TEMPERATURE DEPENDENCE OF CO ADSORPTION IN H-FER ZEOLITE

THEORY **EXPERIMENT**

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ÚOCHB
IOCB PRAGUE

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Motivation

- Obvious discrepancy between calorimetry and VT-IR
  - VT-IR one IR band for all sites – average
  - Calorimetry distinguishes between sites of different adsorption enthalpy

- The apparent agreement between theory and experiment was rather fortuitous:
  - Neglect of dispersion partially compensated by PBE overestimation
  - Thermal correction of $\frac{7}{2}$ RT
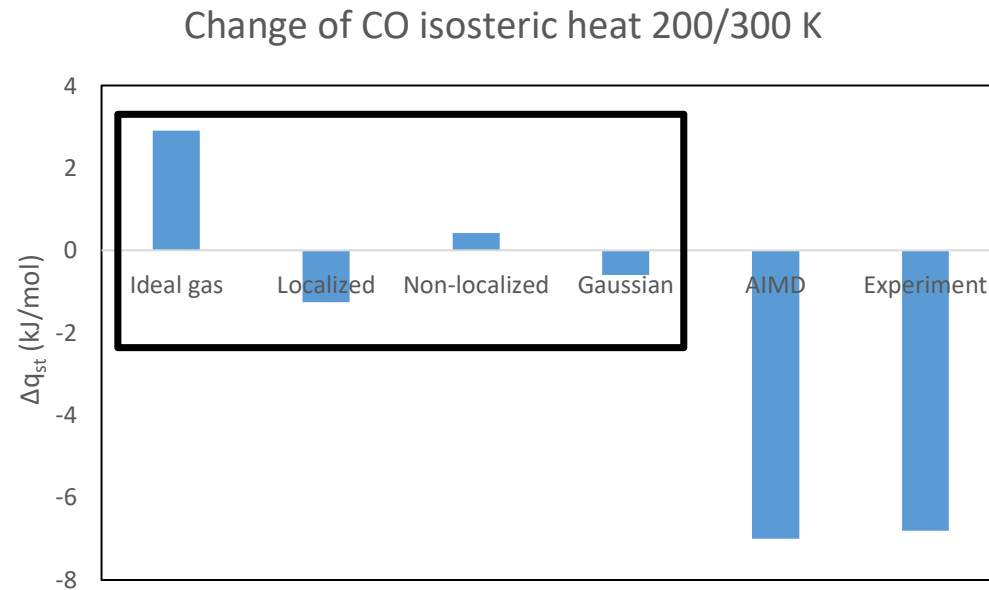   - wrong sign!!!

  HOW TO DO IT RIGHT
  - Account for E_{disp} FER…CO – TRICKY
  - Correcting Brønsted-CO interaction
  - Thermal correction from AIMD
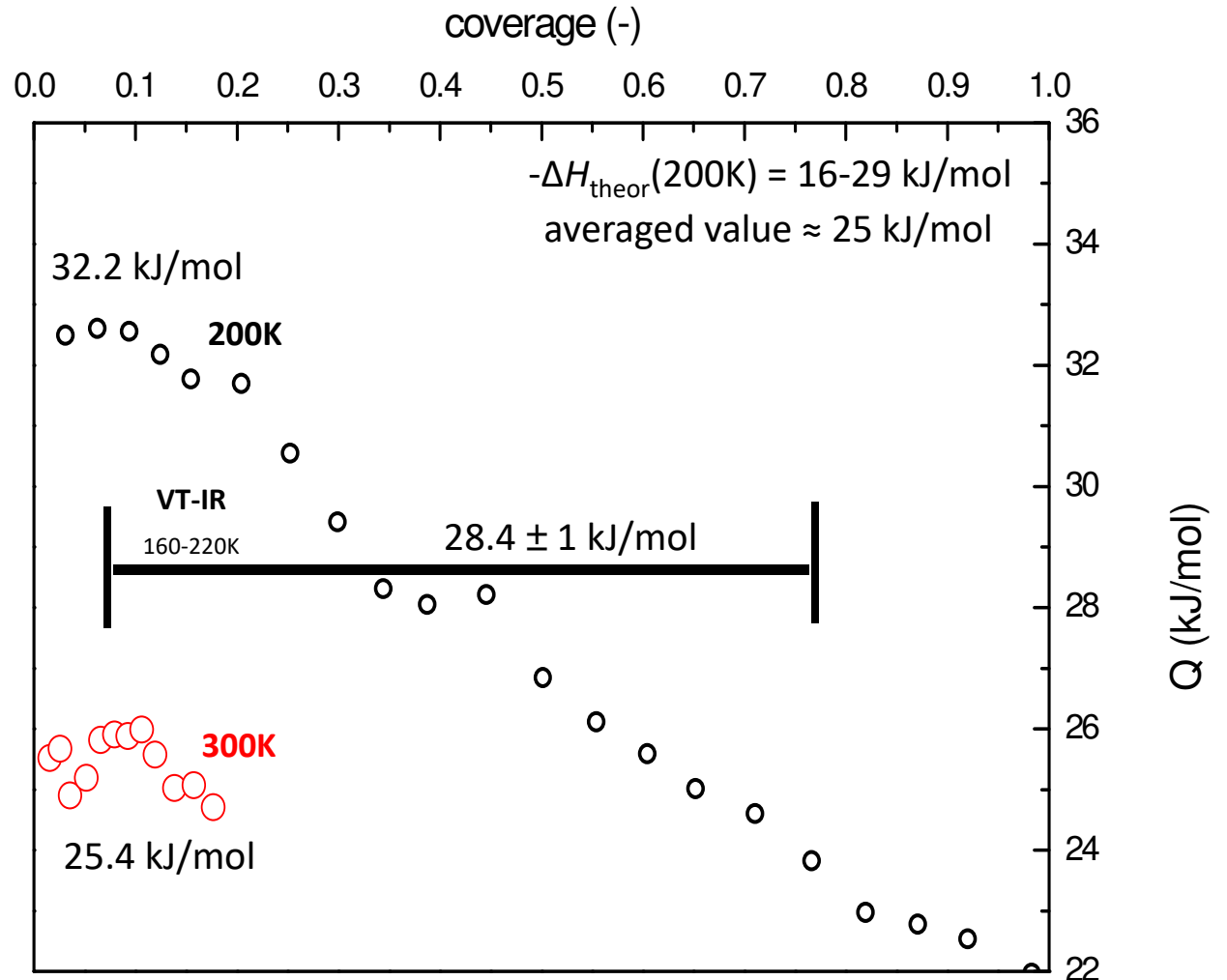
Nachtigall *et al.*, PCCP **11**, 791 (2009)
Arean *et al.*, PCCP **16**, 10129 (2014)

Take home message

Change of CO isosteric heat 200/300 K

Adsorption Models

Ideal gas — thermal correction of 7/2 RT used by Nachtigall *et al.*[1]

Localized — localized adsorption of diatomic molecule at high τ_{vg} (=T/Φ_{vg}).[2]

Non-localized — non-localized (mobile) adsorption at high τ_{vg}.[2]

Gaussian — thermal correction evaluated from Gaussian thermochemistry.[3]

AIMD — evaluated from ab initio molecular dynamics simulation (T_1 site).

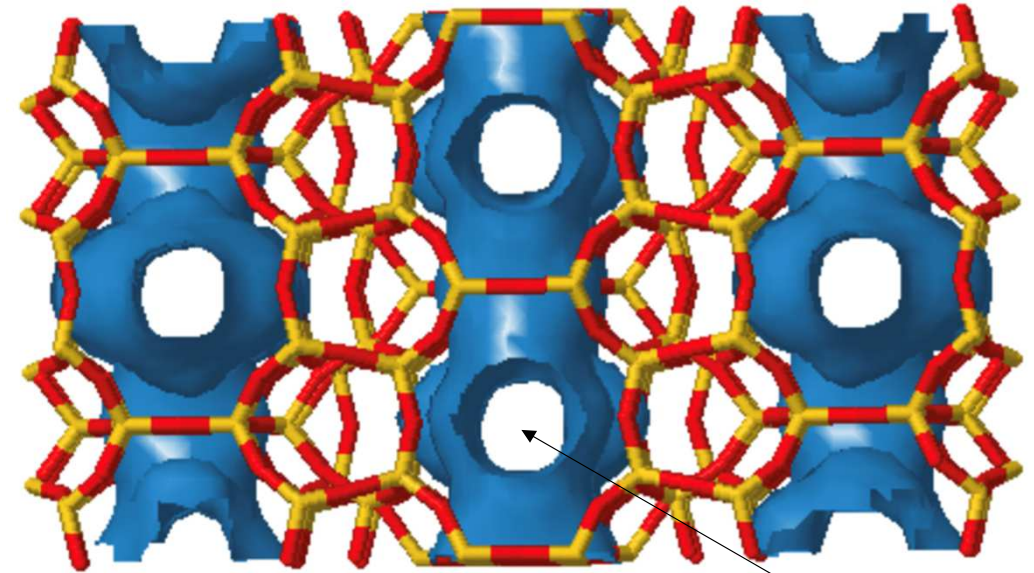Experiment — measured by microcalorimetry (this work).

c-axis view
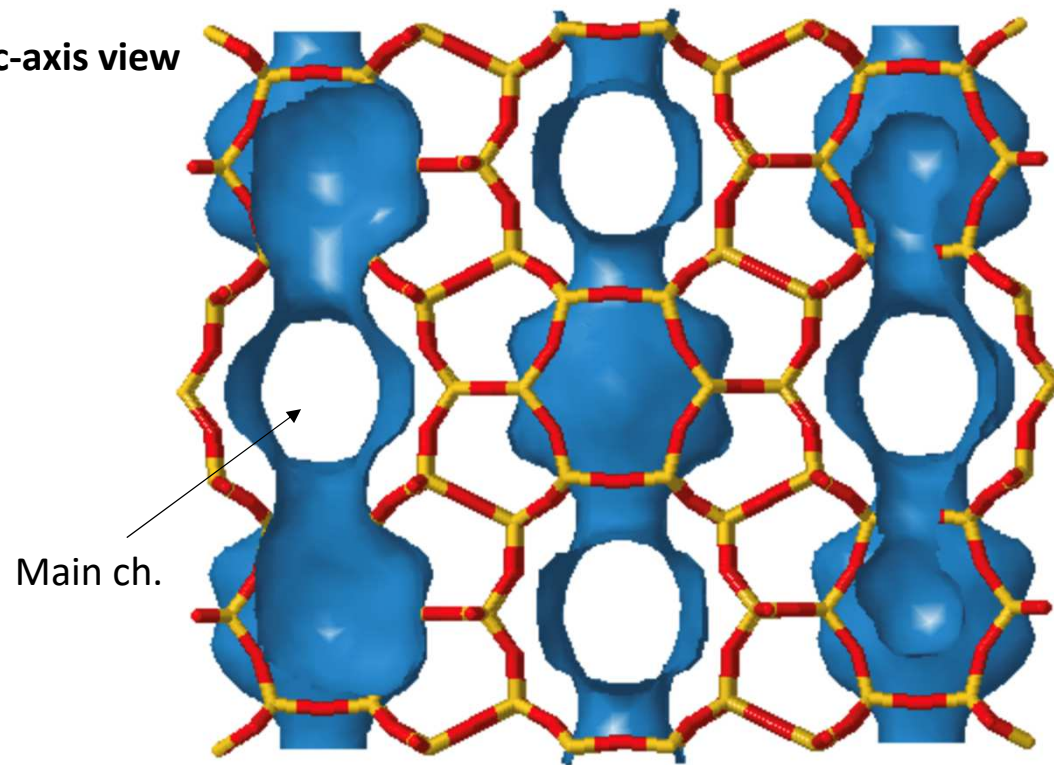
Main ch.

b-axis view

P-cage

Lattice parameters
a= 19.018 Å
b= 14.303 Å
c= 7.541 Å
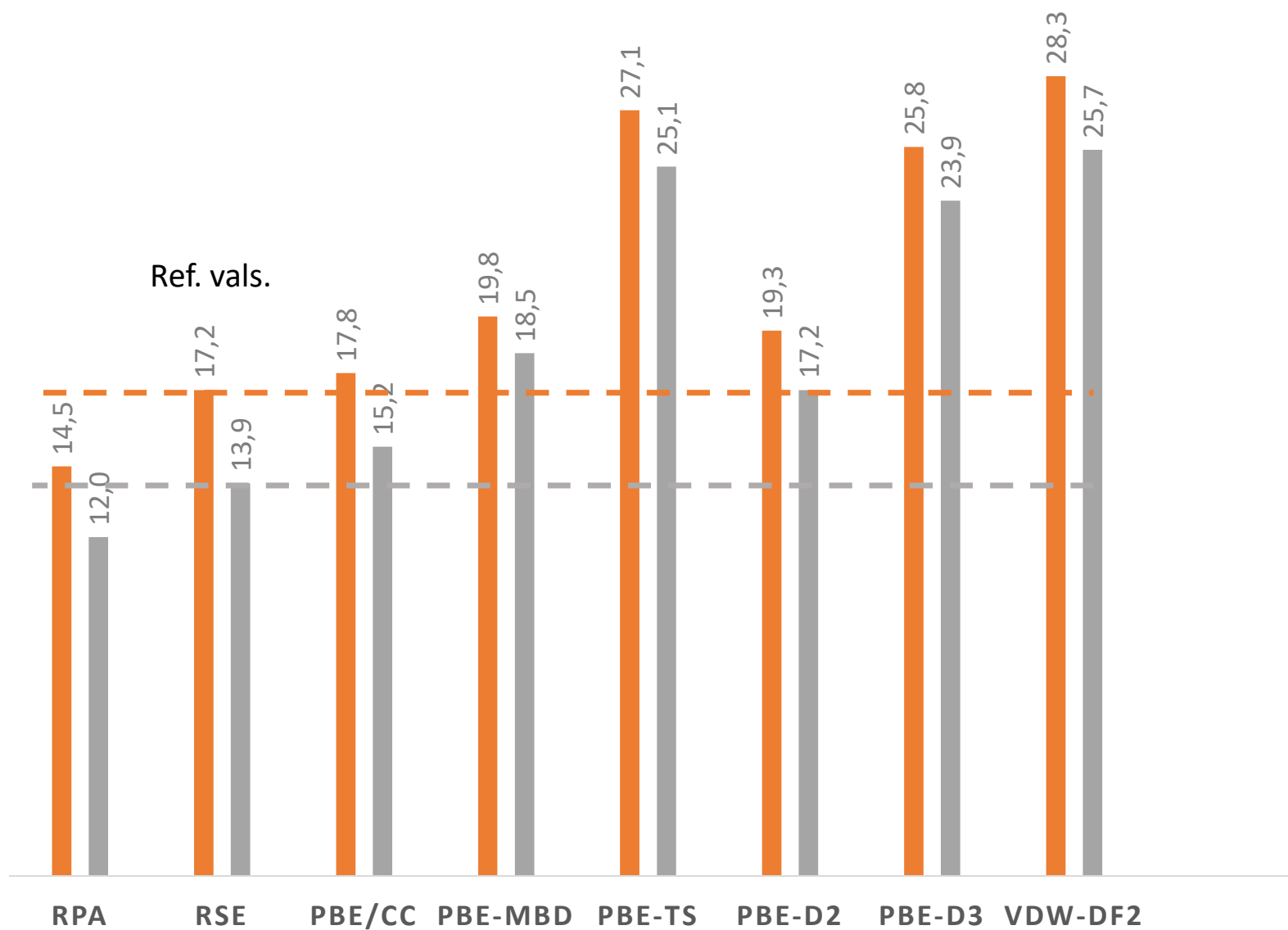α=β=γ= 90°

Symmetry: I_{mmm} (71)
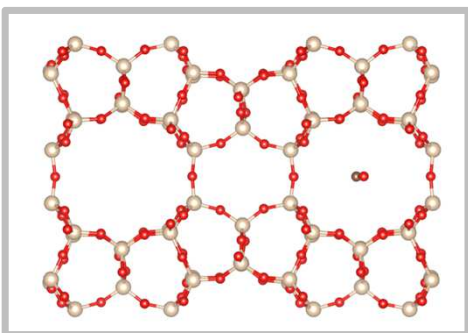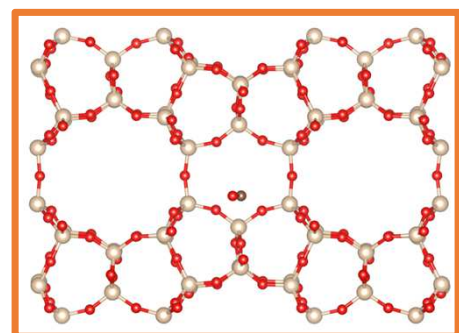T1:T2:T3:T4=16:8:8:4

Synthesis
- Typical Si/Al=8.6, 27.5
- Fully siliceous FER synthesized from amorphous silica - problematic (HF needs to be present)

Performance of ab-initio methods in siliceous FER

**Binding energies in kJ/mol**

P-cage   Main-Channel

Ref. vals.

RPA: 14,5 / 12,0
RSE: 17,2 / 13,9
PBE/CC: 17,8 / 15,2
PBE-MBD: 19,8 / 18,5
PBE-TS: 27,1 / 25,1
PBE-D2: 19,3 / 17,2
PBE-D3: 25,8 / 23,9
VDW-DF2: 28,3 / 25,7

RPA   RSE   PBE/CC   PBE-MBD   PBE-TS   PBE-D2   PBE-D3   VDW-DF2
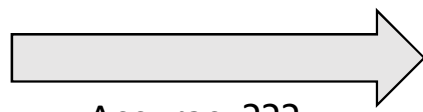
* Thang *et al.*, JPCA **118**, 7526 (2014)

Cluster models & DFT/CC modeling

Binding energies in kJ/mol

model	CCSD(T)	RSE(RPA)	PBE/CC	DFT-D	Δ_{max}[DFT-D – CCSD(T)]
1T..CO	5.7	5.6 (4.4)	5.7	6.0 - 7.1	1.4
2T..CO	6.9	6.9 (5.6)	7.0	7.5 - 9.1	2.2
3T..CO	8.6	8.6 (7.4)	8.6	9.2 - 11.5	2.9

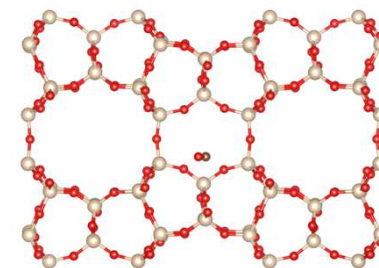~ R^{-6}

problem

minimum

CCSD(T)-PBE [kJ/mol]

R[Ang]
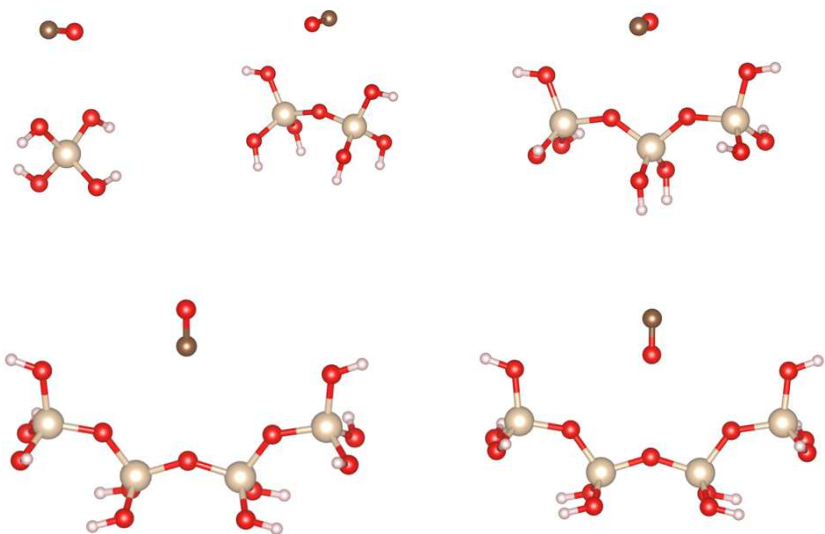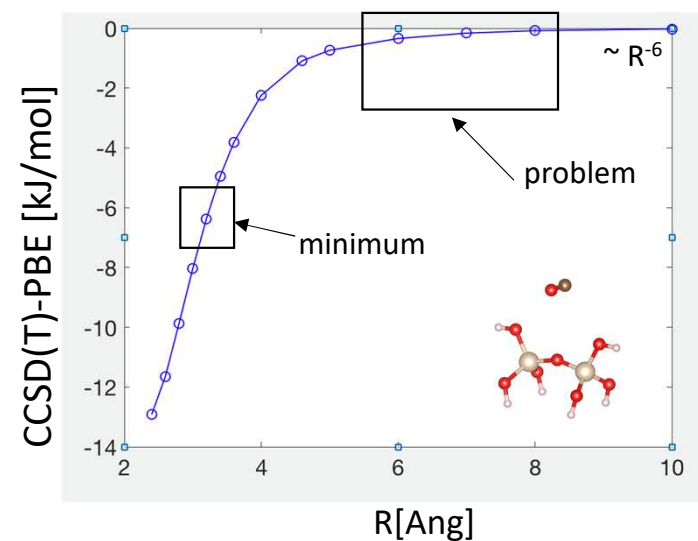
Can we do that???

Accuracy???
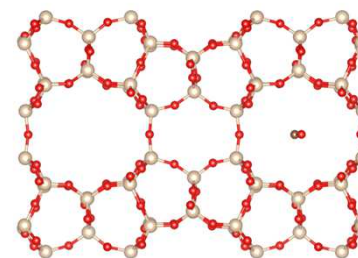
$N_{atom-atom}$ ~ R^3
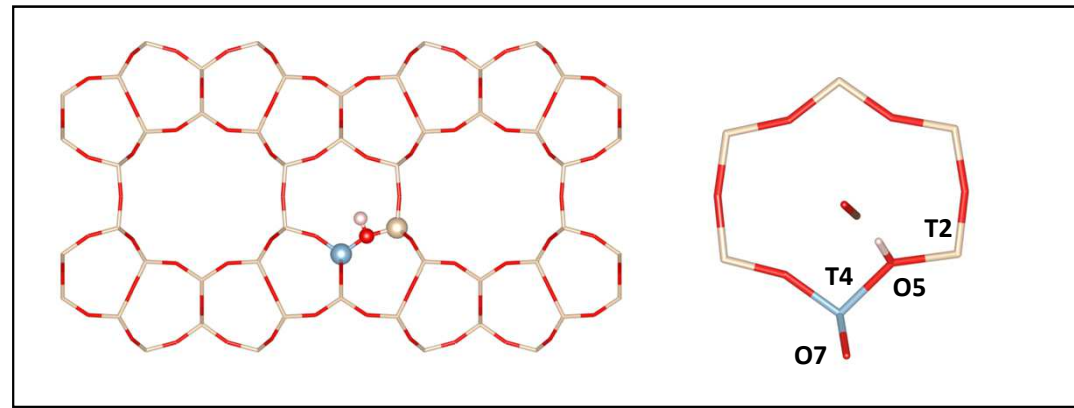
Benchmarks in exteded systems?
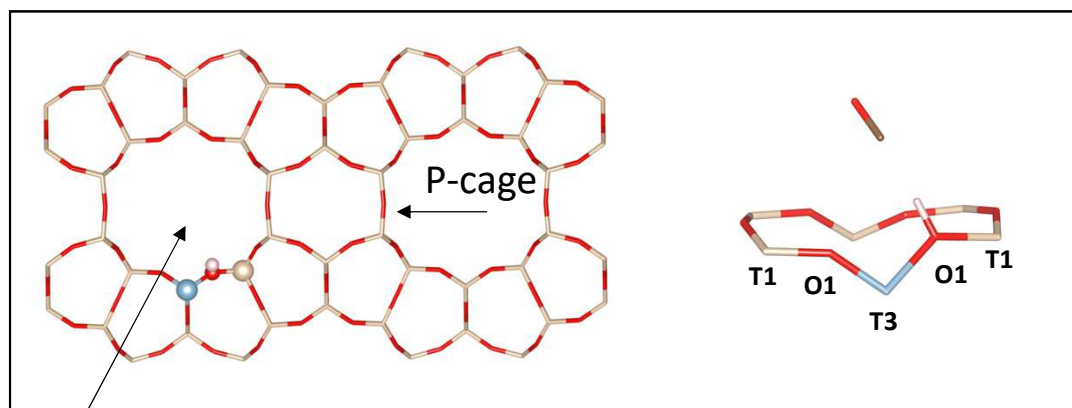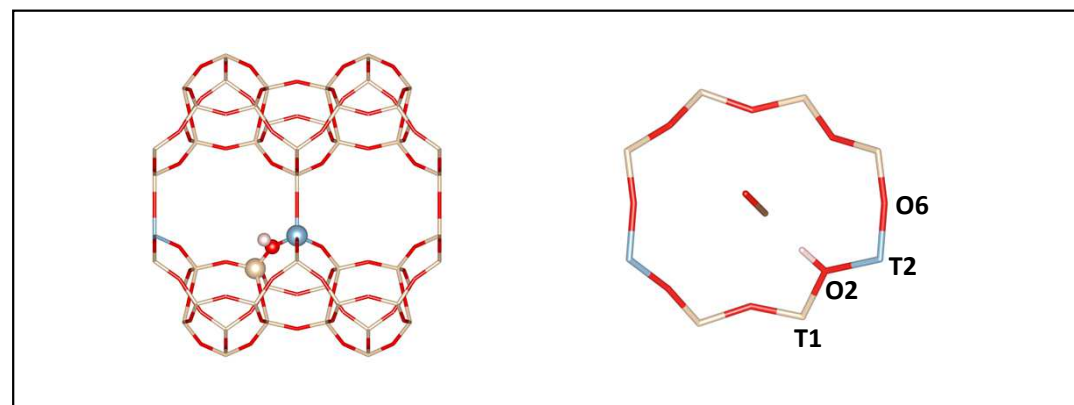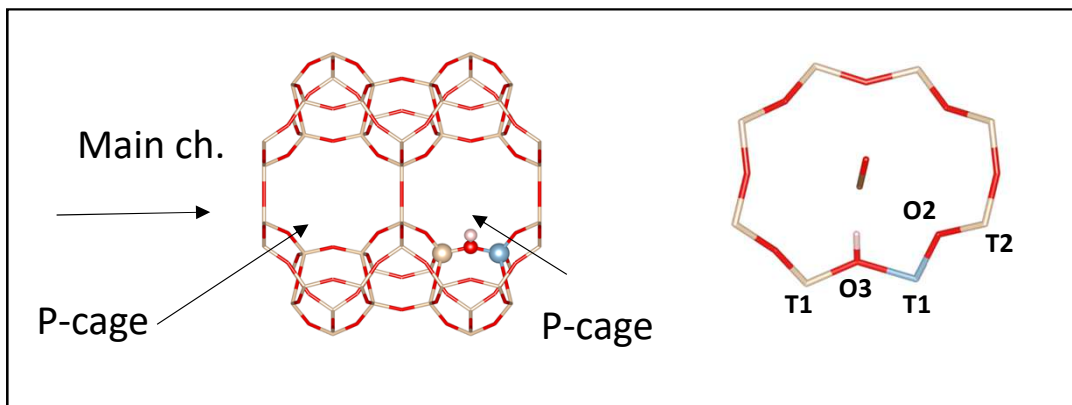
Brønsted-CO interaction

- DFT errors associated with this type of local interaction is an area, where DFT/CC performs quite well.

- Note obvious advantage of using interpolation instead of fitting on dispersion type functional forms.

- Using hybrid func. is better, but still does not fix the problem.
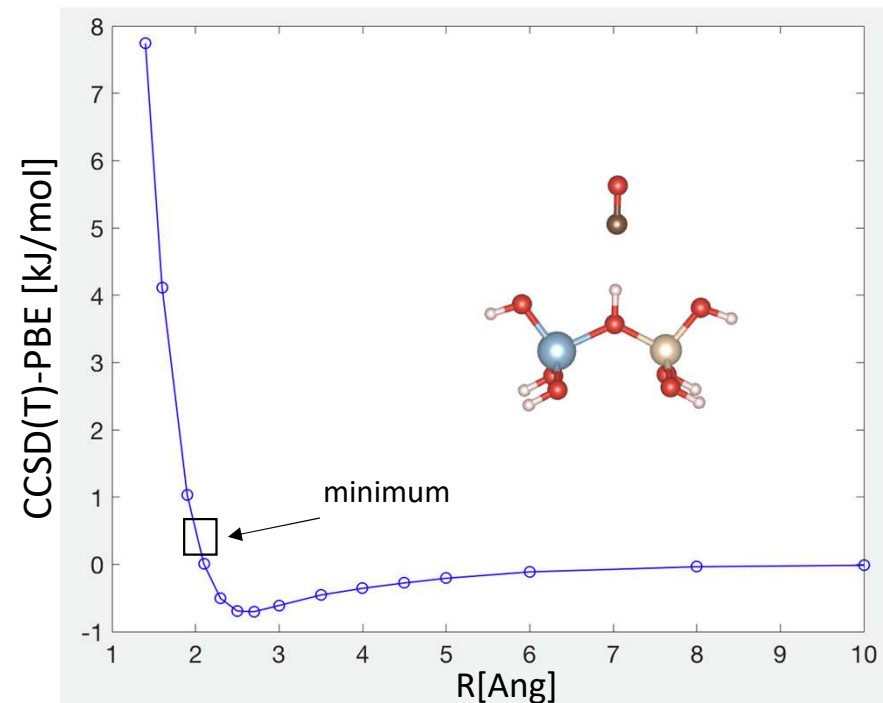
Binding energies in kJ/mol

model	PBE	PBE0	CCSD(T)	RSE(RPA)	PBE/CC	DFT-D	Δ_{max}[DFT-D − CCSD(T)]
2T-HB..CO	26.4	24.2	**25.7**	26.1 (21.0)	25.7	27.9 - 11.5	6.7

H-FER models

Main ch.

P-cage

P-cage

O2
T2
T1   O3   T1

O6
T2
O2
T1

P-cage

Main ch.

T1   O1   O1   T1
T3

T2
T4   O5
O7

Performance of ab-initio methods in H-FER

Binding energies in kJ/mol excluding deformation energy

T1-T4

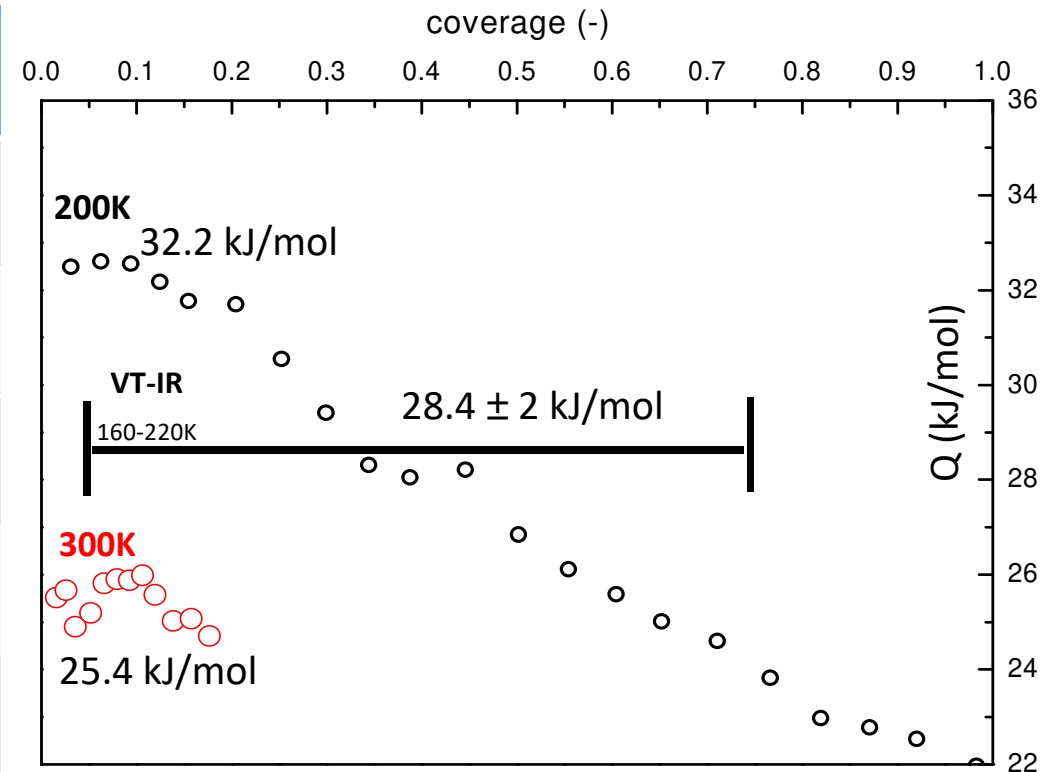| RPA	RSE	PBE/CC	PBE-MBD	PBE-TS	PBE-D2	PBE-D3	vdW-DF2
31	38	38	47	52	45	52	46
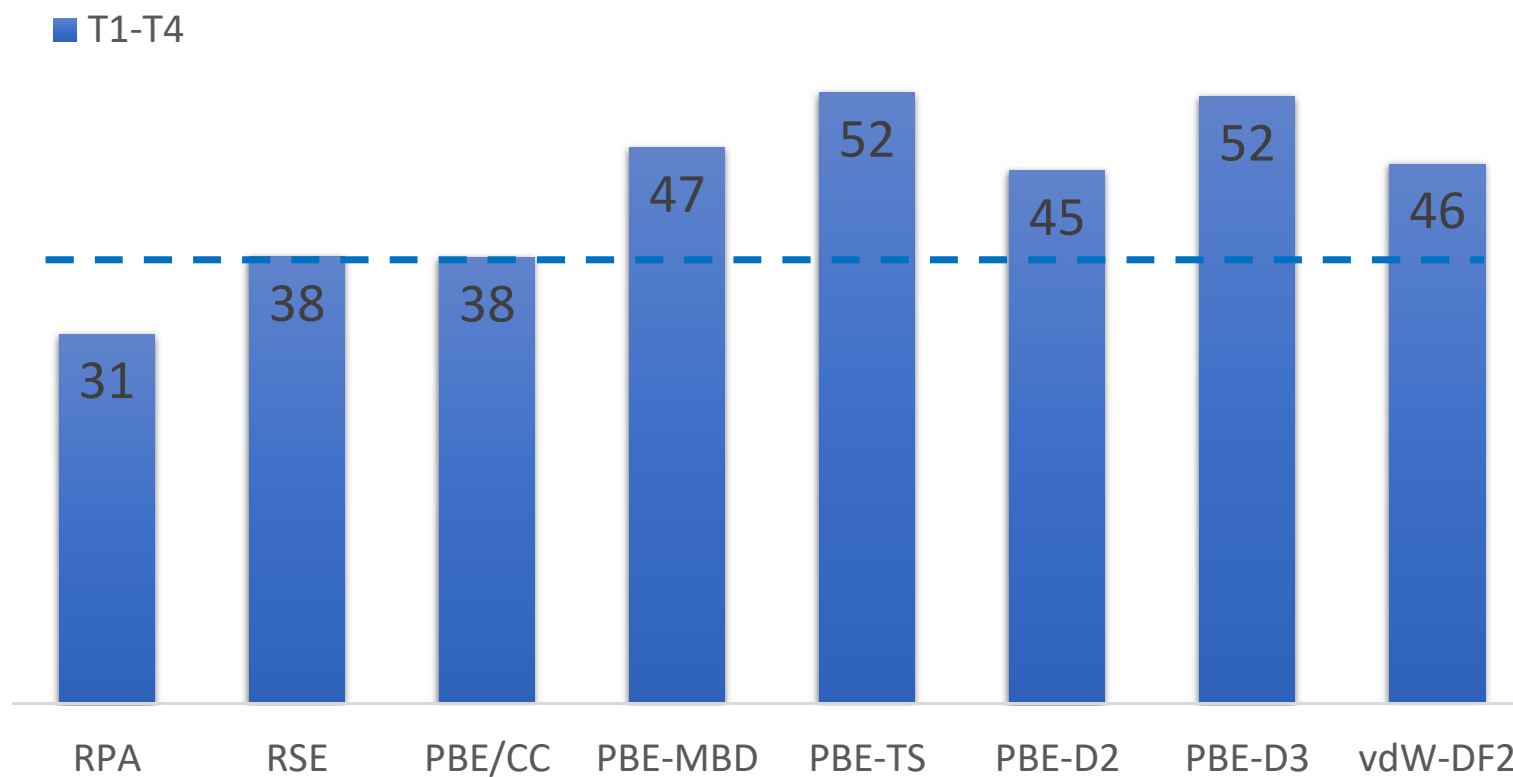
Temperature dependence of adsorption enthalpy

In kJ/mol

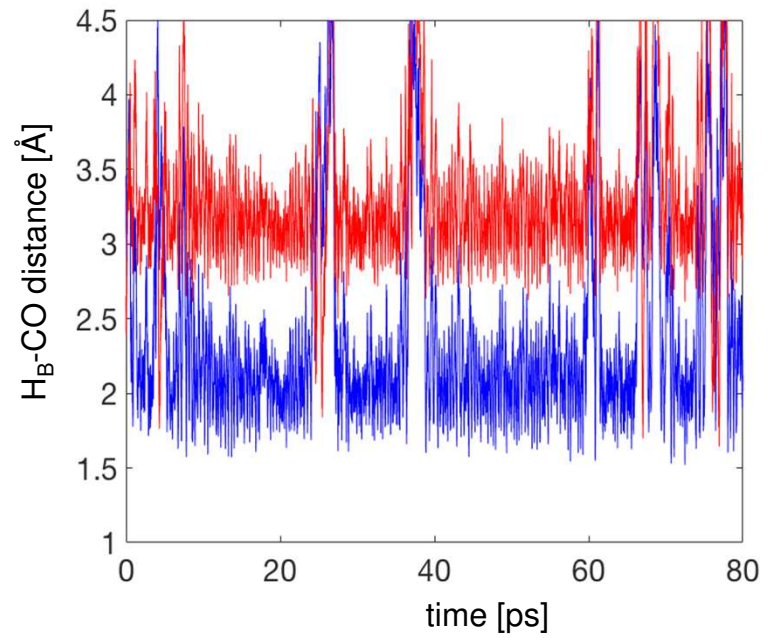| Ads. site	E_{bind}	$-\Delta H(0K)$	$-\Delta H(200K)$	$-\Delta H(300K)$
T1	36.7	33.6	**33.0** (34.2)	**26.0** (33.5)
T2	31.7	28.5	**27.7**	**22.9**
T3	34.6	30.4	**28.4**	**21.9**
T4'	23.9	20.1	**17.4**	x
T4''	35.2	32.3	**30.0**	**28.4**

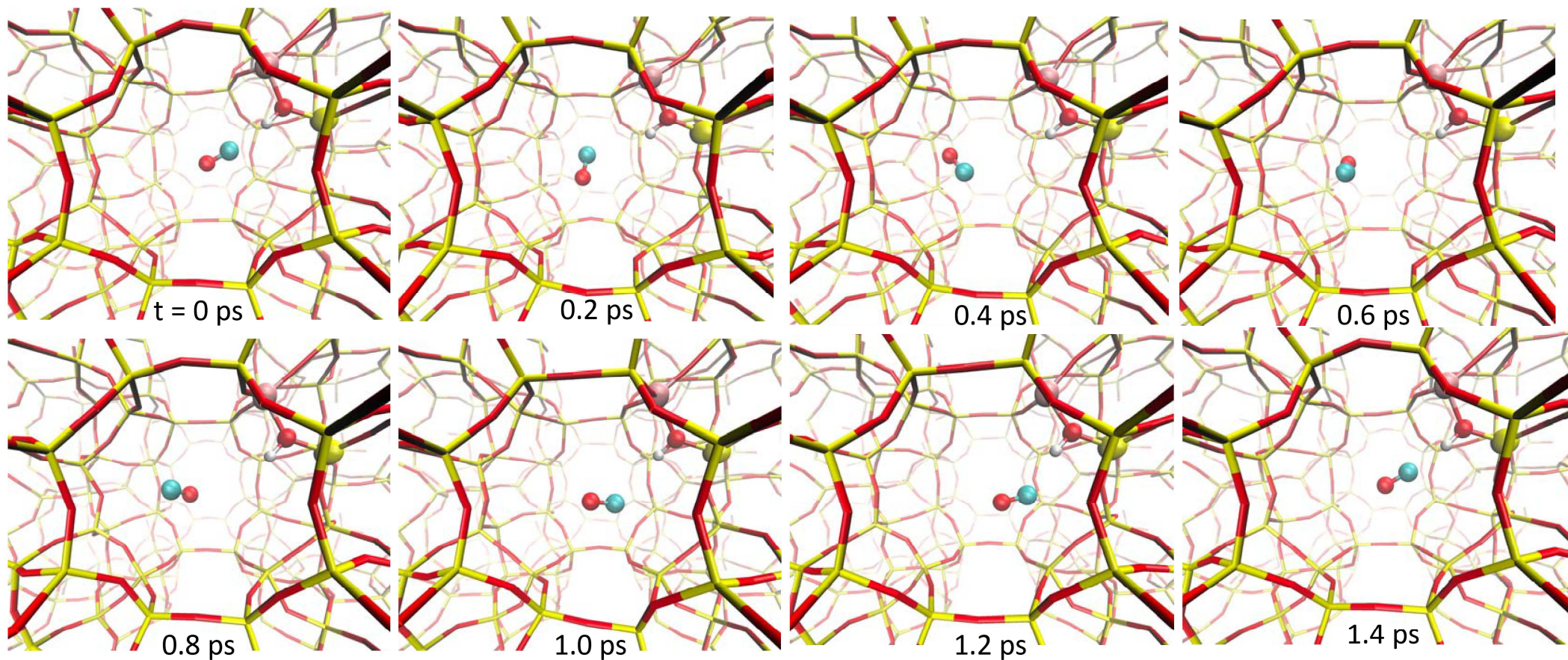# Atomistic insight from MD & limits of the model


200K
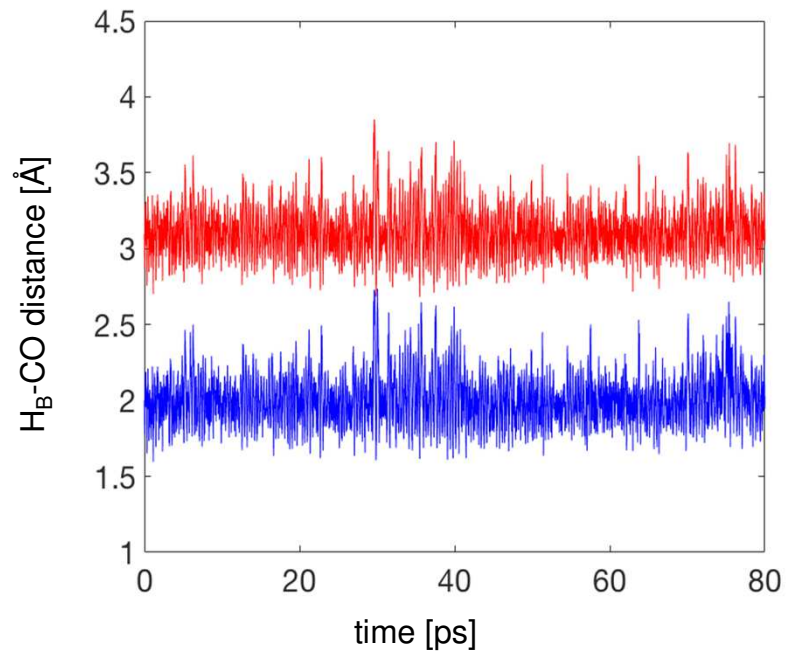
300K

T4'' 300 K simulation - shows confined space effect, thus 200K → 300K behaviour is less prounouced

Conclusions

- Describing the CO energetics with Brønsted acid sites in zeolites is still quite challenging for contemporary computational chemistry

- The following effects needs to be addressed as accurately as possible:
    - CO interaction with the framework (i.e. dispersion)
    - Errors of functional itself upon CO interaction with Brønsted cannot be ignored
    - Thermal effects needs to described via MD rather than using vibrational partition functions or equipartition theorem -> especially at higher temperatures

- Possible generalization?
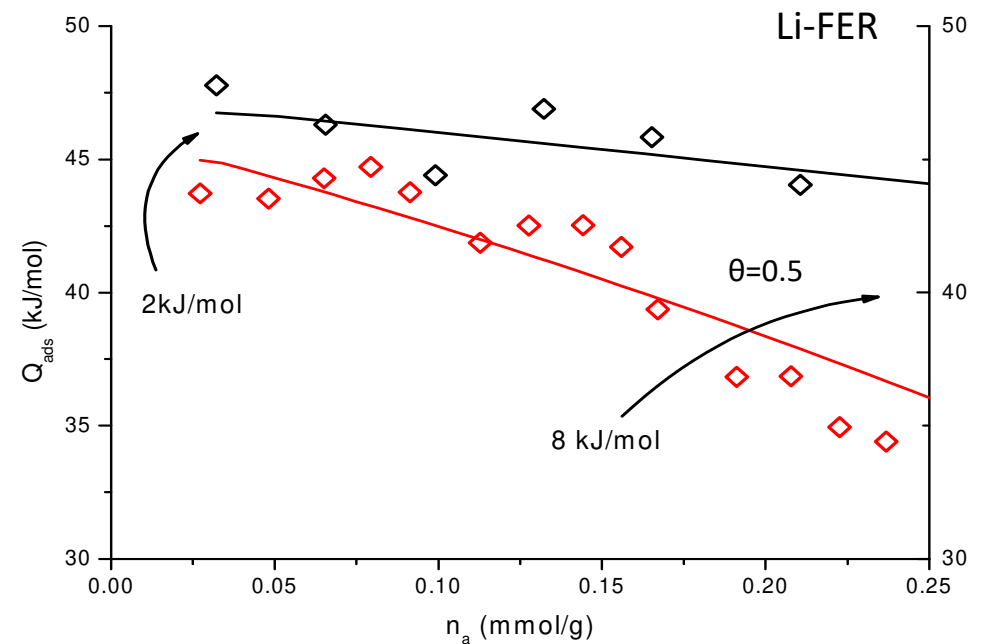
I would like to acknowledge my colleagues:

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- Msc. Michal Trachta
- Prof. Roman Bulánek (exp.)
- Dr. Eva Koudelková (exp.).
- Dr. Jiří Klimeš (RPA)

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Thank you for your attention