Supporting Information

A Combined First-Principles Molecular Dynamics/Density-Functional Theory Study of Ammonia Electrooxidation on Pt(100) Electrode

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Table S1. Zero-point vibrational energy (ZPVE) correction for binding energy (E_{bind})

	E_{bind} without ZPVE, kcal/mol	$\Delta\text{ZPVE} = \text{ZPVE}_X - \text{ZPVE}_{\text{ads}},$ kcal/mol	E_{bind} with ZPVE, kcal/mol
NH ₃ (top)	53.8	-0.3	53.5
NH ₂ (top)	69.2	-2.2	67.0
NH ₂ (bridge)	90.4	-4.3	86.1
NH(bridge)	104.4	-3.7	100.7
N(bridge)	109.8	-1.7	108.1
N ₂ H ₄ (bridge)	72.8	-1.7	71.1
NH ₃ N(bridge)	147.9	-3.8	144.1
N ₂ (hollow)	1.2	-0.5	0.7
N ₂ (bridge)	4.1	-0.7	3.4
N ₂ (top)	7.1	-1.0	6.1

Table S2. Entropic effects in the reactions

Reaction	Vibrational entropy of reactant S_{vib} , cal/mol*K	Vibrational entropy of product S_{vib} , cal/mol*K	ΔS , cal/mol*K	$T\Delta S$, kcal/mol, at T = 300K
NH ₃ adsorption	NH _{3(aq)} 0.164	NH _{3(top)} 12.316	12.152	3.6
NH _{3(top)} oxidation	NH _{3(top)} 12.316	NH _{2(top)} 14.779	2.463	0.7
NH _{2(top)} → NH _{2(bridge)}	NH _{2(top)} 14.779	NH _{2(bridge)} 4.122	-10.657	-3.2
NH _{2(bridge)} oxidation	NH _{2(bridge)} 4.122	NH _(bridge) 3.787	-0.335	-0.10
NH _(bridge) oxidation	NH _(bridge) 3.787	N _(bridge) 3.950	0.163	-0.05
NH _{2(top)} dimerization	NH _{2(top)} - NH _{2(top)} 11.102	N ₂ H _{4(bridge)} 7.656	-3.446	-1.0
NH _(bridge) dimerization	NH _(bridge) - NH _(bridge) 6.131	N ₂ H _{2(hollow)} 5.390	-0.741	-0.2
N _(bridge) dimerization	N _(bridge) - N _(bridge) 6.498	N _{2(hollow)} 3.999	-2.499	-0.75
N _{2(hollow)} → N _{2(bridge)}	N _{2(hollow)} 3.999	N _{2(bridge)} 9.813	5.814	1.7
N _{2(bridge)} → N _{2(top)}	N _{2(bridge)} 9.813	N _{2(top)} 11.050	1.237	0.4
N _{2(top)} → N _{2(aq)}	N _{2(top)} 11.050	N _{2(aq)} 0.000	-11.050	-3.3
NH ₃ -N bond formation	NH _{3(aq)} -N _(bridge) 4.114	NH ₃ N _(bridge) 5.971	1.857	0.6

Figure S1. Energy profile for $\text{NH}_2(\text{top})$ electrooxidation to form $\text{N}(\text{bridge})$ at ca. +0.4 V vs. RHE ($q = 0$). Energies are in kcal/mol.

Figure S2. The $\text{N}(\text{bridge})$ lateral translation to an adjacent Pt site. The TS with four N-Pt bonds has two imaginary frequencies of $i145 \text{ cm}^{-1}$ and corresponds to a second order saddle point. The numbers correspond to the bond lengths in Å. Ambient water molecules are omitted for clarity.

Figure S3. Energy profile (kcal/mol) for $\text{NH}_{2(\text{top})}$ electrooxidation at ca. +0.3 V vs. RHE ($q = -2$).

Table S3. $\text{NH}_{3(\text{top})}$ vibration frequencies*

Mode (scaling factor)	Frequency (ν), cm^{-1}	Frequency in vacuum, cm^{-1}	Cortés Bracho <i>et al.</i> solid/gas interface ¹	Experi- ment on Pt(111) ²
$\nu(\text{N-H})$, asym- metrical stretching (0.976)	3395.17	3666.91	3481	3360

	3173.55	3661.49	3472	
$\nu(\text{N-H})$, sym- metrical stretching (0.976)	3084.91	3522.77	3359	3150
$\delta_a(\text{HNH})$, asymmetric bending mode (0.963)	1576.19	1547.41	1606	1610
	1545.15	1541.72	1595	

$\delta_s(\text{HNH})$, symmetric bending mode (0.963)	1246.12	892.11	1150	1170
$\nu(\text{N-Pt})$, surface stretch mode (1.013)	410.73			360
$T_{ }(\text{Pt-NH}_3)$, NH_3 translated parallel to the $\text{Pt}(100)$ surface (0.973)	206.79 182.36 104.98

	92.62			
ZPVE** (kcal/mol)	21.47	21.20		
Vibrational entropy*** S_{vib} (cal/mol*K)	12.316	0.164		

*The computed harmonic frequencies were scaled by empirical factors to account for anharmonicity effects. [Rauhut, G. and Pulay, P.; J. Phys. Chem. 99,3093 (1995)]

** Zero-point vibrational energy, $ZPVE = \frac{1}{2} hc \sum \nu_i$

*** Vibrational entropy

$$S_{vib} = R \sum_i \left[\frac{(h c \nu_i / k T) \exp(-h c \nu_i / k T)}{1 - \exp(-h c \nu_i / k T)} - \ln(1 - \exp(-h c \nu_i / k T)) \right]$$

Table S4. Vibration frequencies for NH₂(_{top})

Mode (scaling factor)	frequency, cm ⁻¹
$\nu(\text{N-H})$ asymmetrical stretching (0.976)	3349.57
$\nu(\text{N-H})$ symmetrical stretching (0.976)	3205.62
$\delta_s(\text{H-N-H})$, symmetric bending mode (0.963)	1440.11
$\delta(\text{H-N-H})$ NH ₂ swing sym.	687.00

<p>(wagging) (0.808)</p>
<p>$\nu(\text{N-Pt})$ surface stretch mode (1.013)</p>	<p>476.23</p>
<p>twisting (1.002)</p>	<p>439.96</p>
<p>$T_{ }(\text{Pt-NH}_2)$, NH_2 translated</p>	<p>195.73</p>

parallel to the
Pt(100) surface
(0.973)

169.97

133.67

37.37

ZPVE (kcal/mol)	14.49
Vibrational entropy, S_{vib} (cal/mol*K)	14.779

Table S5. Vibration frequencies for NH₂(bridge)

Mode (scaling factor)	frequency, cm ⁻¹	Solid/gas calculation ³	Solid-gas experiment ^{4,5}
v(N-H), N-H stretching (0.976)	3395.12	3479	3388

	3100.49	3379	3298
δ_s (HNH), symmetric bending mode (0.963)
	1480.11	1467	1450
δ (NH),	979.13		

bending mode (0.985)	827.04
$\delta_a(\text{HNH})$, asymmetric bending mode (0.819)	648.26
$\nu(\text{N-Pt})$ surface stretching mode (1.013)	496.66

$\rho(\text{NH}_2)$, rocking mode (1.013)	436.07
$T_{ }(\text{Pt-NH}_2)$, NH_2 translated parallel to the $\text{Pt}(100)$ surface (1.057)	222.16
ZPVE (kcal/mol)	16.56		
Vibrational entropy, S_{vib} (cal/mol*K)	4.122		

Table S6. Vibration frequencies for NH_(bridge)

Mode (scaling factor)	frequency, cm ⁻¹	Solid/gas calculation ³	Solid-gas experiment ⁶
ν(N-H) stretching (0.976)	2984.80	3363	3185

δ(NH), bending mode (0.985)	1010.99	895	930

	717.07
	858	
ρ(NH),	515.65		

<p>rocking mode (1.013)</p>
<p>v(N-Pt) surface stretch mode (1.013)</p>	<p>488.44</p>	<p>430</p>	<p>470</p>

$T_{ }(\text{Pt-NH})$, NH translated parallel to the Pt(100) surface (1.057)	203.24		210 ($T_{x,y}$)
ZPVE** (kcal/mol)	8.46		
Vibrational entropy, S_{vib} (cal/mol*K)	3.787		

Table S7. Vibration frequencies for N_(bridge)

Mode (scaling factor)	frequency, cm ⁻¹
$\nu(\text{N-Pt})$, surface stretch mode (1.013)	550.76
$\rho(\text{N})$, rocking mode (1.013)	494.45
$T_{ }(\text{Pt-N})$, N translated parallel to the Pt(100) surface (1.057)	145.08
ZPVE , kcal/mol	1.70
Vibrational entropy, S_{vib} (cal/mol*K)	3.951

Table S8. Vibration frequencies for $\text{N}_{2(\text{hollow})}$

Mode (scaling factor)	frequency, cm^{-1}	frequency in vacuum, cm^{-1}
$\nu(\text{N-N})$, N-N bond stretch mode (1.013)	1269.29	2509.28
twisting (0.819)	501.23
$\nu(\text{N-Pt})$, surface stretch mode asynchronous (1.013)	413.30

$\rho(\text{N}_2)$, rocking mode (1.013)	360.63
$\nu(\text{N-Pt})$, surface stretch mode synchronous (1.013)	326.19
ZPVE , kcal/mol	4.10	3.59
Vibrational entropy, S_{vib} (cal/mol*K)	3.999	0.000

Table S9. Vibration frequencies for $\text{N}_{2(\text{bridge})}$

Mode (scaling factor)	frequency, cm^{-1}	frequency in vacuum, cm^{-1}
$\nu(\text{N-N})$, N-N bond stretch mode (1.013)	1853.98	2509.28
$\nu(\text{N-Pt})$, surface stretch mode asynchronous (1.013)	330.99
$\nu(\text{N-Pt})$, surface stretch mode synchronous (1.013)	253.46

twisting (0.819)	<p>232.68</p>
$\rho(\text{N}_2)$, rocking mode (1.013)	<p>228.65</p>
$T_{ }(\text{Pt-N}_2)$, N_2 translated parallel to the Pt(100) surface (1.057)	<p>119.94</p>
ZPVE , (kcal/mol)	4.32	3.59
Vibrational	9.813	0.000

entropy, S_{vib} (cal/mol*K)		
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Table S10. Vibration frequencies for N_{2(top)}

Mode (scaling factor)	frequency, cm ⁻¹	frequency in vacuum, cm ⁻¹
v(N-N), N-N bond stretch mode (1.013)	2184.38	2509.28
v(N-Pt), surface stretch mode (1.013)	300.46

$\rho(\text{N}_2)$, rocking mode (1.057)	<p>281.75</p>
	<p>229.83</p>
$T_{ }(\text{Pt-N}_2)$, N_2 translated parallel to the Pt(100) surface (1.057)	<p>129.97</p> <p>109.05</p>

ZPVE, (kcal/mol)	4.63	3.59
Vibrational entropy, S_{vib} (cal/mol*K)	11.050	0.000

Table S11. Vibration frequencies for N₂H₄(ads)

Mode (scaling factor)	frequency, cm ⁻¹	frequency in vacuum, cm ⁻¹	experiment for solid/gas ⁷
v(N-H) N-H bond stretch mode (0.976)	3266.87	3631.59	3156

	3232.80	3618.19

	3078.13	3517.56
	3503.71	
	2972.98
$\delta(\text{HNH})$, HNH bending mode (0.963)	<p>1571.08</p> <p>1552.37</p>	<p>1571.11</p> <p>1549.38</p>	1558
synchronous twisting (0.819)	<p>1161.90</p>	<p>1031.60</p>	1392
wagging (0.808)	<p>1036.66</p>	<p>987.07</p>

	<p>976.11</p> <p>931.81</p>	<p>684.69</p> <p>534.63</p>
$\nu(\text{N-N})$, N-N stretching (1.013)	<p>944.98</p>	<p>1129.54</p>	836
$\rho(\text{NH}_2)$, NH ₂ twisting	<p>607.97</p>		

<p>around axis (N-N) (0.819)</p>	<p>548.44</p>
<p>$\nu(\text{N-Pt})$, N surface stretch mode (1.013)</p>	<p>448.91</p> <p>351.40</p>		<p>355</p>
<p>N-N twisting parallel to the surface (0.819)</p>	<p>209.84</p>	<p>143.05</p>

$T_{ }$ translated perpendicular to (N-N) (1.057)	195.15
ZPVE , (kcal/mol)	33.00	31.31	
Vibrational entropy, S_{vib} (cal/mol*K)	7.656	3.919	

Table S12. $\text{NH}_3\text{N}_{(\text{ads})}$ vibration frequencies

Mode (scaling factor)	frequency, cm^{-1}
v(N-H), stretching (0.976)	3089.92
	2965.48
	2854.79

$\delta_a(\text{HNH})$, asymmetric bending mode (0.963)	<p>1566.47</p>
$\delta_s(\text{HNH})$, symmetric bending mode (0.963)	<p>1530.43</p>
$\rho(\text{NH}_3)$, rocking mode (1.057)	<p>1500.50</p>
	<p>1236.40</p>

	<p>1155.33</p>
<p>v(N-N), N-N bond stretch mode (1.013)</p>	<p>1026.54</p>
<p>v(N-Pt), surface stretch mode (1.013)</p>	<p>416.99</p>
<p>twisting (0.819)</p>	<p>307.94</p>

$T_{ }(\text{Pt-N}_2)$, N_2 translated parallel to the Pt(100) surface (1.057)	254.73
NH_3 wagging (0.808)	240.78
ZPVE , (kcal/mol)	25.94
Vibrational entropy, S_{vib} (cal/mol*K)	5.971

Figure S4. The MD for $\text{NH}_3(\text{aq}) - \text{N}_{(\text{bridge})}$ bond formation at surface potential ca. +0.5 V vs. RHE ($q = +2$). The distances (Å) between N of the ammonia molecule and the Pt surface are shown.

At $t = 0$ fs, the initial position of $\text{NH}_3(\text{aq})$ is taken to be 3.971 Å above the Pt surface with zero velocity with the N-N initial distance of 2.917 Å. The ammonia molecule gains acceleration due to the NH_3 -Pt attraction. At $t = 41.0$ fs, one of the hydrogen atoms on the ammonia molecule forms a hydrogen bond with the bridging nitrogen, and the ammonia molecule accelerating towards the metal surface in the vicinity of the bridging nitrogen. At $t = 87.0$ fs, the ammonia molecule reaches the lowest point corresponding to the N-Pt(100) distance of 3.406 Å and the N-N distance of 2.446 Å. The bridging nitrogen begins to tilt toward a hollow site. At $t = 106.0$ fs, the impinging ammonia molecule is seen to bounce back from the $\text{N}_{(\text{bridge})}$ due to the N-N repulsion at this angle of approach, and the bridging nitrogen continues to tilt toward the hollow site. At about $t = 171.0$ fs, ammonia again begins to accelerate toward the surface when the $\text{N}_{(\text{bridge})}$ is nearly in the hollow site with the $\text{N}_{(\text{bridge})}$ - surface angle of 29 degrees. At $t = 225.0$ fs, the ammonia molecule reaches the surface with the N-Pt(100) distance of 3.370 Å, while the bridging nitrogen moves back to the vertical position. At $t = 325.0$ fs, the bond between $\text{NH}_3(\text{aq})$ and $\text{N}_{(\text{bridge})}$ is seen to form.

Figure S5. Formation of $N_{(\text{bridge})}$ in line with an extant $N_{(\text{bridge})}$ in the process of submonolayer coverage on Pt(100).

Figure S6. Dimerization of $N_{(\text{bridge})}$ across the adjacent rows to form $N_{2(\text{bridge})}$. Energies in kcal/mol.

References

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