synthesis Changed the World. *Nat. Geosci.* **2008**, *1*, 636–639.
- (2) Chen, J. G.; Crooks, R. M.; Seefeldt, L. C.; Bren, K. L.; Morris Bullock, R.; Darensbourg, M. Y.; Holland, P. L.; Hoffman, B.; Janik, M. J.; Jones, A. K.; et al. Beyond Fossil Fuel-Driven Nitrogen Transformations. *Science* **2018**, *360*, No. eaar6611.
- (3) Han, G. F.; Li, F.; Chen, Z. W.; Coppex, C.; Kim, S. J.; Noh, H. J.; Fu, Z.; Lu, Y.; Singh, C. V.; Siahrostami, S.; et al. Mechanochemistry for Ammonia Synthesis under Mild Conditions. *Nat. Nanotechnol.* **2021**, *16*, 325–330.
- (4) Guo, C.; Ran, J.; Vasileff, A.; Qiao, S. Rational Design of Electrocatalysts and Photo(Electro)Catalysts for Nitrogen Reduction to Ammonia (NH₃) under Ambient Conditions. *Energy Environ. Sci.* **2018**, *11*, 45–56.
- (5) Humphreys, J.; Lan, R.; Tao, S. Development and Recent Progress on Ammonia Synthesis Catalysts for Haber–Bosch Process. *Adv. Energy Sustainability Res.* **2021**, *2*, No. 2000043.
- (6) Cao, N.; Zheng, G. Aqueous Electrocatalytic N₂ Reduction under Ambient Conditions. *Nano Res.* **2018**, *11*, 2992–3008.
- (7) Lim, J.; Fernández, C. A.; Lee, S. W.; Hatzell, M. C. Ammonia and Nitric Acid Demands for Fertilizer Use in 2050. *ACS Energy Lett.* **2021**, *6*, 3676–3685.
- (8) Wang, L.; Xia, M.; Wang, H.; Huang, K.; Qian, C.; Maravelias, C. T.; Ozin, G. A. Greening Ammonia toward the Solar Ammonia Refinery. *Joule* **2018**, *2*, 1055–1074.
- (9) David, B.; Bird, F.; Clarke, A.; Davies, P.; Surkovic, E. *Ammonia: Zero-Carbon Fertiliser, Fuel and Energy Store*; 2020.
- (10) Suryanto, B. H. R.; Du, H.-L.; Wang, D.; Chen, J.; Simonov, A.; MacFarlane, D. Challenges and Prospects in the Catalysis of Electrorreduction of Nitrogen to Ammonia. *Nat. Catal.* **2019**, *2*, 290–296.
- (11) Tang, C.; Qiao, S. Z. How to Explore Ambient Electrocatalytic Nitrogen Reduction Reliably and Insightfully. *Chem. Soc. Rev.* **2019**, *48*, 3166–3180.
- (12) Service, R. F. Liquid Sunshine. *Science* **2018**, *361*, 120–123.
- (13) Zhao, X.; Hu, G.; Chen, G. F.; Zhang, H.; Zhang, S.; Wang, H. Comprehensive Understanding of the Thriving Ambient Electrochemical Nitrogen Reduction Reaction. *Adv. Mater.* **2021**, *33*, No. 2007650.
- (14) Andersen, S. Z.; Čolić, V.; Yang, S.; Schwalbe, J. A.; Nielander, A. C.; McEnaney, J. M.; Enemark-Rasmussen, K.; Baker, J. G.; Singh, A. R.; Rohr, B. A.; et al. A Rigorous Electrochemical Ammonia Synthesis Protocol with Quantitative Isotope Measurements. *Nature* **2019**, *570*, 504–508.
- (15) Li, W.; Li, K.; Ye, Y.; Zhang, S.; Liu, Y.; Wang, G.; Liang, C.; Zhang, H.; Zhao, H. Efficient Electrocatalytic Nitrogen Reduction to Ammonia with Aqueous Silver Nanodots. *Commun. Chem.* **2021**, *4*, No. 10.
- (16) Xu, H.; Ithisuphalap, K.; Li, Y.; Mukherjee, S.; Lattimer, J.; Soloveichik, G.; Wu, G. Electrochemical Ammonia Synthesis through N₂ and H₂O under Ambient Conditions: Theory, Practices, and Challenges for Catalysts and Electrolytes. *Nano Energy* **2020**, *69*, No. 104469.
- (17) Foster, S. L.; Bakovic, S. I. P.; Duda, R. D.; Maheshwari, S.; Milton, R. D.; Minter, S. D.; Janik, M. J.; Renner, J. N.; Greenlee, L. F. Catalysts for Nitrogen Reduction to Ammonia. *Nat. Catal.* **2018**, *1*, 490–500.
- (18) Zhang, L.; Ji, X.; Ren, X.; Ma, Y.; Shi, X.; Tian, Z.; Asiri, A. M.; Chen, L.; Tang, B.; Sun, X.; et al. Electrochemical Ammonia Synthesis via Nitrogen Reduction Reaction on a MoS₂ Catalyst: Theoretical and Experimental Studies. *Adv. Mater.* **2018**, *30*, No. 1800191.
- (19) Jin, H.; Li, L.; Liu, X.; Tang, C.; Xu, W.; Chen, S.; Song, L.; Zheng, Y.; Qiao, S.-Z.; Jin, H.; et al. Nitrogen Vacancies on 2D Layered W₂N₃: A Stable and Efficient Active Site for Nitrogen Reduction Reaction. *Adv. Mater.* **2019**, *31*, No. 1902709.
- (20) Song, Y.; Johnson, D.; Peng, R.; Hensley, D. K.; Bonnesen, P. V.; Liang, L.; Huang, J.; Yang, F.; Zhang, F.; Qiao, R.; et al. A Physical Catalyst for the Electrolysis of Nitrogen to Ammonia. *Sci. Adv.* **2018**, *4*, No. e1700336.
- (21) Montoya, J. H.; Tsai, C.; Vojvodica, A.; Nørskov, J. K. The Challenge of Electrochemical Ammonia Synthesis: A New Perspective on the Role of Nitrogen Scaling Relations. *ChemSusChem* **2015**, *8*, 2180–2186.
- (22) Sippel, D.; Rohde, M.; Netzer, J.; Trncik, C.; Gies, J.; Grunau, K.; Djurdjevic, L.; Decamps, L.; Andrade, S. L. A.; Einsle, O. A Bound Reaction Intermediate Sheds Light on the Mechanism of Nitrogenase. *Science* **2018**, *359*, 1484–1489.
- (23) Čorić, I.; Mercado, B. Q.; Bill, E.; Vinyard, D. J.; Holland, P. L. Binding of Dinitrogen to an Iron–Sulfur–Carbon Site. *Nature* **2015**, *526*, 96–99.
- (24) Lukoyanov, D. A.; Yang, Z.-Y.; Dean, D. R.; Seefeldt, L. C.; Raugei, S.; Hoffman, B. M. Electron Redistribution within the Nitrogenase Active Site FeMo–Cofactor During Reductive Elimination of H₂ to Achieve N≡N Triple-Bond Activation. *J. Am. Chem. Soc.* **2020**, *142*, 21679–21690.
- (25) Lu, K.; Xia, F.; Li, B.; Liu, Y.; Razak, I. B. A.; Gao, S.; Kaelin, J.; Brown, D. E.; Cheng, Y. Synergistic Multisites Fe₂Mo₆S₈ Electrocatalysts for Ambient Nitrogen Conversion to Ammonia. *ACS Nano* **2021**, *15*, 16887–16895.
- (26) Akbashev, A. R. Electrocatalysis Goes Nuts. *ACS Catal.* **2022**, *12*, 4296–4301.
- (27) Resasco, J.; Abild-Pedersen, F.; Hahn, C.; Bao, Z.; Koper, M. T. M.; Jaramillo, T. F. Enhancing the Connection between Computation and Experiments in Electrocatalysis. *Nat. Catal.* **2022**, *5*, 374–381.
- (28) Schwarz, K.; Sundararaman, R. The Electrochemical Interface in First-Principles Calculations. *Surf. Sci. Rep.* **2020**, *75*, No. 100492.
- (29) Alsunni, Y. A.; Alherz, A. W.; Musgrave, C. B. Electrocatalytic Reduction of CO₂ to CO over Ag(110) and Cu(211) Modeled by

Grand-Canonical Density Functional Theory. *J. Phys. Chem. C* **2021**, *125*, 23773–23783.

(30) Liu, C.; Qian, J.; Ye, Y.; Zhou, H.; Sun, C. J.; Sheehan, C.; Zhang, Z.; Wan, G.; Liu, Y. S.; Guo, J.; et al. Oxygen Evolution Reaction over Catalytic Single-Site Co in a Well-Defined Brookite TiO₂ Nanorod Surface. *Nat. Catal.* **2021**, *4*, 36–45.

(31) Varley, J. B.; Wang, Y.; Chan, K.; Studt, F.; Nørskov, J. K. Mechanistic Insights into Nitrogen Fixation by Nitrogenase Enzymes. *Phys. Chem. Chem. Phys.* **2015**, *17*, 29541–29547.

(32) Hoffman, B. M.; Lukoyanov, D.; Yang, Z. Y.; Dean, D. R.; Seefeldt, L. C. Mechanism of Nitrogen Fixation by Nitrogenase: The next Stage. *Chem. Rev.* **2014**, *114*, 4041–4062.

(33) Lilova, K.; Perryman, J. T.; Singstock, N. R.; Abramchuk, M.; Subramani, T.; Lam, A.; Yoo, R.; Ortiz-Rodríguez, J. C.; Musgrave, C. B.; Navrotsky, A.; Velázquez, J. M. A Synergistic Approach to Unraveling the Thermodynamic Stability of Binary and Ternary Chevrel Phase Sulfides. *Chem. Mater.* **2020**, *32*, 7044–7051.

(34) Spivey, T. D.; Holewinski, A. Selective Interactions between Free-Atom-like d-States in Single-Atom Alloy Catalysts and Near-Frontier Molecular Orbitals. *J. Am. Chem. Soc.* **2021**, *143*, 11897–11902.

(35) Perryman, J. T.; Hyler, F. P.; Ortiz-Rodríguez, J. C.; Mehta, A.; Kulkarni, A. R.; Velázquez, J. M. X-Ray Absorption Spectroscopy Study of the Electronic Structure and Local Coordination of 1st Row Transition Metal-Promoted Chevrel-Phase Sulfides. *J. Coord. Chem.* **2019**, *72*, 1322–1335.

(36) Singstock, N. R.; Ortiz-Rodríguez, J. C.; Perryman, J. T.; Sutton, C.; Velázquez, J. M.; Musgrave, C. B. Machine Learning Guided Synthesis of Multinary Chevrel Phase Chalcogenides. *J. Am. Chem. Soc.* **2021**, *143*, 9113–9122.

(37) Ortiz-Rodríguez, J. C.; Singstock, N. R.; Perryman, J. T.; Hyler, F. P.; Jones, S. J.; Holder, A. M.; Musgrave, C. B.; Velázquez, J. M. Stabilizing Hydrogen Adsorption through Theory-Guided Chalcogen Substitution in Chevrel-Phase Mo₆X₈ (X = S, Se, Te) Electrocatalysts. *ACS Appl. Mater. Interfaces* **2020**, *12*, 35995–36003.

(38) Perryman, J. T.; Velázquez, J. M. Design Principles for Multinary Metal Chalcogenides: Toward Programmable Reactivity in Energy Conversion. *Chem. Mater.* **2021**, *33*, 7133–7147.

(39) Sundararaman, R.; Letchworth-Weaver, K.; Schwarz, K. A.; Gunceler, D.; Ozhabes, Y.; Arias, T. A. JDFTx: Software for Joint Density-Functional Theory. *SoftwareX* **2017**, *6*, 278–284.

(40) Sundararaman, R.; Goddard, W. A.; Arias, T. A. Grand Canonical Electronic Density-Functional Theory: Algorithms and Applications to Electrochemistry. *J. Chem. Phys.* **2017**, *146*, No. 114104.

(41) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(42) Grimme, S. Semiempirical GGA-Type Density Functional Constructed with a Long-Range Dispersion Correction. *J. Comput. Chem.* **2006**, *27*, 1787–1799.

(43) Sundararaman, R.; Goddard, W. A. The Charge-Asymmetric Nonlocally Determined Local-Electric (CANDLE) Solvation Model. *J. Chem. Phys.* **2015**, *142*, No. 064107.

(44) Ong, S. P.; Richards, W. D.; Jain, A.; Hautier, G.; Kocher, M.; Cholia, S.; Gunter, D.; Chevrier, V. L.; Persson, K. A.; Ceder, G. Python Materials Genomics (Pymatgen): A Robust, Open-Source Python Library for Materials Analysis. *Comput. Mater. Sci.* **2013**, *68*, 314–319.

(45) Kastlunger, G.; Lindgren, P.; Peterson, A. A. Controlled-Potential Simulation of Elementary Electrochemical Reactions: Proton Discharge on Metal Surfaces. *J. Phys. Chem. C* **2018**, *122*, 12771–12781.

(46) Larsen, A. H.; Mortensen, J. J.; Blomqvist, J.; Castelli, I. E.; Christensen, R.; Dulak, M.; Friis, J.; Groves, M. N.; Hammer, B.; Hargus, C.; et al. The Atomic Simulation Environment—a Python Library for Working with Atoms. *J. Phys. Condens. Matter* **2017**, *29*, No. 273002.

(47) Mills, G.; Jónsson, H. Quantum and Thermal Effects in H₂ Dissociative Adsorption: Evaluation of Free Energy Barriers in Multidimensional Quantum Systems. *Phys. Rev. Lett.* **1994**, *72*, 1124.

(48) Henkelman, G.; Uberuaga, B. P.; Jónsson, H. A Climbing Image Nudged Elastic Band Method for Finding Saddle Points and Minimum Energy Paths. *J. Chem. Phys.* **2000**, *113*, 9901.

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