

ELECTRONIC SUPPLEMENTARY INFORMATION

Competition between metal-catalysed electroreduction of dinitrogen, protons, and nitrogen oxides: a DFT perspective

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1. Computational details

The reaction mechanisms for the reduction reactions of N₂ (NRR), NO (NORR), NO₂ (NO₂RR), and N₂O (N₂ORR) into NH₃ catalysed by a series of metals have been studied by means of density functional theory (DFT). The generalised gradient approximation (GGA) with the revised Perdew-Burke-Ernzerhof (RPBE) functional with Pade approximation¹ has been used with a plane-wave cut-off energy of 400 eV,^{2,3} including Grimme's D3 dispersion.^{4,5} The Brillouin zone (periodic boundary conditions) was sampled by 9×9×1 *k*-points using the Monkhorst-Pack scheme. Optimisation calculations were done using energy and force convergence limits equal to 10⁻⁴ eV/atom and |0.01| eV/Å, respectively. For those metals presenting magnetic properties (Fe, Ni, and Co), spin-polarised calculations were imposed in that cases (see **Table S1**). Over the optimised structures, vibrational frequencies were calculated for the Γ point to obtain zero-point energies (ZPE), thermal corrections, and entropy contributions. All optimisation and vibrational frequency calculations have been performed throughout the facilities provided by the Vienna *Ab-Initio* Simulation Package (VASP, version 5.4.4).⁶⁻⁹

Table S1. Magnetic moments (μ) for the optimised geometries of the clean surfaces of Fe, Ni, and Co.

| Layer | Fe | Ni | Co |
|------------------|-------|-------|-------|
| First | 2.594 | 0.649 | 1.757 |
| Second | 2.363 | 0.672 | 1.671 |
| Third | 2.380 | 0.672 | 1.664 |
| Fourth (surface) | 2.611 | 0.650 | 1.745 |

2. DFT characterisation of metal slabs

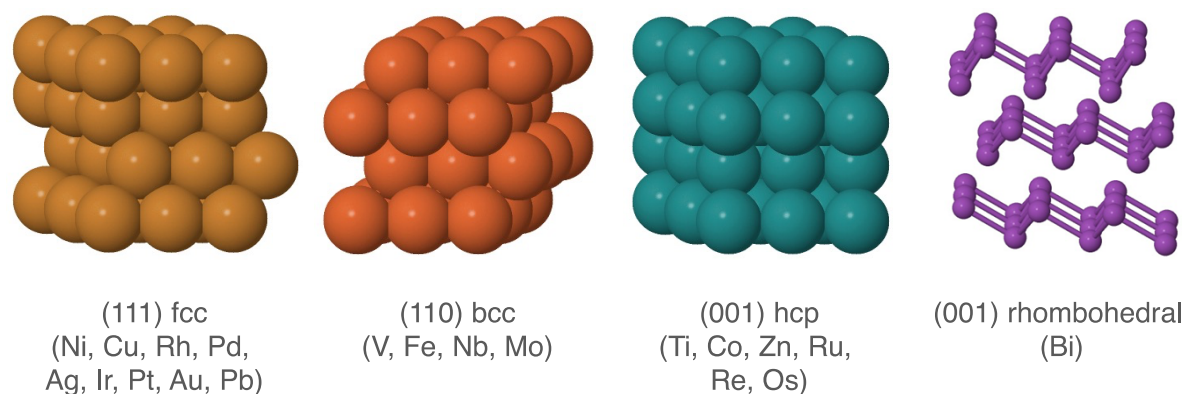


Figure S1. Representative structures for the structural models used in this study.

For this study, an important number of transition metals (*d*-block) has been selected, namely: (i) fcc Ni, Cu, Rh, Pd, Ag, Ir, Pt, and Au; (ii) bcc V, Fe, Nb, and Mo; and (iii) hcp Ti, Co, Zn, Ru, Re, and Os. To this end, we have circumscribed our analysis to the flat (111), (110), and (001) facets for the fcc, bcc, and hcp packings, respectively. We have also included two metals from the *p*-block such as Pb (fcc) and Bi (rhombohedral) with (111) and (001) surfaces in each case. Note that fcc, bcc, and hcp refer to face centred cubic, body centred cubic, and hexagonal closed packed crystal lattices, respectively. In all cases, four layers of 3×3 unit cell (4×3×3, *i.e.*, 36 atoms) have been considered for construction of the metal slabs, with exception of Bi (rhombohedral) in which three layers of 18 atoms each (54 atoms) was considered.

3. Modelling performance

Once optimised the metal slab structures, the catalytic reductions of N₂ (NRR), NO (NORR), NO₂ (NO₂RR), and N₂O (N₂ORR) into NH₃ were investigated by placing the different intermediates on the clean surfaces of the metal slabs. During the optimisation of the adsorbed reactants, products, and intermediates states, no structural constrains have been applied at any case. Over the optimised geometries, vibrational frequencies were calculated to obtain zero-point energies (ZPE), thermal corrections, and entropy contributions. Only in such cases, all atoms from the catalyst were frozen during vibrational frequency calculations, not imposing any constrains for the N, O, or H atoms constituting the adsorbates.

4. Thermochemistry

The free energy is defined by:

$$G = E(+D3) + \int C_p dT - TS$$

where G , E and C_p refer to the free energy, electronic energy, and heat capacity, respectively.

The entropy term can be expressed as the sum of the translational, rotational, vibrational, and electronic contributions as follows:

$$S = S_t + S_r + S_v + S_e$$

Finally, including the intrinsic zero-point energy (ZPE) we obtain the expression used in our calculations:

$$G = E(+D3) + \int C_p dT - T(S_t + S_r + S_v + S_e) + \text{ZPE}$$

Since $S_e \approx 0$ at the fundamental electronic level, Table S2 gathers the thermodynamic quantities for $\text{N}_2(\text{g})$, $\text{NO}(\text{g})$, $\text{NO}_2(\text{g})$, $\text{N}_2\text{O}(\text{g})$, $\text{H}_2\text{O}(\text{g})$, $\text{H}_2(\text{g})$, and $\text{NH}_3(\text{g})$ species at standard conditions (25 °C, 1 atm):

Table S2. Thermodynamic quantities, in eV, for $\text{N}_2(\text{g})$, $\text{NO}(\text{g})$, $\text{NO}_2(\text{g})$, $\text{N}_2\text{O}(\text{g})$, $\text{H}_2\text{O}(\text{g})$, $\text{H}_2(\text{g})$, and $\text{NH}_3(\text{g})$ species at standard conditions (25 °C, 1 atm, *i.e.*, 298.15 K and 1 bar of fugacity) using the RPBE+D3 functional.

| Species | $E(+D3)$ | $\int C_p dT$ | $-TS$ | ZPE | G |
|--------------------------------|----------|---------------|-------|------|--------|
| $\text{N}_2(\text{g})$ | -16.24 | 0.09 | -0.59 | 0.15 | -16.59 |
| $\text{NO}(\text{g})$ | -11.95 | 0.09 | -0.62 | 0.12 | -12.36 |
| $\text{NO}_2(\text{g})$ | -17.77 | 0.12 | -0.73 | 0.23 | -18.15 |
| $\text{N}_2\text{O}(\text{g})$ | -20.74 | 0.12 | -0.68 | 0.30 | -21.00 |
| $\text{H}_2\text{O}(\text{g})$ | -14.07 | 0.10 | -0.58 | 0.57 | -14.07 |
| $\text{H}_2(\text{g})$ | -7.02 | 0.09 | -0.40 | 0.27 | -7.02 |
| $\text{NH}_3(\text{g})$ | -19.47 | 0.11 | -0.60 | 0.91 | -19.05 |

In the case of solids and adsorbates, translational and rotational motions can be neglected, therefore, $S_t \approx 0$ and $S_r \approx 0$. In this sense, all entropy contributions come from vibrations: $S = S_v$. Similarly, translational and rotational contributions to the heat capacity are neglected. Therefore, free energies for the different adsorbates have been calculated as to:

$$G = E(+D3) + \int C_p dT - TS_v + \text{ZPE}$$

The adsorption and desorption of a given species 'X', corresponding to the chemical equations $* + X \rightleftharpoons *X$ and $*X \rightleftharpoons * + X$, respectively, can be expressed in terms of their relative binding free energies as to:

$$\Delta G_{b,ads} = G(*X) - G(*) - G(X)$$

$$\Delta G_{b,des} = G(X) + G(*) - G(*X)$$

The relative reaction free energy for each elementary reduction reaction, for instance the first hydrogenation step in NRR, *i.e.*, $*N_2 + H^+/e^- \rightleftharpoons *N_2H$, can be expressed as to:

$$\Delta G_R = G(*N_2H) - G(*N_2) - \mu(H^+/e^-)$$

And similarly for other elementary reduction reactions. However, in the frame of the proton-coupled electron transfer (PCET) approach,¹⁰ *i.e.*, both proton and electron reach the catalytic surface in a concerted way, all energy values have been referred using the computational hydrogen electrode (CHE) model for the H^+/e^- transfer, considering the chemical potential of the H^+/e^- pair in aqueous solution as the half of the H_2 gas molecule at standard hydrogen electrode (SHE) conditions, *i.e.*, $f(H_2) = 1$ bar, $U = 0$ V, and $\text{pH} = 0$, being $f(H_2)$ and U the fugacity of H_2 and the external applied potential, respectively.

$$\mu(H^+/e^-) = \frac{1}{2} \mu(H_2)$$

Therefore:

$$\Delta G_R = G(*N_2H) - G(*N_2) - \mu(H^+/e^-) = G(*N_2H) - G(*N_2) - \frac{1}{2} \mu(H_2)$$

5. Comparison of HER calculations

In 2005, Nørskov and co-workers reported calculated hydrogen adsorption energies in a series of metals.¹¹ We have reproduced these data applying our methodology at the RPBE+D3 level of theory and we have observed a very good linear correlation between Nørskov's data (RPBE level, without dispersion) and ours being $R^2 = 0.93$, $R^2 = 0.99$ if excluding Ni since it seems in

its magnetic (spin-polarised) properties were not taking into account at ref.¹¹ In addition, Co is out in this comparison since Nørskov *et al.*¹¹ have considered it as fcc, when it is really hcp.

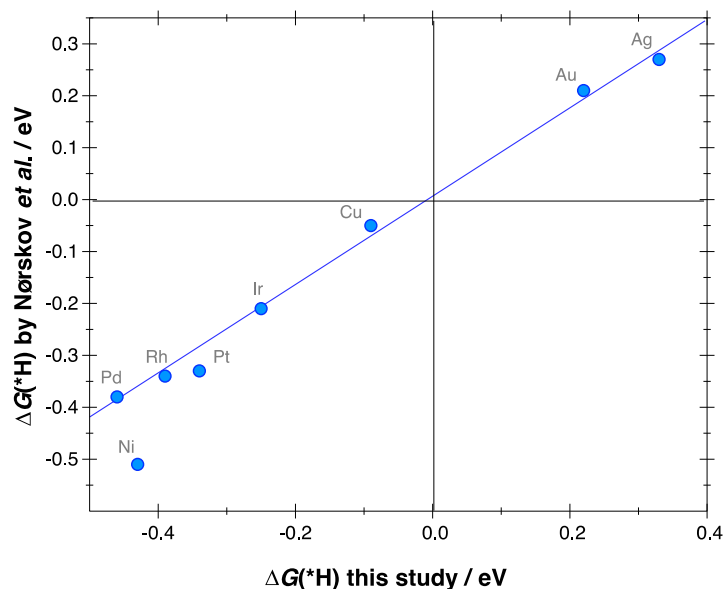


Figure S2. Comparison of $\Delta G(*H)$ calculated by Nørskov and co-workers¹¹ and by us.

6. Relative free reaction energies

Table S3. Relative free energies, ΔG (eV), for the different states considered along the HER, NRR, NORR, NO₂RR, and N₂ORR processes. In order to facilitate the reading of the numbers, those free energies with positive values (*i.e.*, non-spontaneous) have been shaded in soft grey colour.

| Metal | HER | NRR | | NORR | | | | | |
|-------|-------|-----------------|-------------------|-------|-------|-------|-------|------------------|------------------|
| | *H | *N ₂ | *N ₂ H | *NO | *NOH | *N | *NH | *NH ₂ | *NH ₃ |
| Ni | -0.43 | 0.04 | 1.23 | -1.81 | -1.30 | -2.84 | -3.37 | -3.36 | -3.61 |
| Cu | -0.09 | ^a | 2.13 | -0.51 | -0.18 | -1.25 | -2.45 | -2.96 | -3.37 |
| Rh | -0.39 | -0.08 | 0.87 | -1.85 | -1.41 | -2.96 | -3.32 | -3.31 | -3.65 |
| Pd | -0.46 | 0.19 | 1.27 | -1.69 | -0.96 | -2.40 | -2.75 | -2.90 | -3.52 |
| Ag | 0.33 | 0.26 | 2.58 | 0.14 | 0.79 | 0.16 | -1.32 | -2.31 | -3.11 |
| Ir | -0.25 | 0.07 | 0.98 | -1.29 | -1.11 | -2.67 | -3.15 | -3.23 | -3.76 |
| Pt | -0.34 | 0.27 | 1.19 | -1.27 | -0.92 | -2.41 | -2.85 | -3.01 | -3.72 |
| Au | 0.22 | 0.40 | 2.59 | 0.27 | 0.77 | -0.14 | -1.34 | -2.20 | -4.16 |
| V | -0.91 | -0.14 | -2.00 | -2.81 | -3.13 | -5.53 | -5.30 | -4.52 | -3.73 |
| Fe | -0.61 | -0.08 | 0.01 | -2.19 | -2.06 | -3.96 | -4.15 | -3.67 | -3.49 |
| Nb | -0.76 | 0.00 | -1.39 | -2.58 | -2.69 | -5.05 | -4.83 | -4.12 | -3.58 |
| Mo | -0.59 | -0.19 | -0.73 | -2.29 | -2.35 | -4.31 | -4.48 | -4.10 | -3.68 |
| Ti | -0.95 | -0.18 | -2.77 | -2.95 | -3.18 | -5.31 | -5.41 | -4.69 | -3.96 |
| Zn | 0.66 | 0.41 | 2.47 | 0.19 | 0.35 | -1.29 | -2.20 | -2.71 | -3.06 |

| | | | | | | | | | |
|----|-------|-------|------|-------|-------|-------|-------|-------|-------|
| Ru | -0.49 | -0.18 | 0.78 | -2.04 | -1.87 | -3.77 | -3.85 | -3.58 | -3.71 |
| Re | -0.68 | -0.15 | 0.48 | -2.06 | -2.08 | -3.98 | -4.23 | -3.72 | -3.71 |
| Os | -0.42 | -0.17 | 0.99 | -1.64 | -1.73 | -3.64 | -3.84 | -3.65 | -3.91 |
| Co | -0.43 | 0.01 | 1.02 | -1.83 | -1.39 | -3.09 | -3.46 | -3.37 | -3.53 |
| Pb | 0.87 | 0.40 | 2.62 | 0.16 | 0.64 | -0.54 | -1.55 | -2.26 | -2.91 |
| Bi | 1.04 | 0.31 | 2.87 | 0.34 | 1.19 | 0.33 | -0.87 | -1.89 | -2.84 |

| Metal | NO ₂ RR | | | N ₂ ORR | | |
|-------|--------------------|--------------------|-------|--------------------|--------------------|-----------------|
| | *NO ₂ | *NO ₂ H | *NO | *N ₂ O | *N ₂ OH | *N ₂ |
| Ni | -1.07 | -0.90 | -3.07 | 0.19 | -0.22 | -2.60 |
| Cu | -0.88 | -0.50 | -1.77 | 0.43 | 0.45 | ^a |
| Rh | -1.14 | -1.09 | -3.11 | 0.15 | -0.17 | -2.73 |
| Pd | -0.73 | -0.82 | -2.95 | 0.33 | 0.29 | -2.46 |
| Ag | -0.63 | -0.36 | -1.11 | 0.43 | ^a | -2.38 |
| Ir | -0.99 | -1.00 | -2.55 | 0.32 | 0.31 | -2.58 |
| Pt | -0.63 | -0.90 | -2.53 | 0.44 | 0.28 | -2.38 |
| Au | -0.22 | -0.40 | -0.99 | 0.47 | 1.02 | -2.24 |
| V | -2.31 | -2.73 | -4.07 | -0.07 | -6.32 ^b | -2.79 |
| Fe | -1.45 | -1.19 | -3.45 | 0.11 | -0.08 | -2.72 |
| Nb | -2.23 | -2.45 | -3.84 | 0.05 | -5.21 ^b | -2.64 |
| Mo | -2.17 | -1.71 | -3.55 | -0.08 | -0.45 | -2.83 |
| Ti | ^a | ^a | -4.21 | -0.18 | -7.82 ^b | -2.82 |
| Zn | -0.75 | -0.36 | -1.07 | 0.47 | 0.98 | -2.24 |
| Ru | -1.55 | -1.20 | -3.30 | 0.03 | -0.45 | -2.82 |
| Re | -1.55 | -1.28 | -3.32 | 0.01 | -0.56 | -2.80 |
| Os | -1.97 | -1.60 | -2.90 | 0.07 | -0.36 | -2.81 |
| Co | -1.19 | -0.87 | -3.09 | 0.17 | -0.24 | -2.64 |
| Pb | -0.62 | -0.27 | -1.10 | 0.47 | ^a | -2.25 |
| Bi | -0.34 | -0.25 | -0.92 | 0.53 | ^a | -2.33 |

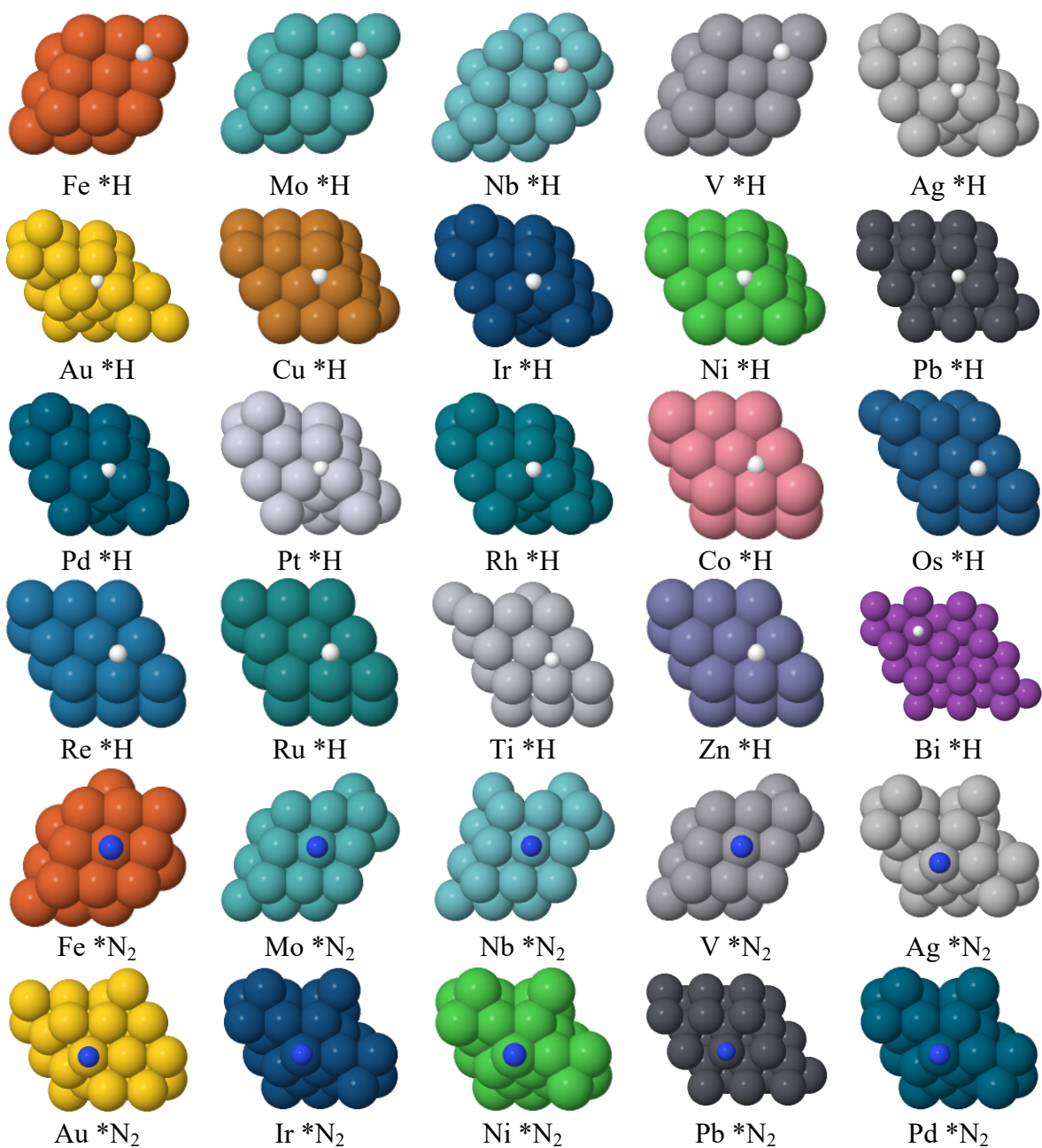
(^a) Minimum not described. (^b) N₂OH species is decomposed into N₂ + OH during optimisation.

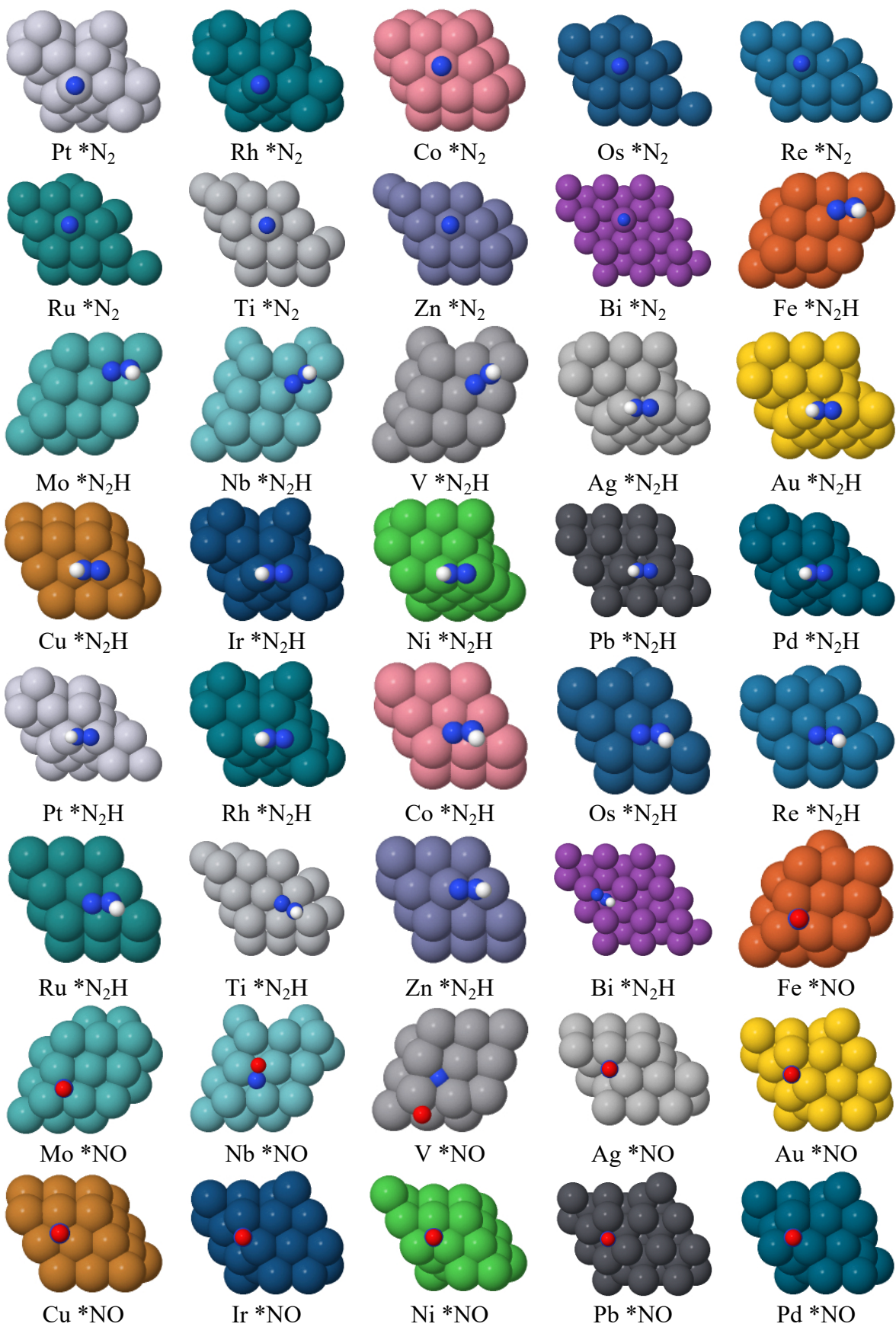
Table S4. Maximum relative ΔG values ($\Delta\Delta G$) and NH₃ desorption free energies (eV) required for the NORR. Note that free energies and redox potentials are related *via* $\Delta G = -nF\varepsilon$.

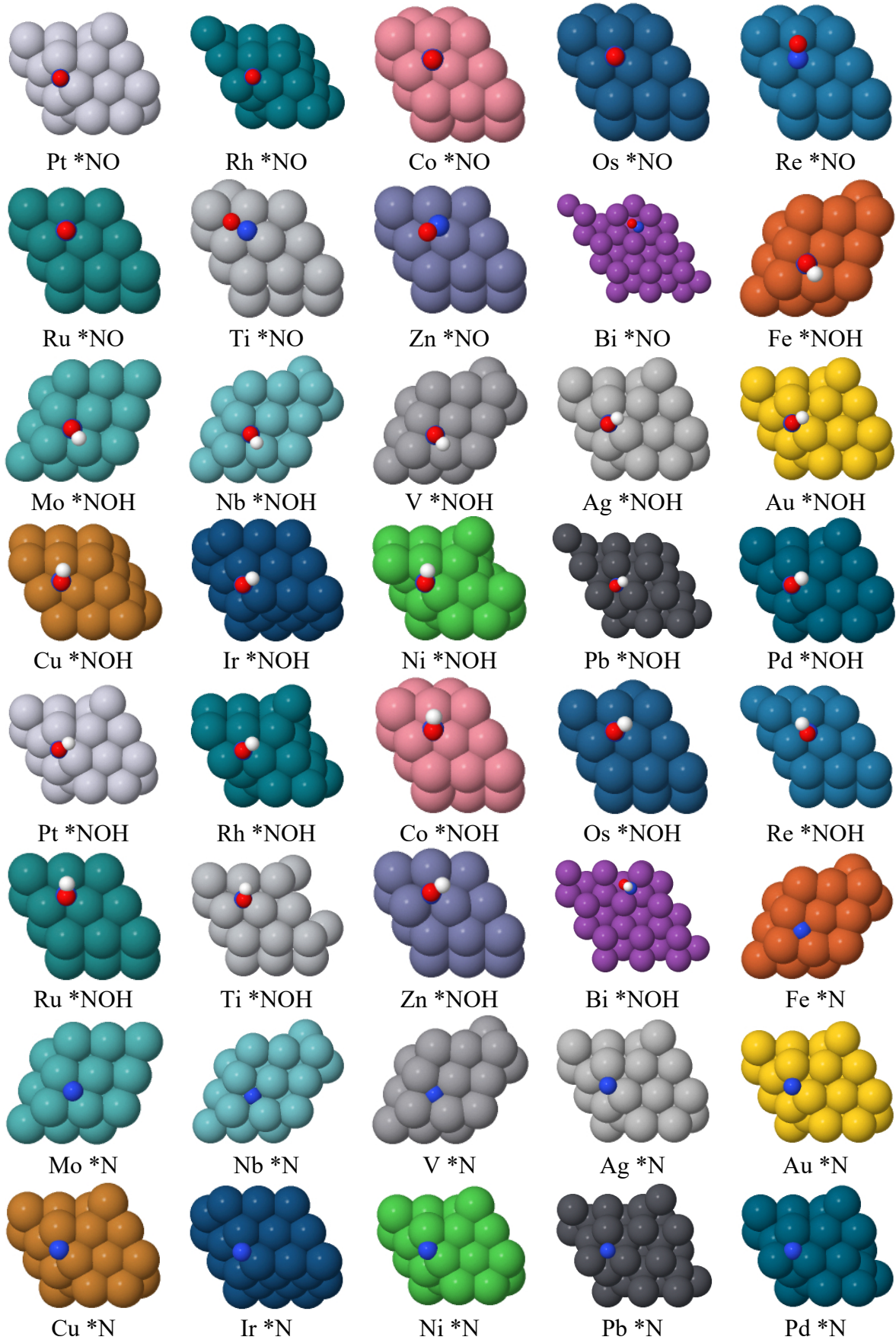
| Metal | Rel. ΔG_{max} | Limiting state | $\Delta G_d(*NH_3)$ |
|-------|-----------------------|------------------|---------------------|
| Ni | 0.51 | *NOH | 0.40 |
| Cu | 0.33 | *NOH | 0.16 |
| Rh | 0.44 | *NOH | 0.44 |
| Pd | 0.73 | *NOH | 0.31 |
| Ag | 0.65 | *NOH | -0.11 |
| Ir | 0.18 | *NOH | 0.55 |
| Pt | 0.35 | *NOH | 0.51 |
| Au | 0.50 | *NOH | 0.95 |
| V | 0.80 | *NH ₃ | 0.52 |
| Fe | 0.48 | *NH ₂ | 0.28 |
| Nb | 0.71 | *NH ₂ | 0.36 |

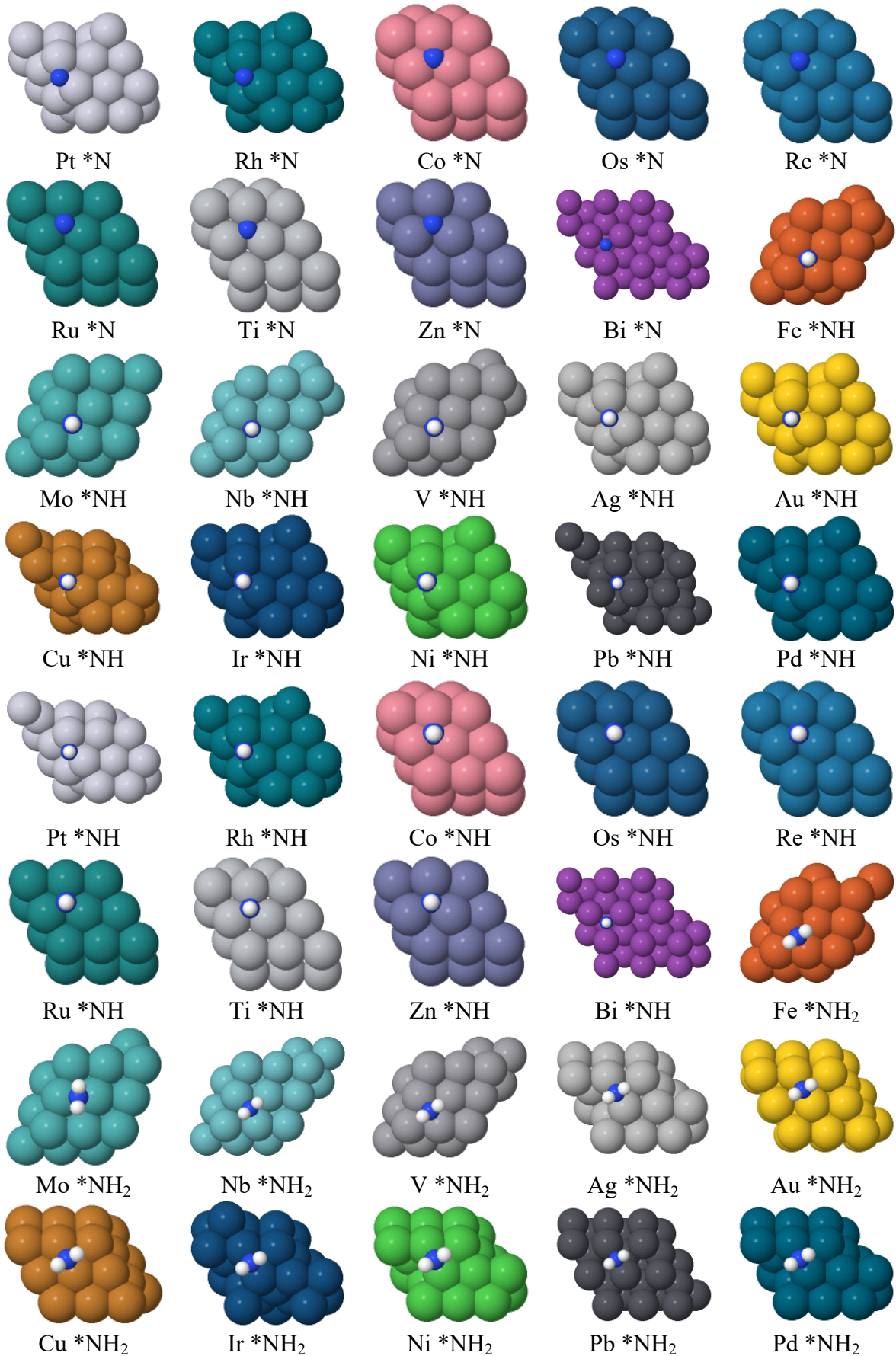
| | | | |
|----|------|------------------|-------|
| Mo | 0.42 | *NH ₃ | 0.47 |
| Ti | 0.73 | *NH ₂ | 0.75 |
| Zn | 0.16 | *NOH | -0.16 |
| Ru | 0.27 | *NH ₂ | 0.50 |
| Re | 0.51 | *NH ₂ | 0.50 |
| Os | 0.19 | *NH ₂ | 0.70 |
| Co | 0.44 | *NOH | 0.31 |
| Pb | 0.48 | *NOH | -0.30 |
| Bi | 0.85 | *NOH | -0.38 |

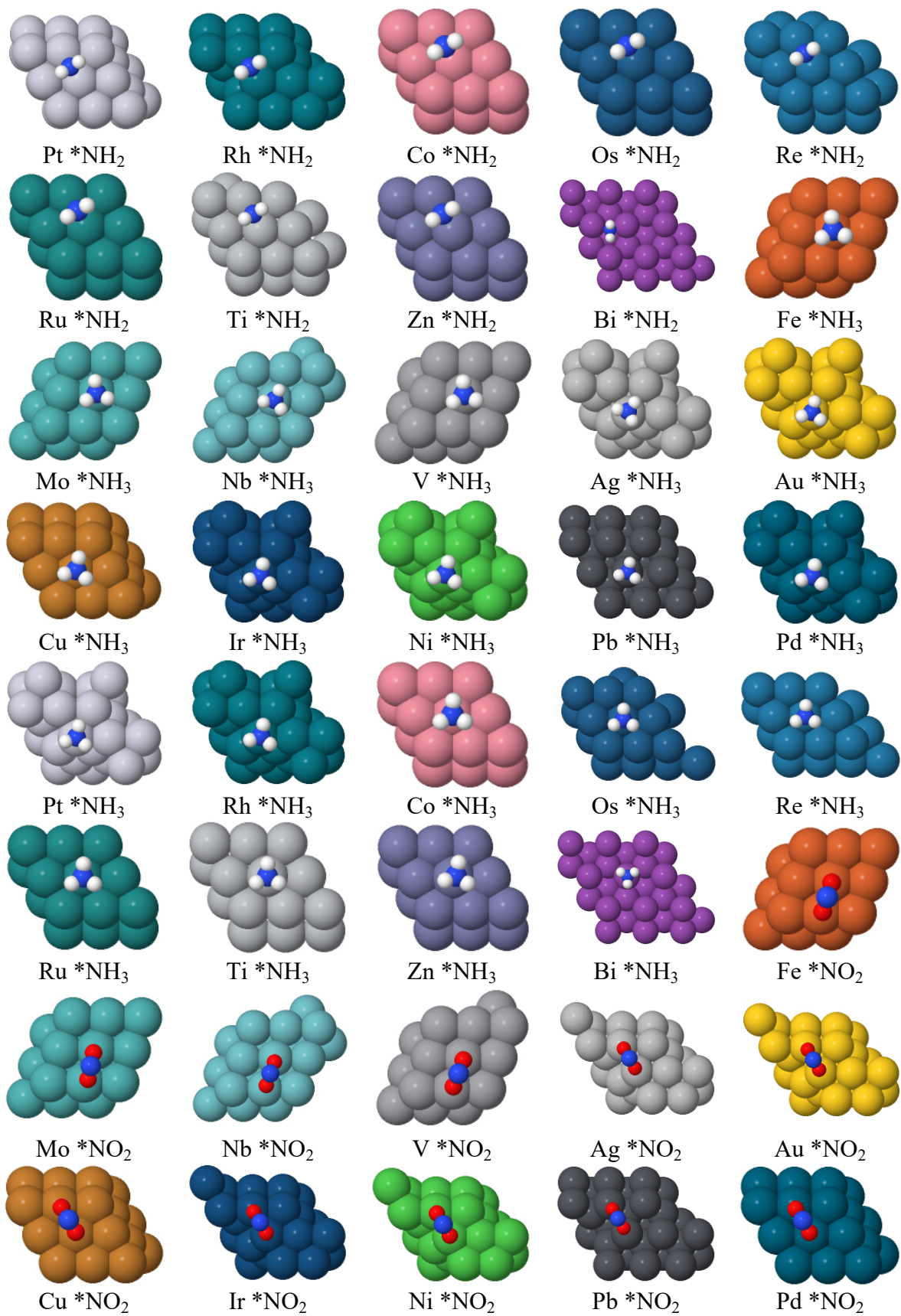
7. Optimised structures

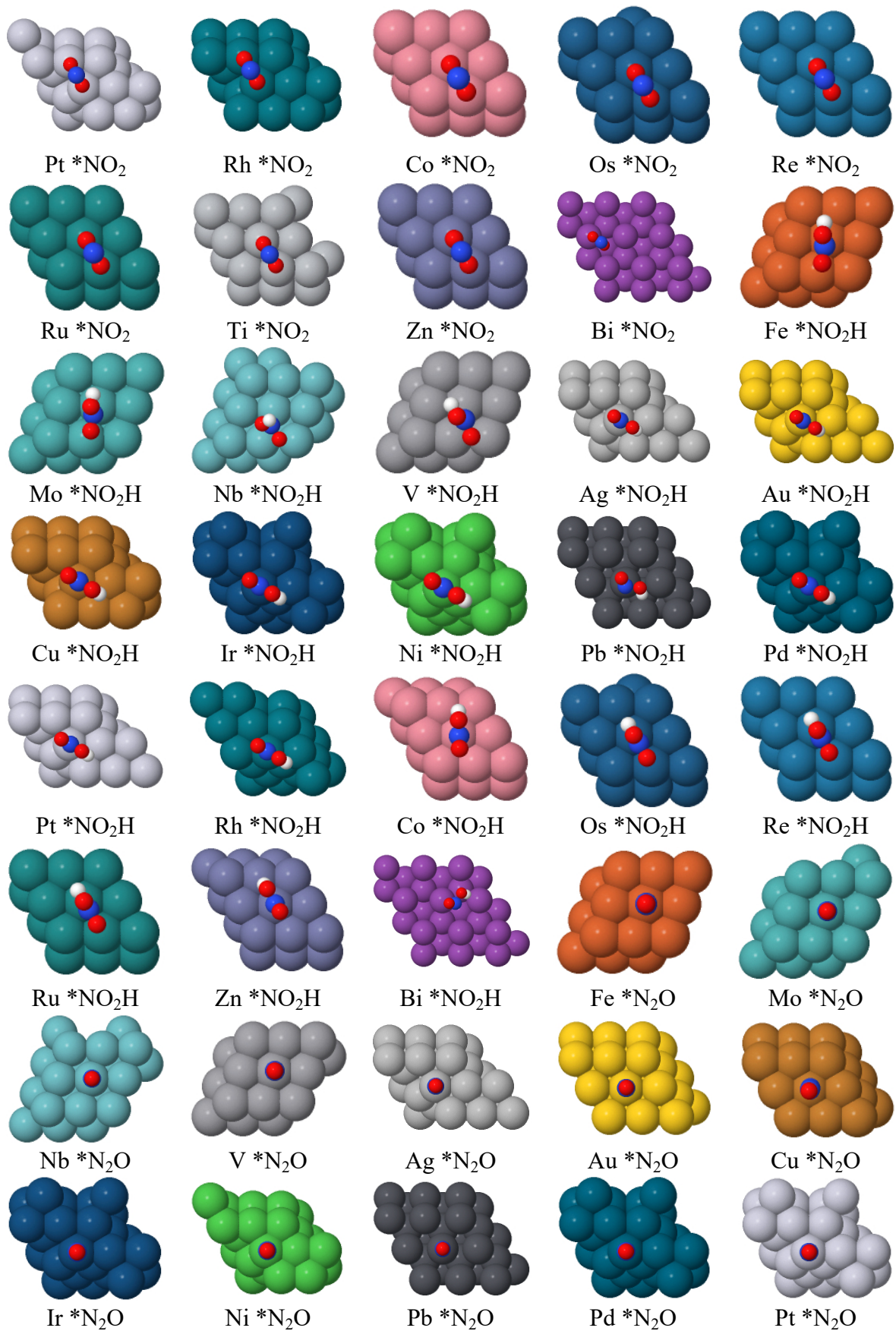












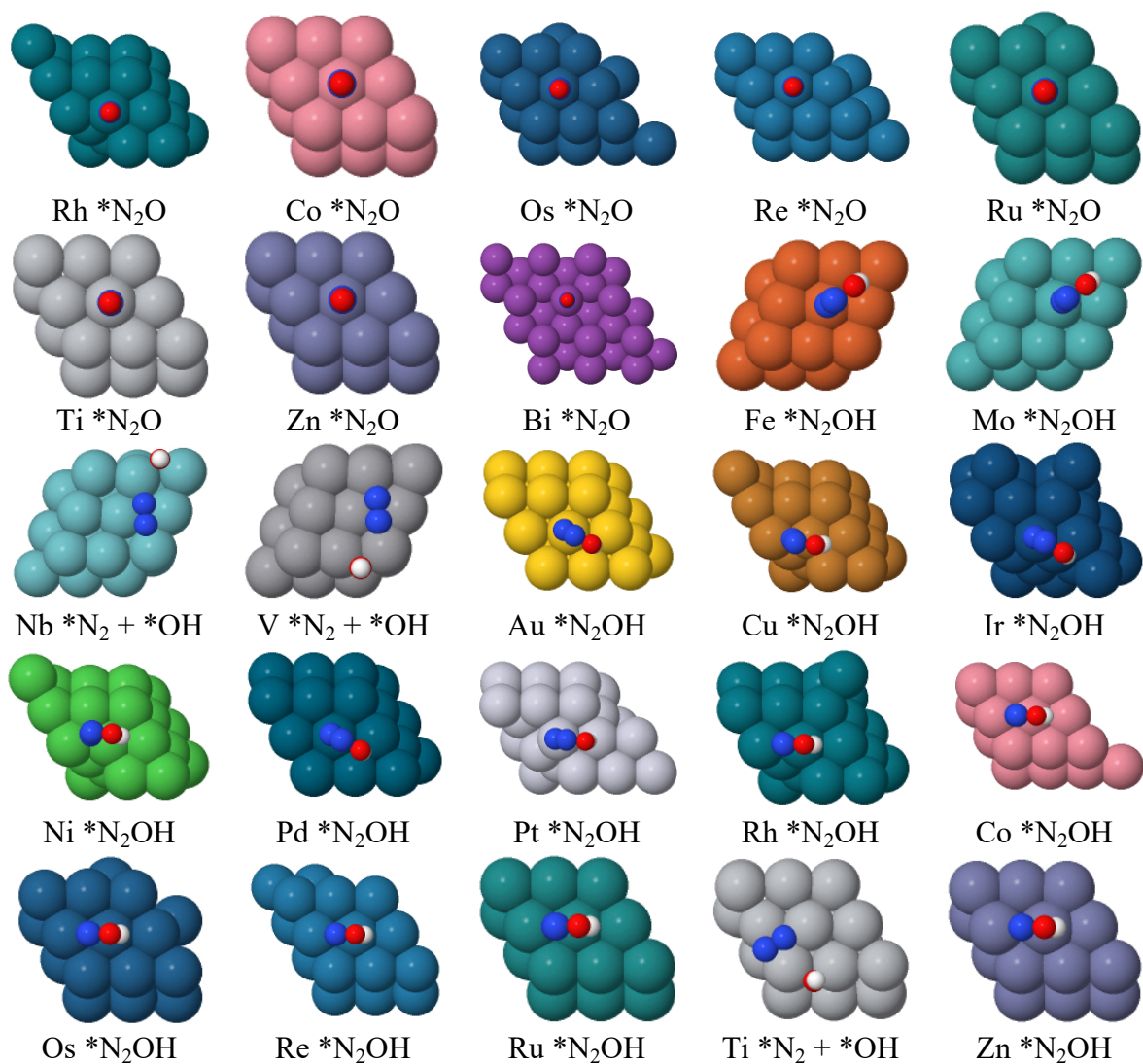
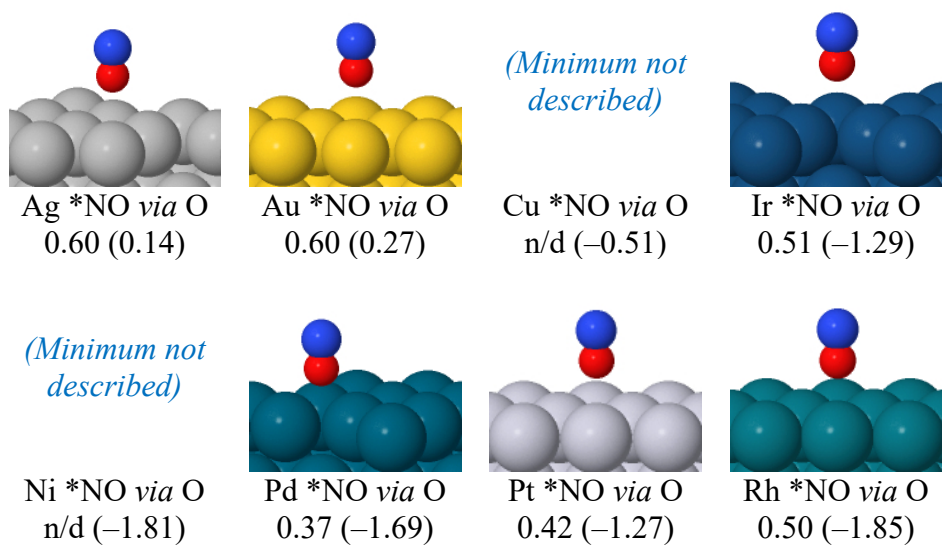


Figure S3. Optimised structures for the HER, NRR, NORR, NO₂RR, and N₂ORR.



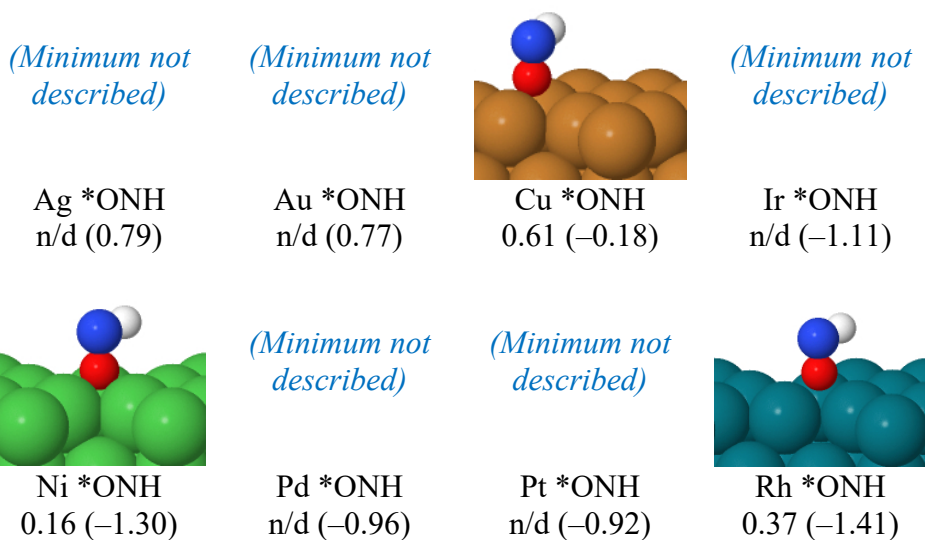


Figure S4. Optimised structures for the binding of NO and ONH species in NORR when they take place *via* the O atom in selected *d*-metals, specifically those with fcc packing. Free energies are in eV, being those in parenthesis referred to the binding of NO and NOH species when taking place *via* the N atom (for comparison).

References

- 1 B. Hammer, L. B. Hansen and J. K. Nørskov, *Phys. Rev. B*, 1999, **59**, 7413–7421.
- 2 P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953–17979.
- 3 G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758–1775.
- 4 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
- 5 S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456–1465.
- 6 G. Kresse and J. Hafner, *Phys. Rev. B*, 1993, **47**, 558–561.
- 7 G. Kresse and J. Hafner, *Phys. Rev. B*, 1994, **49**, 14251–14269.
- 8 G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169–11186.
- 9 G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, **6**, 15–50.
- 10 S. Hammes-Schiffer, *Chem. Rev.*, 2010, **110**, 6937–6938.
- 11 J. K. Nørskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandelov and U. Stimming, *J. Electrochem. Soc.*, 2005, **152**, J23.