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# Theoretical insights into the electroreduction mechanism of N<sub>2</sub> to NH<sub>3</sub> from an improved Au(111)/H<sub>2</sub>O interface model†

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An improved H coverage-dependent Au(111)/H<sub>2</sub>O electrochemical interface model is proposed in this paper, which is firstly used to study electroreduction mechanisms of N<sub>2</sub> into NH<sub>3</sub> at the thermodynamical equilibrium potential in cooperation with electronic structure analysis. The results show that the associative mechanism is more favorable on Au(111) and therein alternating and distal pathways may be able to parallelly occur in gas phase and the present simulated electrochemical interface. The initial N<sub>2</sub> reduction into the N<sub>2</sub>H intermediate is the rate determining step, which may be able to be regarded as the origin of the observed experimentally high overpotential during N<sub>2</sub> electroreduction. The presence of an electrochemical environment can significantly change the N<sub>2</sub> reduction pathway and decrease the barrier of the rate determining step, which can be ascribed to the significant electron accumulation and interaction between N<sub>2</sub> molecules and H<sub>2</sub>O clusters. The theoretical results display excellent consistency with the available experimental data, confirming the rationality of the present proposed electrochemical model. The comparison of the barrier between the hydrogen evolution reaction and rate determining step well explains why the activity of Au electrodes is usually unsatisfactory. Accordingly, a single descriptor can be proposed, in which an ideal electrocatalyst should be able to reduce the barrier for initial N<sub>2</sub> electroreduction into N<sub>2</sub>H. In this way, N<sub>2</sub> electroreduction pathways can be facilitated and the yield of NH<sub>3</sub> can be enhanced. We believe that the present study can represent progress to study N<sub>2</sub> electroreduction mechanisms from an improved electrochemical model.

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## 1. Introduction

NH<sub>3</sub> as a promising carbon-free alternative energy carrier can be employed in fertilizers, production of important chemicals, NH<sub>3</sub> fuel cells and indirectly hydrogen fuel cells.<sup>1–3</sup> At present, NH<sub>3</sub> is synthesized primarily by reaction of N<sub>2</sub> with H<sub>2</sub> on an Fe/Ru-based catalyst through the industrial Haber–Bosch (HB) process under harsh conditions such as high temperatures and pressures,<sup>4,5</sup> which is an energy intensive chemical process and consumes *ca.* 2% of annual global energy because of the stability and chemical inertness of N<sub>2</sub> molecule.<sup>6–8</sup> By contrast, the electrochemical reduction of N<sub>2</sub> into NH<sub>3</sub> with proton and electron transfer in an aqueous environment is more energy efficient and attracts extensive interest in recent years since it can be operated at ambient conditions and powered by

renewable electricity.<sup>9–14</sup> Unfortunately, the required large overpotential and competing hydrogen evolution reaction lead to low faradaic efficiency and poor selectivity for N<sub>2</sub> electroreduction into NH<sub>3</sub> on most electrocatalysts, thus impeding its practical applications.<sup>15–18</sup> The poor activity of the cathode electrocatalyst may put a major limitation on production of NH<sub>3</sub> product in significant yields at ambient conditions. To achieve the rational design of more selective and active electrocatalysts, the system understanding on electroreduction mechanism of N<sub>2</sub> into NH<sub>3</sub> is extremely urgent and essential.

Although tremendous efforts in recent years, N<sub>2</sub> electroreduction mechanism remains elusive. The present most studies on N<sub>2</sub> electroreduction reaction primarily focus on the synthesis of electrocatalysts including metals such as Pt, Ru, Fe, Au, Pd, Rh, Fe, Ni, Mo and Bi,<sup>19–30</sup> alloys such as Pt–Ru,<sup>31</sup> metal nitrides and sulfides,<sup>32,33</sup> and carbon-based materials.<sup>34–38</sup> However, these reported electrocatalysts suffer from low NH<sub>3</sub> faradaic efficiency and N<sub>2</sub> electroreduction reaction is still plagued. Based on these previous studies, the development of more active and selective electrocatalysts is highly desired but remains challenging. Study of N<sub>2</sub> electroreduction reaction mechanism will help design electrocatalysts with high activity and selectivity. In the most recent reviews from Shao *et al.* and

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Zhang *et al.*,<sup>39,40</sup> N<sub>2</sub> electroreduction mechanisms and reaction intermediates that obtained in experiments by various spectroscopy techniques are summarized. Currently, it is generally accepted that there are two main reaction mechanisms for N<sub>2</sub> electroreduction into NH<sub>3</sub>, namely, dissociative pathways and associative pathways. N≡N bond in N<sub>2</sub> molecule is broken to form N atoms on electrocatalyst surface before hydrogenation in dissociative mechanism, whereas the hydrogenation of N<sub>2</sub> molecule occurs before N≡N bond is broken in associative mechanism. It is currently believed that the dissociative mechanism is dominant in the HB process of N<sub>2</sub> reduction into NH<sub>3</sub>.<sup>15,41</sup> An associative distal or alternating mechanism may be followed during N<sub>2</sub> electroreduction into NH<sub>3</sub> through experimental identification of some intermediates. For example, using surface-enhanced infrared absorption spectroscopy, Shao *et al.*, studied for the first time N<sub>2</sub> electrochemical reduction reaction mechanism on Au thin film, in which the adsorbed N<sub>2</sub>H<sub>y</sub> (1 ≤ y ≤ 4) species was detected at potentials below 0 V (vs. RHE),<sup>42</sup> thus indicating that N<sub>2</sub> electroreduction may follow the associative alternating and distal mechanisms on Au surface. Combining surface-enhanced infrared absorption spectroscopy with electrochemical measurements, the adsorbed N<sub>2</sub>H<sub>x</sub> (0 ≤ x ≤ 2) species was detected at potentials below 0.2 V (vs. RHE) on Ru thin film in the subsequent study from Shao *et al.*, and notably increased coverage of N<sub>2</sub>H<sub>x</sub> was observed as the potential decreasing from 0.2 to −0.4 V, thus the associative distal mechanism may be able to be concluded.<sup>20</sup> By performing isotope-labelled experiments, Yin *et al.*, found only a trace amount of N<sub>2</sub>H<sub>4</sub> intermediate during N<sub>2</sub> electroreduction on bismuth surface, suggesting that associative distal mechanism may be more favorable.<sup>30</sup> Despite of understanding of N<sub>2</sub> electroreduction reaction mechanism is of importance for rationally designing more efficient electrocatalysts, the experimental studies are very rare at present in this area since low selectivity makes experimental determination of mechanism rather difficult.

Because of the experimental limitations to identify intermediates and complexity of N<sub>2</sub> electroreduction process involving 6 elementary reaction steps, theoretical calculations have become a powerful tool for studying electrocatalytic reactions by employing density functional theory (DFT).<sup>43,44</sup> DFT calculations can give mechanistic information that is not accessible based on experiments alone and identify favored reaction intermediates. Theoretical work by Skúlason *et al.* and Montoya *et al.* thermodynamically indicated that the associative distal mechanism would be more favorable since more positive reaction free energies are expected for the associative alternating mechanism by combining DFT calculations with the computational hydrogen electrode model.<sup>15,45</sup> Their findings had shown that the potential limiting step is N<sub>2</sub> reductive protonation to the adsorbed N<sub>2</sub>H species on the transition metal surface with relatively weak N adsorption such as Pt, Pd, Ag, Au, Ni, Co and Ru during N<sub>2</sub> electroreduction into NH<sub>3</sub>, whereas the potential limiting step is determined by the protonation of the adsorbed NH into NH<sub>2</sub> species for more reactive transition metals, such as Mo. On the basis of DFT-based computational hydrogen electrode model, the electrocatalytic activity of various binary transition metals are systematically examined in recent theoretical work from Zhao

*et al.*,<sup>46</sup> and the binary FeRh catalyst was thought to have the optimal catalytic performance due to its lowest limiting potential and best suppressing effect on hydrogen evolution reaction during N<sub>2</sub> electroreduction reaction. Furthermore, their study indicated that N<sub>2</sub> reduction reaction prefers to proceed through associative distal mechanisms than alternating pathways on the FeRh catalyst. These above theoretical studies assumed that activation barriers of reaction pathways is related with reaction free energies on different transition metal surfaces and only considered various elementary step thermodynamics, whereas the potential-dependent kinetic barriers that predicting catalytic activity were not further calculated. Most recently, Janik *et al.* calculated explicitly the potential-dependent activation barriers for elementary electroreduction reactions included in associative distal and alternating pathways during N<sub>2</sub> electroreduction using their previously developed method,<sup>47–49</sup> and concluded that the alternating mechanism by direct surface hydrogenation may be more favorable on late transition metals due to smaller barriers at 0 V (vs. RHE),<sup>50,51</sup> in which N<sub>2</sub> electroreduction into N<sub>2</sub>H species is rate determining step of overall reaction. However, despite various theoretical efforts, N<sub>2</sub> electroreduction mechanisms are still not systematically understood and mechanistic inconsistencies remain exist. Furthermore, the key factor such as solvent effect was not included in previous theoretical studies on N<sub>2</sub> electroreduction mechanisms. Thus, the modeling of electrocatalytic reaction systems occurred at the complex electrode/aqueous interfaces remains a subject of ongoing discussion.

In the present paper, Au electrocatalyst is selected due to its excellent durability, relatively high faradaic efficiency and low hydrogen evolution reaction activity in N<sub>2</sub> electroreduction. Furthermore, electrocatalytic N<sub>2</sub> reduction reaction on the Au surface is indeed possible under ambient conditions.<sup>25,52</sup> Our previous validated explicit solvation model with two relaxed H<sub>2</sub>O bilayer structure is employed to simulate solvent effect,<sup>53–55</sup> which allows us to better model the interactions among adsorbates, surface and solvents and determine the kinetic barriers for various elementary reaction steps. Thus, an improve H coverage-dependent Au(111)/H<sub>2</sub>O electrochemical interface model is proposed, by which the electroreduction mechanisms of N<sub>2</sub> into NH<sub>3</sub> can be identified. Simultaneously, solvation effect on N<sub>2</sub> reduction mechanisms is also considered in this work. Our present used model is differentiated from previous theoretical work on N<sub>2</sub> electroreduction into NH<sub>3</sub>. The available experimental results on Au electrodes will be used to examine whether the currently employed computational model is enough accurate by comparing with our present theoretical study.

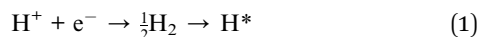
## 2. H coverage-dependent Au(111)/H<sub>2</sub>O interface model

### 2.1 Determination method of equilibrium potentials

Surface and solvation model, and computational parameters included in computational details have been represented in detail in ESI (see Fig. S1).<sup>†</sup> It is known that the hydrogen evolution reaction and proton-coupled electron transfer usually occur during N<sub>2</sub> electroreduction on the Au electrodes, thereby



the surface adsorbed H atoms as the intermediate may be involved.<sup>24,25,53</sup> Moreover, the difference of electrostatic potential in electric double layer can be controlled and adjusted by changing number of the surface adsorbed H atoms.<sup>56–58</sup> Thus, the H coverage-dependent equilibrium potentials can be determined and potential-dependent N<sub>2</sub> electroreduction mechanisms can be speculated. The surface adsorbed H atom can be formed during N<sub>2</sub> electroreduction by following eqn (1):



At different H coverage conditions, the Gibbs free energy of eqn (1),  $\Delta G(\theta)$  can be calculated by eqn (2) on the basis of the methodology proposed by Nørskov *et al.*, Chen *et al.* and Strasser *et al.* for oxygen reduction, hydrogen evolution and CO<sub>2</sub> electrochemical reduction reactions,<sup>56,59–63</sup> in which  $\Delta E(\theta)$ ,  $\Delta S(\theta)$ ,  $\Delta \text{ZPE}$  and  $k_{\text{B}}T \ln(\theta/1 - \theta)$  represent the differential adsorption energy of surface adsorbed H atoms, entropy change, zero-point energy change and the contributions of configuration entropy to  $\Delta G(\theta)$ , respectively. Herein, coverage  $\theta = n/N$ , in which  $n$  is the number of surface adsorbed H atoms and  $N$  is the total number of surface Au atoms. Thus, the H coverage-dependent equilibrium potential  $U$  (vs. RHE) can be determined at Au(111)/H<sub>2</sub>O interface when the Gibbs free energy,  $\Delta G(\theta)$  is equal with zero.

$$\Delta G(\theta) = \Delta E(\theta) + eU - T\Delta S(\theta) + \Delta \text{ZPE} + k_{\text{B}}T \ln(\theta/1 - \theta) \quad (2)$$

According to eqn (3), the differential adsorption energy of surface adsorbed H atoms,  $\Delta E(\theta)$  can be calculated, where  $E(\theta)_{\text{M}_{\text{Hn}}}$  is the total energy of the Au surface with different coverage of adsorbed H atoms.

$$\begin{aligned} \Delta E(\theta) &= \partial E(\theta)_{\text{M}_{\text{Hn}}} / \partial n - \frac{1}{2}E_{\text{H}_2} \\ &= \partial E(\theta)_{\text{M}_{\text{Hn}}} / N\partial\theta - \frac{1}{2}E_{\text{H}_2} \end{aligned} \quad (3)$$

The contributions from ZPE and entropy changes together to  $\Delta G(\theta)$  are estimated to be *ca.* 0.24 eV at standard temperature

(298 K) based on the available data from previous literature.<sup>64</sup> Therefore, combining eqn (2) with eqn (3), the eqn (4) can be obtained. The values of  $E(\theta)_{\text{M}_{\text{Hn}}}$  and  $E_{\text{H}_2}$  is directly available *via* DFT calculations. A series of values of  $E(\theta)_{\text{M}_{\text{Hn}}}$  can be calculated by changing the coverage of surface adsorbed H atoms on Au(111). At the different coverages, the values of  $\Delta E(\theta)$  can be obtained by differentiating the plots of  $\partial E(\theta)_{\text{M}_{\text{Hn}}}/N$  against  $\theta$  on the basis of eqn (3).

$$\begin{aligned} \Delta G(\theta) &= \left[ \partial E(\theta)_{\text{M}_{\text{Hn}}} / N\partial\theta - \left( \frac{1}{2}E_{\text{H}_2} - eU \right) \right] \\ &\quad + k_{\text{B}}T \ln(\theta/1 - \theta) \end{aligned} \quad (4)$$

## 2.2 Relationship between H coverage and equilibrium potentials

In the present study, we consider various possible surface adsorption configurations of H atoms and coverage dependence. It is observed that H atoms prefer to adsorb at 3-fold face-centered cubic hollow (fcc) sites on Au(111) so that they can stay away from each other in order to minimize the repulsive reactions when H coverage ( $\theta_{\text{H}}$ ) is below and equal with 1 monolayer (ML) (see Fig. S2†). The coverages of H atoms above 1 ML are not further analyzed on Au(111) because of the observed spontaneous formations of hydrate proton by adsorbed H atoms with adjacent H<sub>2</sub>O molecules caused by strong repulsive interactions among adsorbed H atoms. Fig. 1(a) exhibits a reasonable polynomial relationship between the differential adsorption energy of surface adsorbed H atoms,  $\Delta E(\theta)$  and  $\theta_{\text{H}}$ , indicating that the Langmuir adsorption isotherms may be followed on Au(111). Thereby,  $\Delta E(\theta)$  can be calculated at any  $\theta_{\text{H}}$  through polynomial fitting of  $\Delta E(\theta) \sim \theta_{\text{H}}$  data. We can calculate the equilibrium potentials ( $U$ ) based on the eqn (4) at any  $\theta_{\text{H}}$  and then the polynomial relationships between  $\theta_{\text{H}}$  and  $U$  can be obtained on Au(111). It is found that the more negative equilibrium potentials can be obtained with the increasing H coverage, as shown in Fig. 1(b). In fact, the previous theoretical study from Skúlason *et al.* also showed that most surfaces will be fully covered with the adsorbed H atoms at more negative

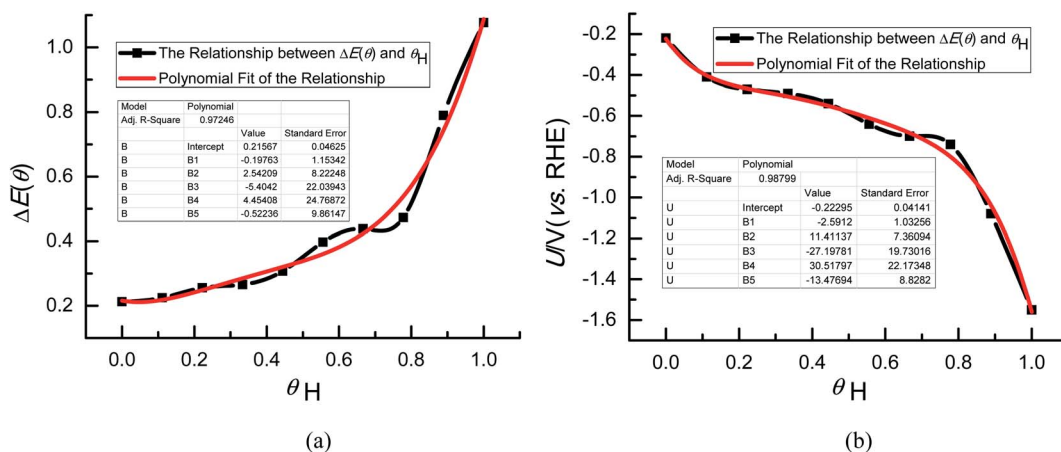


Fig. 1 (a) The relationship between the differential adsorption energy of H atoms and H coverage ( $\theta_{\text{H}}$ ),  $\Delta E(\theta)$ ; (b) the relationship between the calculated equilibrium potentials ( $U$ ) and H coverage ( $\theta_{\text{H}}$ ).



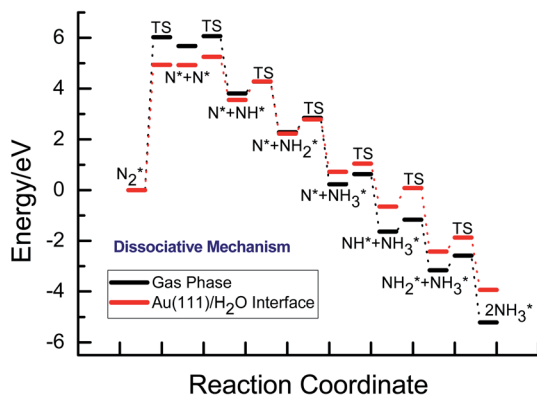


Fig. 2 Overall energy pathway diagram of N<sub>2</sub> reduction and electro-reduction into NH<sub>3</sub> via dissociative mechanism on Au(111) in gas phase and the present simulated Au(111)/H<sub>2</sub>O electrochemical interface.

electrode potentials,<sup>56</sup> confirming the reasonability of our present proposed H coverage-dependent Au(111)/H<sub>2</sub>O electrochemical interface model to some degree. The equilibrium potential is calculated as *ca.*  $-0.22$  V (vs. RHE) when  $\theta_{\text{H}}$  is equal with zero based on the polynomial relationship between  $\theta_{\text{H}}$  and  $U$ , which is the closest to the thermodynamical value of *ca.*  $-0.06$  V (vs. RHE) for N<sub>2</sub> electroreduction under ambient conditions,<sup>20</sup> thus being regarded as the thermodynamical equilibrium potential. Our present study will focus on the electroreduction mechanisms of N<sub>2</sub> into NH<sub>3</sub> at the thermodynamical required equilibrium potential with the aim of applying the present proposed H coverage-dependent Au(111)/H<sub>2</sub>O interface model. The mechanistic understanding on N<sub>2</sub> electroreduction can provide scientific guideline for rational design of efficient electrocatalysts. The potential-dependent N<sub>2</sub> electroreduction mechanisms will be further studied in our future work.

### 3. Results and discussion

#### 3.1 N<sub>2</sub> reduction mechanism on Au(111) in gas phase

For comparison and consideration of solvation effect on N<sub>2</sub> reduction mechanisms, we firstly present calculated results of N<sub>2</sub> reduction to NH<sub>3</sub> via dissociative and associative

mechanisms on Au(111) in gas phase. In dissociative mechanism, N<sub>2</sub> is initially dissociated to form the adsorbed N atoms on Au(111) with an extremely high activation barrier of *ca.* 6.02 eV, as can be seen in Fig. 2. Subsequently, the adsorbed N atoms are further reduced to form NH<sub>3</sub> molecules via serial surface hydrogenation steps with corresponding barriers of *ca.* 0.40, 0.47 and 0.57 eV, respectively. By comprehensively scrutinizing the overall energy pathway diagram of N<sub>2</sub> reduction into NH<sub>3</sub> in gas phase, N<sub>2</sub> dissociation pathway is rate determining step of overall reaction in dissociative mechanism on Au(111).

Fig. 3 shows the overall energy pathway diagram of N<sub>2</sub> reduction into NH<sub>3</sub> via associative alternating and distal mechanisms in gas phase. In these both mechanisms, the activation barrier is calculated as *ca.* 2.10 eV for the first hydrogenation step of N<sub>2</sub> molecule into the adsorbed N<sub>2</sub>H species. Beginning with the further reduction of N<sub>2</sub>H, there may be two possibilities to occur. One is N<sub>2</sub>H hydrogenation to form the surface adsorbed NHHH species, which is defined alternating pathways; another is N<sub>2</sub>H hydrogenation to form the surface adsorbed NNH<sub>2</sub> species, being defined as distal pathways. The required barrier for the formation of NHHH species is *ca.* 0.17 eV in alternating pathways. NHHH species can further be reduced to form the adsorbed NHHH<sub>2</sub> species with an activation barrier of *ca.* 0.26 eV. Two possibilities are considered for NHHH<sub>2</sub> subsequent further reduction, the adsorbed NH<sub>2</sub>NH<sub>2</sub> and NHHH<sub>3</sub> species may be formed via surface hydrogenation. The corresponding barrier is 0.31 and 0.21 eV, respectively, which is extremely low and surmountable at room temperature, indicating that NHHH<sub>2</sub> further reduction into NH<sub>2</sub>NH<sub>2</sub> and NHHH<sub>3</sub> species may be parallel pathways in alternating pathways. NH<sub>2</sub>NH<sub>2</sub> further reduction to form the first NH<sub>3</sub> molecule may be able to be separated into two elementary reaction steps, namely, NH<sub>2</sub>NH<sub>2</sub> species surface hydrogenation into the adsorbed NH<sub>2</sub>NH<sub>3</sub> species, and subsequent formation of the adsorbed NH<sub>2</sub> species and NH<sub>3</sub> product via N–N bond cleavage. The calculated barrier is *ca.* 0.37 and 1.66 eV, respectively, as shown in Fig. 3(a). Surface hydrogenation of NH<sub>2</sub> intermediate can finally leads to production of the second NH<sub>3</sub> molecule.

In distal pathways, surface hydrogenation of NNH<sub>2</sub> intermediate is possible to form the adsorbed NNH<sub>3</sub> and NHHH<sub>2</sub> species. However, the significant higher barrier for formation of

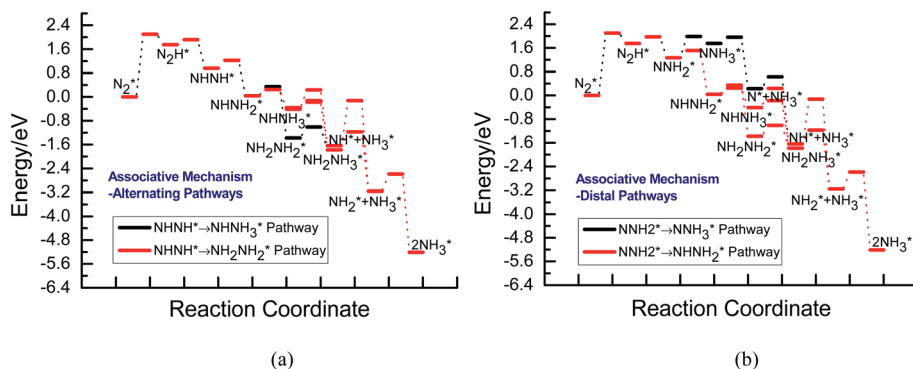


Fig. 3 Overall energy pathway diagram of N<sub>2</sub> reduction into NH<sub>3</sub> via associative mechanism on Au(111) in gas phase: (a) alternating pathways; (b) distal pathways.

**Table 1** Activation barriers ( $\Delta E_{\text{act}}$ , eV) and reaction energies ( $\Delta E_{\text{reac}}$ , eV) for the possible elementary reaction steps involved in  $\text{N}_2$  reduction pathways on Au(111) in gas phase

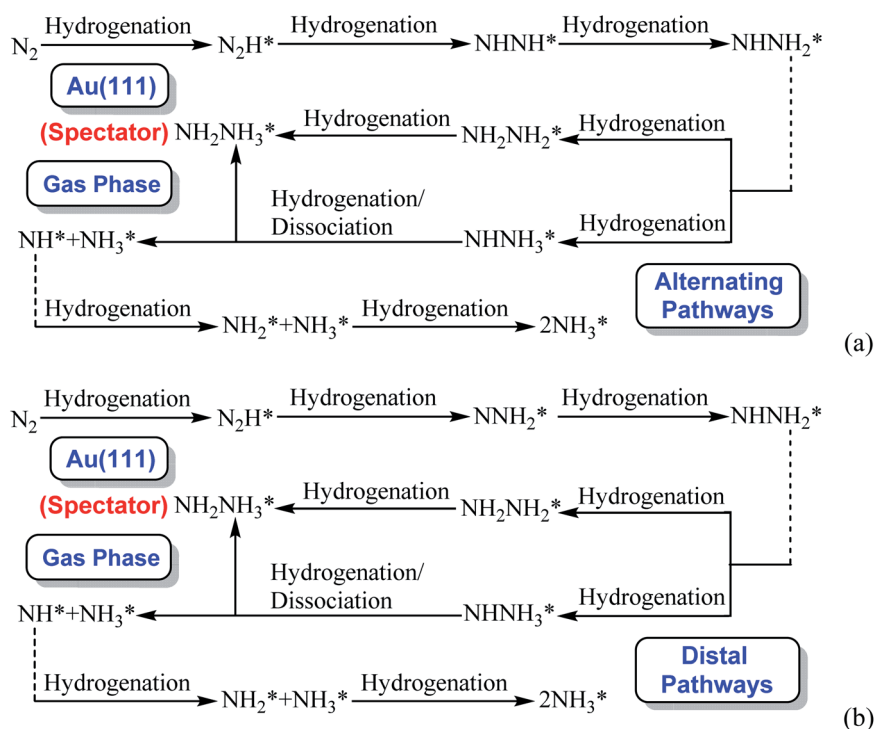
Elementary reaction steps <sup>a</sup>	$\Delta E_{\text{act}}$ , eV	$\Delta E_{\text{reac}}$ , eV
$\text{N}_2 + * \rightarrow \text{N}^* + \text{N}^*$	6.02	5.67
$\text{N}^* + \text{H}^* \rightarrow \text{NH}^*$	0.40	-1.87
$\text{NH}^* + \text{H}^* \rightarrow \text{NH}_2^*$	0.47	-1.52
$\text{NH}_2^* + \text{H}^* \rightarrow \text{NH}_3^*$	0.57	-2.05
$\text{N}_2 + \text{H}^* \rightarrow \text{N}_2\text{H}^*$	2.10	1.75
$\text{N}_2\text{H}^* + \text{H}^* \rightarrow \text{NHNH}^*$	0.17	-0.79
$\text{N}_2\text{H}^* + \text{H}^* \rightarrow \text{NNH}_2^*$	0.22	-0.48
$\text{NHNH}^* + \text{H}^* \rightarrow \text{NHNH}_2^*$	0.26	-0.92
$\text{NNH}_2^* + \text{H}^* \rightarrow \text{NHNH}_2^*$	0.24	-1.23
$\text{NNH}_2^* + \text{H}^* \rightarrow \text{NNH}_3^*$	0.72	0.48
$\text{NHNH}_2^* + \text{H}^* \rightarrow \text{NH}_2\text{NH}_2^*$	0.31	-1.42
$\text{NHNH}_2^* + \text{H}^* \rightarrow \text{NHNH}_3^*$	0.21	-0.45
$\text{NNH}_3^* \rightarrow \text{N}^* + \text{NH}_3^*$	0.21	-1.52
$\text{NH}_2\text{NH}_2^* + \text{H}^* \rightarrow \text{NH}_2\text{NH}_3^*$	0.37	-0.40
$\text{NHNH}_3^* + \text{H}^* \rightarrow \text{NH}_2\text{NH}_3^*$	0.24	-1.37
$\text{NHNH}_3^* \rightarrow \text{NH}^* + \text{NH}_3^*$	0.65	-1.23
$\text{NH}_2\text{NH}_3^* \rightarrow \text{NH}_2^* + \text{NH}_3^*$	1.66	-1.38

<sup>a</sup> The asterisk (\*) indicates that the species is adsorbed on the Au(111) surface.

$\text{NNH}_3$  than  $\text{NHNH}_2$  is observed (0.72 eV vs. 0.24 eV), indicating that the  $\text{NNH}_3$  formation is kinetically inhibited, as shown in Fig. 3(b). Starting with  $\text{NHNH}_2$  further reduction, the first  $\text{NH}_3$  molecule may be produced *via* two elementary reaction steps involving hydrogenation into the adsorbed  $\text{NHNH}_3$  species and

its subsequent N–N bond scission with the formations of the adsorbed  $\text{NH}$  species and  $\text{NH}_3$  product, and the corresponding barrier is calculated as *ca.* 0.21 and 0.65 eV. The adsorbed  $\text{NH}_2\text{NH}_2$  intermediate is also possible to be formed through  $\text{NHNH}_2$  surface hydrogenation with the surmountable barrier of *ca.* 0.31 eV at room temperature in distal pathways. As above elaborated,  $\text{NH}_2\text{NH}_2$  species can further be reduced into the adsorbed  $\text{NH}_2$  species and the first  $\text{NH}_3$  molecule *via* surface hydrogenation and N–N bond scission. The adsorbed  $\text{NH}$  and  $\text{NH}_2$  intermediates can finally lead to the second  $\text{NH}_3$  molecule *via* surface hydrogenation in distal pathways. However, we note that the extremely high barrier is required for N–N bond cleavage in  $\text{NH}_2\text{NH}_3$  species to form  $\text{NH}_3$  product (*ca.* 1.66 eV) in associative alternating and distal mechanisms, thereby it can be concluded that  $\text{NH}_2\text{NH}_3$  species is only a spectator during  $\text{N}_2$  reduction in gas phase due to its easy formation *via*  $\text{NHNH}_3$  and  $\text{NH}_2\text{NH}_2$  hydrogenation. The corresponding energetics of for the possible elementary reaction steps involved in  $\text{N}_2$  reduction pathways on Au(111) in gas phase are summarized in Table 1.

By scrutinizing the overall energy pathway diagram of associative alternating and distal mechanisms (see Fig. 3),  $\text{N}_2$  hydrogenation into  $\text{N}_2\text{H}$  species is rate determining step with the barrier of *ca.* 2.10 eV, suggesting that both alternating and distal pathways may be parallel and operable on Au(111) in gas phase. It is found that the barrier of rate determining step for the associative mechanism is notably lower than that of dissociative mechanism by comparing the barriers between these both mechanisms (*ca.* 2.10 eV vs. 6.02 eV), suggesting that the associative mechanism including the adsorbed  $\text{NHNH}$ ,  $\text{NNH}_2$ ,  $\text{NH}_2\text{NH}_2$ ,  $\text{NHNH}_3$  and  $\text{NH}_2\text{NH}_3$  intermediates is more favorable.



**Fig. 4** The optimal associative mechanisms on Au(111) in gas phase: (a) alternating pathways *via*  $\text{NHNH}$  species; (b) distal pathways *via*  $\text{NNH}_2$  species (\* represents surface adsorption).



The optimal associative mechanisms including alternating and distal pathways on Au(111) in gas phase are summarized in Fig. 4. Images of reactants, products and transition states for  $N_2$  reduction into  $NH_3$  via the optimal associative mechanisms are included in ESI, as shown in Fig. S3–S13.<sup>†</sup> However, we also note that the required barrier for initial  $N_2$  hydrogenation is extremely high, which may be able to ascribed to weakly bonded  $N_2$  molecule on Au(111) with the adsorption energy of *ca.*  $-0.03$  eV. Furthermore,  $N\equiv N$  bond length of  $N_2$  on Au(111) is almost identical with that of isolated  $N_2$  molecule, *ca.*  $1.11$  Å.

### 3.2 $N_2$ electroreduction mechanism at Au(111)/ $H_2O$ interface

Our present proposed H coverage-dependent Au(111)/ $H_2O$  electrochemical interface model is utilized to simulate  $N_2$  electroreduction pathways, including dissociative and associative mechanisms. The present calculated thermodynamically required equilibrium potential of *ca.*  $-0.22$  V (vs. RHE) when  $\theta_H$  is equal with zero is focused. Fig. 1 shows the overall energy pathway diagram of  $N_2$  electroreduction into  $NH_3$  through dissociative mechanism. The largest barrier for this mechanism is initial  $N\equiv N$  bond scission to form the adsorbed N atoms with an activation barrier of *ca.*  $4.90$  eV at  $-0.22$  V (vs. RHE), thus being rate determining step of overall reaction. Although the barrier for  $N_2$  dissociation is significantly decreased at Au(111)/ $H_2O$  electrochemical interface by comparing with that in gas phase ( $4.90$  eV vs.  $6.02$  eV), it is still extremely high and difficult to be overcome. An activation barrier of *ca.*  $1.75$  eV is required for initial  $N_2$  electroreduction into  $N_2H$  species at the present simulated Au(111)/ $H_2O$  interface in associative mechanisms, as can be seen in Fig. 5. The barrier for  $N_2H$  further electroreduction into the surface adsorbed  $NHNH$  and  $NNH_2$  species in alternating and distal pathways is calculated as *ca.*  $0.22$  and  $0.01$  eV, respectively, suggesting that both  $NHNH$  and  $NNH_2$  species are possible key intermediates during  $N_2$  electroreduction on Au(111) because of extremely low formation barriers.

Beginning with  $NHNH$  further electroreduction in alternating pathways, we find that the adsorbed  $NHNH_2$  species is unstable at Au(111)/ $H_2O$  interface, which can be spontaneously

electrochemically reduced to form the surface adsorbed  $NH_2NH_2$  species by proton-coupled electron transfer with the surmountable barrier of *ca.*  $0.24$  eV at room temperature, as shown in Fig. 5(a). The first  $NH_3$  molecule can be produced by further electroreduction of  $NH_2NH_2$  species through two elementary reaction steps including  $NH_2NH_3$  formation and its subsequent N–N bond scission. The corresponding barrier is calculated as *ca.*  $0.48$  and  $0.69$  eV, respectively. It is noted that the barrier for  $NH_2NH_3$  further electroreduction into the adsorbed  $NH_2$  species and  $NH_3$  product is significantly decreased at Au(111)/ $H_2O$  interface compared with that in gas phase ( $0.69$  eV vs.  $1.66$  eV), suggesting that the presence of electrochemical interface may be able to alter  $N_2$  reduction mechanisms. The formed  $NH_2$  species can finally lead to production of the second  $NH_3$  molecule with an activation barrier of *ca.*  $0.56$  eV. Starting with  $NNH_2$  intermediate formed in distal pathways, it is found that the adsorbed  $NHNH_2$  and  $NNH_3$  species observed in gas phase are unstable at Au(111)/ $H_2O$  interface, which can be also spontaneously electrochemically reduced to form the surface adsorbed  $NH_2NH_2$  and  $NHNH_3$  intermediates by proton-coupled electron transfer process. The required barrier for  $NNH_2$  electroreduction into  $NH_2NH_2$  and  $NHNH_3$  is calculated as only *ca.*  $0.11$  and  $0.05$  eV, respectively, as shown in Fig. 5(b), suggesting that  $NH_2NH_2$  and  $NHNH_3$  species is possible intermediate in distal pathways. Similarly,  $NH_2NH_2$  intermediate can be further electrochemically reduced to form the adsorbed  $NH_2$  species and the first  $NH_3$  molecule via above-mentioned two elementary reaction steps. Two possibilities are also considered for further electroreduction of  $NHNH_3$  intermediate at Au(111)/ $H_2O$  interface, one is  $NH_2NH_3$  formation, and another is formation of the adsorbed  $NH$  species and production of the first  $NH_3$  molecule via N–N bond scission. It is found that the required barrier for the former is notably lower than that of the latter ( $0.24$  eV vs.  $0.94$  eV), indicating that  $NH_2NH_3$  formation is more favorable. Thus, we can conclude that the first  $NH_3$  molecule is possible to be produced by N–N bond scission of  $NH_2NH_3$  species at Au(111)/ $H_2O$  interface, rather than  $NHNH_3$  species as observed in gas phase, again suggesting that the influence of electrochemical interface containing solvation effect on  $N_2$  reduction pathways. The corresponding energetics of for various possible reaction steps involved during

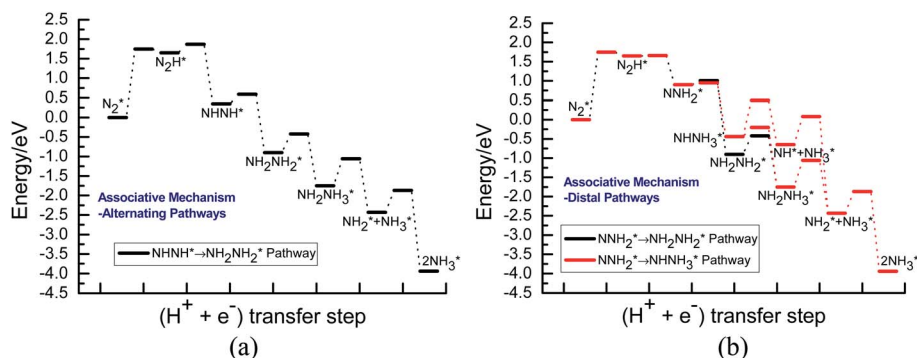


Fig. 5 Overall energy pathway diagram of  $N_2$  electroreduction into  $NH_3$  via associative mechanism at the present proposed Au(111)/ $H_2O$  interface: (a) alternating pathways; (b) distal pathways.

**Table 2** Activation barriers ( $\Delta E_{\text{act}}$ , eV) and reaction energies ( $\Delta E_{\text{reac}}$ , eV) for various possible reaction steps involved in  $\text{N}_2$  electroreduction pathways at Au(111)/ $\text{H}_2\text{O}$  interface

Reaction steps <sup>a</sup>	$\Delta E_{\text{act}}$ , eV	$\Delta E_{\text{reac}}$ , eV
$\text{N}_2 + * \rightarrow \text{N}^* + \text{N}^*$	4.93	4.92
$\text{N}^* + (\text{H} + \text{e}^-) \rightarrow \text{NH}^*$	0.33	-1.37
$\text{NH}^* + (\text{H} + \text{e}^-) \rightarrow \text{NH}_2^*$	0.73	-1.78
$\text{NH}_2^* + (\text{H} + \text{e}^-) \rightarrow \text{NH}_3^*$	0.56	-1.51
$\text{N}_2 + * + (\text{H} + \text{e}^-) \rightarrow \text{N}_2\text{H}^*$	1.75	1.65
$\text{N}_2\text{H}^* + (\text{H} + \text{e}^-) \rightarrow \text{NHNH}^*$	0.22	-1.30
$\text{N}_2\text{H}^* + (\text{H} + \text{e}^-) \rightarrow \text{NNH}_2^*$	0.01	-0.75
$\text{NHNH}^* + 2(\text{H} + \text{e}^-) \rightarrow \text{NH}_2\text{NH}_2^*$	0.24	-1.25
$\text{NNH}_2^* + 2(\text{H} + \text{e}^-) \rightarrow \text{NH}_2\text{NH}_2^*$	0.11	-1.80
$\text{NNH}_2^* + 2(\text{H} + \text{e}^-) \rightarrow \text{NHNH}_3^*$	0.05	-1.34
$\text{NH}_2\text{NH}_2^* + (\text{H} + \text{e}^-) \rightarrow \text{NH}_2\text{NH}_3^*$	0.48	-0.85
$\text{NHNH}_3^* + (\text{H} + \text{e}^-) \rightarrow \text{NH}_2\text{NH}_3^*$	0.24	-1.31
$\text{NHNH}_3^* \rightarrow \text{NH}^* + \text{NH}_3^*$	0.94	-0.21
$\text{NH}_2\text{NH}_3^* \rightarrow \text{NH}_2^* + \text{NH}_3^*$	0.69	-0.68

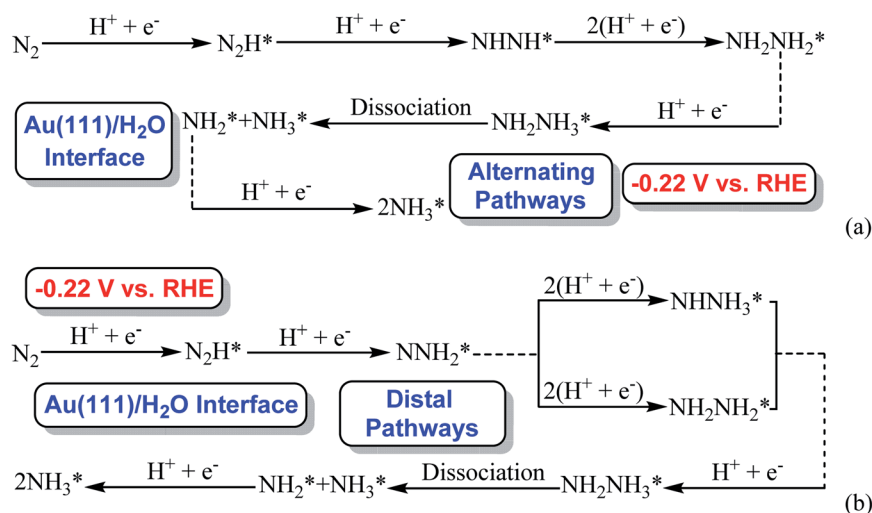
<sup>a</sup> The asterisk (\*) indicates that the species is adsorbed on the Au(111) surface.

$\text{N}_2$  electroreduction at Au(111)/ $\text{H}_2\text{O}$  interface are summarized in Table 2.

By scrutinizing the overall energy pathway diagram, our present simulation results reveal that the rate determining step for  $\text{N}_2$  electroreduction into  $\text{NH}_3$  via associative alternating and distal mechanisms at Au(111)/ $\text{H}_2\text{O}$  interface is  $\text{N}_2$  electroreduction into form the adsorbed  $\text{N}_2\text{H}$  species, suggesting that these both mechanisms may be able to parallelly occur. The corresponding barrier is significantly lower than that of rate determining step in the dissociative mechanism (1.75 eV vs. 4.90 eV). Thus, it can be concluded that the associative mechanisms are more facile to occur at the present simulated Au(111)/ $\text{H}_2\text{O}$  interface. The optimal associative alternating and distal mechanisms are summarized in Fig. 6. Images of

reactants, products and transition states for  $\text{N}_2$  electroreduction into  $\text{NH}_3$  via the optimal associative mechanisms at the present simulated Au(111)/ $\text{H}_2\text{O}$  interface are included in ESI, as shown in Fig. S14–S23.†

Our present calculated  $\text{N}_2$  electroreduction mechanisms at Au(111)/ $\text{H}_2\text{O}$  electrochemical interface are partially inconsistent with the previous theoretical study from Janik *et al.*, in which only alternating pathway via  $\text{NHNH}$  species is favorable on late transition metals at 0 V (vs. RHE) with rate determining step of  $\text{N}_2$  electroreduction into  $\text{N}_2\text{H}$  species by calculating explicitly the potential-dependent barriers for elementary electroreduction reactions (see Fig. 7).<sup>51</sup> Furthermore, the predicted  $\text{NHNH}_2$  species on late transition metals at 0 V (vs. RHE) is found to may be unstable at Au(111)/ $\text{H}_2\text{O}$  interface, which can be spontaneously reduced to form adsorbed  $\text{NH}_2\text{NH}_2$  species by proton-coupled electron transfer with the surmountable barrier at room temperature. The difference of interface model may lead to partially inconsistent  $\text{N}_2$  electroreduction mechanisms, in which only a  $\text{H}_2\text{O}$  molecule is employed to simulate solvent effect in previous theoretical work from Janik *et al.*, being insufficient to model interactions among solvent, adsorbates and surface. However, our present theoretical results can be confirmed by the most recent experimental study from Shao *et al.*, in which the adsorbed intermediates such as  $\text{N}_2\text{H}$ ,  $\text{NHNH}$ ,  $\text{NNH}_2$ ,  $\text{NH}_2\text{NH}_2$ ,  $\text{NH}_2\text{NH}_3$  and  $\text{NH}_2$  may be able to be formed during  $\text{N}_2$  electroreduction on the Au electrodes at potentials of ca. -0.10 V (vs. RHE) or lower due to detected  $\text{N}_2\text{H}_y$  ( $1 \leq y \leq 4$ ) reaction species using the surface-enhanced infrared absorption spectroscopy technique,<sup>42</sup> further validating the rationality of our present employed Au(111)/ $\text{H}_2\text{O}$  interface model. Simultaneously, we also note that the presence of electrochemical interface makes the barrier of rate determining step in the associative mechanisms decrease compared with that in gas phase (1.75 eV vs. 2.10 eV), indicating that the presence of solvent effect could help stabilize the adsorbed  $\text{N}_2\text{H}$  species and lower the corresponding barrier value to ca. 1.75 eV. Even so, barrier of 1.75 eV is still high for  $\text{N}_2$  electroreduction, making



**Fig. 6** The optimal associative mechanisms at the present simulated Au(111)/ $\text{H}_2\text{O}$  interface: (a) alternating pathways via  $\text{NHNH}$  species; (b) distal pathways via  $\text{NNH}_2$  species (\* represents surface adsorption).



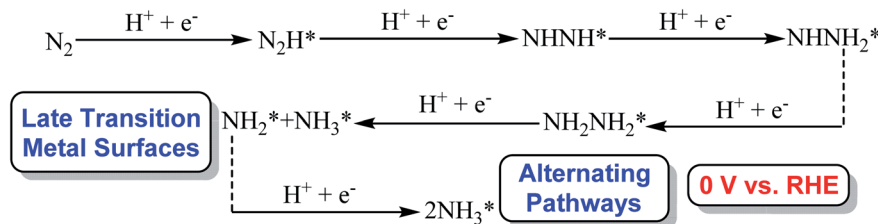


Fig. 7 The optimal associative alternating pathways *via* NHNH species on late transition metal surfaces at 0 V (vs. RHE) from previous work conducted by Janik *et al.* (\* represents surface adsorption).<sup>51</sup>

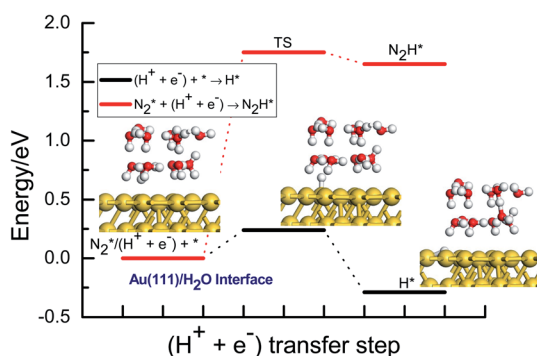


Fig. 8 Energy pathway diagram of competitive hydrogen evolution reaction and initial  $N_2$  electroreduction into  $N_2H$  species at the present proposed Au(111)/ $H_2O$  electrochemical interface.

this process be still challenging, which may be able to be regarded as origin of experimentally observed high overpotential. The almost not changed  $N\equiv N$  bond length of *ca.* 1.11 Å at Au(111)/ $H_2O$  interface again shows weakly adsorbed  $N_2$  molecule compared with that of isolated  $N_2$  molecule.

The potential of the hydrogen evolution reaction is very approximate to the thermodynamically required potential for  $N_2$  electroreduction under ambient conditions. Therefore, overcoming the undesirable hydrogen evolution reaction competition may become the critical challenge during  $N_2$  electroreduction at present, which can greatly reduce the faradaic efficiency of reaction. Herein, the barrier of hydrogen evolution reaction is evaluated by using our present proposed H coverage-dependent Au(111)/ $H_2O$  interface model at  $-0.22$  V (vs. RHE) and compared with that of rate determining step for the optimal associative mechanisms during  $N_2$  electroreduction into  $NH_3$  to quantify the challenge in designing the high efficient electrocatalysts. As can be seen in Fig. 8, the calculated activation barrier of *ca.* 0.24 eV is remarkably lower than that of initial  $N_2$  electroreduction into  $N_2H$  intermediate (*ca.* 1.75 eV). Furthermore, we also observe that the formed  $N_2H$  intermediate may be unstable, which can be facile to back to  $N_2$  molecule with extremely low barrier of *ca.* 0.10 eV. The present comparison and analysis can well explain why the catalytic activity of Au electrodes is usually unsatisfactory although the relatively high faradaic efficiency can be achieved experimentally during  $N_2$  electroreduction.<sup>24,25,42</sup> Accordingly, the single descriptor may be able to be proposed to scale catalytic activity of electrocatalysts for  $N_2$  electroreduction, in which an ideal

electrocatalyst should be able to reduce barrier for initial  $N_2$  electroreduction into  $N_2H$  intermediate. In this way,  $N_2$  electroreduction pathways can be facilitated and the yield of  $NH_3$  can be enhanced.

### 3.3 Origin of solvation effect on $N_2$ reduction mechanisms

As above discussed, the presence of electrochemical interface including solvation effect could change  $N_2$  reduction mechanism, especially it can reduce the barrier of rate determining step. To ascertain the origin of difference of  $N_2$  reduction mechanisms at gas phase and the present simulated electrochemical interface on Au(111), the charge density difference analyses are carried out in our present work taking example for  $N_2$  adsorption on Au(111). It is observed that there is almost not significant electron accumulation and interaction between  $N_2$  molecule and surface Au atoms under gas- and aqueous-phase environment, as shown in Fig. 9, confirming the above-mentioned weakly binding  $N_2$  molecule on Au(111) and almost identical  $N\equiv N$  bond length compared with isolated  $N_2$  molecule, thus explaining why high barrier is required for initial  $N_2$  reduction. However, the significant electron interactions are found between  $N_2$  and  $H_2O$  cluster at the present simulated electrochemical interface. The existence of H bonds and interactions of  $N_2$  with  $H_2O$  molecules at the Au(111)/ $H_2O$  interface may lead to easier initial  $N_2$  electroreduction, as observed decreased barrier value.

Based on the above conclusions, we can conclude that the decreased barrier for rate determining step may be able to be ascribed to electronic interactions between  $N_2$  and  $H_2O$  cluster. Therefore, the quantitative analysis of electronic structures will facilitate well understanding the origin of solvation effect on  $N_2$  electroreduction mechanisms. According to projected electron densities of states, the Löwdin charge (the number of valence electron) of  $N_2$  can be obtained from Löwdin population analyses on Au(111) in gas phase and at the present simulated electrochemical interface. Table 3 gives the electron gains ( $\Delta q$ ) for  $N_2$  molecule, respectively, which could be obtained by subtracting the Löwdin charge of isolated  $N_2$  molecule from that in the optimized structure. Simultaneously,  $\Delta q$  of  $H_2O$  cluster at the present simulated electrochemical interfaces are also given in Table 3 compared with that of free  $N_2$  adsorbed Au(111)/ $H_2O$  interface. A positive value of  $\Delta q$  will imply a gain of electron by the component. It can be found that only slight electron transfer occurs between  $N_2$  molecule and Au(111) surface in gas phase due to little electron gains of total, s and p orbitals of  $N_2$ , as



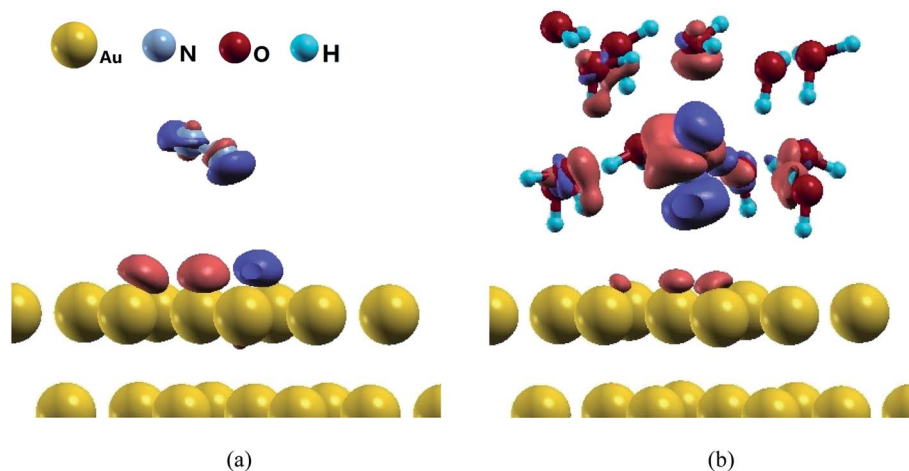


Fig. 9 The charge density difference maps for  $N_2$  (a) in gas-phase and (b) at the Au(111)/ $H_2O$  interface.

**Table 3** The electron gains ( $\Delta q$ ) of total, s and p orbitals of  $N_2$  molecule on Au(111) and at the present simulated Au(111)/ $H_2O$  interface;  $\Delta q$  of total, s and p orbitals of  $H_2O$  cluster in  $N_2$  adsorbed Au(111)/ $H_2O$  interface

		Difference of electron ( $\Delta q$ )		
		Total	s	p
Au(111)	$N_2$	−0.0284	−0.0271	−0.0013
Au(111)/ $H_2O$ interface	$N_2$	−0.0147	−0.0385	+0.0238
	$H_2O$ cluster	+0.0188	+0.0384	−0.0195

found weakly bonded  $N_2$  molecule on Au(111) with the adsorption energy of only *ca.* −0.03 eV, confirming the above observed no significant electron accumulation and interaction based on the charge density difference analyses. However, we notice that the nature of electronic interactions at the Au(111)/ $H_2O$  interface is practically not the same as that observed in gas phase. The significant electron transfer occurs between  $N_2$  molecule and  $H_2O$  cluster, namely, the total net electrons of  $H_2O$  cluster are positive because s orbital can gain more electrons although p orbital loses electrons, whereas the total net electrons of  $N_2$  is negative, in which s orbital loses electrons and p orbital gains electrons. Thus, it can be concluded that the notable different electron interactions on Au(111) in gas phase and at the electrochemical interface may result in the difference of  $N_2$  reduction mechanisms.

## 4. Conclusions

In the present paper, an improved H coverage-dependent Au(111)/ $H_2O$  electrochemical interface model is proposed, which is firstly used to study electroreduction mechanisms of  $N_2$  to  $NH_3$  at the thermodynamical equilibrium potential cooperated with electronic structure analysis. The calculated results show that the associative mechanism is more favorable on Au(111) and therein alternating and distal pathways may be

able to parallelly occur in gas phase and the present simulated electrochemical interface. The initial  $N_2$  reduction into  $N_2H$  intermediate is rate determining step, which may be able to be regarded as the origin of observed experimentally high overpotential during  $N_2$  electroreduction. However, the presence of electrochemical environment can significantly change  $N_2$  reduction pathway and decrease the barrier of rate determining step, in which  $NHNH_2$  and  $NNH_3$  species observed in gas phase are unstable at Au(111)/ $H_2O$  interface, which can be spontaneously electrochemically reduced to form adsorbed  $NH_2NH_2$  and  $NHNH_3$  intermediates by proton-coupled electron transfer process. The significant electron accumulation and interaction between  $N_2$  molecule and  $H_2O$  cluster may result in different  $N_2$  electroreduction pathways and the decreased barrier of rate determining step. The theoretical results display excellent consistency with the available experimental data, confirming the rationality of the present used Au(111)/ $H_2O$  interface model. The comparison of barrier between hydrogen evolution reaction and rate determining step well explains why the catalytic activity of Au electrodes is usually unsatisfactory although the relatively high faradaic efficiency can be experimentally achieved. Accordingly, the single descriptor may be able to be proposed, in which an ideal electrocatalyst should be able to reduce barrier for initial  $N_2$  electroreduction into  $N_2H$  intermediate. In this way,  $N_2$  electroreduction pathways can be facilitated and the yield of  $NH_3$  can be enhanced. We believe that the present study represents a progress to systematically study  $N_2$  electroreduction mechanisms based on an improved electrochemical interface model.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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