

A density functional theory study on NO-H₂O co-adsorption on Cu(111)

Thanh Ngoc Pham,^{1*} Yuji Hamamoto,^{1,2} Kouji Inagaki,^{1,2} Ikutaro Hamada,^{1,2} and Yoshitada Morikawa^{1,2,3}

¹Department of Precision Engineering, Osaka University, 2-1 Yamada-Oka, Suita, Osaka 565-0871, Japan,
²Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Katsura, Kyoto 615-8520, Japan.

³Research Center for Ultra-Precision Science and Technology, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita 565-0871, Osaka, Japan

*Email: thanh@cp.prec.eng.osaka-u.ac.jp

I. Introduction

- The complex formation of nitric oxide (NO) with some common gases in three-way catalyst environment (e.g. NH₃, H₂O. etc.) is important for the selectivity of the NO reduction reaction.
- Recently, the formation of NO-H₂O complex on Cu(111) is observed experimentally [1].
- It found that NO-H₂O interaction is stronger than NO-NO and H₂O-H₂O interactions, leading to the formation of a mixed NO-H₂O complex on Cu(111) [1]
- To shed light on the experimental observation of NO-H₂O/Cu(111), we studied the adsorption of small $mNO-nH_2O$ complexes ($n = 1 - 4$, $m = 1 - 4$) on Cu(111) [2]

[1] H. Koshida et al, J. Phys. Chem C **122**, 8894 (2018)
 [2] T. N. Pham et al. Phys Rev Mat. Under review

II. Computational details

- DFT with STATE (Simulation Tool for Atom TEchnology) package. [3]
- Plane-wave basis set with cut-off energies of 36 and 400 Ry for wave functions and augmented charge density.
- K-points: 5 x 5 x 1
- Eight-layer slab model for Cu(111) with a vacuum thickness of 16 Å

$$E_{ads}(nNO-mH_2O) = E_{nNO-mH_2O/Cu}^{tot} - [E_{Cu}^{tot} + nE_{NO}^{tot} + mE_{H_2O}^{tot}]$$

$$E_b(nNO-mH_2O) = E_{nNO-mH_2O/Cu}^{tot} - nE_{NO/Cu}^{tot} - mE_{H_2O/Cu}^{tot} + (n+m-1)E_{Cu}^{tot}$$

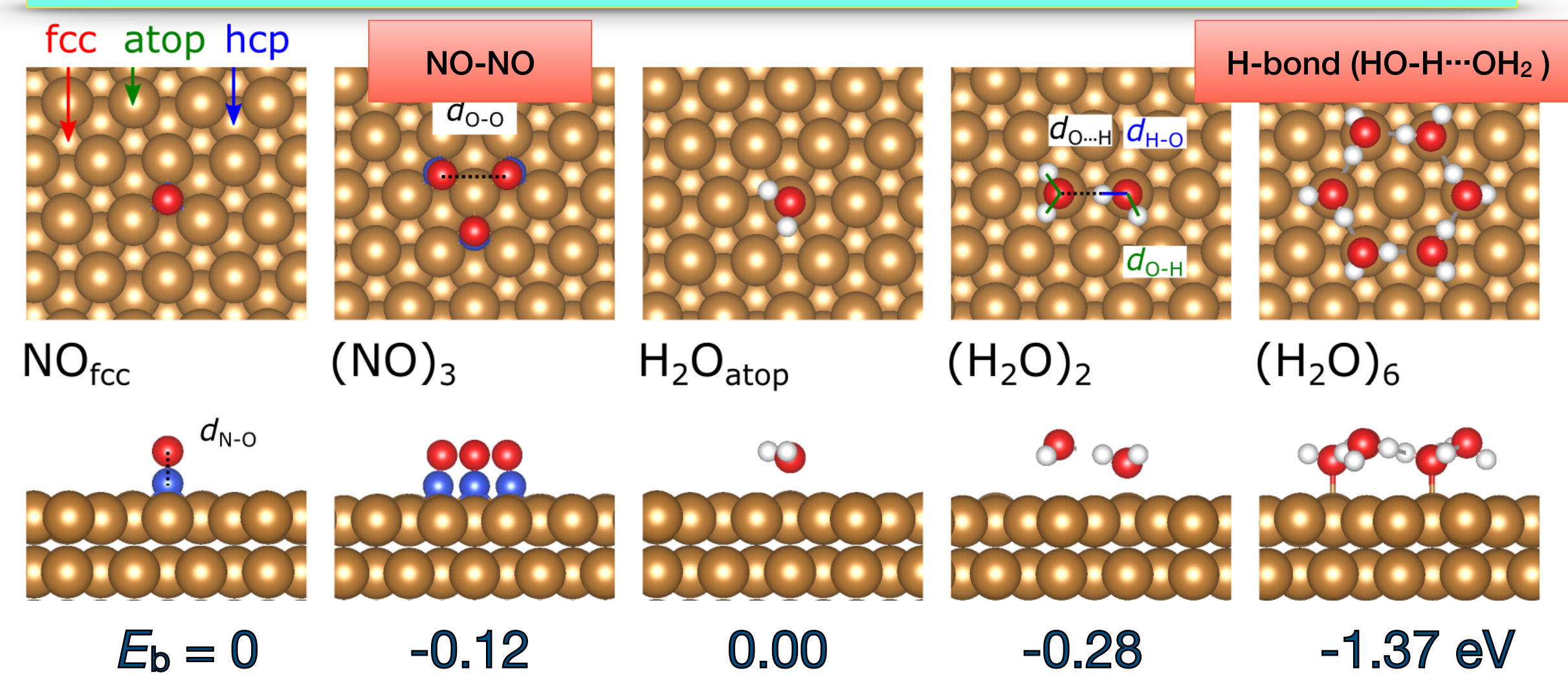
[3] Y. Morikawa, Phys. Rev. B **51**, 802, (1995)

IV. Conclusions

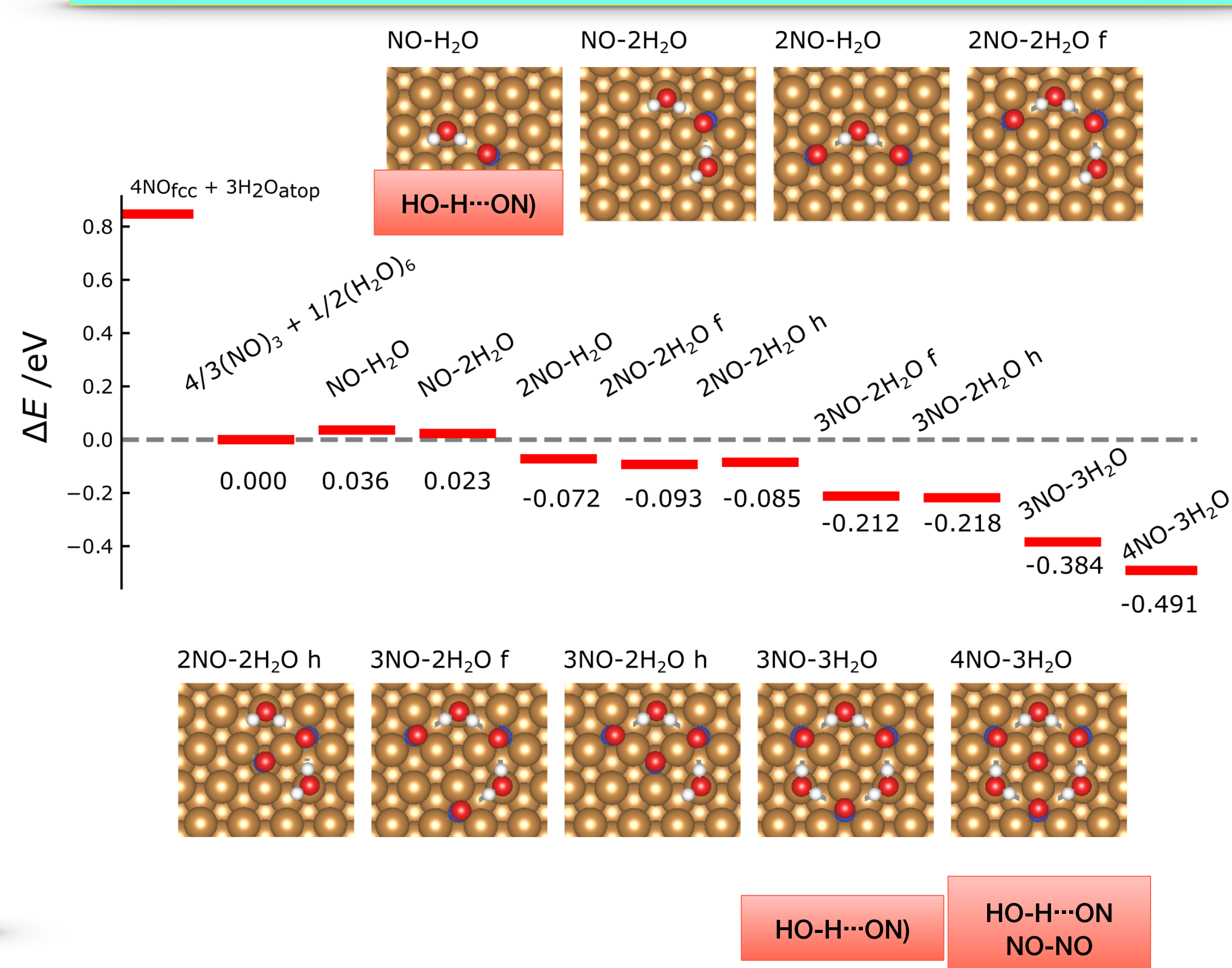
- We confirm the NO-H₂O interaction is stronger than NO-NO and H₂O-H₂O interaction.
- NO-H₂O interaction mainly arises from direct hydrogen bondings between H₂O and negatively charged NO by back-donation process.

III. Results and discussion

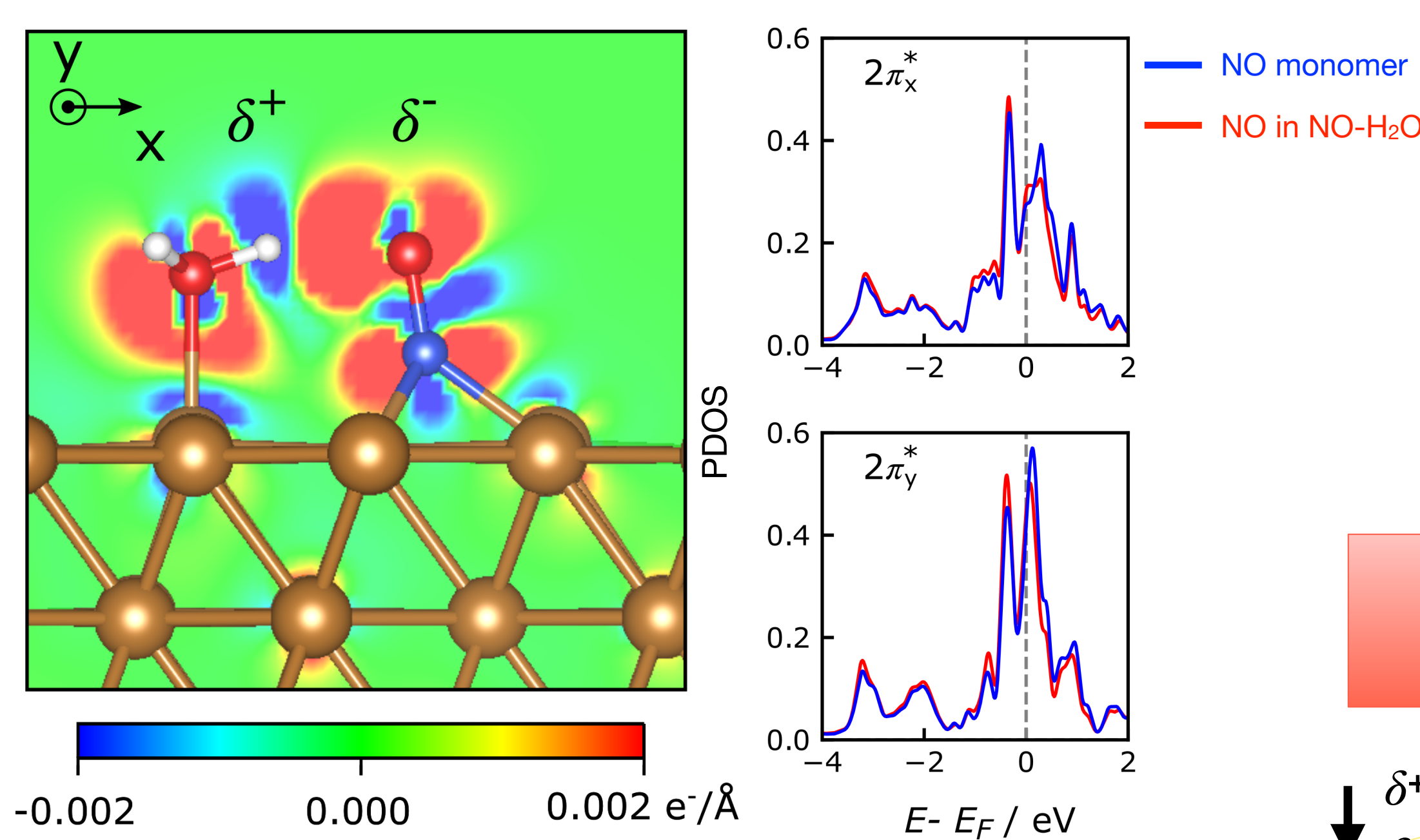
A. NO and H₂O clusters on Cu(111)



B. NO-H₂O co-adsorption on Cu(111)



C. Intermolecular interaction

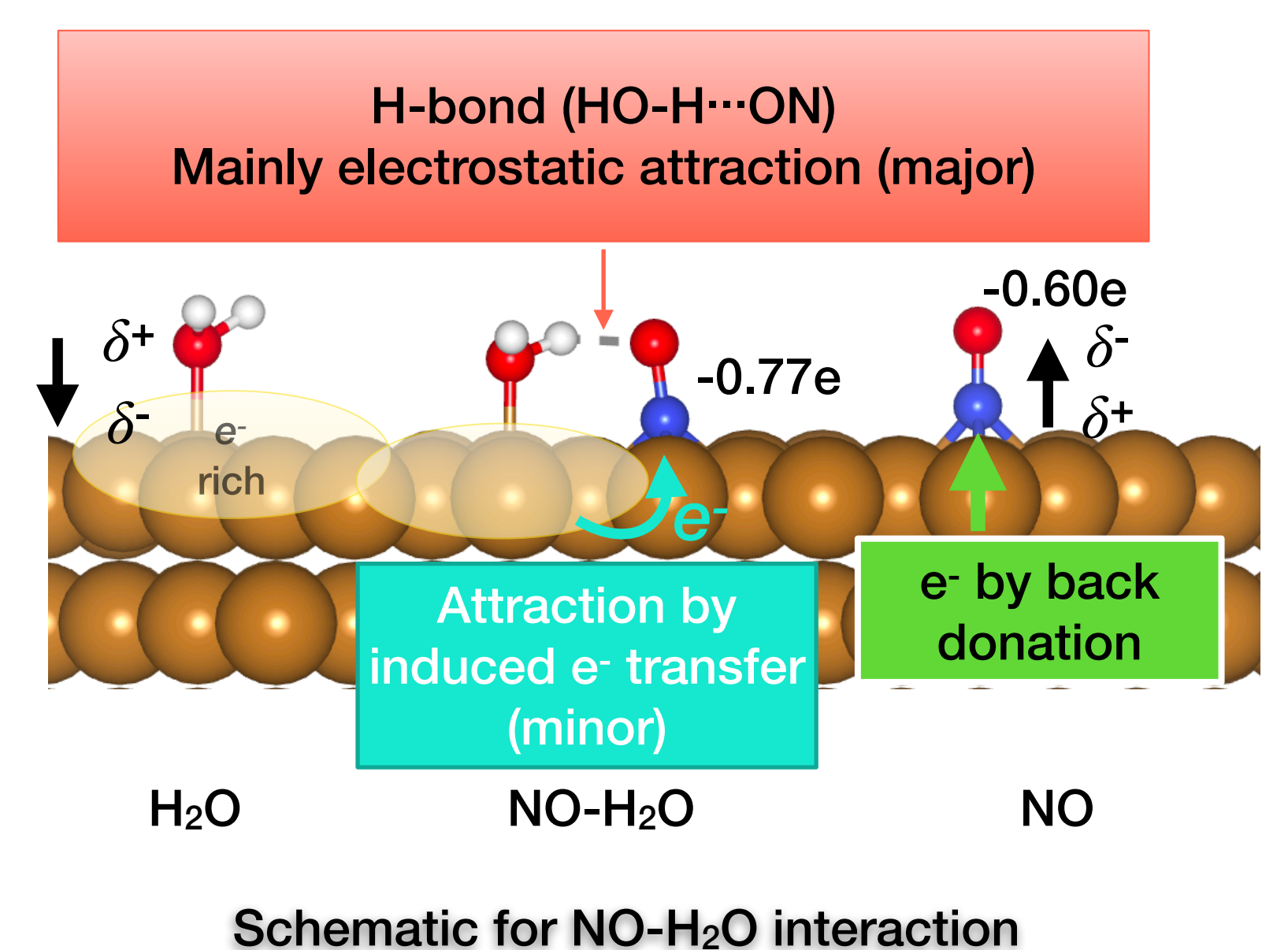


	E_b /eV	$\Delta q(\text{NO})/e$	$\Delta q(\text{H}_2\text{O})/e$
NO monomer	0	-0.60	
H ₂ O monomer	0		0.02
NO-H ₂ O	-0.222	-0.77	0.02

Δq : effective Bader charge
 $\Delta q = Z - q$,
 Where Z and q are total valance and Bader electrons

$$\Delta\rho_{\text{NO-H}_2\text{O}} = \rho_{\text{NO-H}_2\text{O}/\text{Cu}} - \rho_{\text{NO}/\text{Cu}} - \rho_{\text{H}_2\text{O}/\text{Cu}} + \rho_{\text{Cu}}$$

H-bond (electrostatic attraction between H₂O and negatively charged NO) mainly stabilizes the co-adsorption and enhances the back donation to 2π* orbitals



Schematic for NO-H₂O interaction

JHPCN

ID: EX22202

Title: First-principles multiscale simulation of sintering process of perovskite-supported metal nanoclusters