1	Supporting Information:		
2			
3	First-principles Analysis of Coverage, Ensemble, and Solvation		
4	Effects on Selectivity Trends in NO Electroreduction on Pt <sub>3</sub> Sn Alloys		
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10	transfer, selectivity, coverage effects, solvation effects		
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### 13 1. Solvation Corrections

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Table S1. Solvation energy corrections for binding energies of adsorbed surface species. The values are adopted from the data reported by Clayborne *et. al.*<sup>1</sup>.

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Species	Solvation Energy (eV)
N	-0.1
NH	-0.30
NH <sub>2</sub>	-0.24
H <sub>2</sub> NO	-0.24
NH <sub>3</sub>	-0.16
ОН	-0.41
HNO	-0.23
NOH	-0.31
HNOH	-0.47
NH <sub>2</sub> OH	-0.41

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In the case of low coverages of adsorbed NO\* (no spectator NO\* present on the surface), the solvation correction is included for all the intermediates considered in the analysis. In case of high

coverages, with 5/9 ML total coverage of NO-containing species, solvation corrections are

23 included only for NOH\* and intermediates binding to on-top sites, such as OH\* and NH<sub>2</sub>OH\*.

### 25 2. Most Stable Configurations of Adsorbates



- Figure S1. Most stable adsorption configurations of adsorbates at low coverage (no spectator NO\*
  species present).
- 28 29





Figure S2. Most stable configuration of different adsorbates at high coverage (4/9 ML of spectator

- 32 NO\* plus the adsorbate itself).
- 33

#### 3. Water Shuttling Model 34

A water shuttling model is utilized to capture some features of proton transfer from a double layer 35 36 to a surface in a real electrochemical system. The key assumption in the model is that, during the proton transfer event, the proton has to come close enough to the surface of the catalyst that there 37 in principle should exist an equilibrium between H\* present on the surface and the proton in the 38 39 bilayer. Under these assumptions, the proton transfer can be modeled via a shuttling mechanism, 40 wherein the H\* present on the surface shuttles through a water molecule to complete the proton 41 transfer event. This process is depicted in Figure S3. In our previously published work on similar 42 chemistry on Pt(111) (Clayborne, A.; Chun, H.-J.; Rankin, R. B.; Greeley, J. Elucidation of Pathways for NO Electroreduction on Pt(111) From First Principles. Angew. Chem. 2015, 127 43 44 (28), 8373–8376), we found that the comparison between the barriers estimated using a water 45 shuttling model with a single water molecule and with a full bilayer of water molecules were in reasonable agreement, with differences ranging from 0.1-0.2 eV, suggesting that predicted 46 47 reactivity trends will not be substantially altered by the number of water molecules that are 48 explicitly included in the water shuttling calculations.

The barriers from the water shuttling model are used as the blue pathways in the free energy 49 50 diagrams reported in the main manuscript.

51 To illustrate how the voltage dependence is estimated for these barriers, consider the 52 following hydrogenation reaction:

53

$$X^* + H^* \rightarrow XH^* + *$$

54 Let us assume that a BEP relationship exists for the above reaction which can be written as:

 $\Delta G_1^{\neq} = \beta \times \Delta G_1 + \alpha$ 55 Where  $\Delta G_1^{\neq \prime}$  is the activation energy,  $\Delta G_1^{\prime}$  is the adsorption energy w.r.t. to surface hydrogen 56 (H\*), and ' $\alpha' \& \beta'$  represent the slope and the intercept for the relationship. A further assumption 57 58 can be made that a similar BEP exists for the corresponding electrochemical hydrogenation, which 59 can be written as follows:

relation  $\begin{array}{c} X^{*} + H^{+} + e^{-} \rightarrow XH^{*} \\ \text{then} \\ \Delta G_{2}^{\neq} = \beta \times \Delta G_{2} + \alpha \end{array}$ 60 be The written 61 BEP as: 62

where  $\Delta G_2^{\neq \prime}$  is the electrochemical activation energy and  $\Delta G_2^{\prime}$  is the adsorption energy w.r.t. to the proton electron pair (H<sup>+</sup> + e<sup>-</sup>). Subtracting the two BEP relationships, we obtain 63 64

$$\Delta G_2^{\neq} = \Delta G_1^{\neq} + \beta \times (\Delta G_2 - \Delta G_1)$$

In the above equation, 
$$\Delta G_1^{\neq \prime}$$
 can be calculated using the water shuttling model, and  $\beta'$  can be  
assumed to be 0.5, representing the transfer coefficient in Butler-Volmer formulism. The term in  
the bracket can then be expanded as:  
$$\Delta G_2 - \Delta G_1 = \mu_{\text{II}} + \mu_$$

$$\Delta G_2 - \Delta G_1 = \mu_{H^*} - \mu_{H^+ + e^-} - \mu_* = \mu_{H^*} - \mu_{0.5H_2(g)} - \mu_* + eU$$

where U is the potential w.r.t. SHE and  $'\mu_{*}'$ ,  $'\mu_{H^{*}}'$  and  $'\mu_{H_2(g)}'$  are the DFT calculated energies for 70

71 the clean surface, the H\*, and the gas phase H<sub>2</sub> molecule. Finally, the electrochemical activation 72 energy can be written as:

$$\Delta G_2^{\neq} = \Delta G_1^{\neq} + \beta \times (\mu_{H^*} - \mu_{0.5H_2(g)} - \mu_* + eU)$$





Figure S3. Schematic for water shuttling model using a single water molecule to transfer hydrogen to the metal surface. For color coding of different atoms refer to legend in Figure S1.

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### 4. Structure Generation Algorithm 85

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87 We use an in-house code to generate all the high coverage structures. The low symmetry of the 88 Pt<sub>3</sub>Sn alloy makes it challenging to track all such possible configurations, and to overcome this 89 barrier, we employ our own python-based algorithm to screen through different possible 90 geometries of the reaction intermediates. The algorithm can be summarized as follows:

- 91 1. Identify the possible adsorption sites.
- 2. Find the elements in the 1<sup>st</sup> and 2<sup>nd</sup> coordination shells to determine the environment of the 92
- 93 site
- 94 3. Compare the environment of different sites to determine symmetrically equivalent sites.
- 95 4. Populate unique sites
- 96
- 97 Below, we present structures for some of the most stable configurations that are found for the
- 98 different coverages of NO. The structures, along with their energies relative to the most stable 99 structure, are shown in Figures S4, S5 and S6.



### High Coverage 2-NO and 3-NO

- 103
- 104 in Figure S1.
- 105
- 106

Figure S4. Selected configurations with 2/9 (top row) and 3/9 (bottom row) ML of NO on the 101

<sup>102</sup>  $Pt_3Sn(111)$  surface. Numbers indicate the energy of the configurations, in eV, with respect to the most stable configuration at each NO coverage. For color coding of different atoms refer to legend

## High Coverage 4-NO and 5-NO



1070.100.110.110.11108Figure S5. Selected configurations with 4/9 (top row) and 5/9 (bottom row) ML of NO on the109Pt<sub>3</sub>Sn(111) surface. Numbers indicate the energy of the configurations, in eV, with respect to the110most stable configuration at each NO coverage. For color coding of different atoms refer to legend111in Figure S1.

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- 113

## High Coverage 6-NO



114

Figure S6. Selected configurations with 6/9 ML of NO on the Pt<sub>3</sub>Sn(111) surface. Numbers indicate the energy of the configurations, in eV, with respect to the most stable configuration at

the indicated coverage. For color coding of different atoms refer to legend in Figure S1.

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- 119



121 To calculate the coverage dependent phase diagram, the most stable configurations for a given

122 coverage were first calculated using the evolutionary algorithm approach. Then, the free energy of 123

a given configuration was plotted as a function of the partial pressure of NO, using the formulae:

124  

$$\Delta G = \frac{1}{9} \times \left[ E_{n \times NO^*} - E_* + n \times (ZPE_{NO^*} - TS_{NO^*} - \mu_{NO(g)}) \right]$$
125  

$$\mu_{NO(g)} = E_{NO(g)} + ZPE_{NO(g)} - TS_{NO(g)} + kT \times \ln\left(\frac{P}{P^0}\right)$$

where,  $E_{nNO^*}$  and  $E_*$  represent the DFT calculated energies for the most stable structure containing 126 'n' NO atoms on the surface, and the clean surface respectively. ZPE(NO<sup>\*</sup>), TS<sub>NO<sup>\*</sup></sub> and  $\mu_{NO(g)}$ 127 represent the zero-point energy and the entropy change of the adsorbed NO on the surface, and the 128 chemical potential of gas phase NO respectively.  $E_{NO(g)}$ ,  $ZPE_{NO(g)}$ ,  $TS_{NO(g)}$  and  $kT \times \ln \left(\frac{P}{D^0}\right)$ 129 represent the DFT calculated energy of a single NO molecule, the entropy of gas phase NO using 130 131 standard tables and the pressure correction respectively. The entropy of adsorbed NO is taken to be zero in this case as it binds strongly to the surface. The prefactor of '1/9' is included to account 132 133 for area normalization w.r.t. to the total number of available surface atoms, and in this case the 134 number is calculated given that only 'Pt' atoms bind NO. 135

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### 5. Capacitor-based cell extrapolation method 137

For certain electrochemical reactions where a water shuttling approach is not sufficient, we use a 138 139 capacitor-based model to calculate the barrier for proton transfer events happening directly from a double layer present above the catalyst surface. This scheme was developed to overcome the 140 spurious changes taking place in the work-function <sup>2,3</sup> when using a small size unit cell to describe 141 charge transfer reactions. This effect is unphysical, as in a real system the charge transfer takes 142 143 place over a very large surface, and that event does not affect the workfunction of the cell. In other words, the process in a real system takes place under constant potential. To overcome this problem, 144 145 Rossmeisl and coworkers proposed a scheme based on simple capacitor-based model, with the assumption that the electrochemical and chemical steps in a reaction mechanism are separable, and 146 147 used it to calculate the thermodynamic free energy and the corresponding barriers for proton transfer reactions in the Hydrogen Evolution reaction over the Pt(111) surface <sup>2</sup> at constant 148 149 potentials. Under the analysis, different sizes of unit cells were simulated with either the initial 150 state or the final state of the different cells having a similar proton coverage (protons/surface 151 atoms). Then, a simple capacitor-based model was used to extrapolate to the case of an infinite 152 sized unit cell, which would then represent the case of the reaction happening at constant potential. 153 We adopt a similar scheme for some of the reactions in this study. A schematic of the three 154 different sized unit cells considered is shown below:

- 155
- 156



Figure S7. Schematic showing the different sizes of unit cells considered to calculate the electrochemical N--O bond breaking barrier for the intermediates NOH and HNOH using the extrapolation method. For color coding of different atoms refer to legend in Figure S1.

161 In our analysis, we consider constant coverage of protons in the initial state for the high coverage 162 cases and constant coverage in the final state for the low coverage cases. The high coverage case 163 has a work-function of about 4.3 V vs. vacuum for our system, which is about -0.1 V vs. SHE. 164 This is desirable as we are interested in reactions taking place in the lower potential region, with 165 voltages around 0.0 V vs. SHE. Note that controlling the workfunction of the cell quantitatively is 166 very challenging, and the aim is to try to get barriers in the range of potentials of interest. Figures 167 S8 and S9 below show the plots for free energy change calculated as a function of the change in 168 workfunction for the cases of high coverage NOH and HNOH N--O bond breaking. The best fit 169 slopes for both the cases are close to 0.5. The intercepts for the models can be used as the corrected 170 free energy and the transition state energy in the limit of infinite sized unit cell, the workfunction 171 of which will not be affected by charge transfer. The intercept values for the transition states are 172 used as the transition state energy for the magenta pathways considered in Figure 3 in the main 173 manuscript. The initial and final state energies for these elementary steps are calculated using the 174 standard SHE scheme for all thermodynamic calculations.

175 For the case of low coverage NOH and HNOH N--O bond breaking, we performed the cell 176 extrapolation method with the case of constant final state. The change in workfunction for those 177 cases was relatively small, and we considered only the biggest cell (48 and 24 atoms on the surface 178 for the cases of HNOH and NOH respectively) to calculate the transition state energies. There is 179 no barrier for NOH bond breaking, while the HNOH bond breaking barrier is of the order of 0.20 180 eV respectively. These barriers are also in good agreement with those calculated using the water-181 shuttling model shown in Figure S13 and S14 (0.2 and 0.25 eV for the NOH and HNOH cases, 182 respectively). The initial, transition, and final state for the barrier calculated using a water bilayer 183 are shown in Figure S10 and S11.

184 The choice of barrier estimation method for different elementary reaction steps was made to 185 balance the need to obtain accurate barriers with computational efficiency. In particular, while the 186 water shuttling approach to barrier estimation is more facile to implement, there are cases where 187 it fails to capture realistic features of the charge transfer transition state, and a method that 188 rigorously treats the structure of the electrochemical double layer, such as the bilayer/capacitor 189 model, must instead be used. An example is the electrochemically-assisted N-O bond breaking 190 in the intermediate HNOH, in which adsorbed HN\* and water are products (this is the likely step 191 controlling product selectivity in our reaction network). In this case, at high NO coverages, the 192 coadsorbed NO's restrict possible configurations of H\* and H2O such that they cannot be close to 193 one other, which is a crucial requirement of the water shuttling model. However, we note that, in 194 other reactions where the water shuttling method is able to provide a reasonable description of the

195 transition state structure, calculated barriers between the water shuttling and double layer/capacitor 196 methods can agree reasonably well. For example, for electrochemically-assisted N-O bond 197 breaking in the intermediate HNOH at low NO coverages, when spectator NO molecules do not 198 interact with the transition state, the two schemes yield transition states with similar structures; 199 indeed, the structures involve no proton transfer and are reminiscent of a simple chemical 200 dissociation step, with additional stability provided by hydrogen bonding from the additional water 201 molecule present (see Figures S10 and S14). The corresponding barriers are also quite comparable, 202 at 0.25 and 0.20 eV.

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- 204



Figure S8. Results of free energy and activation energy calculated using the extrapolated unit cell method for the electrochemical N--O bond breaking of the intermediate NOH. Left side figure shows the thermodynamic reaction energy (difference between the final state and the initial state), and the right side figure shows the activation state energy (difference between transition state energy and the initial state) plotted against workfunction change for different sized unit cells.

212





215 Figure S9. Results of free energy and activation energy calculated using the extrapolated unit cell 216 method for the electrochemical N--O bond breaking of the intermediate HNOH. Left side figure 217 shows the thermodynamic reaction energy (difference between the final state and the initial state), 218 and the right side figure shows the activation state energy (difference between transition state 219 energy and the initial state) plotted against the workfunction change for different sized unit cells.





Figure S10. Schematic showing the initial, transition, and final states for the electrochemical N--222 O bond breaking barrier for the intermediate HNOH calculated using the extrapolated bilayer 223 method. For color coding of different atoms refer to legend in Figure S1.

## NOH Water Shuttling N--O breaking



225

Figure S11. Schematic showing the initial, transition, and final states for the electrochemical N--O bond breaking barrier for the intermediate NOH calculated using the extrapolated bilayer method. For color coding of different atoms refer to legend in Figure S1.

### 230 6. Barriers for selected reactions

- 231 6.1. N--O bond breaking in HNO
- 232 Shown below are the initial, transition, and final state configurations for N--O bond dissociation
- 233 for the intermediate HNO (Figure S12).

# HNO N--O breaking

234

Figure S12. Schematic showing the initial, transition, and final state for the HNO N--O bond breaking barrier for the intermediate HNO. For color coding of different atoms refer to legend in Figure S1.

238

The barrier for the above pathway is calculated to be  $\sim 1.2$  eV, and it is prohibitive at room temperature. A similar barrier is observed for the N--O bond breaking barrier for the intermediate NO.

242

6.2. Water Shuttling model for N--O bond breaking in NOH and HNOHintermediates

245 The figures below (S13 and S14) show the electrochemical N--O bond breaking pathway for the 246 intermediates NOH and HNOH at low coverage calculated using the water shuttling model. The 247 barriers calculated are on the order of 0.2 and 0.25 eV, respectively. The barrier estimate agrees 248 well with that calculated using the extrapolated bilayer method (see Section 5, Figures S10 and 249 S11). It can be observed in the case of HNOH N--O bond breaking, the transition state is very 250 similar to what would be observed for chemical bond breaking (without significant charge 251 transfer), and it stabilized by hydrogen bonds of the water. This feature is also seen in the barriers 252 calculated using the cell extrapolation method, which takes into account explicit bilayer-type water 253 (Figure S10).



Figure S13. Schematic showing the initial, transition and final state for the electrochemical N--O

- 257 bond breaking barrier for the intermediate NOH calculated using the water shuttling model. For
- color coding of different atoms refer to legend in Figure S1.

# HNOH Water Shuttling N--O breaking

IS







Figure S14. Schematic showing the initial, transition, and final states for the electrochemical N-O bond breaking barrier for the intermediate HNOH calculated using the water shuttling model.
For color coding of different atoms refer to legend in Figure S1.

263

### 264 6.3. NH<sub>3</sub> Pathways

We considered pathways for  $NH_3$  production at low coverages. The barrier for the rate determining step comes from the reduction of NH to  $NH_2$ ; the barrier is on the order of 0.5 eV and is surmountable at room temperatures. The initial, transition, and final states for  $NH_3$  formation can be seen below in Figure S15:

269

Elementary Step	Initial state	Transition state	Final State
N -> NH (barrier: 0.16 eV)			
NH -> NH <sub>2</sub> (Rate Limiting with barrier 0.5 eV at 0.0 V vs. SHE)			
NH <sub>2</sub> -> NH <sub>3</sub> (barrier: 0.34 eV)			

270

Figure S15. Schematic showing the initial, transition, and final states for  $NH_3$  production from N via the water shuttling model. Note that the final state configuration for the intermediates, N\*, NH\* and  $NH_2$ \* and  $NH_3$ \* are also the most stable configurations for these intermediates. The initial state in case of  $NH_3$ \* formation ( $NH_2$ \*) is in a metastable configuration. For color coding of different atoms refer to legend in Figure S1.

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6.4 NOH and HNOH reduction to HNOH and NH<sub>2</sub>OH and NH<sub>2</sub>OH N—O
dissociation

The NOH to HNOH barrier at high coverages involves a rotation of the N-O bond of NOH, tilting the O atom towards the Sn, following which protonation takes place to form HNOH. The tilted state is isoenergetic with the initial state. The barrier to rotate the N-O bond is 0.45 eV and is the

- rate limiting step for this process. Both the barriers to rotate and then the protonation are shown
- 283 below:
- 284



Figure S16a. Schematic showing the initial, transition, and final states for the rotation of NOH to

287 an isoenergetic state with OH pointing towards the Sn. For color coding of different atoms refer to

288 legend in Figure S1.





Figure S16b. Schematic showing the initial, transition, and final states for the electrochemical
 reduction of rotated NOH to HNOH. For color coding of different atoms refer to legend in Figure
 S1.

- 293
- 294
- 295 HNOH to NH<sub>2</sub>OH formation involves HNOH starting from a metastable position with N on top of
- 296 Pt, which then undergoes proton transfer. The metastable state is  $\sim 0.15$  eV metastable compared
- 297 to the most stable state. The initial, transition and final state images are shown below in Figure
- 298 S17:



299

Figure S17. Schematic showing the initial, transition, and final states for the electrochemical
 reduction of meta-stable HNOH to NH<sub>2</sub>OH. For color coding of different atoms refer to legend in
 Figure S1.

303

304 The NH<sub>2</sub>OH chemical bond dissociation transition state is similar to that of HNOH chemical bond dissociation, with the intermediate OH\* interacting with a Sn atom. The corresponding barrier is 305 306 0.67 eV and, motivated by the result that the electrochemical HNOH bond breaking transition state 307 is very similar to the corresponding chemical bond breaking transition state, the electrochemical 308 barrier for N-O activation in NH2OH\* can be assumed to be of this order, as well (the main 309 assumption in this conclusion is that the transition state lies close to the surface, with the important 310 interaction being the interaction of Sn with the OH group). This magnitude is, in turn, larger than 311 nearly all barriers to form N-H bonds calculated in the reaction network, suggesting that NH<sub>2</sub>OH\* 312 will preferentially form NH<sub>3</sub>OH<sup>+</sup> as a product. The initial, transition and final state images are 313 shown in Figure S18.

# NH<sub>2</sub>OH -> NH<sub>2</sub> + OH (chemical dissociation)



- 314 315 Figure S18. Schematic showing the initial, transition, and final states for chemical dissociation of intermediate NH<sub>2</sub>OH to NH<sub>2</sub> and OH. For color coding of different atoms refer to legend in Figure
- 316
- 317 S1.
- 318

### 319 7. Gas phase results

320 Table S2 below presents the reaction steps considered to understand the effect of catalyst on the

- 321 gas product N<sub>2</sub>O formed at potentials of  $\sim 0.3$  V vs. SHE.
- 322

Reaction	Barrier (High Coverage) (eV)	
$NO^{+}NO^{+} \rightarrow cis(NO-NO^{+})$	0.65 (thermodynamic)	
$NO^{*}+NOH^{*}\rightarrow cis(NO-NOH^{*})$	0.4	
$cis(NO-NOH^*)+H^++e^- \rightarrow N_2O^*+H_2O$	0.45	
$N^{*}+NO^{*}\rightarrow N_{2}O^{*}$	0.35	

Table S2. Estimated barriers at high coverages for the different reactions considered to understand the gas phase formation.

The initial, transition, and final state images of the reactions considered in Table S2 are shown below in Figures S19, S20, and S21.

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### 8. Kinetic pathways for different reactions considered 325

### NO+NOH->NO-NOH



326 327

Figure S19. Initial, transition and final state configuration for the NO-NOH dimerization. For color 328 coding of different atoms refer to legend in Figure S1.

## $NO-NOH->N_2O + H_2O$



329 330 Figure S20. Initial, transition and final state configuration for electrochemical NO-NOH breaking

- into N<sub>2</sub>O and H<sub>2</sub>O. For color coding of different atoms refer to legend in Figure S1. 331
- 332
- 333



334 335 Figure S21. Initial, transition and final state configuration for electrochemical N\* and NO coupling into  $N_2O$ . For color coding of different atoms refer to legend in Figure S1.

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