Modeling of surface properties of lamellar zeolites

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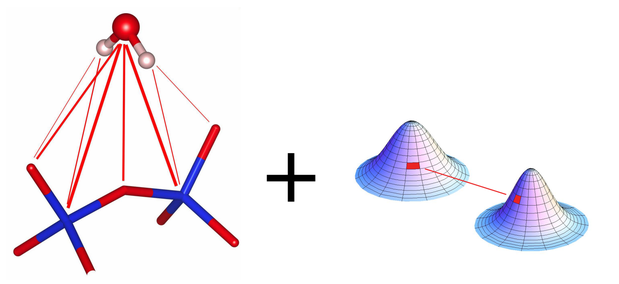
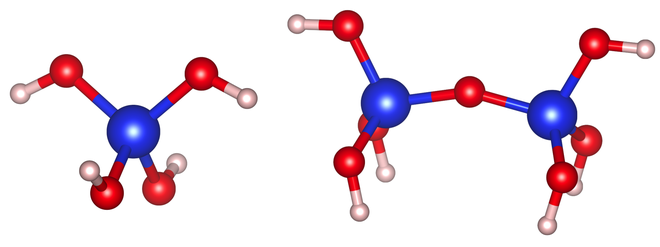
Introduction

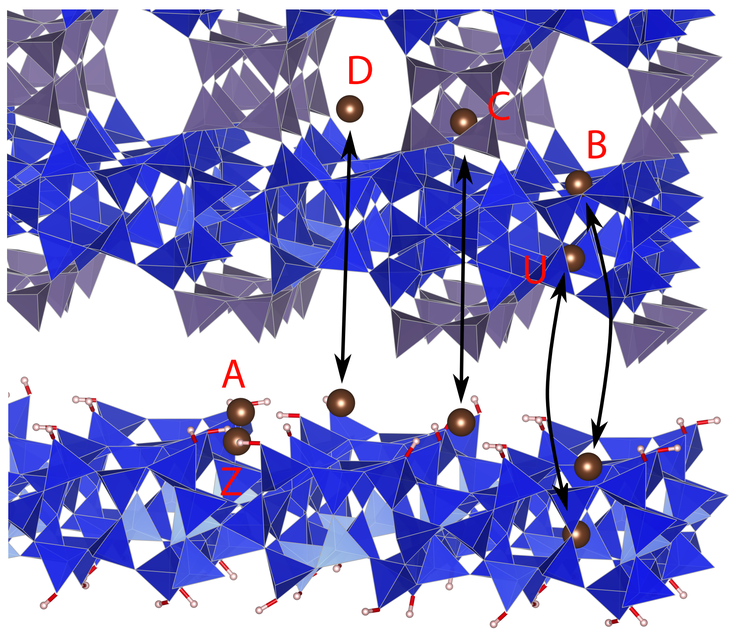
- 3D zeolites UTL or ITH can be broken down to 2D lamellae by dissolving their D4R bridging units.[1,2]
- Proper treatment of van der Waals forces is crucial in modeling physisorption of small molecules on 2D zeolites.
- We use the empirical DFT/CC method[3] simplified by a physical model for dispersion.



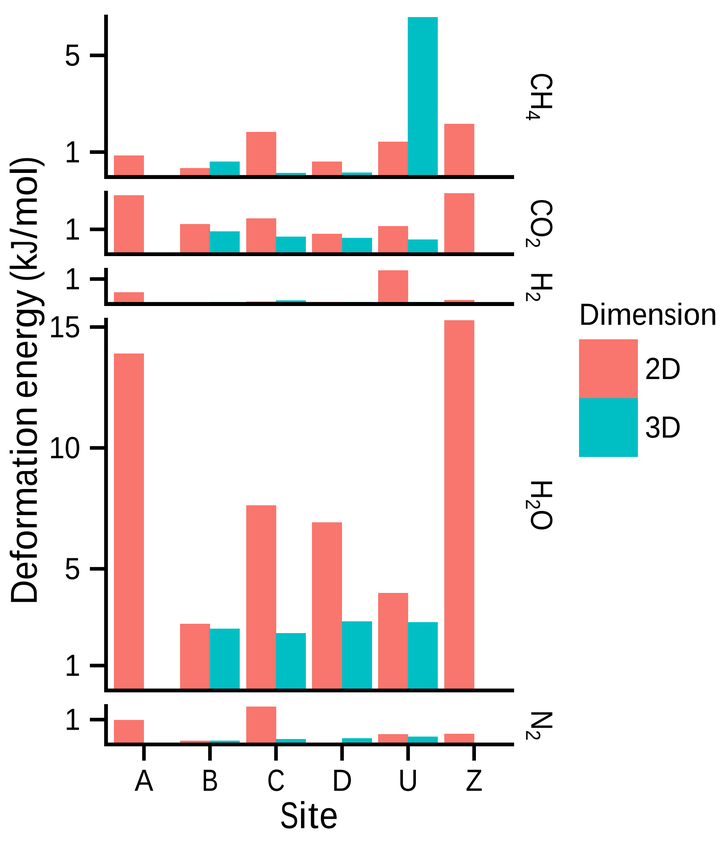
Studied systems



- 1T and 2T models of the silica framework are used for parametrization of our method.
- Binding energies of molecules at several specific sites of 2D-UTL, 2D-ITH and 3D-ITH were calculated.

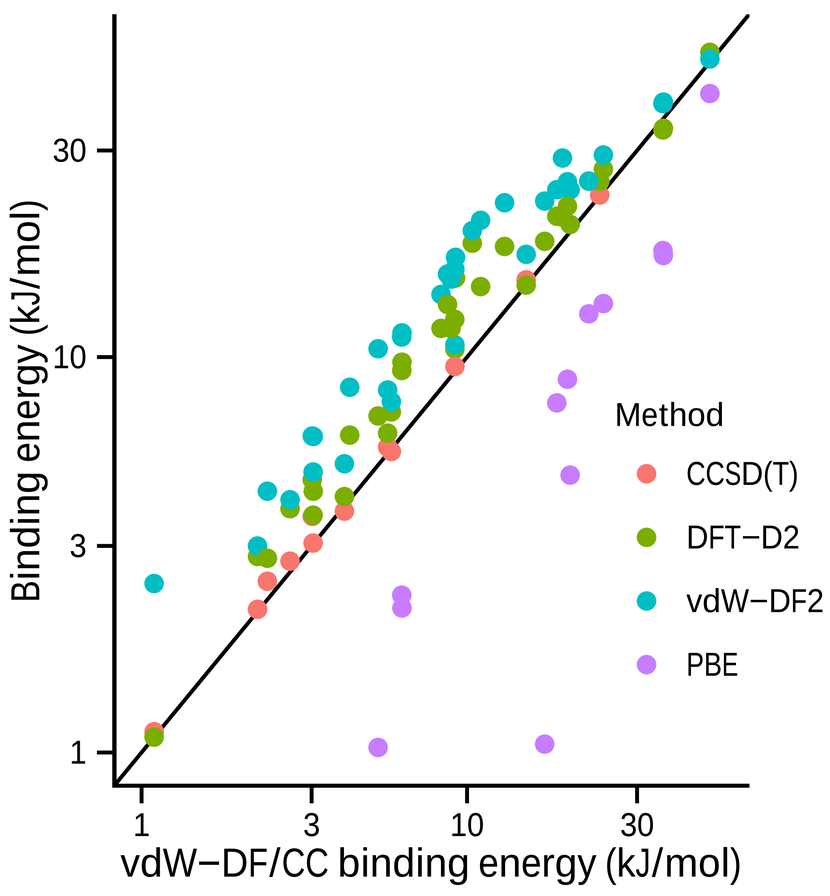


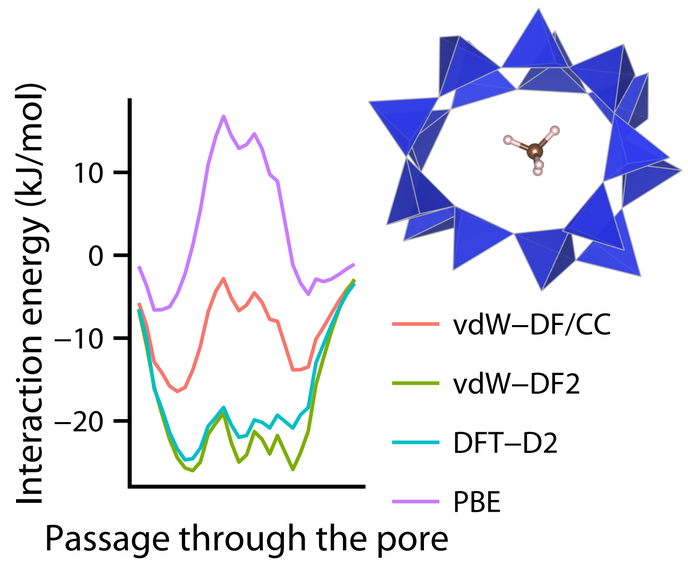
Deformation energy



- Deformation energy is significant for water interacting with silanol groups via hydrogen bonds.

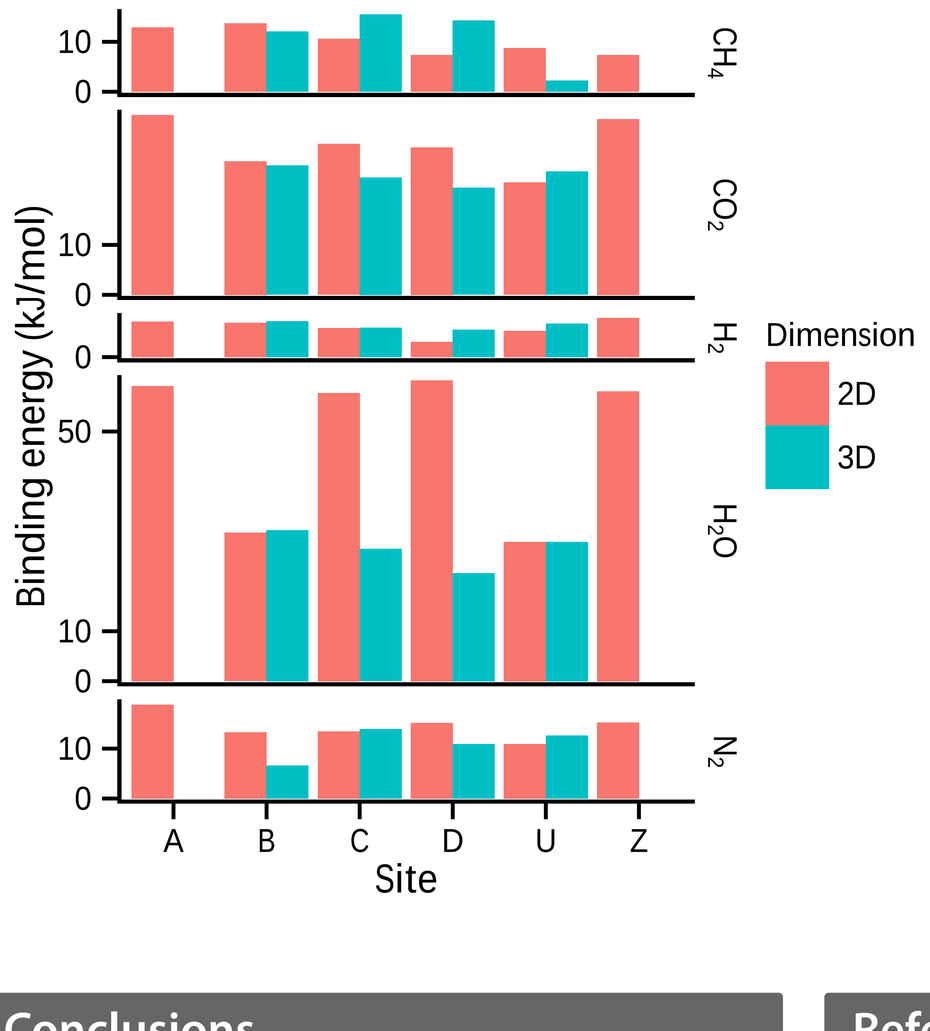
Comparison of dispersion-corrected DFT methods





- Two widely used methods for dispersion interaction, DFT-D2 and vdW-DF2, overestimate binding energies in the studied systems.
- The error can be as much as 100% in case of CH_4 or N_2.
- DFT-D2 and vdW-DF2 predict an energy minimum in the middle of the cross-lamellar pore in ITH.
- Our method predicts a barrier which prevents the passage through the pore.
- Our method provides binding energies with the accuracy of 1 kJ/mol (several percent).
- The behaviour of the methods is consistent between the 2T model and a full zeolite, indirectly proving the transferability of our method.

Effects of 3D to 2D transformation of ITH on binding energies



- Sites B, C, D and U are present in both 2D- and 3D-ITH, while sites A and Z are unique for 2D-ITH (on ''silanol hills'' formed after dissolving the D4Rs).
- Several effects contribute to the changes in binding energies:
  - Hydrogen-bond and electrostatic interactions with silanol groups of the 2D zeolite (H_2O, CO_2).
  - Confined space effect enhances dispersion interaction in the 3D zeolite.
  - 2D zeolite is more flexible to accommodate larger molecules (inner sites, CH_4).

Conclusions

- Standard methods for describing van der Waals forces in DFT are not only inaccurate, but can provide qualitatively wrong results.
- Both the framework and surface of 2D zeolites are more flexible than those of their 3D counterparts.
- The dominant feature of the surface of 2D zeolites is the presence of silanol groups, which strongly interact with polar molecules, especially water.

References

1. Roth, W. J. *et al. J. Am. Chem. Soc.* **133**, 6130 (2011).
2. Grajciar, L., Bludský, O., Roth, W. J. & Nachtigall, P. *Catal. Today* **204**, 15 (2012).
3. Bludský, O., Rubeš, M., Soldán, P. & Nachtigall, P. *J. Chem. Phys.* **128**, 114102 (2008).

Acknowledgment

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Further information

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