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Molecular modeling of adsorption of nitrogen and hydrazine in different surfaces

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OUTLINE

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- ❑ METHODS
  DFT calculations
- ❑ RESULTS
  N_2 and N_2H_4 on different surfaces
- ❑ CONCLUSIONS

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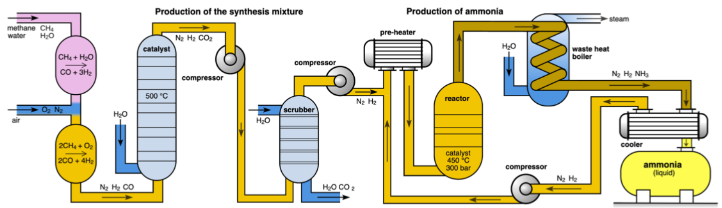
INTRODUCTION

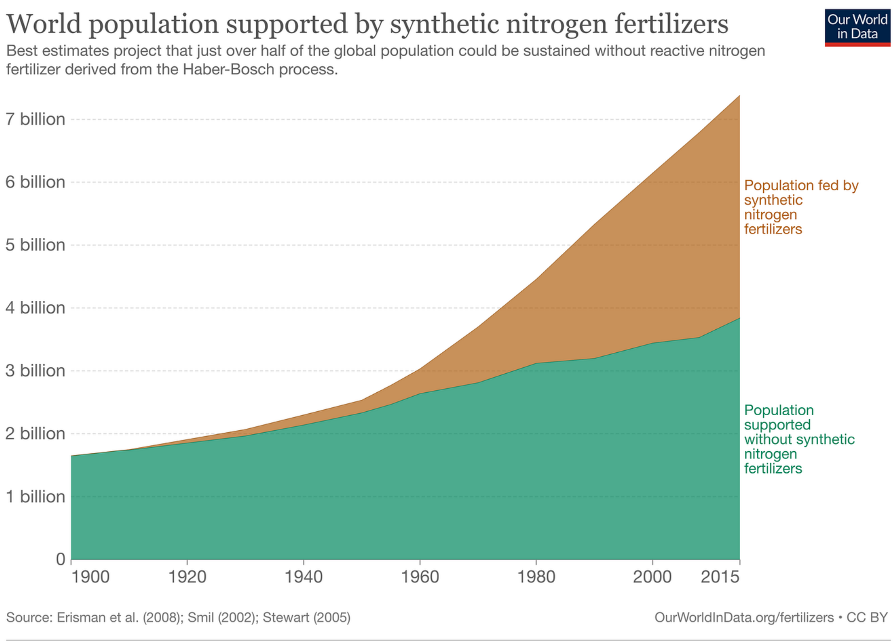
- NH_3 is widely used in various industries: Pharmaceutical, fertilizer production, dye synthetic fiber, food and agricultural, textile industries, nitric acid



- Most of the industrial NH_3 production uses Haber−Bosch technology



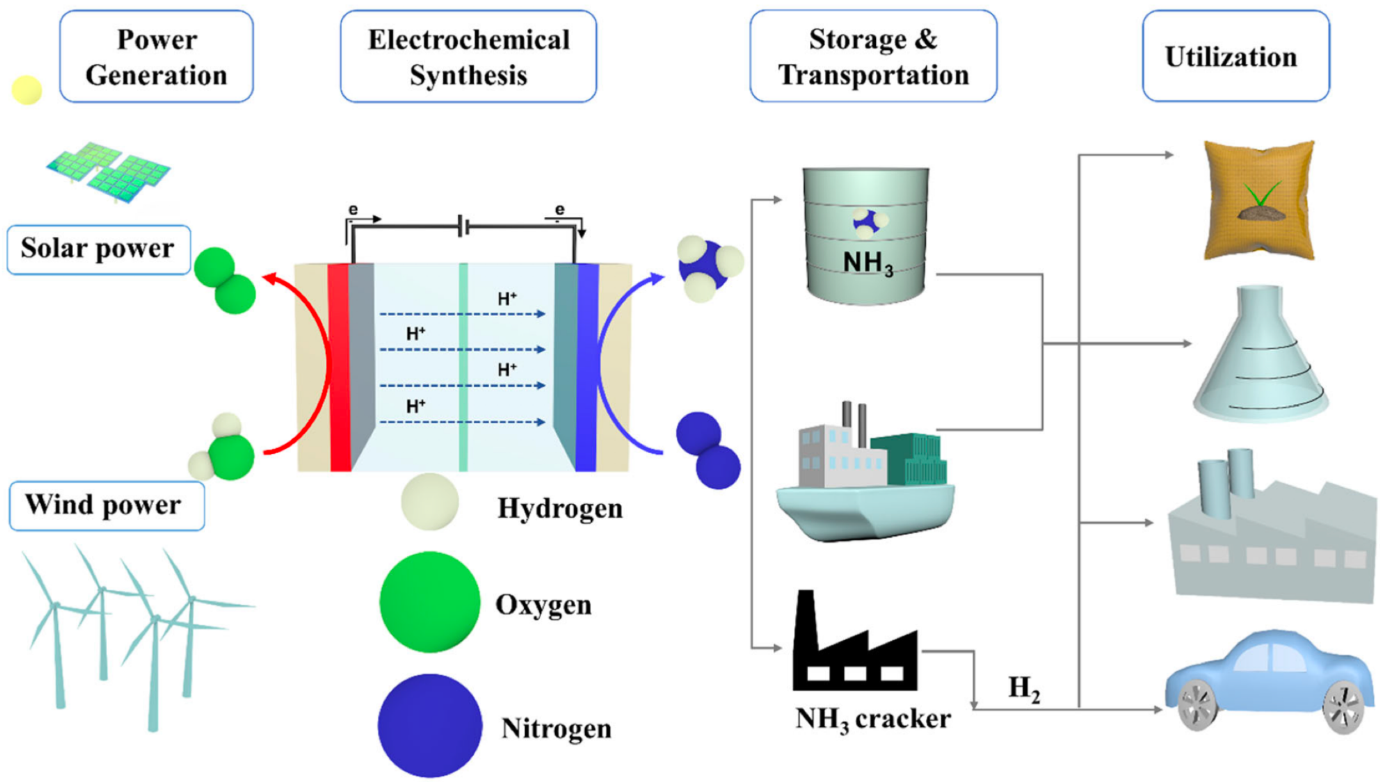
H−B consumes a large number of fossil fuels, ~300 million tons of CO_2 annually.



- A sustainable and economically viable process is required for the production of NH_3

several approaches: plasma technology, biochemical photocatalytic, photo-electrocatalysis, electrochemical, and chemical looping

- The electrochemical nitrogen reduction reaction (ENRR) process has excellent properties and opens a new avenue for carbon-free NH_3 production from N_2 directly.

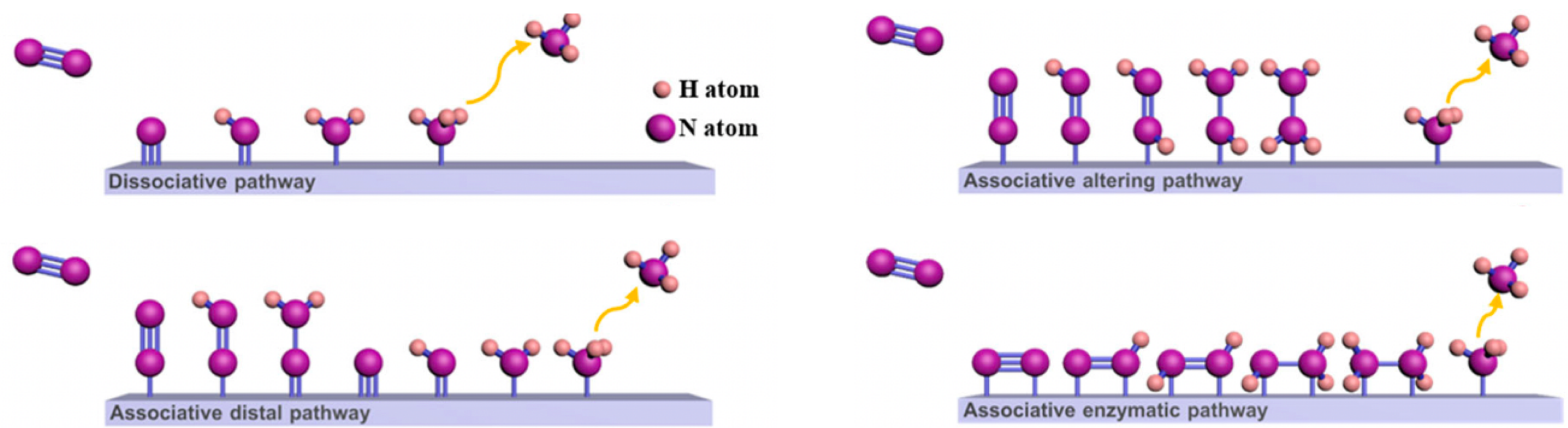


- There are several challenges to using ENRR in industrial green ammonia production
- Improving the catalytic activity of the electrodes:
  - Identify the active sites
  - understand the reaction mechanisms

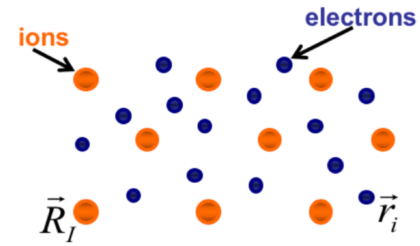
  two key aspects of the study of electrocatalytic reactions.

- Here, a catalyst plays a great role in breaking the N≡N triple bond because the N_2 molecule has a high bond energy (9.75 eV) with nonpolar characteristics.

- The electrocatalytic ENRR mainly engages three basic steps: (1) the adsorption of N_2 near the active surface area of the catalyst, (2) the hydrogenation process, and (3) the desorption of NH_3 molecules.



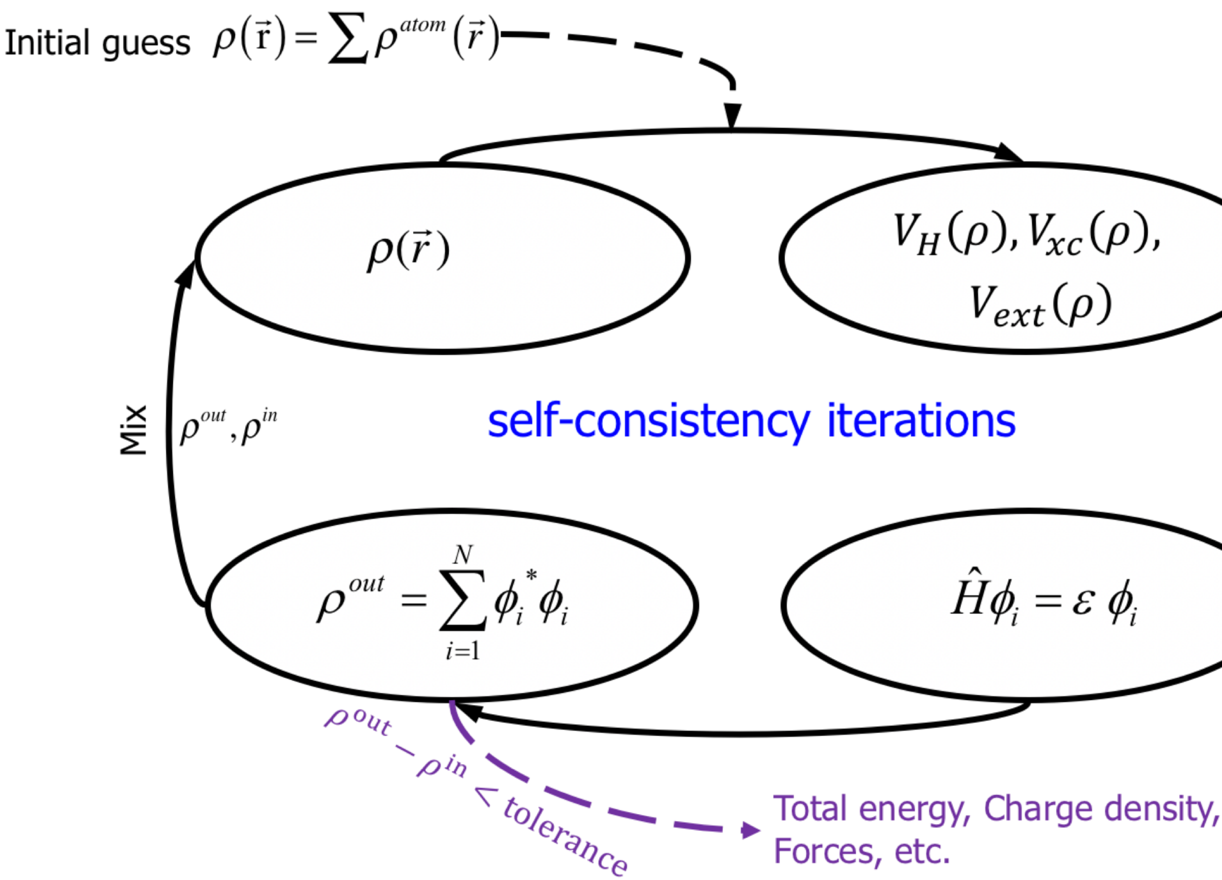
METHODS

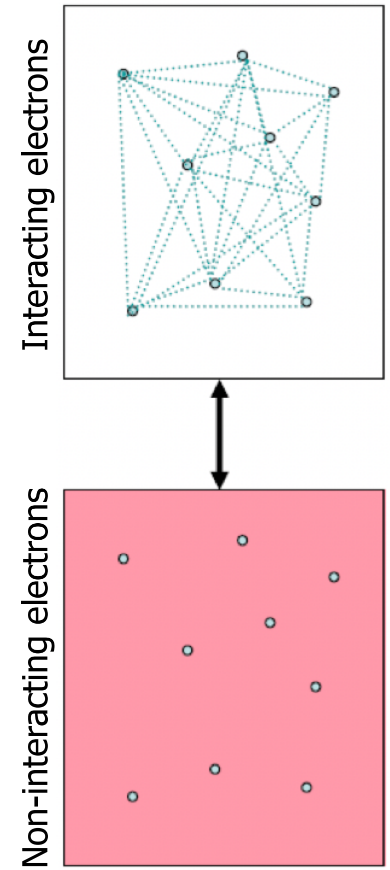


- Density Functional Theory (DFT) in the Khon-Sham formalism

  mapping from an interacting electron system to a non-interacting one

$$E[\rho] = T_0[\rho] + V_H[\rho] + V_{xc}[\rho] + V_{ext}[\rho] \geq E_{GS}$$





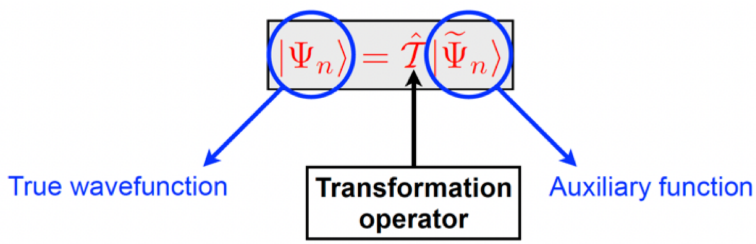
It is a program for modeling materials at the atomic scale, from first principles.

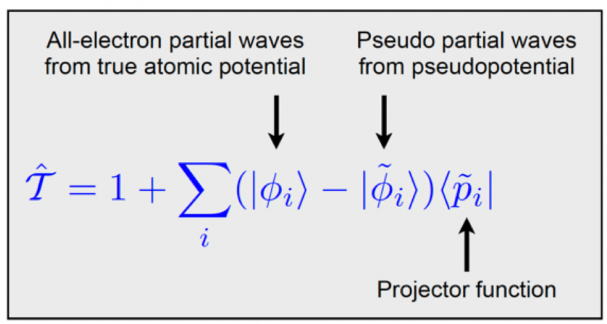
https://www.vasp.at

$$\left[\frac{1}{2}\nabla^2 + v_H(\vec{r}) + v_{ext}(\vec{r}) + v_{xc}(\vec{r})\right]\psi_{n\vec{k}}(\vec{r}) = \epsilon_{n\vec{k}}\psi_{n\vec{k}}(\vec{r})$$

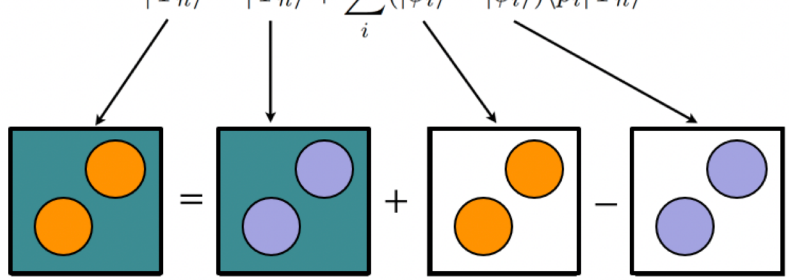
plane wave basis sets: $\psi_{n\vec{k}}(\vec{r}) = \frac{1}{\Omega}\sum_{\vec{G}} C_{n\vec{k}}(\vec{G})e^{i(\vec{k}+\vec{G})\cdot\vec{r}}$

- LAPW (Linearized Augmented Plane wave)



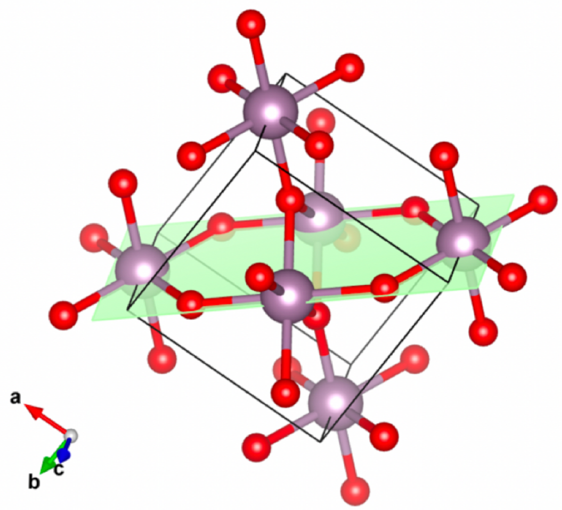


$$|\Psi_n\rangle = |\tilde{\Psi}_n\rangle + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle)\langle\tilde{p}_i|\tilde{\Psi}_n\rangle$$

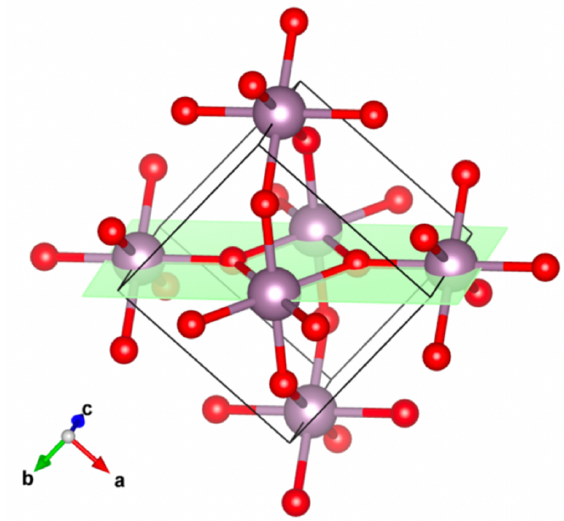


RESULTS

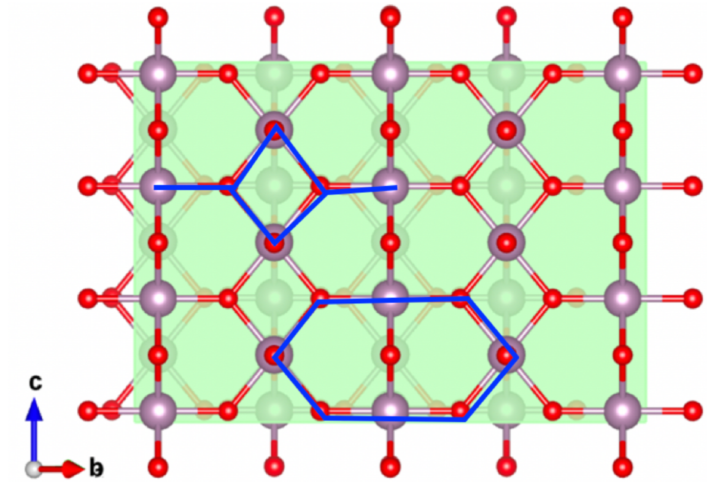
Molybdenum dioxide (MoO_2) {110} surfaces



$(1\bar{1}0)$



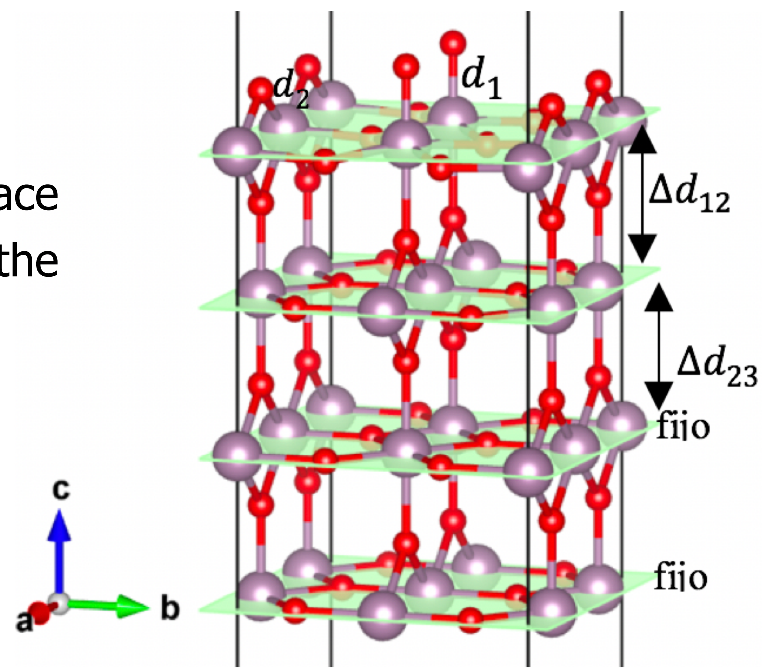
(110)



View of the plane $(1\bar{1}0)$ from direction $[1\bar{1}0]$

The O-terminated surface has a lower energy than the Mo-terminated one.

$\Delta E \sim 54.2\ \mathrm{meV/atom}$



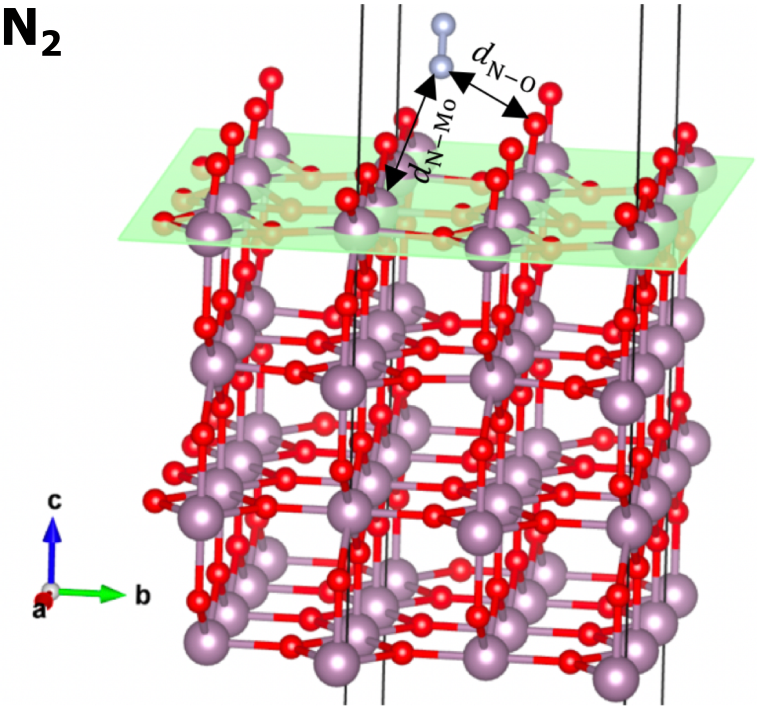
$\Delta d_{12} = +1.08\%$

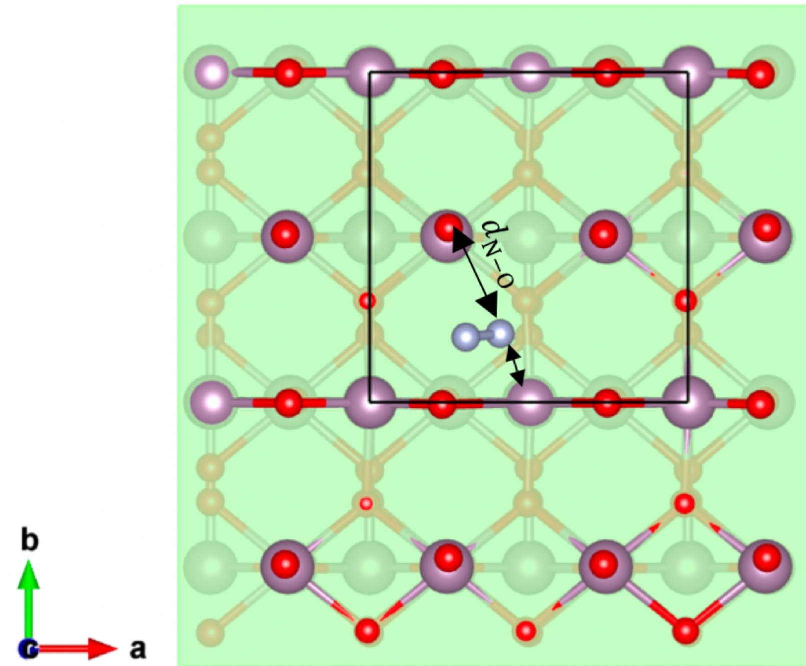
$\Delta d_{23} = -0.04\%$

$d_1 = 2.02 \rightarrow 1.71 Å$

$d_2 = 2.10 \rightarrow 1.96 Å$

SURF + N_2





$$d_{N-\text{plano}Mo} = 3.24\ \text{Å}$$

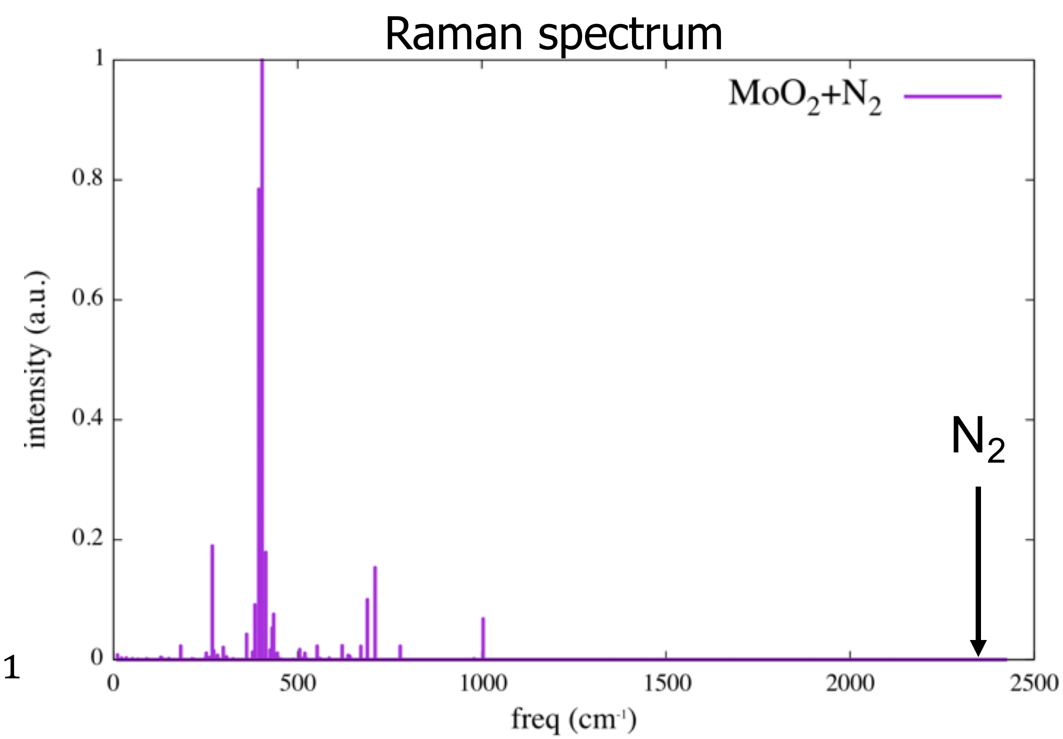
$$d_{N-O} = 2.83\ \text{Å}$$

$$d_{N-Mo} = 3.76\text{Å}$$

$$\theta_{N_2} = 39°\ \text{respect to Z}$$

$$E_{ad} = -0.57\ \text{eV} = -13.1\ \text{kcal/mol}$$

$$f = 2488.7 \rightarrow 2423.0\ \text{cm}^{-1}$$



SURF + N_2H_4

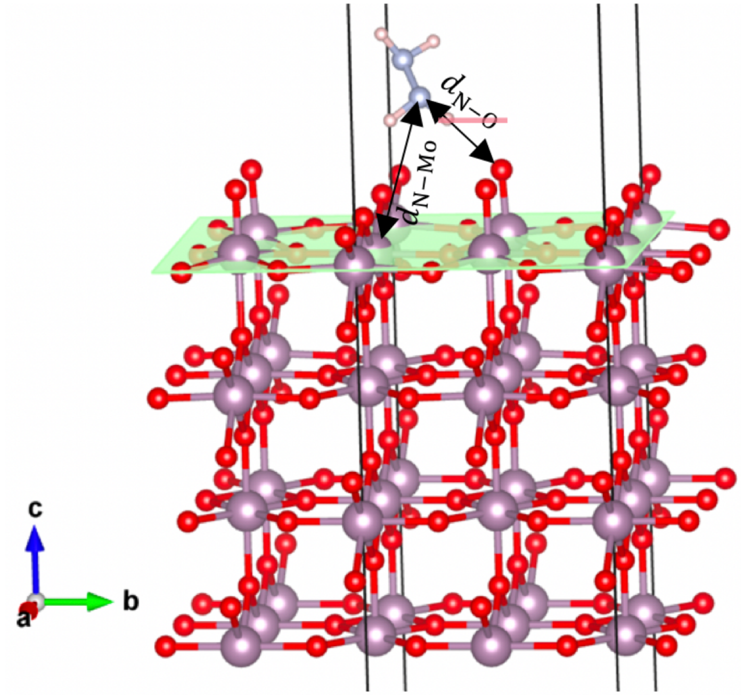
$$d_{N-\text{plano}Mo} = 3.87\text{Å}$$

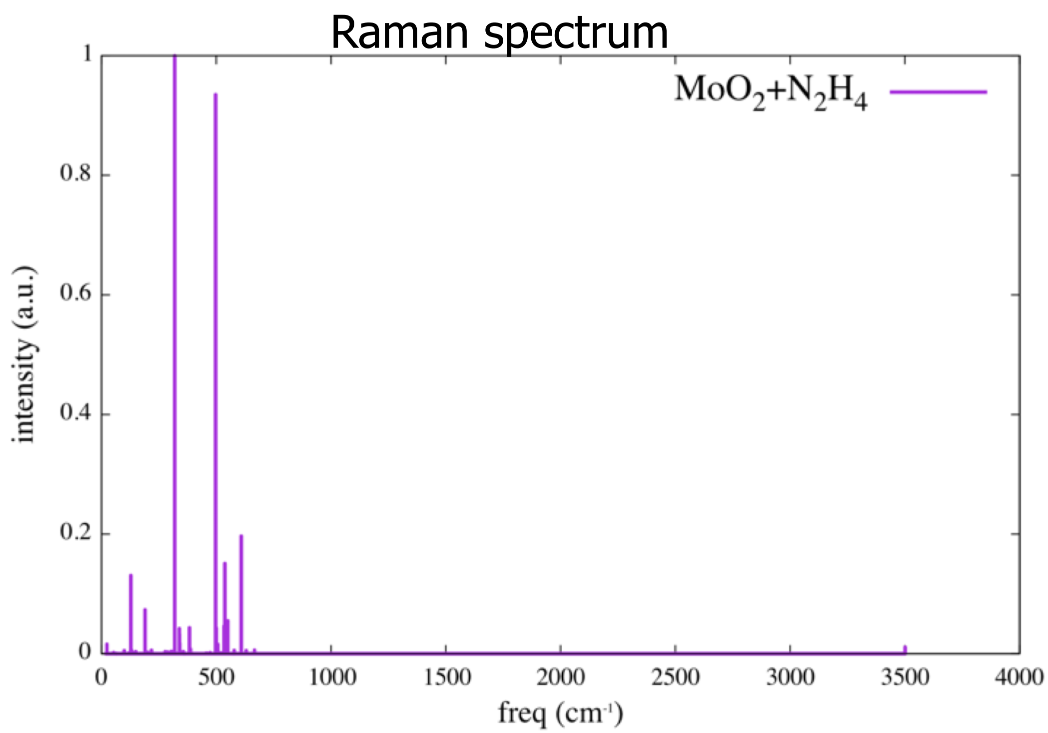
$$d_{N-O} = 3.27\ \text{Å}$$

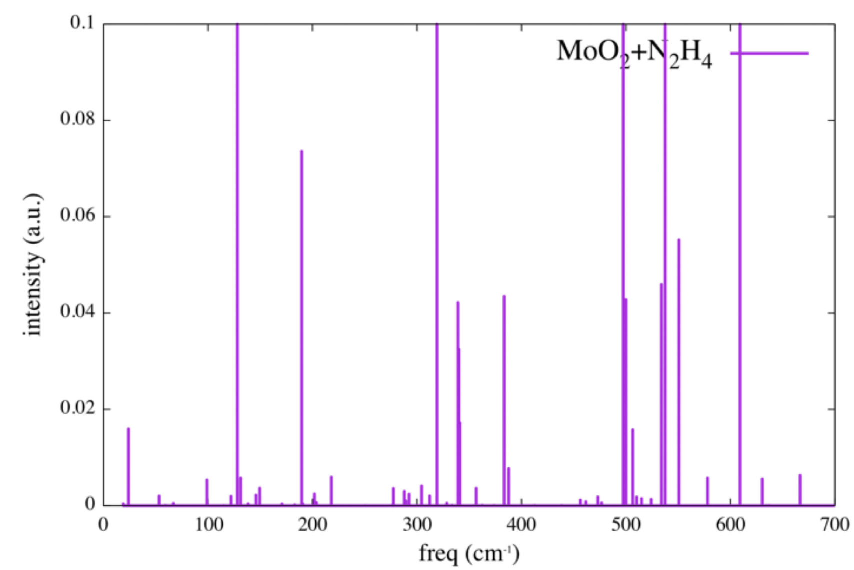
$$d_{N-Mo} = 4.39\text{Å}$$

$$\theta_{N_2} = 53° \text{ respect to Z}$$

$$E_{ad} = -0.78\ \text{eV} = -18.0\ \text{kcal/mol}$$





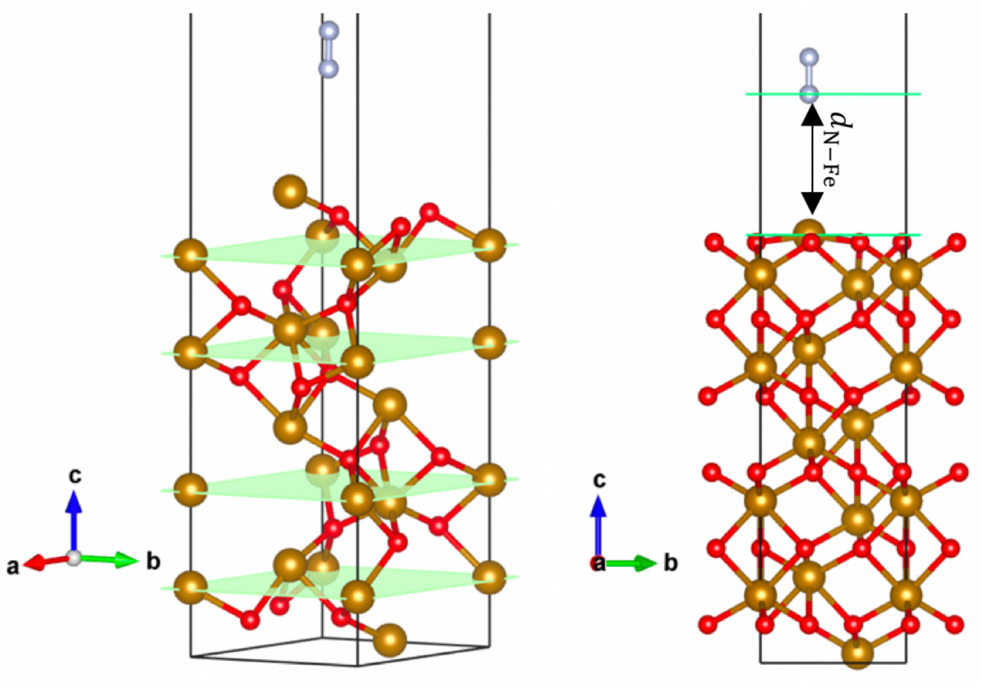


$$f_{N_2H_4} = 649.0, 1302.6\ \text{cm}^{-1}$$

Hematite (Fe_3O_4) (001) surface

$$\gamma = \frac{E_{slab} - N\, E_{bulk}/atom}{2A} = 0.1304\,\frac{\mathrm{eV}}{\text{Å}^2} = 1.51\,\frac{\mathrm{J}}{\mathrm{m}^2}$$

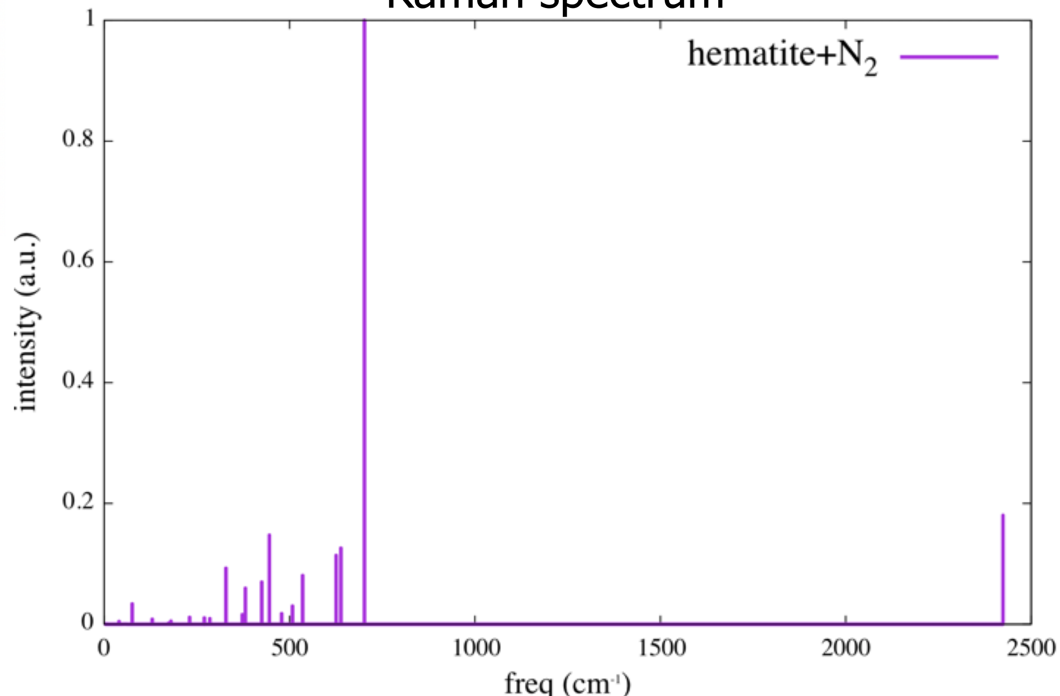
SURF + N_2



$$d_{N-\mathrm{plano}Mo} = 4.25\ \text{Å}$$

$$\theta_{N_2} = 0°\ \text{respect to Z}$$

Raman spectrum



$$d_{N-Fe} = 4.28\ \text{Å}$$

$$E_{ad} = -0.45635\ \mathrm{eV} = -10.5\ \mathrm{kcal/mol}$$

$$f = 2488.7 \rightarrow 2424.0\ \mathrm{cm}^{-1}$$

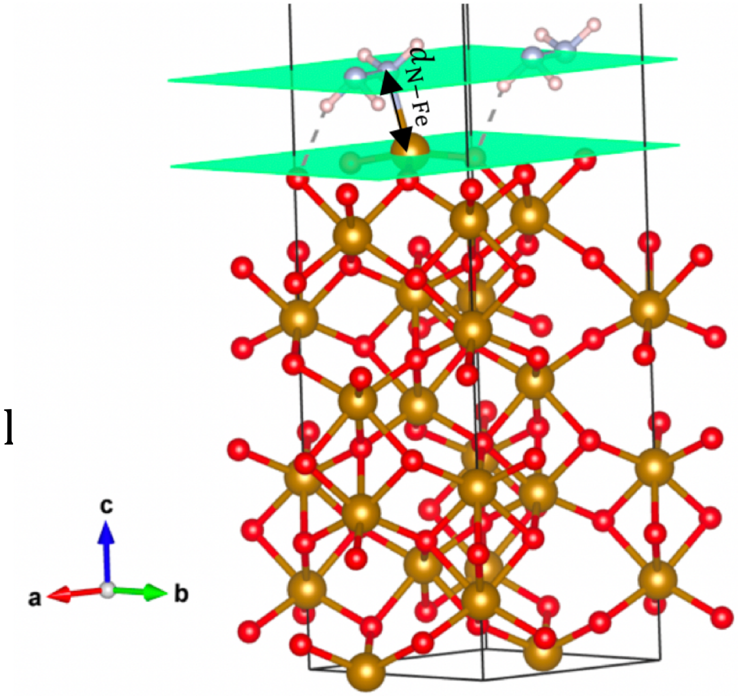
SURF + N_2H_4

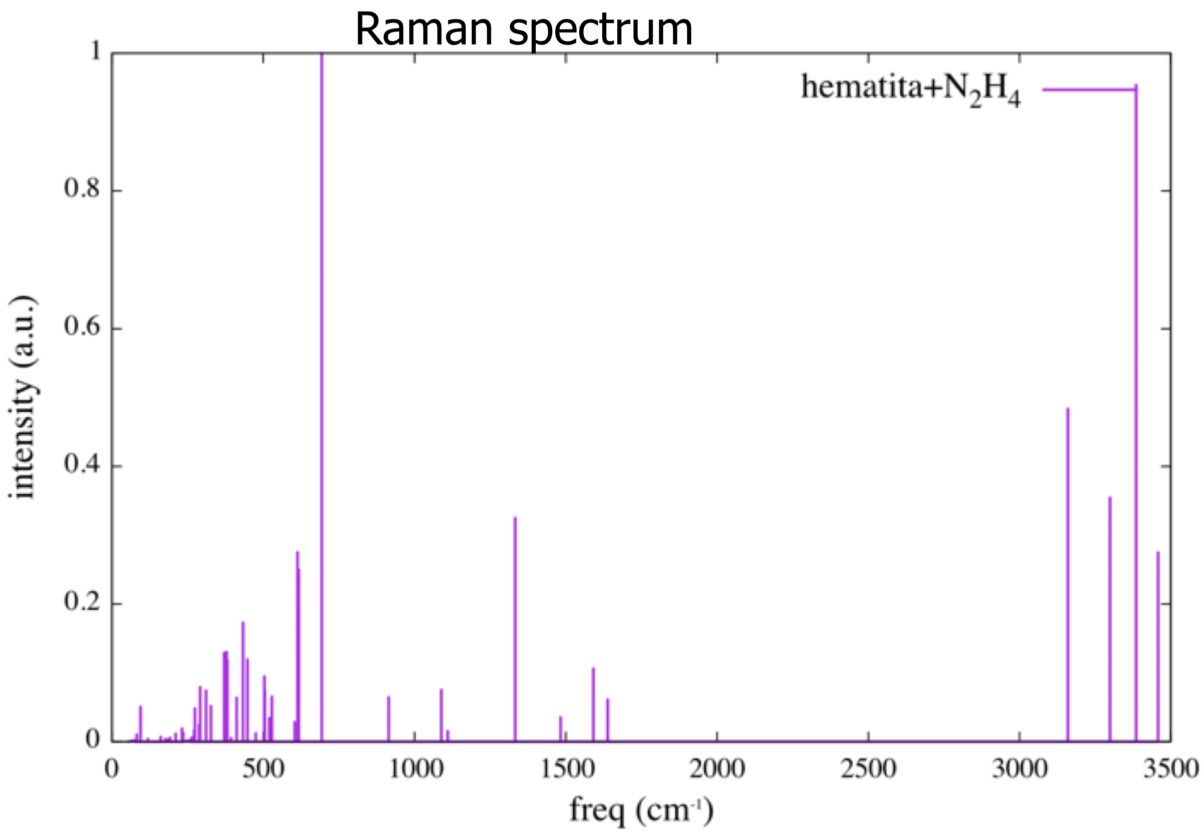
$$d_{N-\text{plano}Mo} = 2.10\ \text{Å}$$

$$d_{N-Fe} = 2.18\ \text{Å}$$

$$\theta_{N_2} = 87.4°\ \text{respect to Z}$$

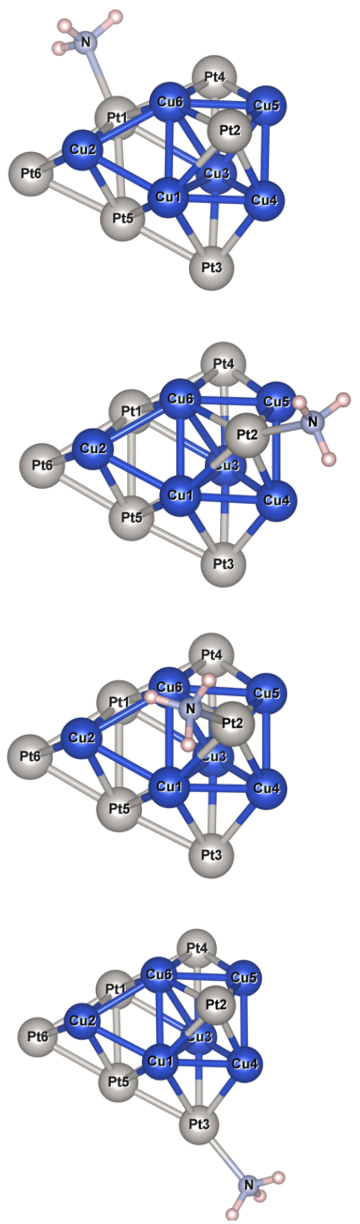
$$E_{ad} = -2.402\ \text{eV} = -55.4\ \text{kcal/mol}$$





$$f_{N_2H_4} = 649.0, 1302.6\ \text{cm}^{-1}$$

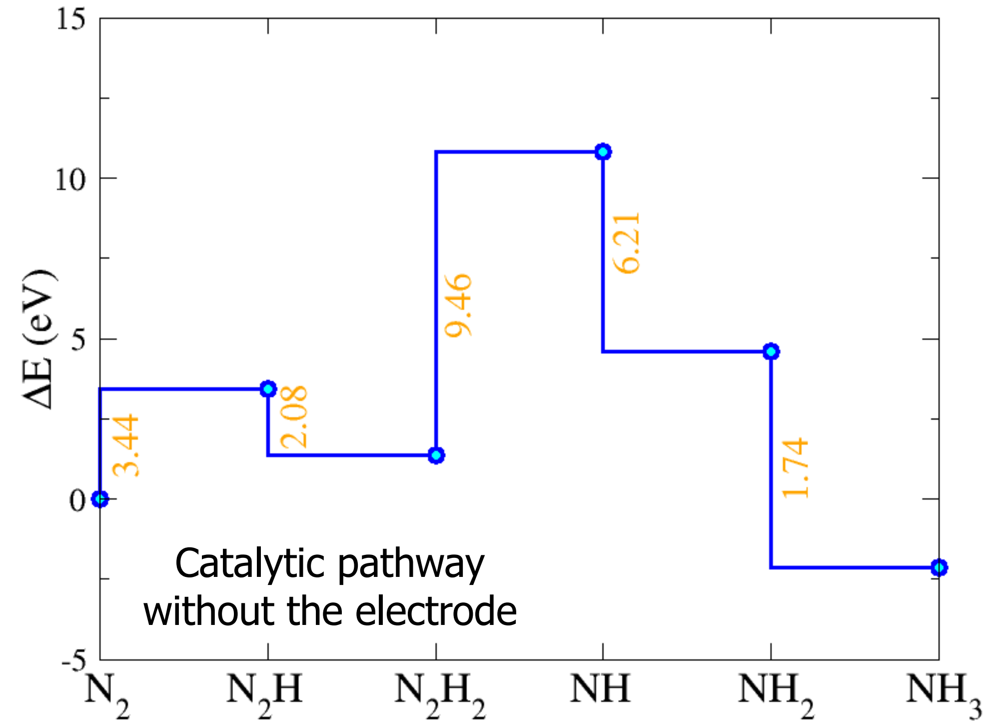
Cluster Pt_6Cu_6

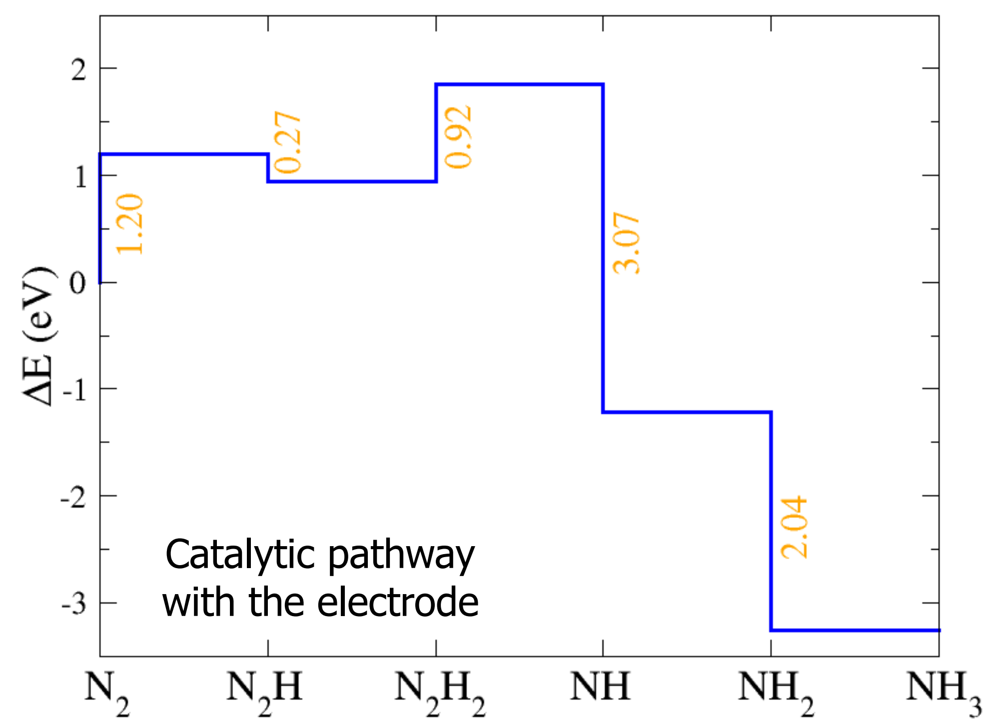


Position	Eads
Cu2pos1	-1.125929
Pt1pos2	-1.016581
Pt2pos1	-0.903967
Pt2pos2	-0.874522
Pt3pos1	-0.995788
Pt4pos2	-0.992262
Pt5pos2	-1.06035
Pt6pos1	-1.094506

$$N_2 + H \rightarrow N_2H$$
$$N_2H + H \rightarrow N_2H_2$$
$$N_2H_2 \rightarrow NH$$
$$NH + H \rightarrow NH_2$$
$$NH_2 + H \rightarrow NH_3$$

Molecule	E_{ads} (eV)
N_2	-0.619142
N_2H	-2.852163
N_2H_2	-1.041679
NH	-4.7911373
NH_2	-3.220889
NH_3	-0.874522





Conclusiones

- We have presented an initial theoretical study of the N_2 reduction mechanism via hydrazine formation on MoO_2 and Fe_2O_3 surfaces.

- The mechanism is similar to the associative altering pathway but with an inclination angle of the molecules for MoO_2.

- The cluster has a significant catalytic activity in the ammonia decomposition reaction

- DFT calculations play a crucial role in understanding catalytic mechanisms and providing guidelines for the design of new efficient electrocatalysts.

Acknowledgments

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- **And to you for your attention**

GRACIAS !!!!