First-principles dynamics and free energy methods for flexible materials

François-Xavier Coudert
Chimie ParisTech

Rodolphe Vuilleumier, Anne Boutin
École normale supérieure

@fxcoudert
www.coudert.name

Chimie ParisTech

Summary — our toolbox

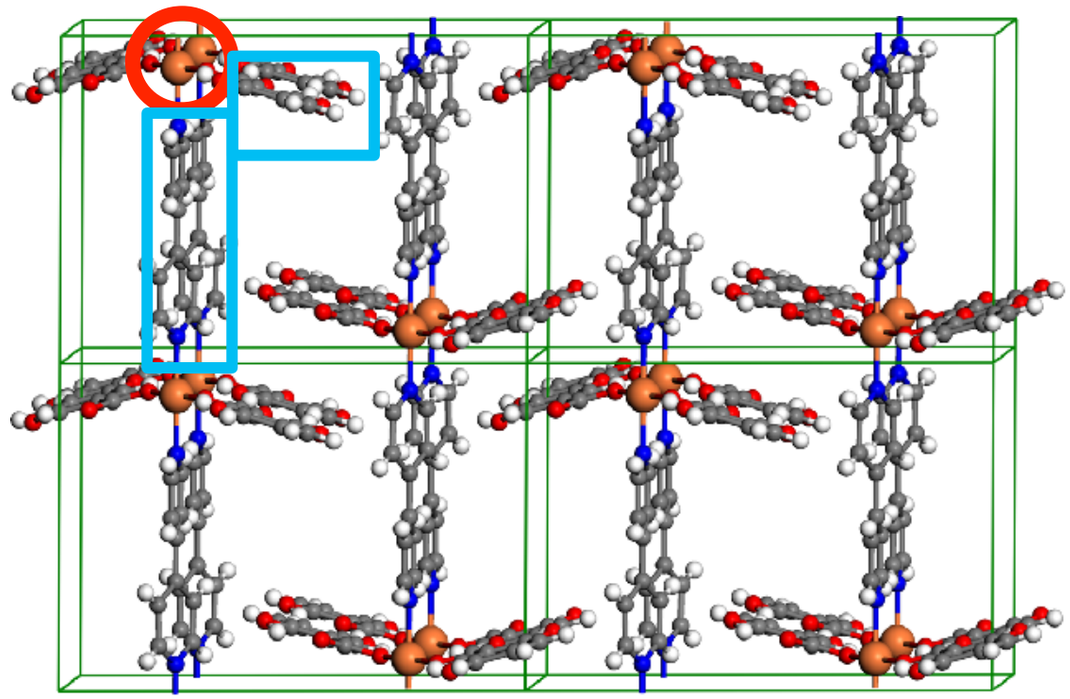
From smaller to large time / length scale

- Structure & energetics: quantum chemistry calculations
- Vibrations & deformations: harmonic / elastic approximations
- Local dynamics: *ab initio* molecular dynamics (CPMD)
- Long-time dynamics, diffusion : parameterized molecular dynamics
- Thermodynamics, open systems : Monte Carlo methods
- Multi-scale modeling: Lattice Boltzmann models with physical/chemical insight

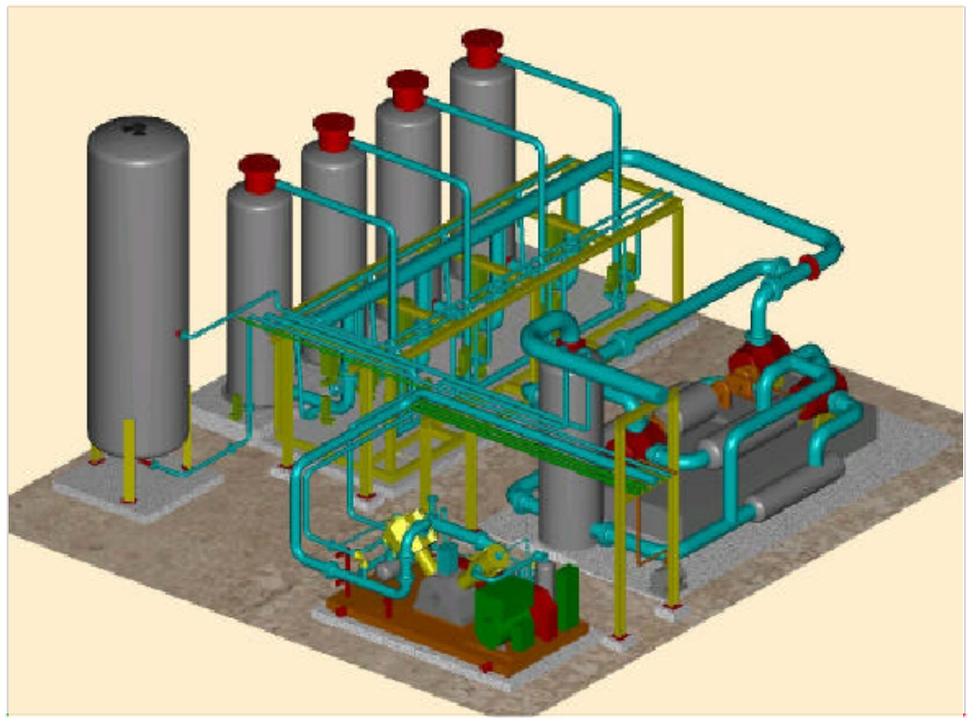
Multiple theoretical tools = multiples points of view for a given phenomenon

Metal–Organic Frameworks

Cristalline, organic–inorganic hybrid nanoporous materials



- Flexibility of coordination chemistry: pore geometry and topology
- Versatility of organic chemistry: pore size and internal surface



- Applications: gas adsorption, catalysis, sensing, delivery, …
- **High structural flexibility of their frameworks**
- **Important limitation for applications: hydrothermal & mechanical stability**

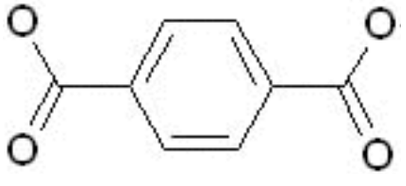
Metal–Organic Frameworks

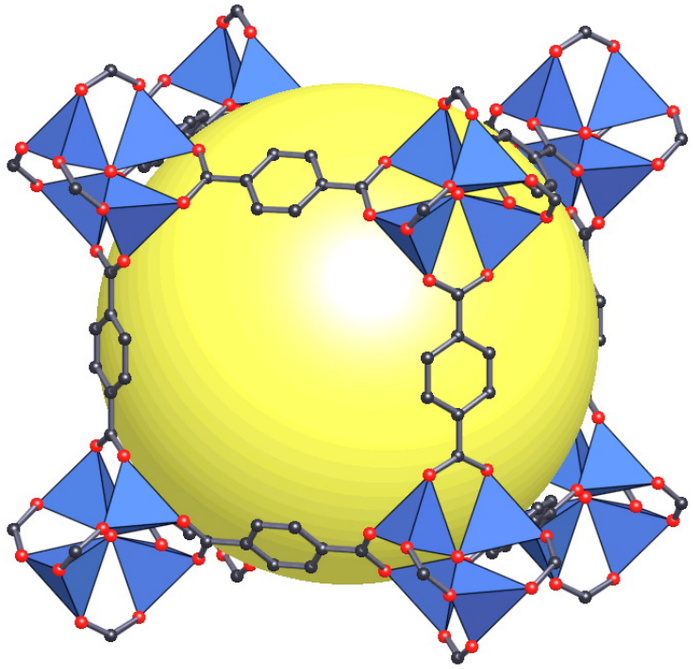
MOF-5

=

Zn_4O

+



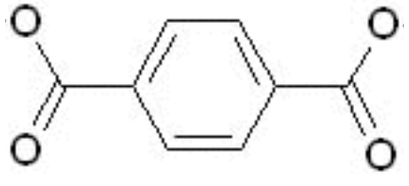


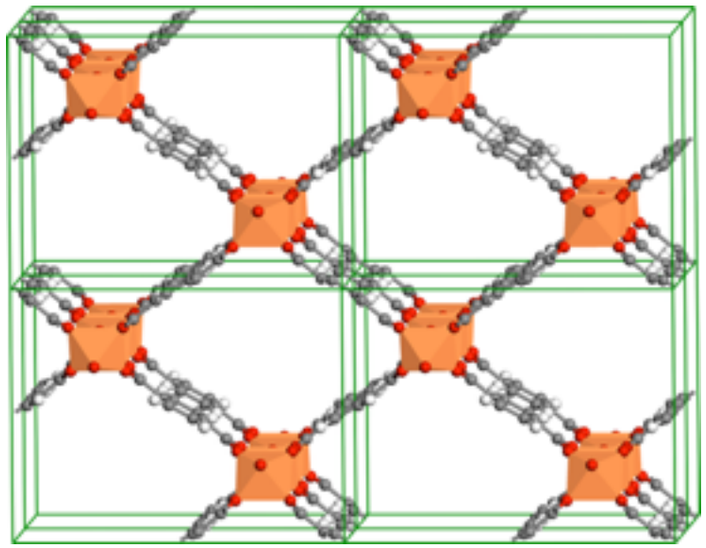
MIL-53 (Cr)

=

Cr(OH)

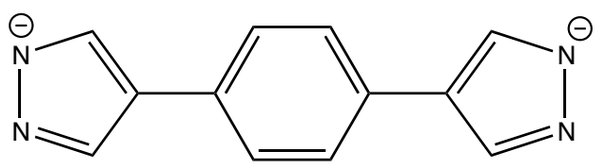
+

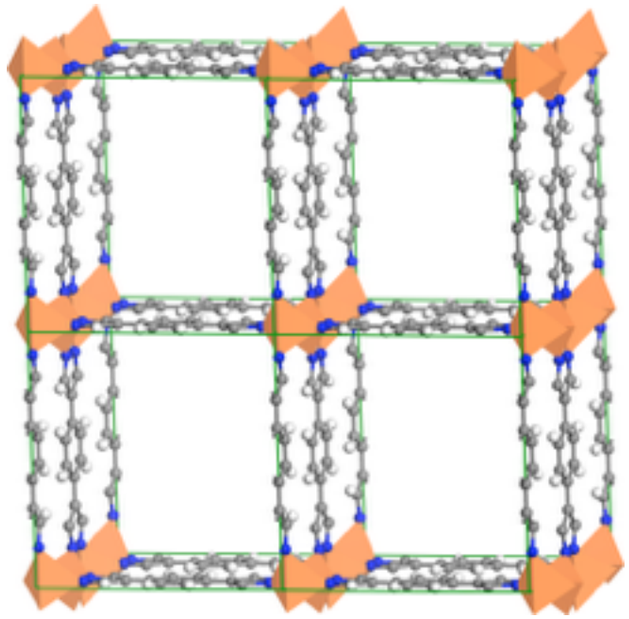




Co^{2+}

+

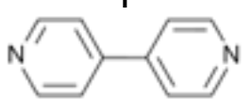


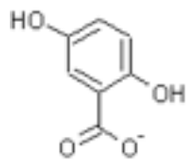


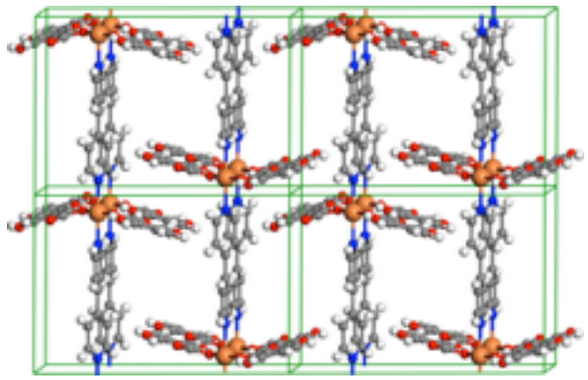
Metal–Organic Frameworks

Cu^{2+}

+

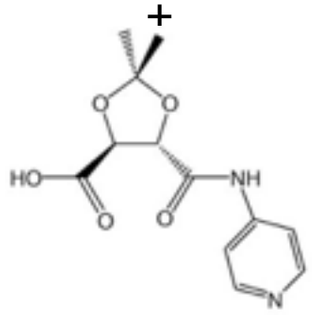


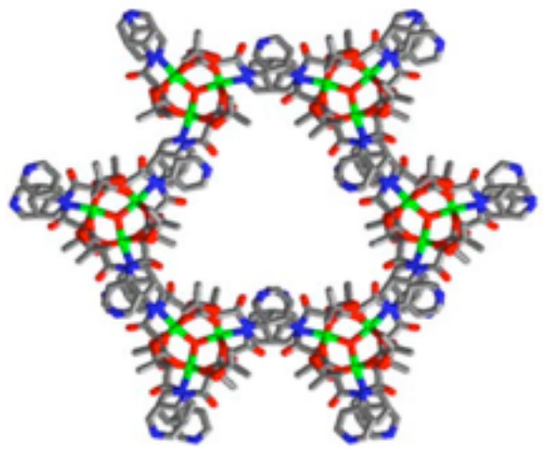




Zn^{2+}

+



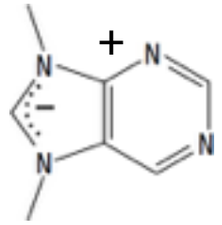


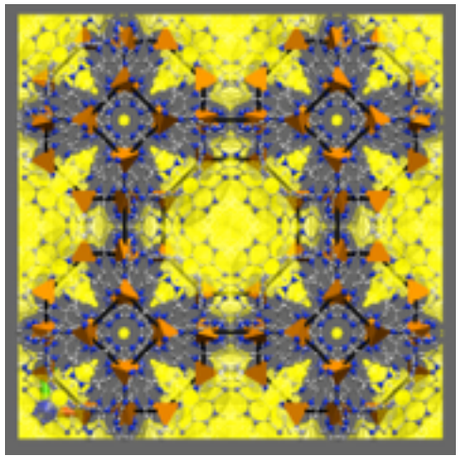
ZIF-20

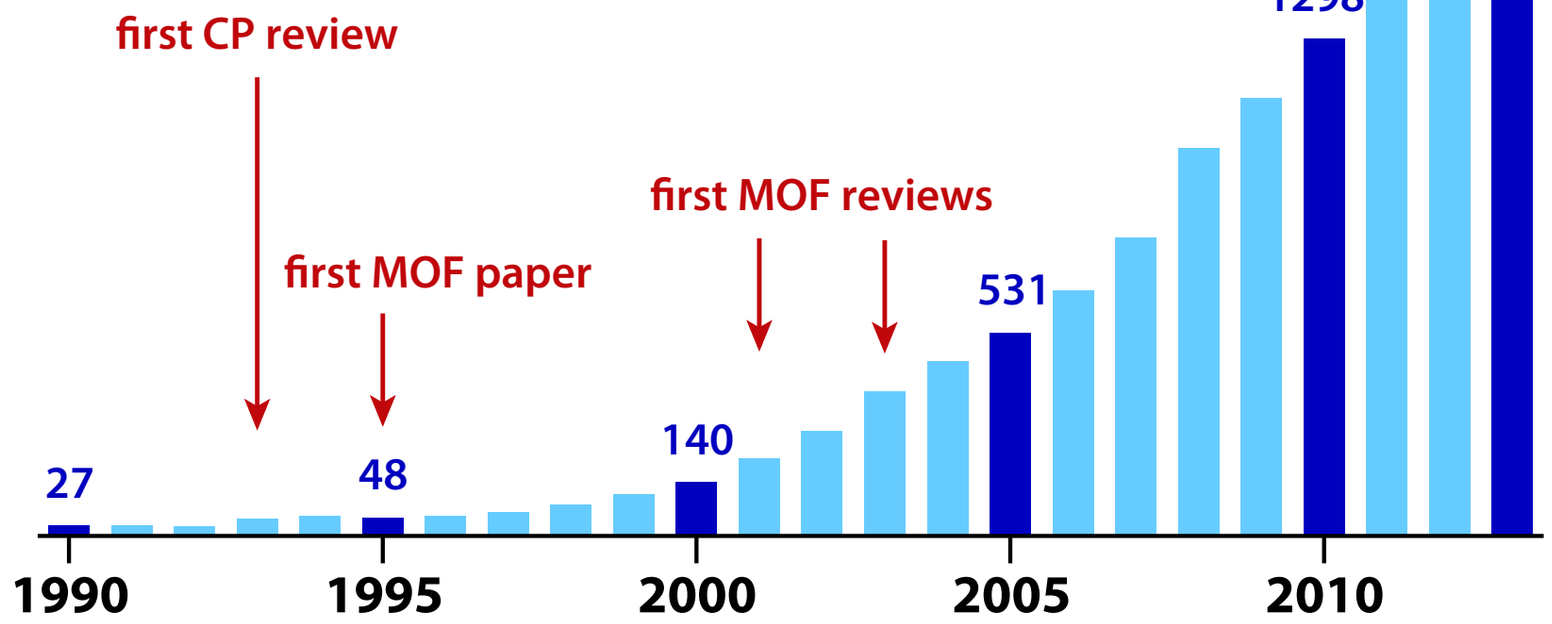
=

Zn^{2+}

+







Soft Porous Crystals

nature chemistry

REVIEW ARTICLE

PUBLISHED ONLINE: 23 NOVEMBER 2009 | DOI: 10.1038/NCHEM.444

Soft porous crystals

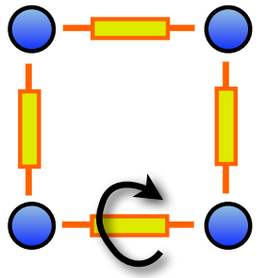
Satoshi Horike[1,2], Satoru Shimomura[1] and Susumu Kitagawa*[1-3]

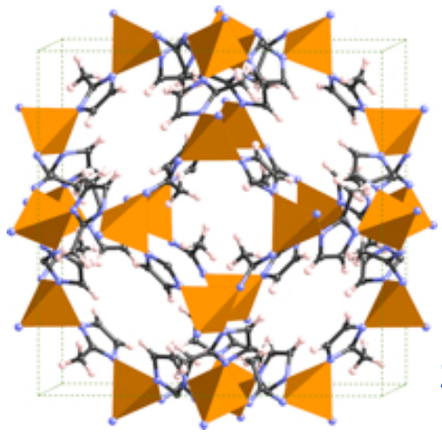
The field of host–guest complexation is intensely attractive from diverse perspectives, including materials science, chemistry and biology. The uptake and encapsulation of guest species by host frameworks are being investigated for a wide variety of purposes, including separation and storage using zeolites, and recognition and sensing by enzymes in solution. Here we focus on the concept of the cooperative integration of 'softness' and 'regularity'. Recent developments on porous coordination polymers (or metal–organic frameworks) have provided the inherent properties that combine these features. Such soft porous crystals exhibit dynamic frameworks that are able to respond to external stimuli such as light, electric fields or the presence of particular species, but they are also crystalline and can change their channels reversibly while retaining high regularity. We discuss the relationship between the structures and properties of these materials in view of their practical applications.

"Soft porous crystals are defined as porous solids that possess both a highly ordered network and **structural transformability**. They are bistable or multistable crystalline materials with long-range structural ordering, a **reversible transformability between states**, and permanent porosity"

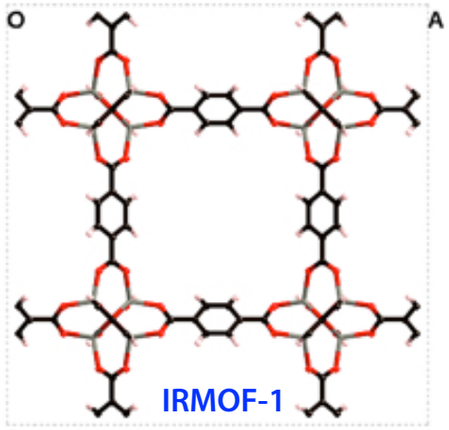
Soft Porous Crystals

intraframework dynamics



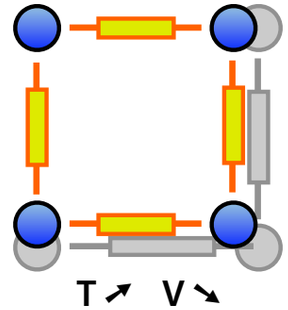


ZIF-8

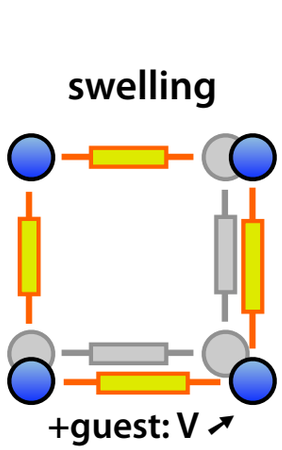


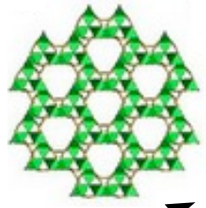
IRMOF-1

negative thermal expansion



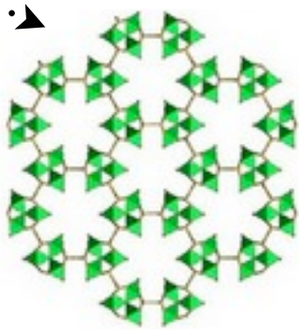
swelling



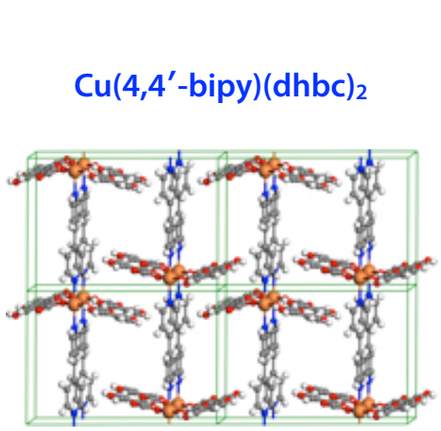


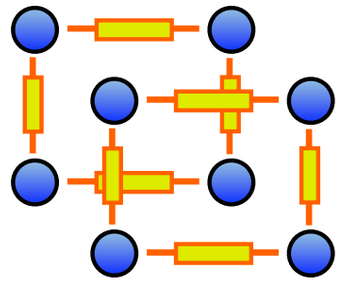
solvent

MIL-88

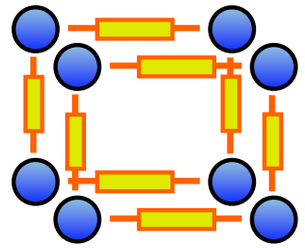


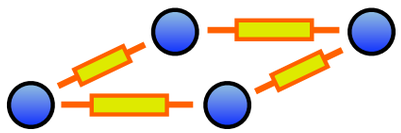
Cu(4,4′-bipy)(dhbc)$_2$



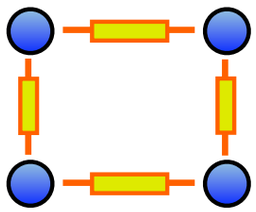


gate opening

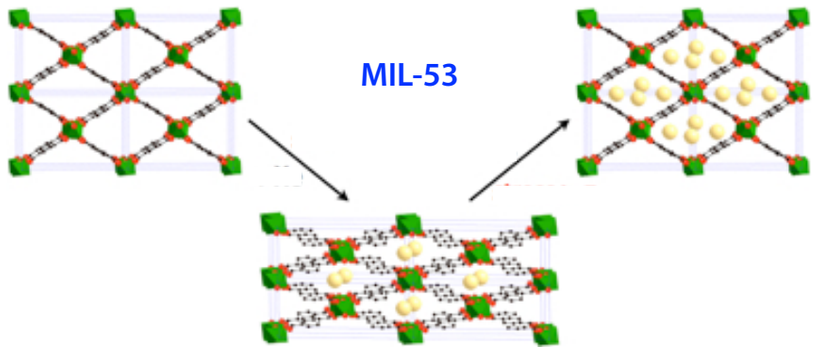




breathing



MIL-53



Coudert et al, *ChemPhysChem* **2011**

Thermodynamics

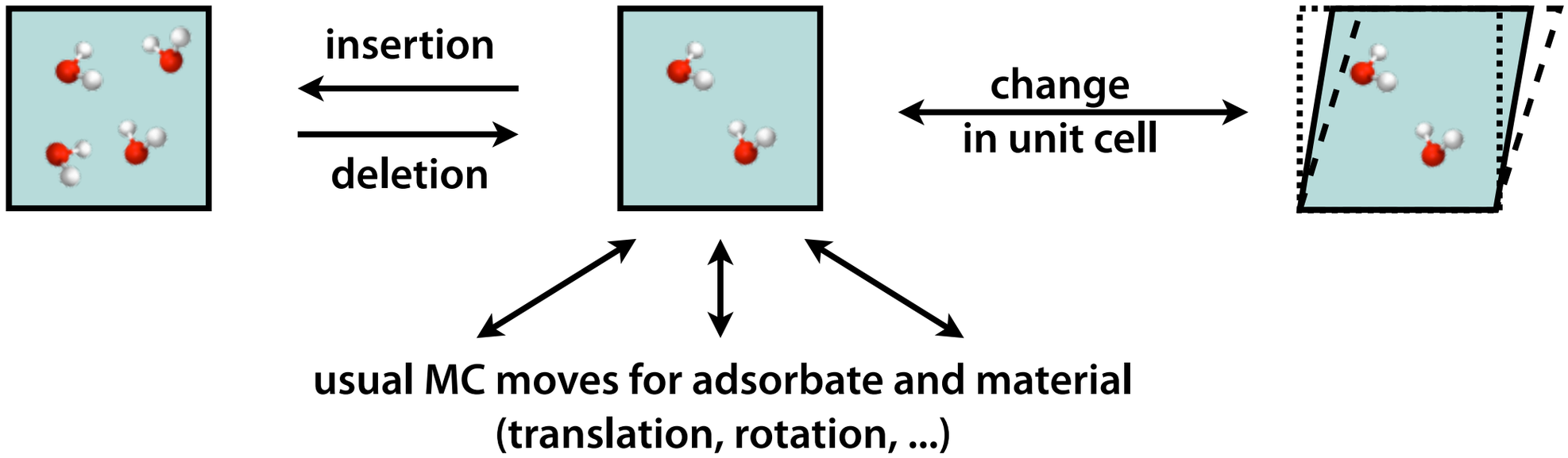
The osmotic ensemble: $(N_{mat}, \mu_{ads}, P, T)$

$$\Omega_{os} = U - TS - \mu_{ads}N_{ads} + PV$$

Both V and N_{ads} can vary

Coudert et al, *JACS* **2009**
Coudert et al, *JACS* **2010**

Direct Monte Carlo simulation:



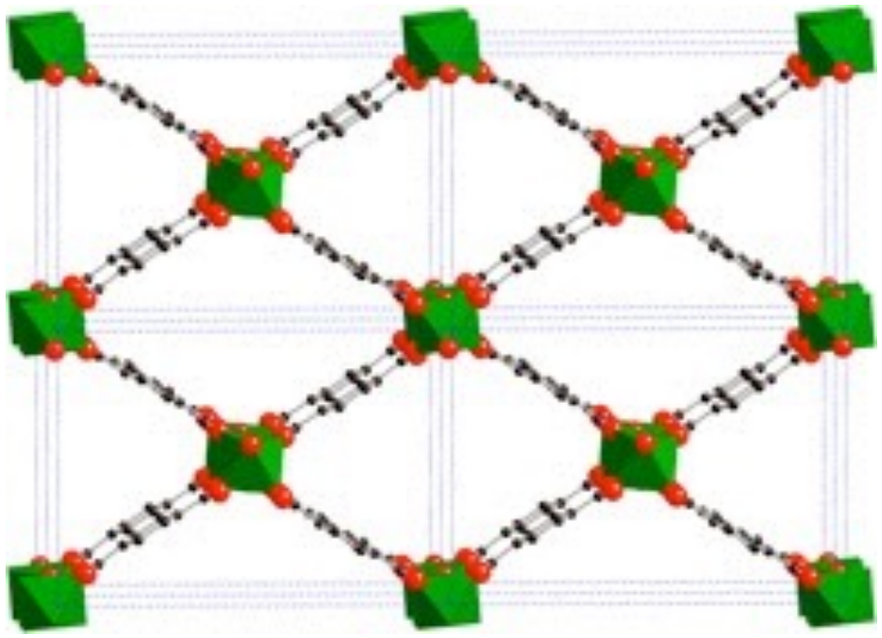
- Correctly describes adsorption in flexible materials
- Basis for Monte Carlo simulations
  - **Flexible forcefield for the material**
  - **Convergence is difficult… ΔN & ΔV changes are coupled!**

Bousquet, Coudert et al, *J. Chem. Phys.* **2012**

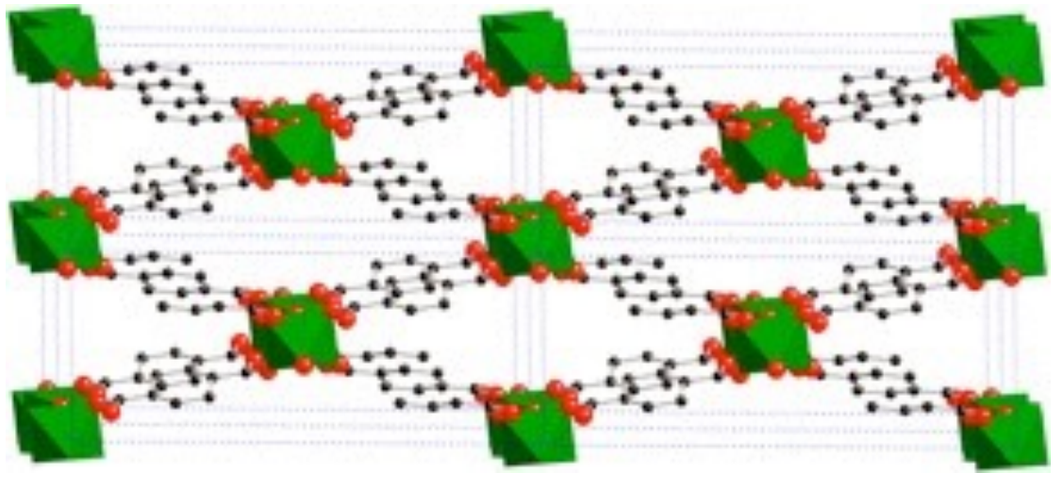
Breathing of MIL-53

- $M(OH)(O_2C–C_6H_4–CO_2)$, M = Al, Cr, …
- Group of prof. Férey, Versailles

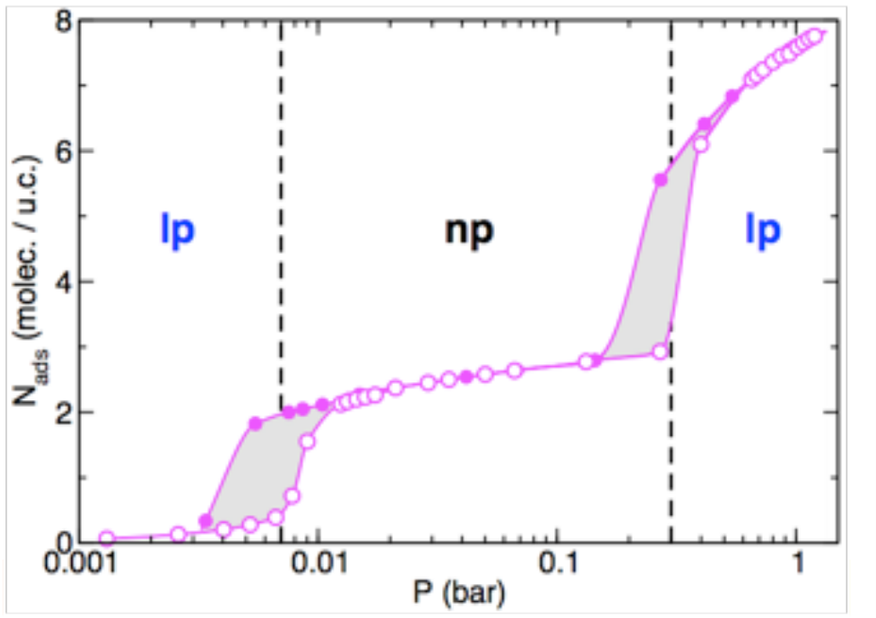
large-pore (**lp**) form
stable empty at high T



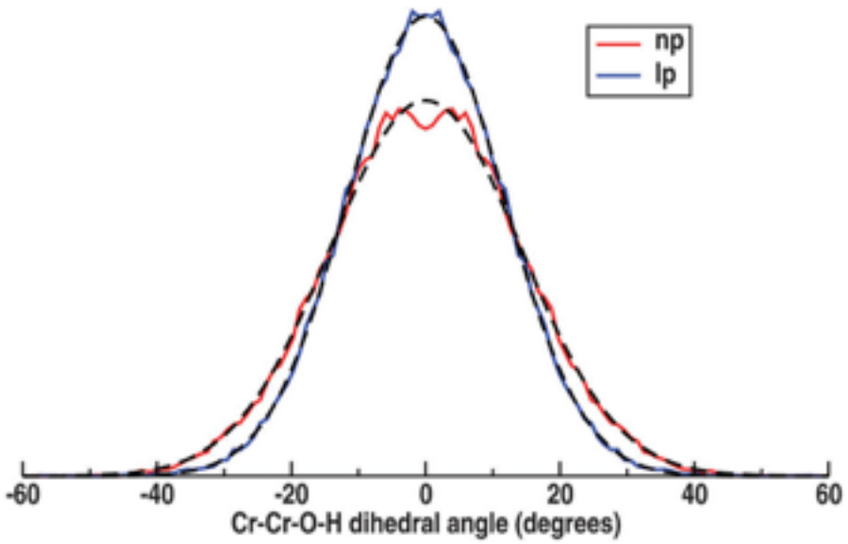
narrow-pore (**np**) form
stable empty at low T



Breathing phenomenon:
lp → **np** → **lp** transitions
upon (some) gas adsorption



- Describing the structure of each phase + adsorbate
- Structural & dynamic properties



PCCP

RSC Publishing

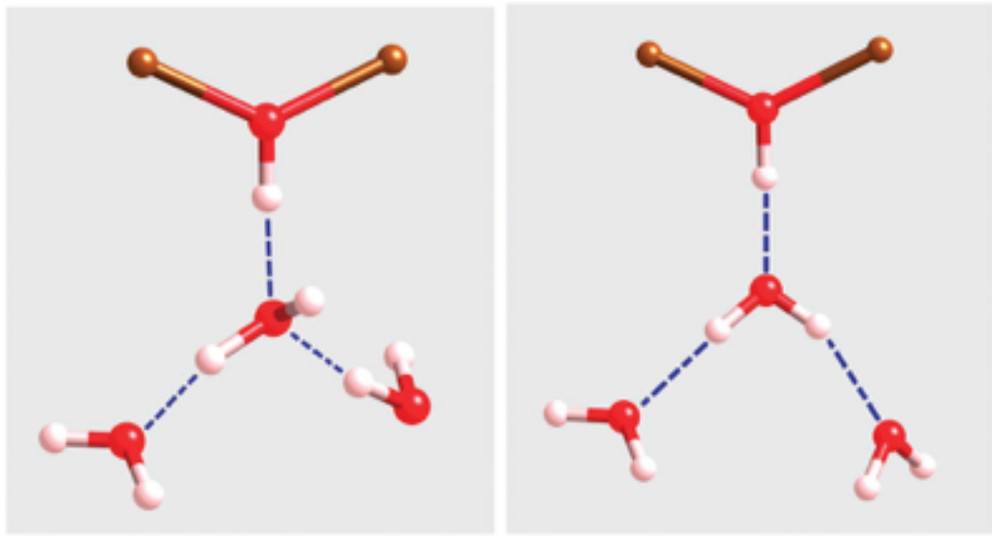
PAPER

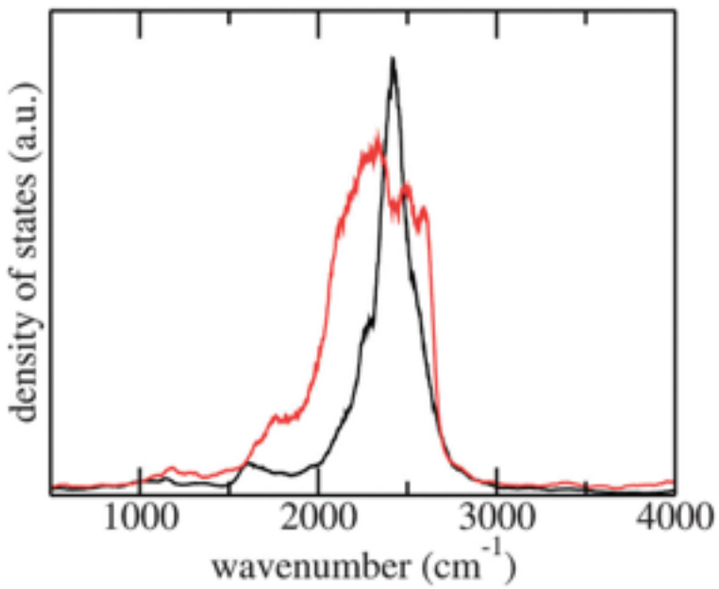
View Article Online
View Journal | View Issue

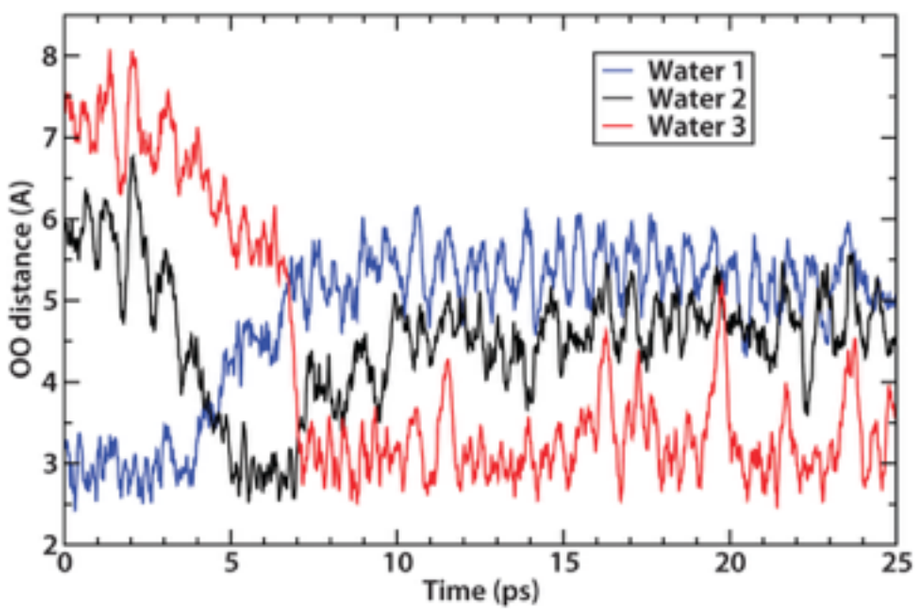
Cite this: *Phys. Chem. Chem. Phys.*, 2013, **15**, 19049

Investigation of structure and dynamics of the hydrated metal–organic framework MIL-53(Cr) using first-principles molecular dynamics

Volker Haigis,*[a] François-Xavier Coudert,[b] Rodolphe Vuilleumier[a] and Anne Boutin[a]







THE JOURNAL OF CHEMICAL PHYSICS **141**, 064703 (2014)

Challenges in first-principles *NPT* molecular dynamics of soft porous crystals: A case study on MIL-53(Ga)

Volker Haigis,[1,a)] Yacine Belkhodja,[1] François-Xavier Coudert,[2] Rodolphe Vuilleumier,[1] and Anne Boutin[1]

[1]*Ecole Normale Supérieure-PSL Research University, Département de Chimie, Sorbonne Universités – UPMC Univ Paris 06, CNRS UMR 8640 PASTEUR, 24, rue Lhomond, 75005 Paris, France*

[2]*PSL Research University, Chimie ParisTech – CNRS, Institut de Recherche de Chimie Paris, 75005 Paris, France*

(Received 3 March 2014; accepted 17 July 2014; published online 8 August 2014)

- *NPT* dynamics: failure
- But… a well-documented failure, for others to see

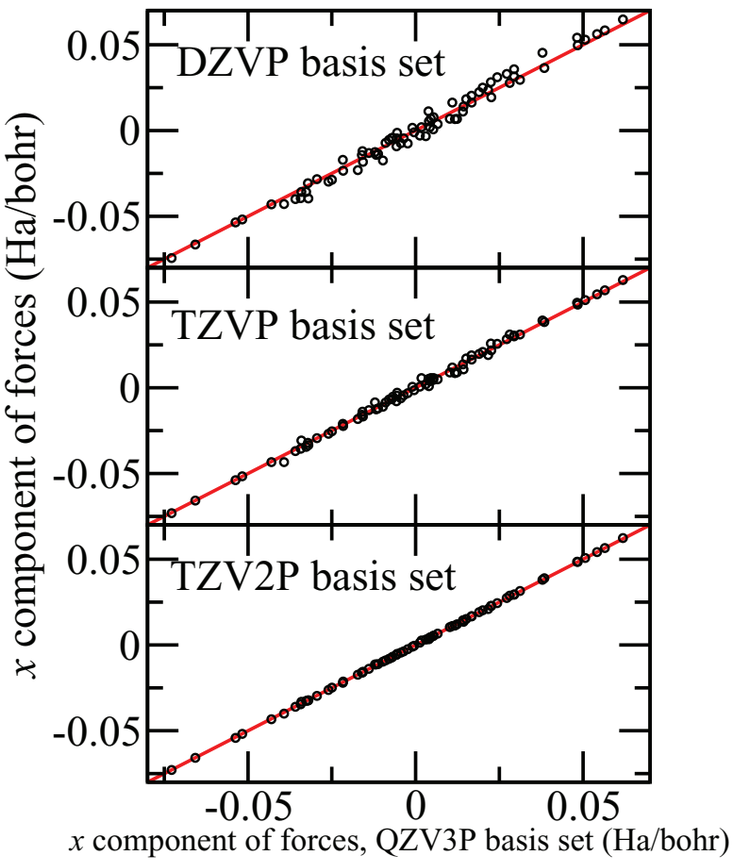
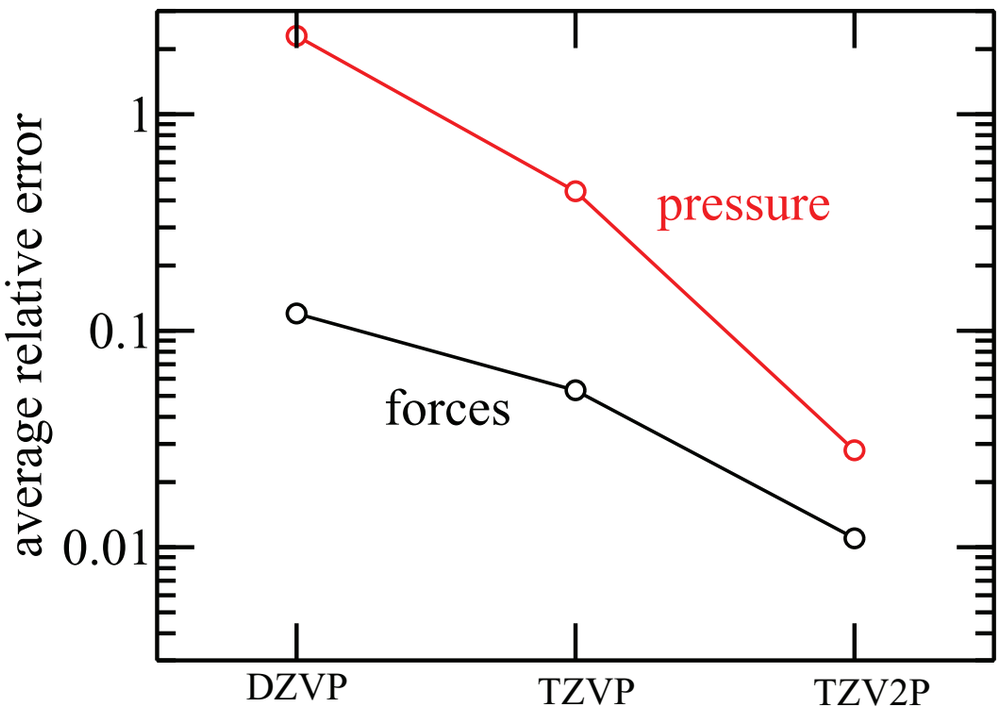


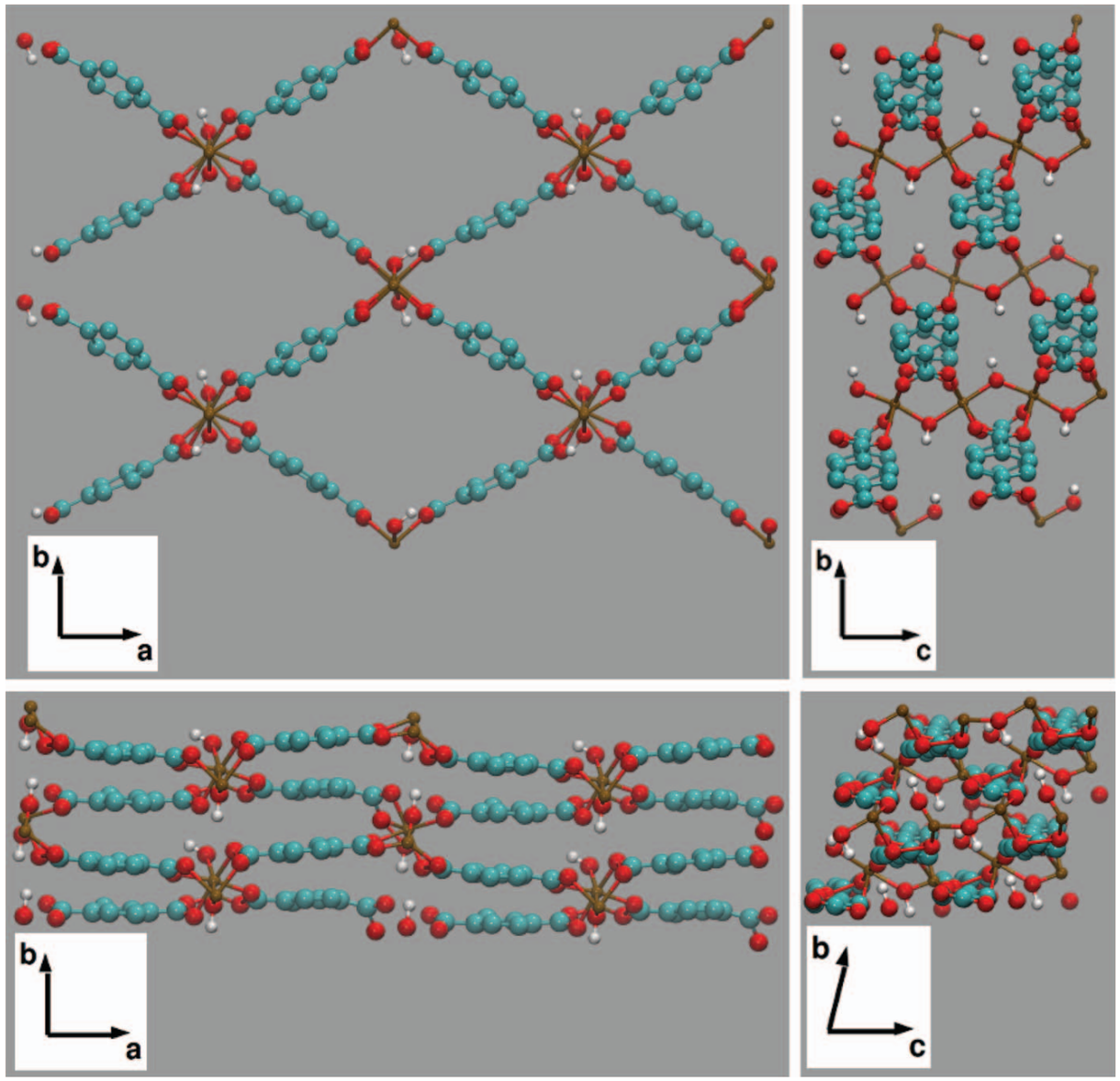
TABLE I. Convergence of forces (mean relative error) by element with respect to the plane-wave cutoff. As reference, a cutoff of 2500 Ry was used.

	280 Ry	600 Ry
Ga	607%	10.7%
O	12.7%	4.2%
C	0.64%	0.02%
H	0.11%	0.00%



Dispersive interactions...

- Semi-local XC functionals tested: BLYP, PBE
- Possibly with Grimme dispersion corrections: "D2" (2006), "D3" (2010)



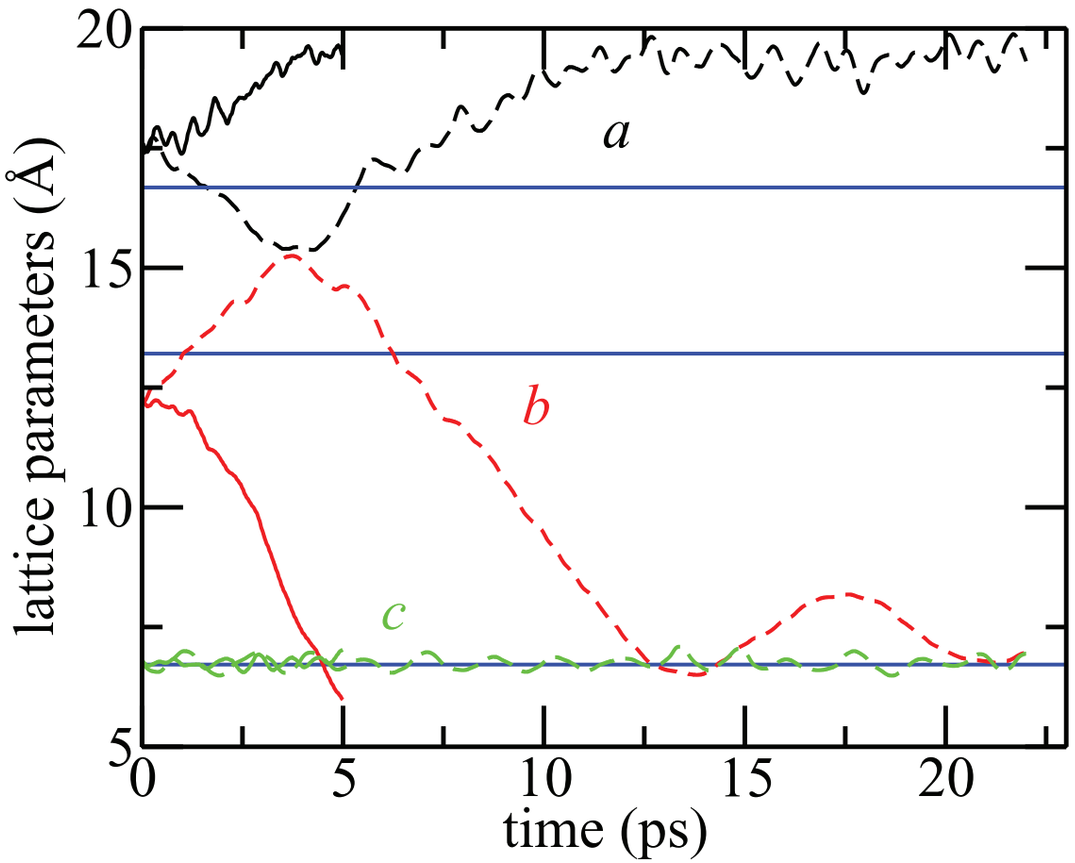


FIG. 3. Evolution of the cell parameters at 1 bar, 600 K, with the Grimme dispersion correction (solid line: D2,[45] dashed line: D3[52]). The experimental lattice parameters[33] for the large-pore phase are shown as blue lines.

Dispersive interactions...

- Semi-local XC functionals tested: BLYP, PBE
- Possibly with Grimme dispersion corrections: "D2" (2006), "D3" (2010)
- Possibly tweaking / scaling the dispersion corrections???

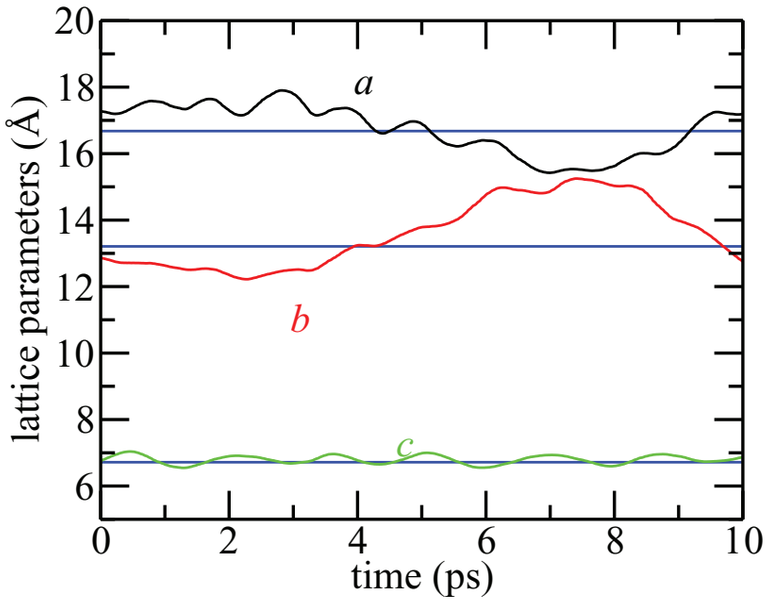


FIG. 5. Evolution of the cell parameters at 1 bar, 600 K, with the modified Grimme dispersion correction (global scaling factor $s_6 = 0.2$). The experimental lattice parameters[33] for the large-pore phase are shown as blue lines.

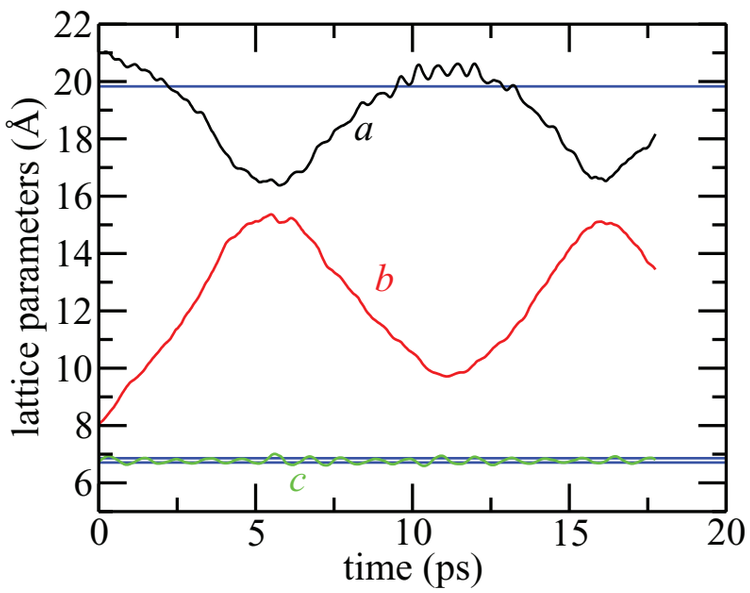


FIG. 6. Evolution of the cell parameters at 1 bar, 300 K, with the modified Grimme dispersion correction (global scaling factor $s_6 = 0.2$). The experimental lattice parameters[33] for the narrow-pore phase are shown as blue lines.

Dispersive interactions...

- Semi-local XC functionals tested: BLYP, PBE
- Possibly with Grimme dispersion corrections: "D2" (2006), "D3" (2010)
- Nonlocal XC functional: Dion 2004 ("vdW-DF")

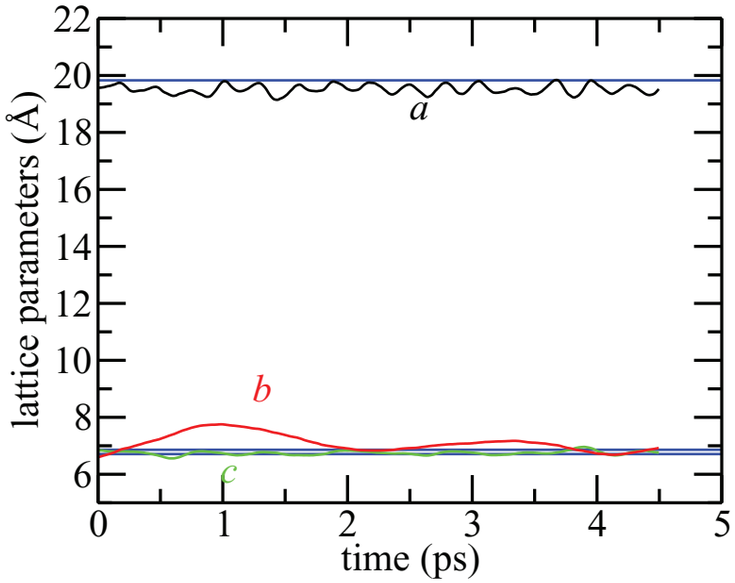


FIG. 7. Evolution of the cell parameters of the narrow-pore phase, at 1 bar and 300 K, with the Dion exchange-correlation functional. The experimental lattice parameters[33] for the narrow-pore phase are shown as blue lines.

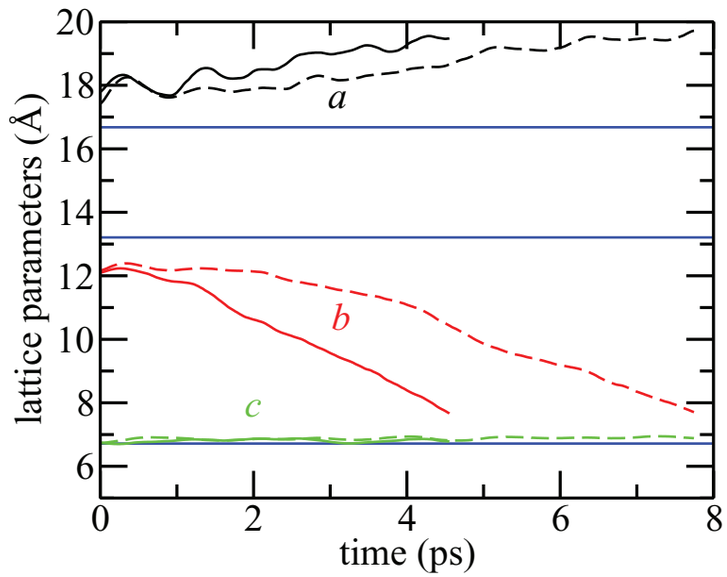
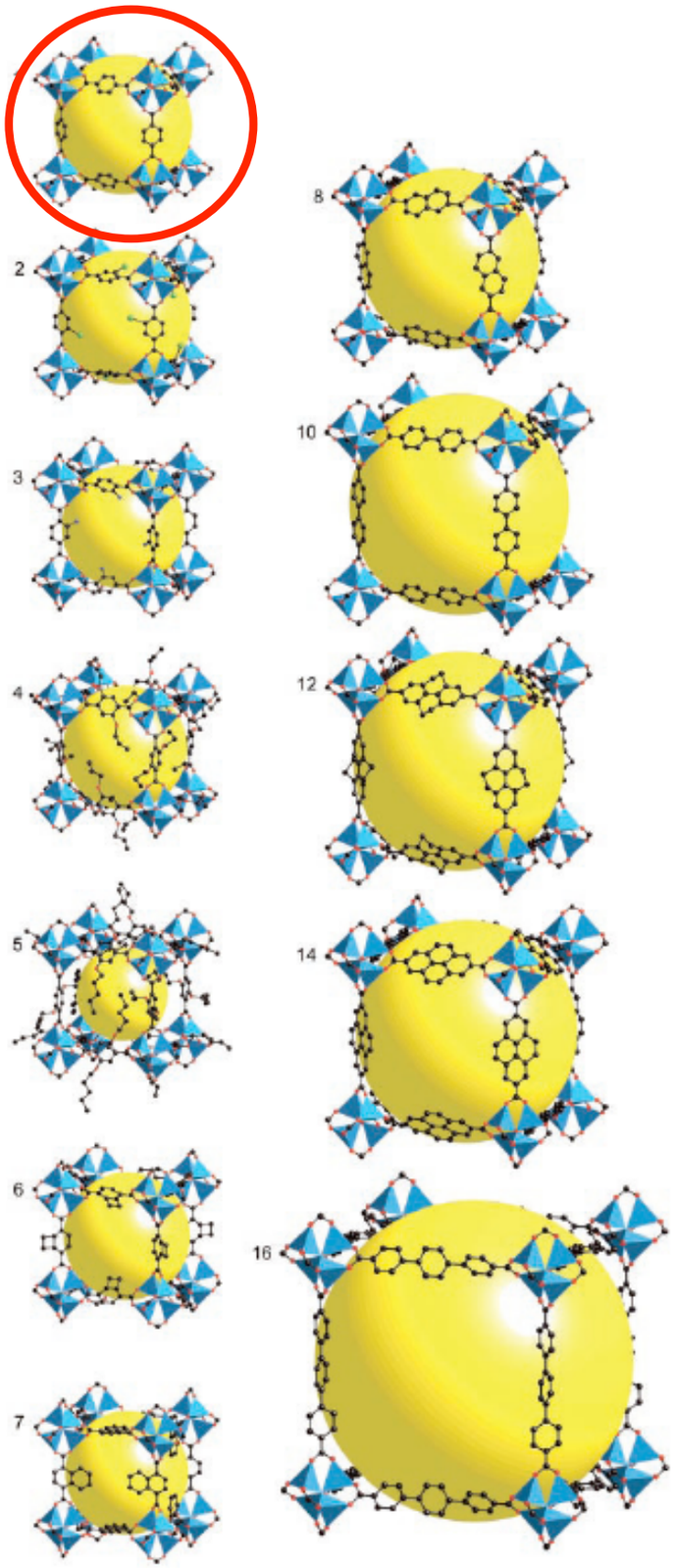


FIG. 8. Evolution of the cell parameters at 1 bar, 600 K, with the Dion exchange-correlation functional. Full and dashed lines represent simulations using a single unit cell and a 1 × 1 × 2 supercell, respectively. The experimental lattice parameters[33] for the large-pore phase are shown as blue lines.

TABLE III. Structural parameters of the hydrated narrow-pore phase of MIL-53(Ga), obtained from first-principles molecular dynamics simulations in the *NPT* ensemble.

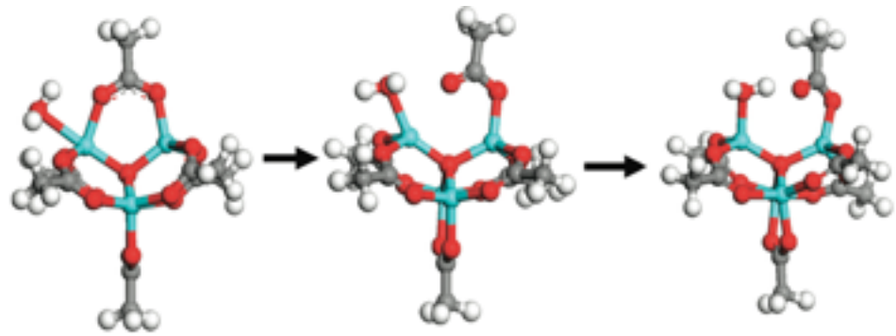
	a (Å)	b (Å)	c Å)	α (deg)	β (deg)	γ (deg)	Volume (Å^3)
sim.	19.38	8.10	6.79	90	97	90	1056
exp.[33]	19.72	7.58	6.69	90	103	90	972

Water stability of MOF-5



What was known about MOF-5 and water?

- Exposed to wet air: collapses in an hour
- Transition state was calculated by quantum chemistry:



$\Delta E^{\neq}$ = 50 kJ/mol

Low et al, *JACS* **2009**

Questions unanswered

- Is that actually the mechanism?
- Why is that activation energy so high?
- Impact of hydration rate?

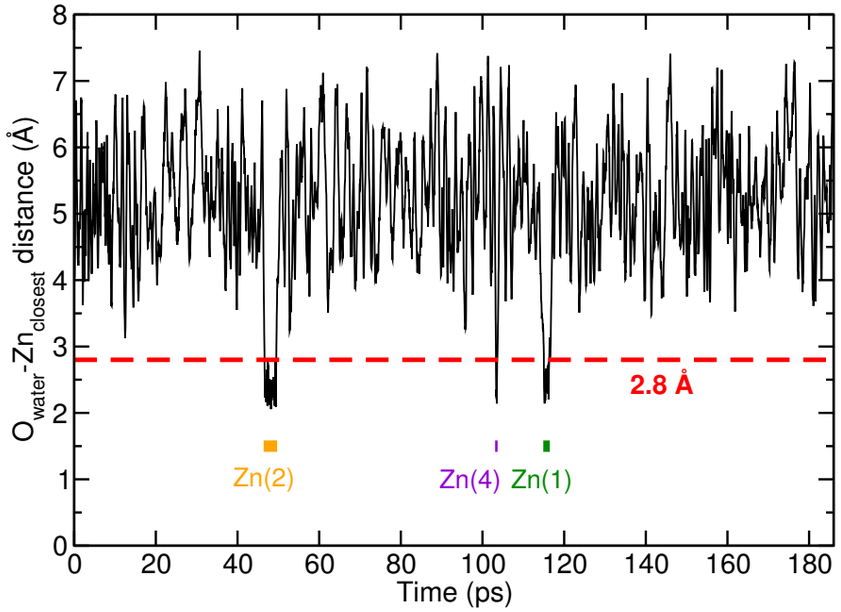
Tools available

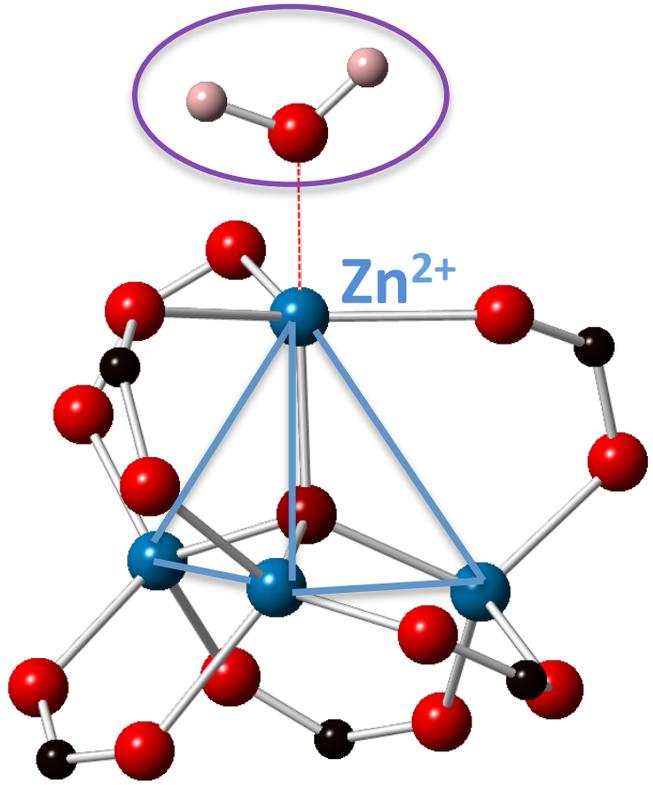
- Hydrophobicity/hydrophilicity: Grand Canonical Monte Carlo
- Reactivity: Car–Parrinello MD

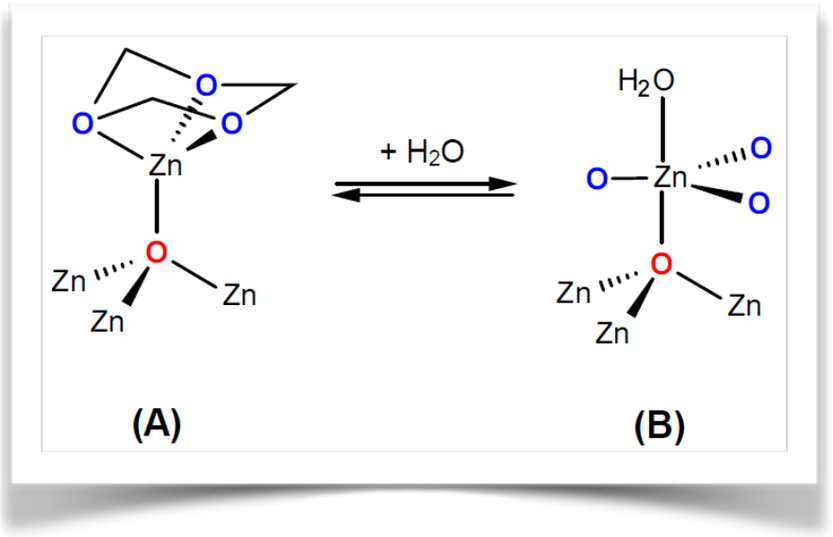
Water stability of MOF-5

At low water loading

- Hydrophobic material
- Hydrated state, 5-coordinated Zn^{2+}
- Short lifetime, low activation energy
- … not further spontaneous evolution





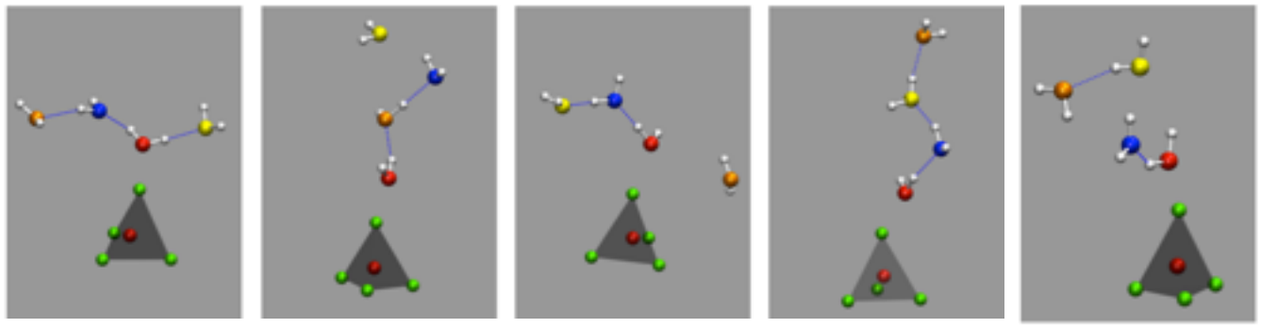


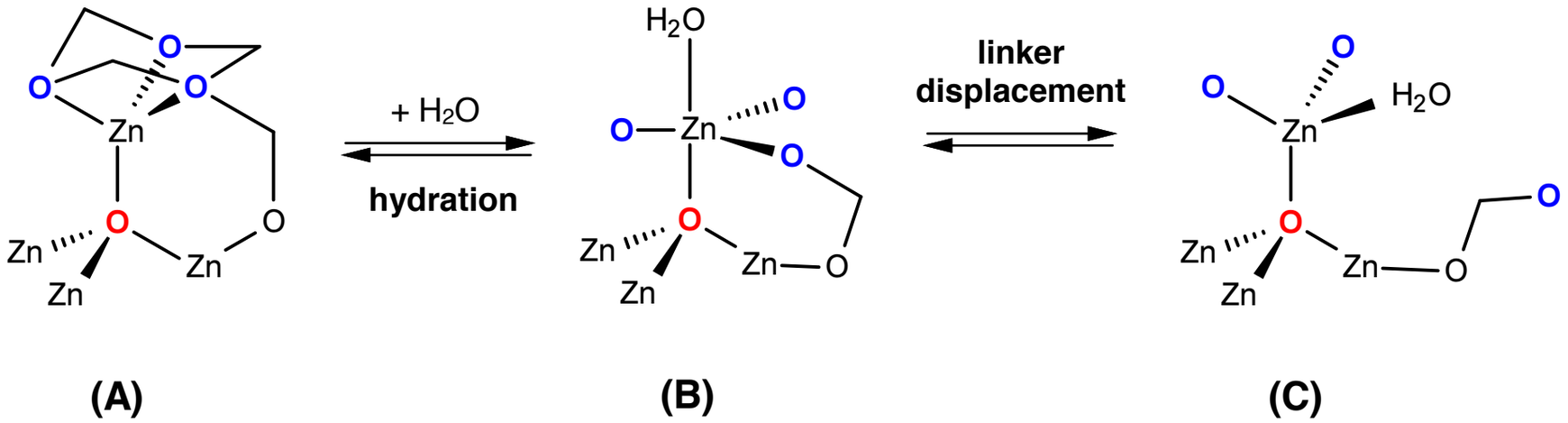
De Toni, FXC et al, *ChemPhysChem* **2012**

Water stability of MOF-5

At higher water loading

- Hydration is rapid and non-reversible
- Hydrated state stabilized by H bonds
- Second step of the mechanism: linker displacement





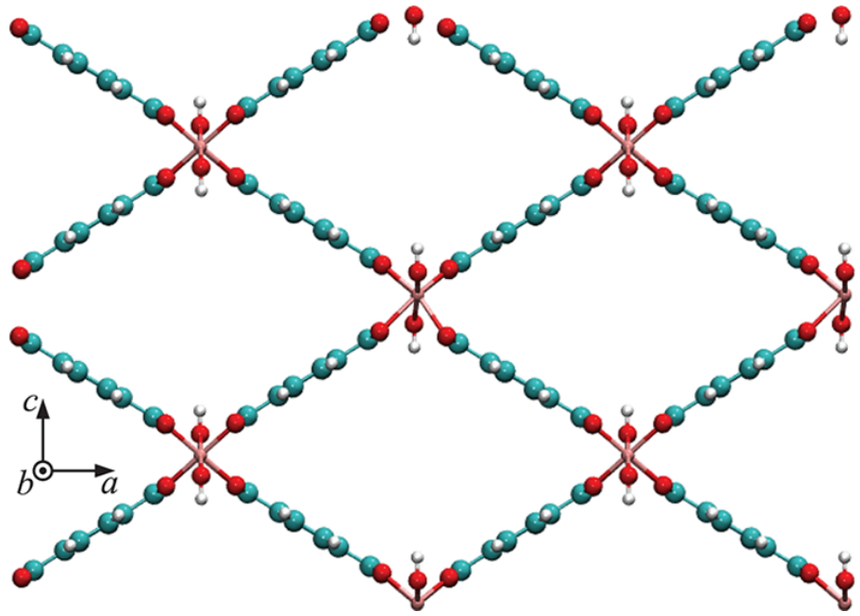
Conclusions drawn

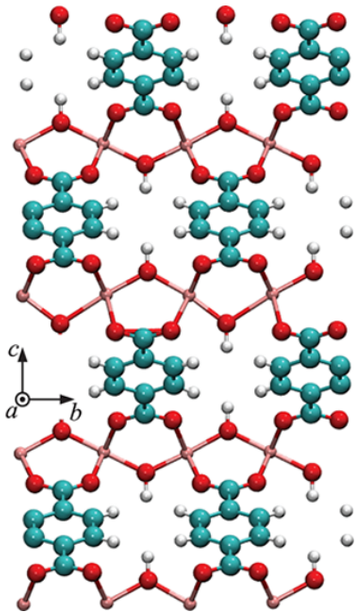
- Mechanism proposed in the literature: confirmed
- Influence of water collective effects: yes
- Activation energies from calculations with one water: overly simple

De Toni, FXC et al, *ChemPhysChem* **2012**

Water stability of MIL-53

- Step 1: identify weak point of the framework





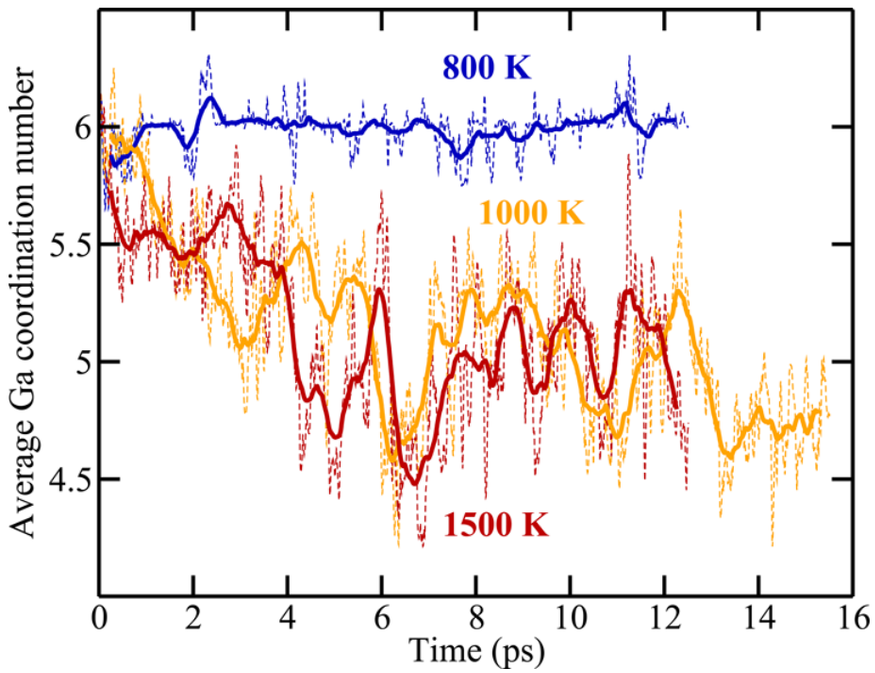


Figure 2. Evolution of the average coordination of Ga by O in nonhydrated MIL-53(Ga) at three different temperatures (dashed lines): 800 K (blue), 1000 K (orange), and 1500 K (red). For better visibility, we also plot the running averages over a time interval of 0.5 ps (solid lines). The cutoff distance for Ga−O coordination is at 2.8 Å, corresponding to the first minimum of the Ga−O radial distribution function at 800 K. In order to obtain a continuous evolution in time, we applied a small Fermi−Dirac-like smearing to the cutoff distance.

Haigis et al, *J Phys Chem Lett* **2015**

Water stability of MIL-53

- Step 2: metadynamics, with Ga–O distance as coordinate

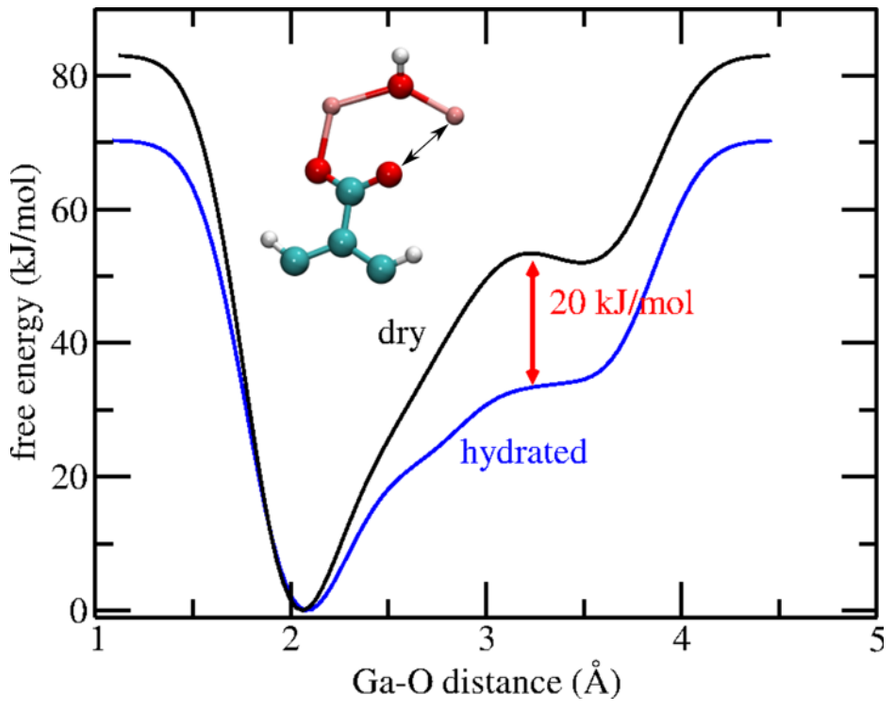
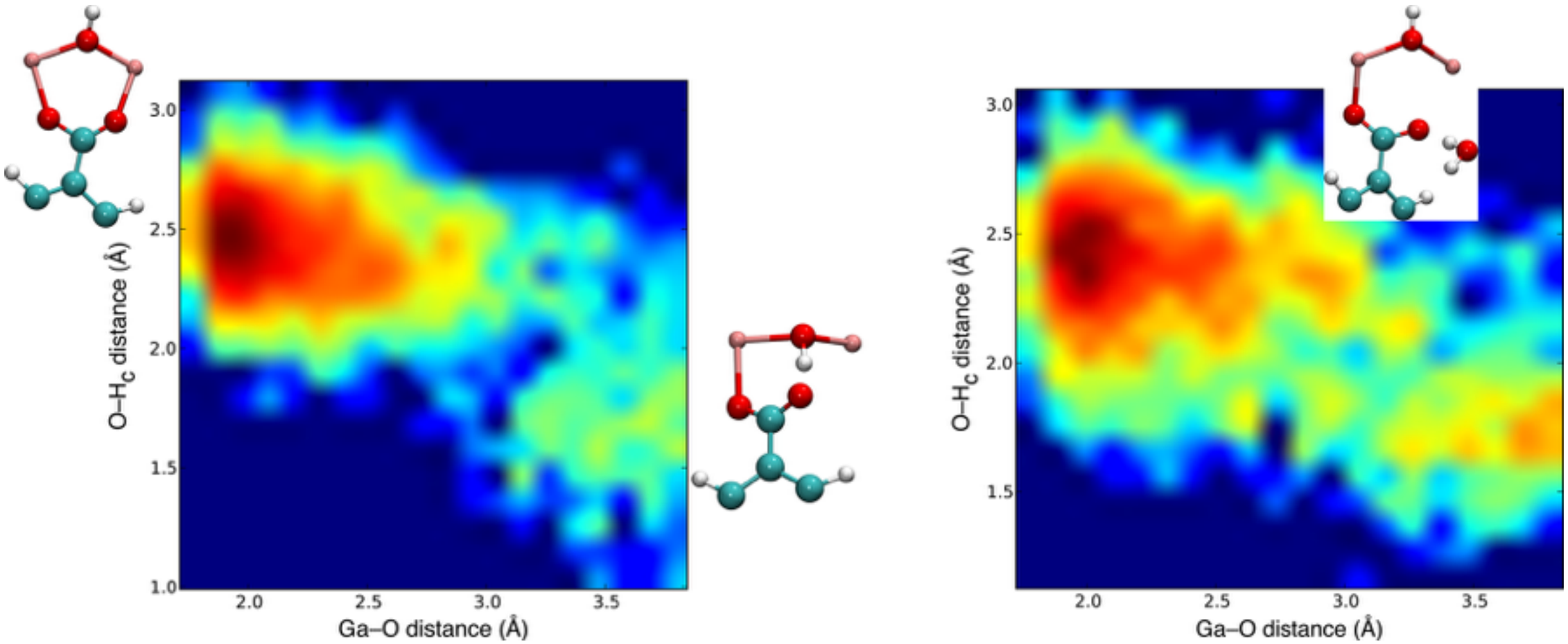


Figure 3. Free energy profiles of Ga−O bond breaking for dry (black) and hydrated (blue) MIL-53(Ga) at 650 K. The minimum of each curve has been set to zero. The black arrow in the structure model indicates the metadynamics variable, i.e., the Ga−O distance. Atomic color code: Ga (pink), O (red), C (turquoise), H (white). Note that for computational purposes, the sampled Ga−O distances were limited to about 3.8 Å, hence the free-energy profiles at larger distances are not physical (see text).

Haigis et al, *J Phys Chem Lett* **2015**

Water stability of MIL-53

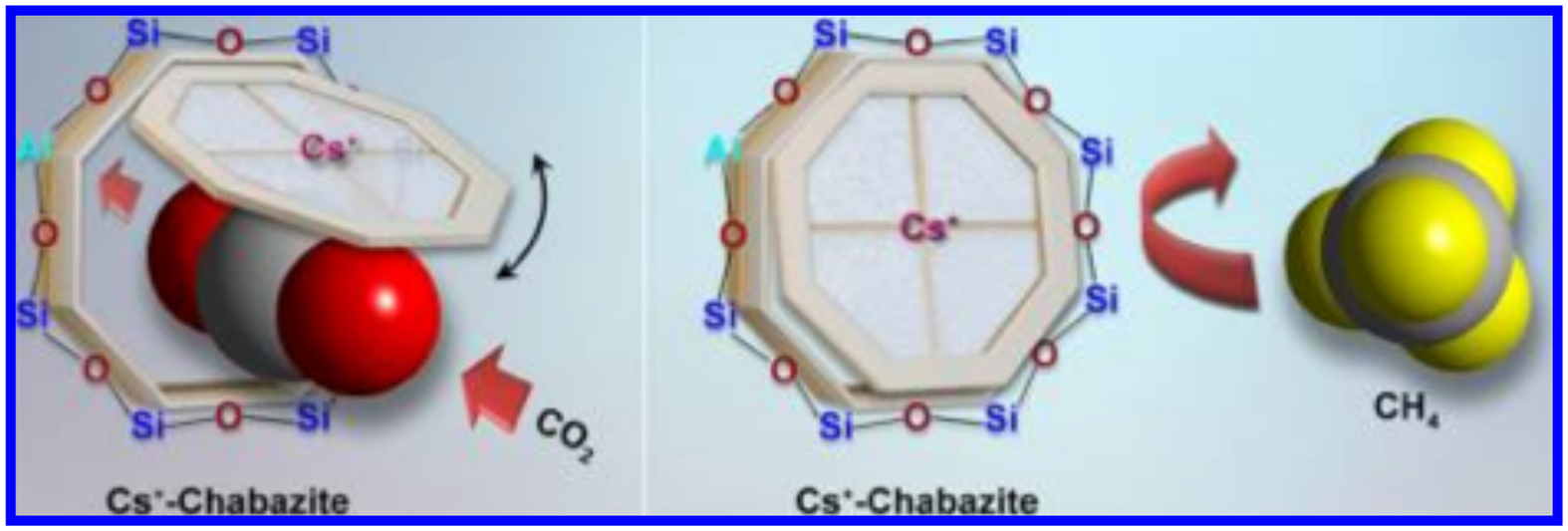
- Step 2 (bis): metadynamics analysis, microscopic insight



- Step 3: influence of pressure… *NPT* metadynamics, ongoing

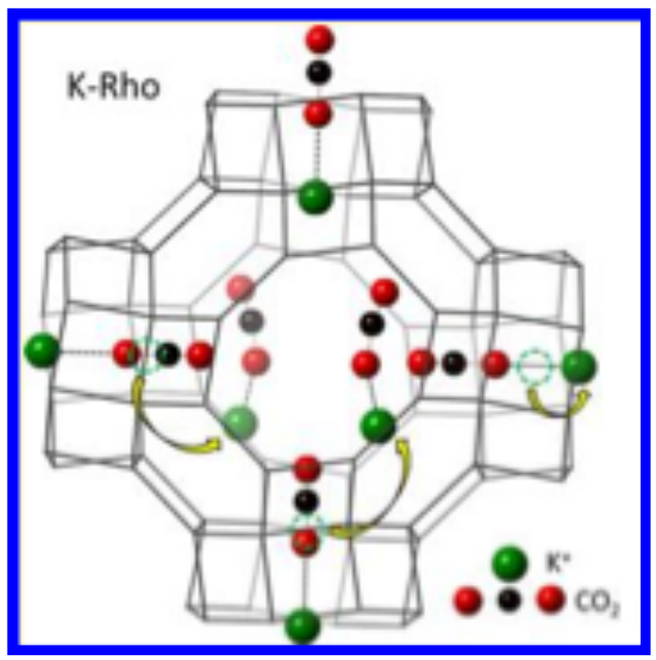
Haigis et al, *J Phys Chem Lett* **2015**

CO_2 opens “Trapdoors” in zeolites



Discriminative Separation of Gases by a “Molecular Trapdoor” Mechanism in Chabazite Zeolites.

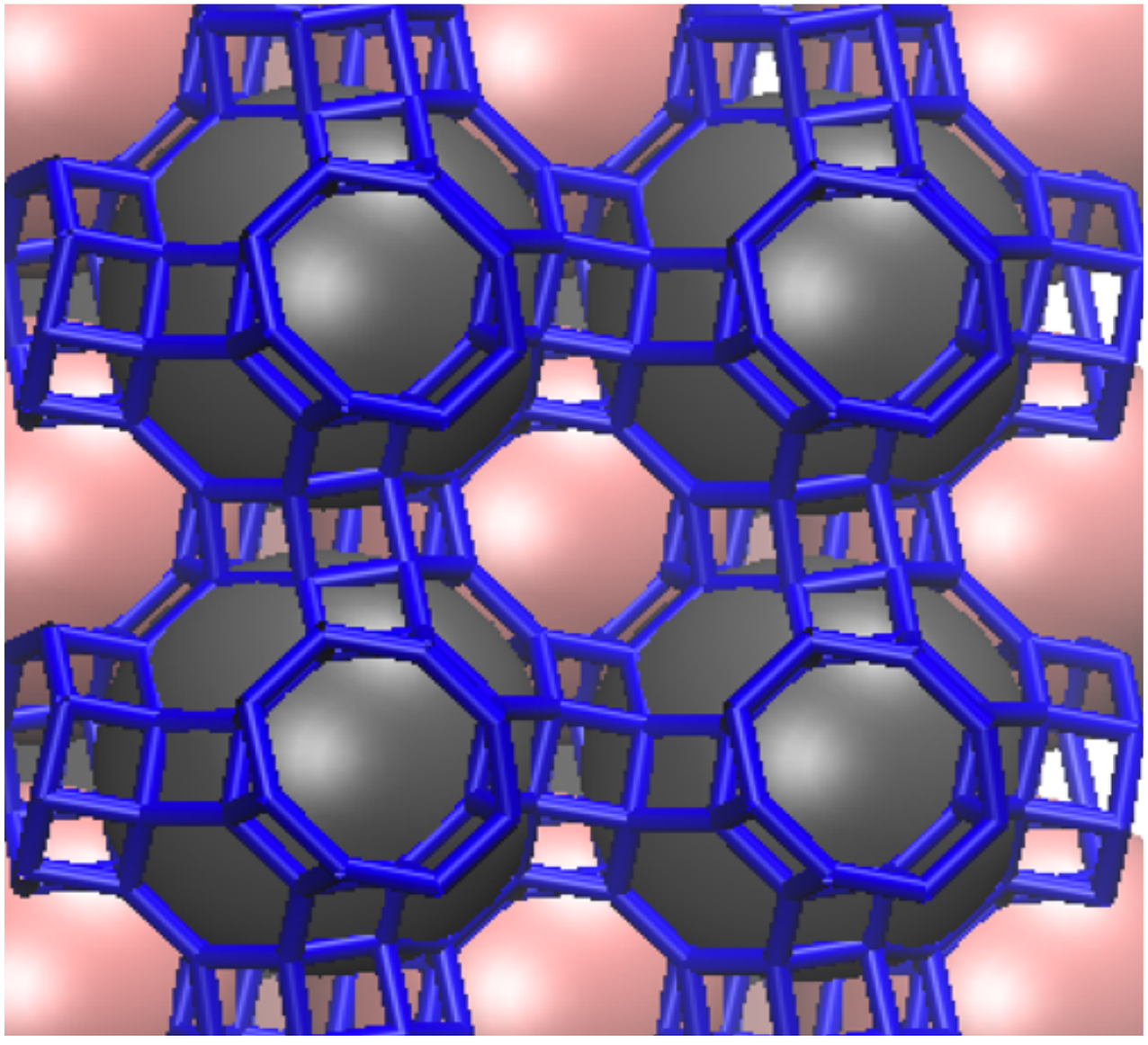
Webley et al. JACS 2012, 134, 19246

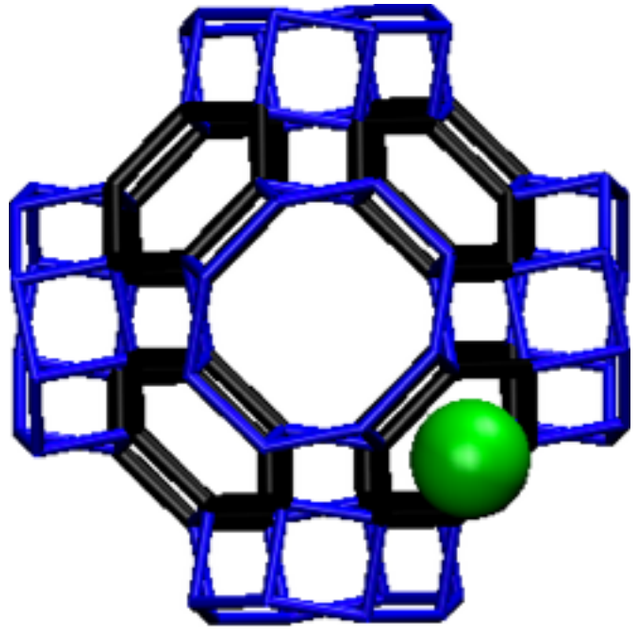


Cation Gating and Relocation during the Highly Selective “Trapdoor” Adsorption of CO_2 on Univalent Cation Forms of Zeolite RHO. Wright et al. Chem Mater 2014, 26, 2052.

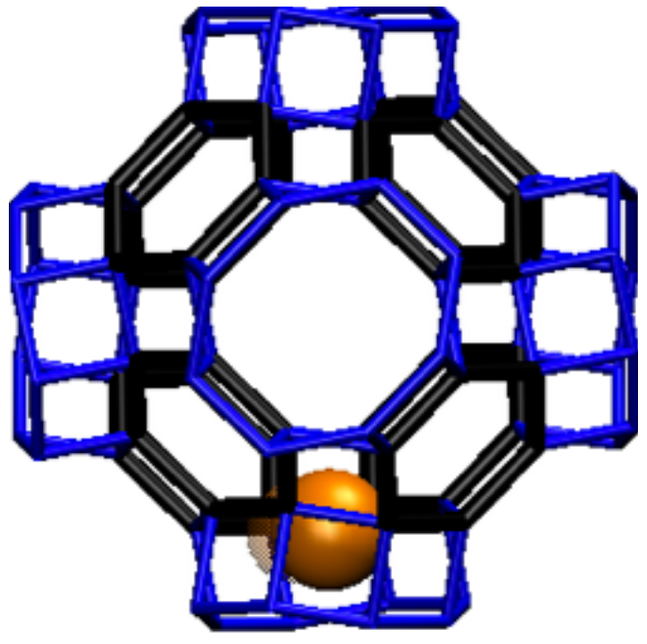
Zeolite Rho: a highly selective adsorbent for CO_2/CH_4 separation induced by a structural phase modification. Corma et al. Chem Commun 2012, 48, 215.

Na-RHO Zeolite





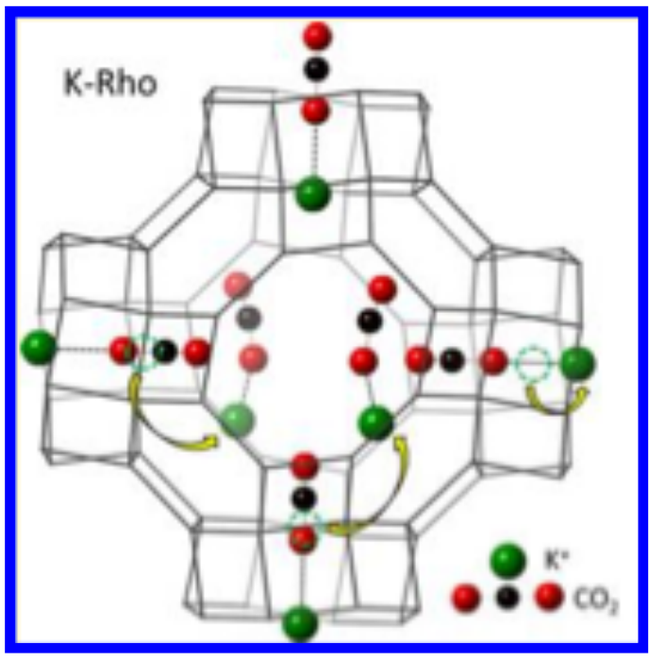
8 S6R per UC



12 S8R per UC

How does CO_2 open "Trapdoors" in Na-RHO zeolite?

Cation Gating and Relocation during the Highly Selective "Trapdoor" Adsorption of CO_2 on Univalent Cation Forms of Zeolite RHO. Wright et al. Chem Mater 2014, 26, 2052.



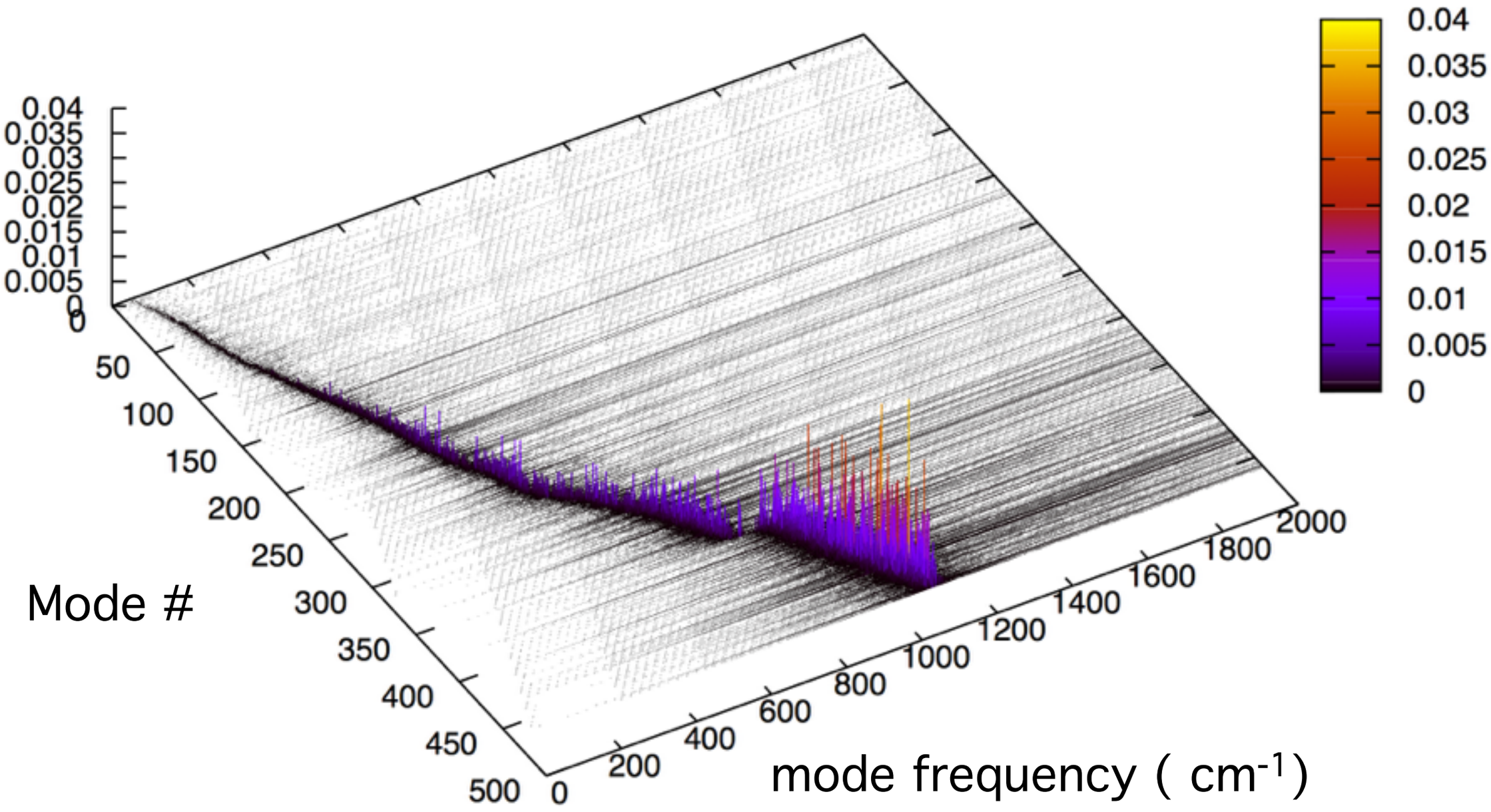
- X-ray results suggest that CO_2 interaction with Cation opens the trapdoor

Atomistic Simulations of CO2 during "Trapdoor" Adsorption onto Na-Rho Zeolite. Kohen et al. in Molecular Modeling and the Materials Genome: Selected Papers from the 2015 Foundations of Molecular Modeling and Simulation Conference, R.Q. Snurr, C.S. Adjiman, D.A. Kofke, Eds., Springer, in press.

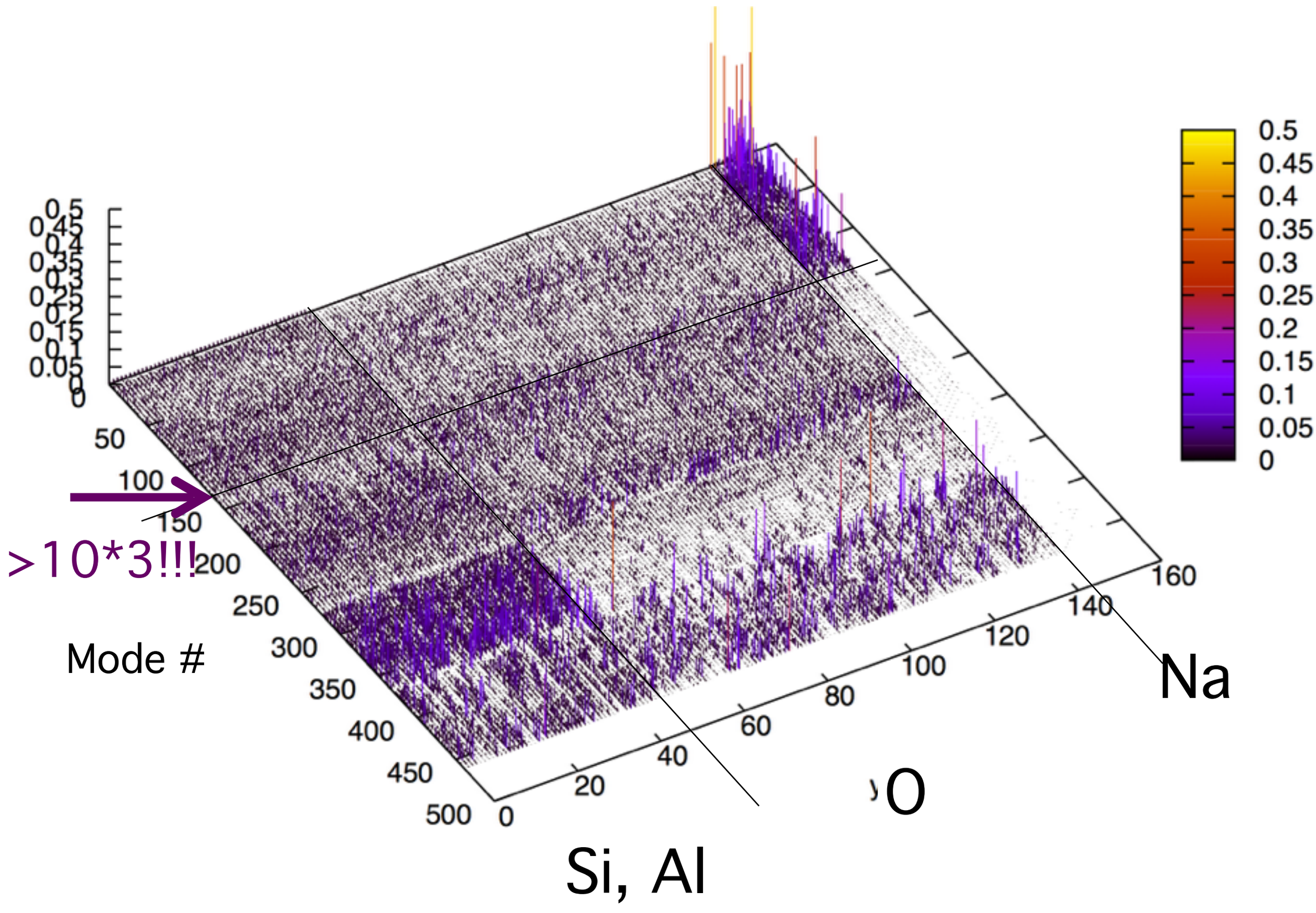
- CO_2 preferred site is in the S8R just as for Na^+
- Maybe CO_2 squeezes by cations in Na-RHO zeolite rather than opening the cation trapdoor

Na-RHO effective normal modes

(Vuilleumier J. Chem. Phys. 144106 2006)



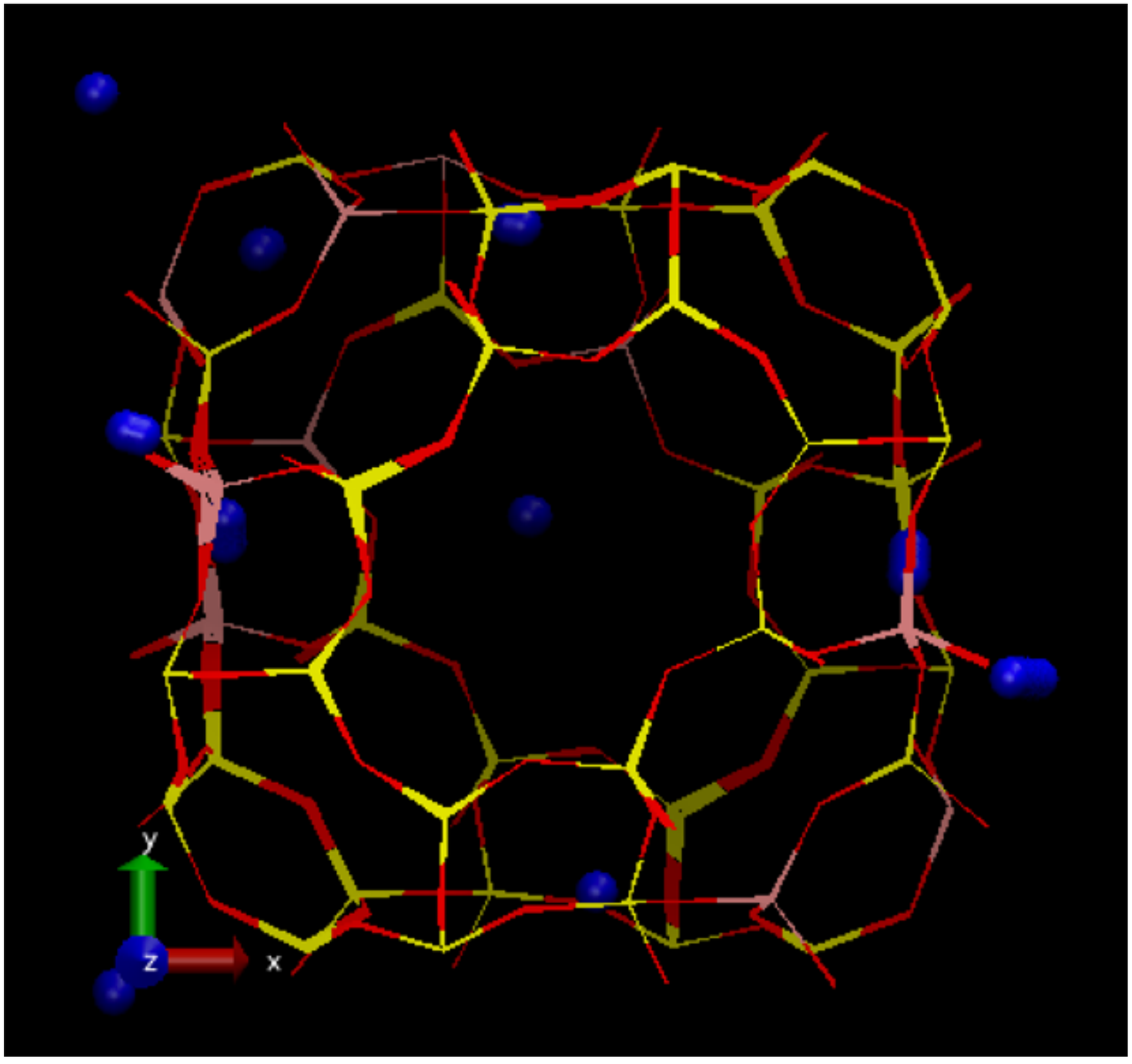
Na-RHO effective normal modes



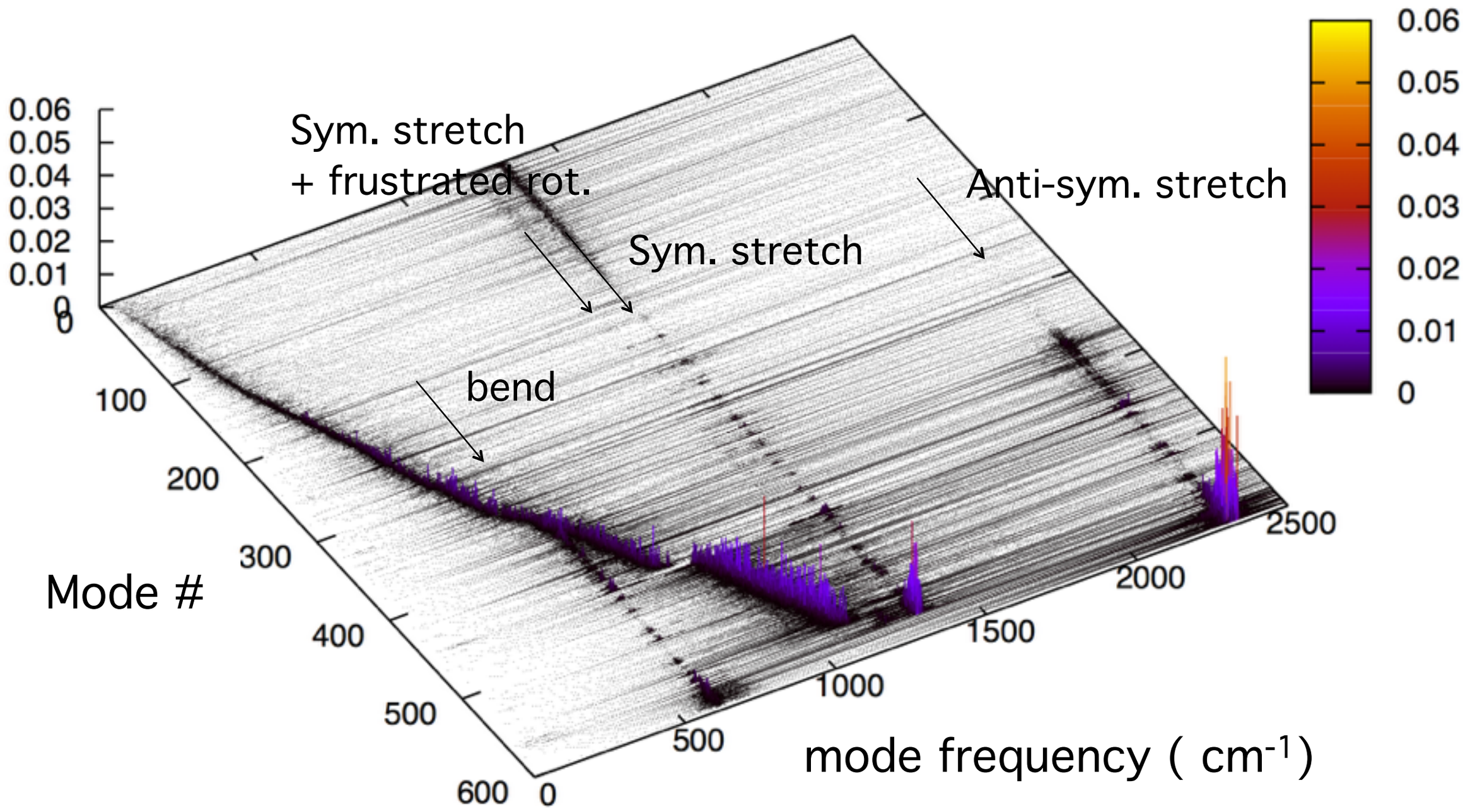
>10*3!!!

Na-RHO effective normal modes

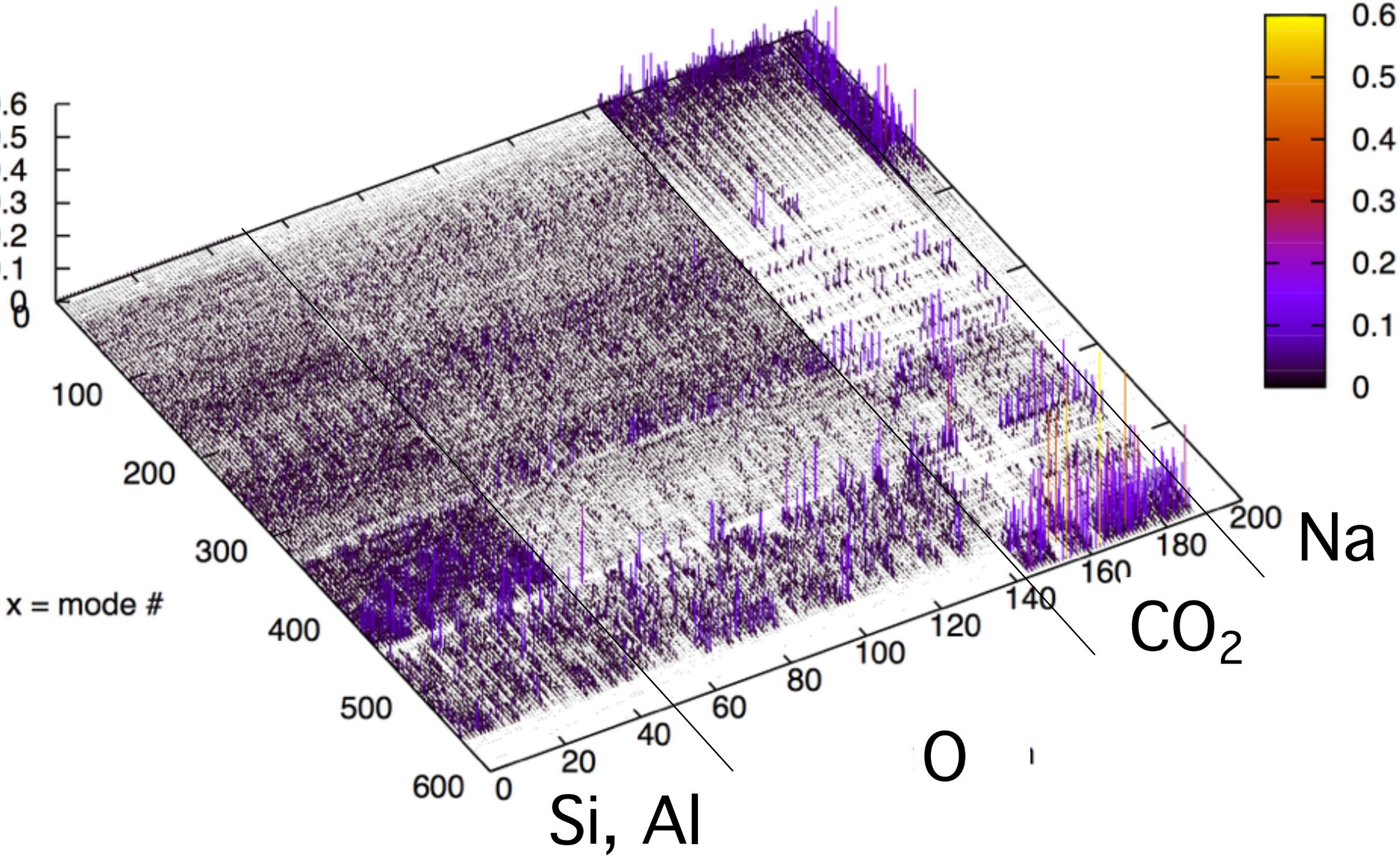
Mode #100



1atm CO_2 within Na-RHO: effective normal modes

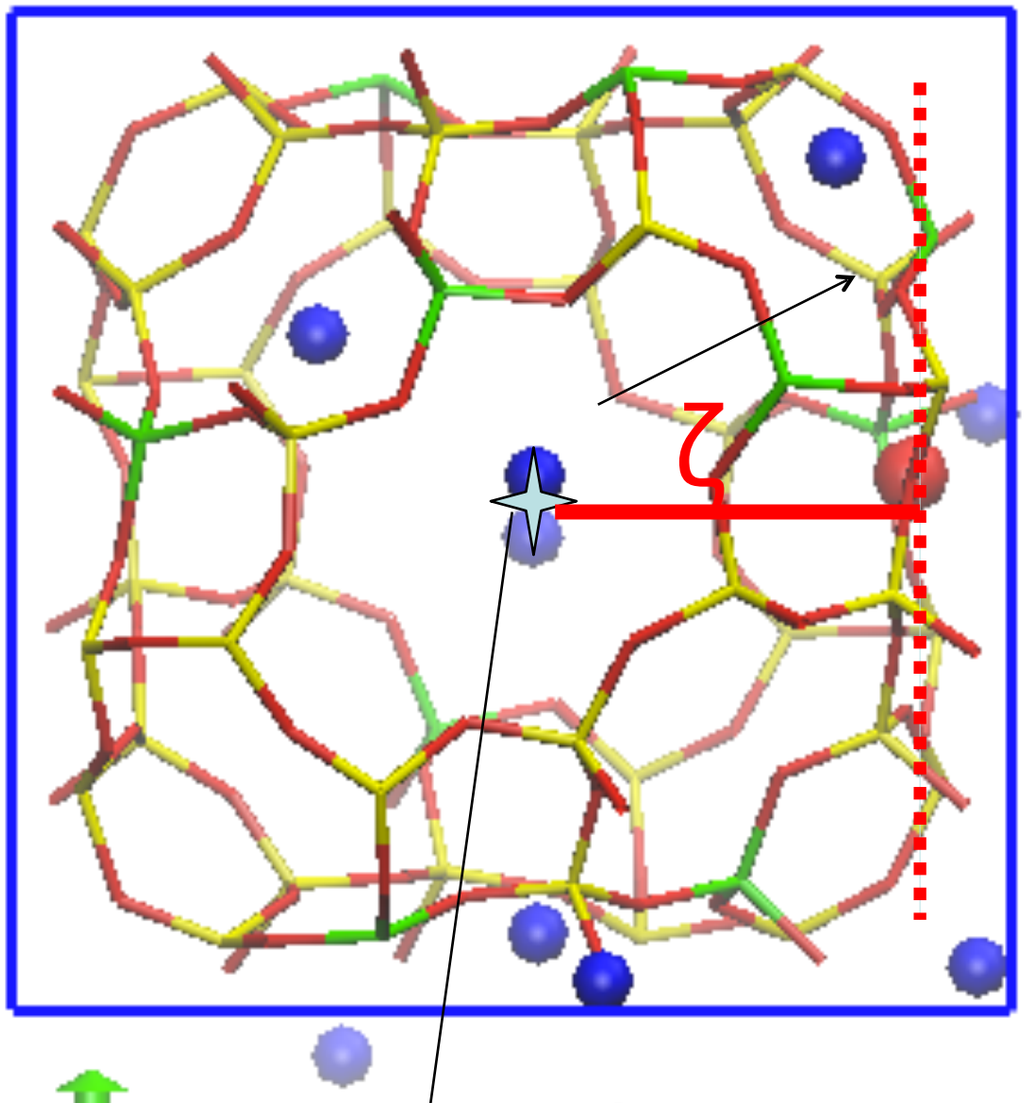


1atm CO_2 within Na-RHO: effective normal modes



Na-RHO Constrained AIMD simulations using CP2K

To Calculate Free Energy Profiles using the blue moon ensemble method (Carter et al. Chem Phys Let 1989)



Framework center of mass

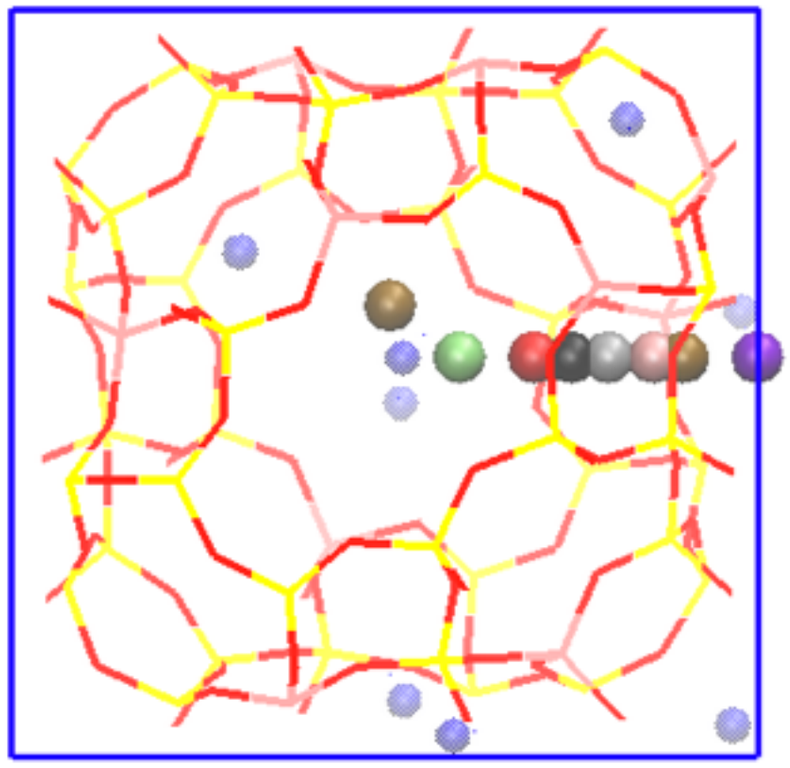
ζ is constrained during AIMD runs

for this simple constraint:

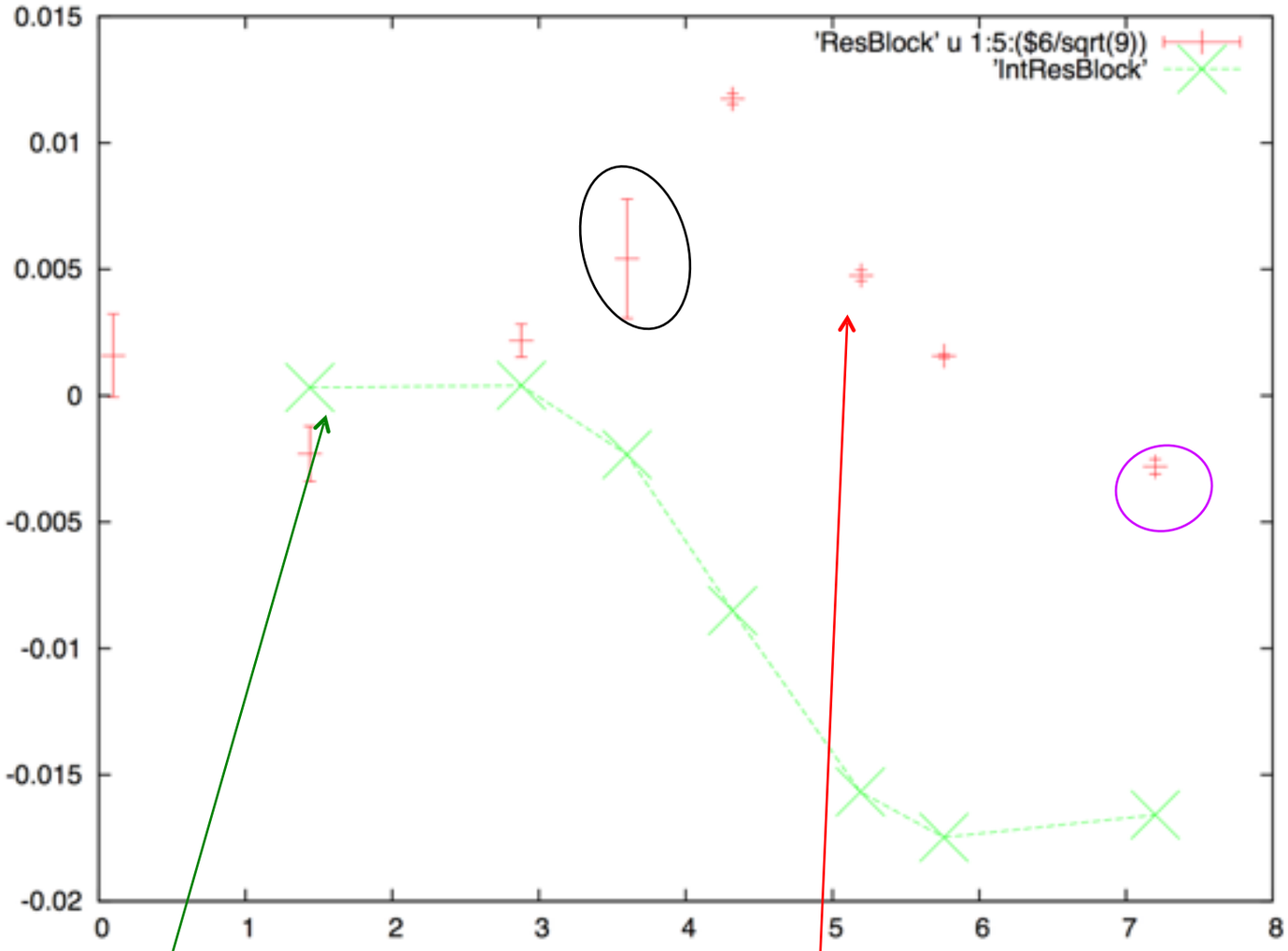
$$F(\zeta) = \int_{\zeta min}^{\zeta max} < f(\zeta) > d\zeta$$

Force required to keep ζ constrained (get as Lagrangian multiplier from SHAKE)

Na-RHO Constrained AIMD simulations using CP2K



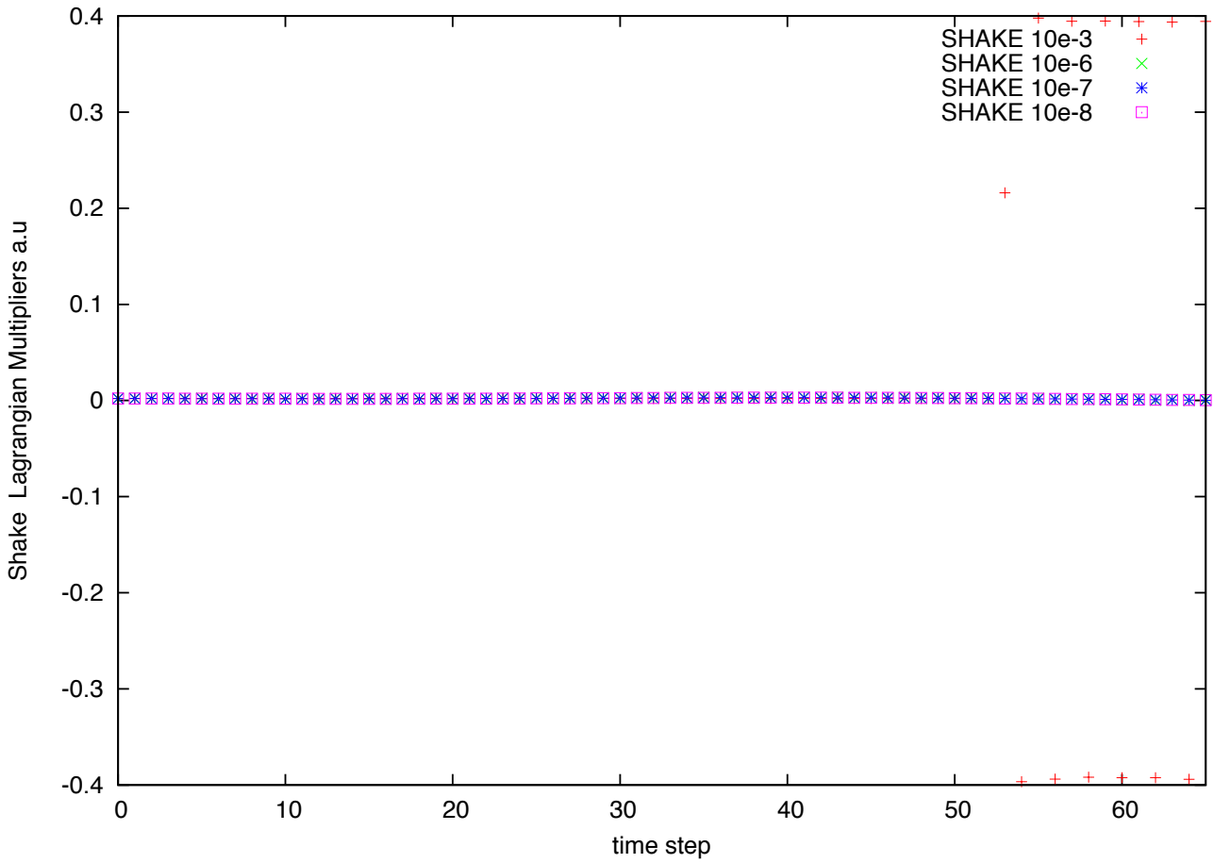
a.u.

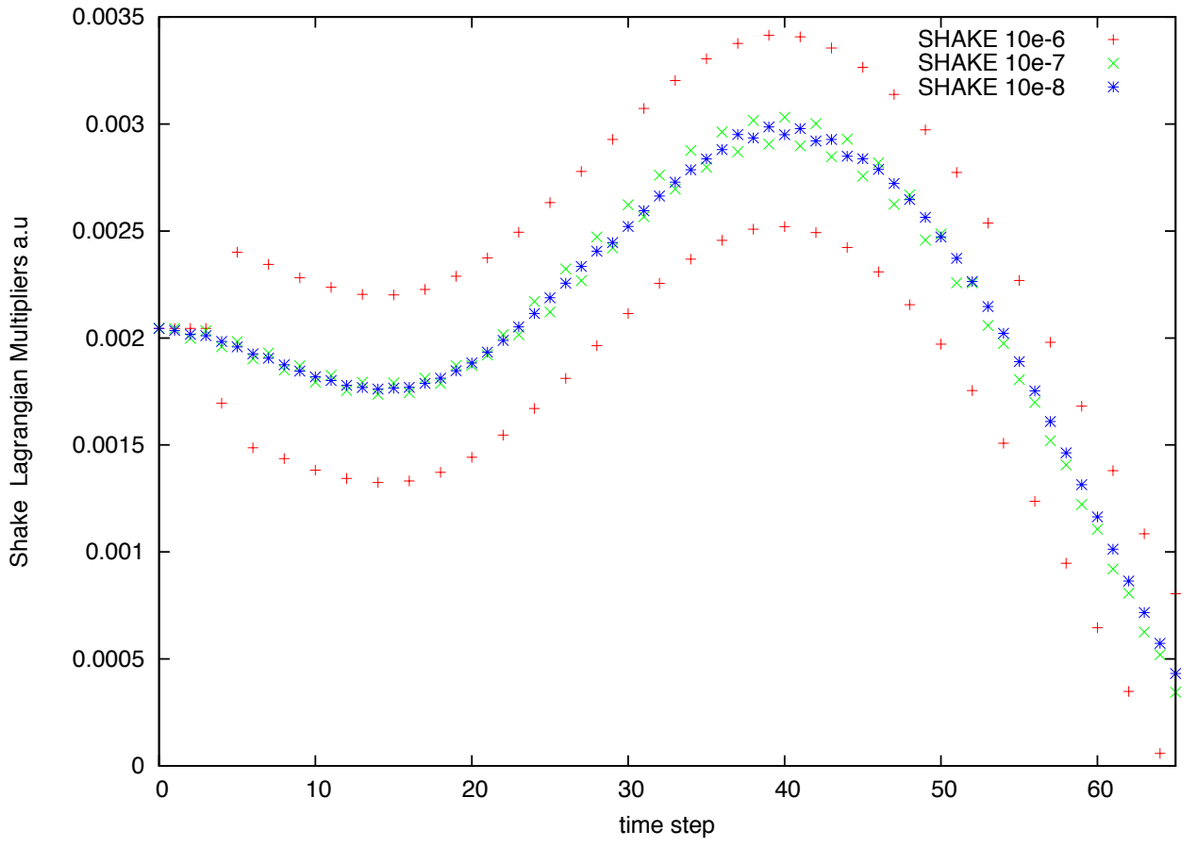


ζ

$$F(\zeta) = \int_{\zeta min}^{\zeta max} < f(\zeta) > d\zeta$$

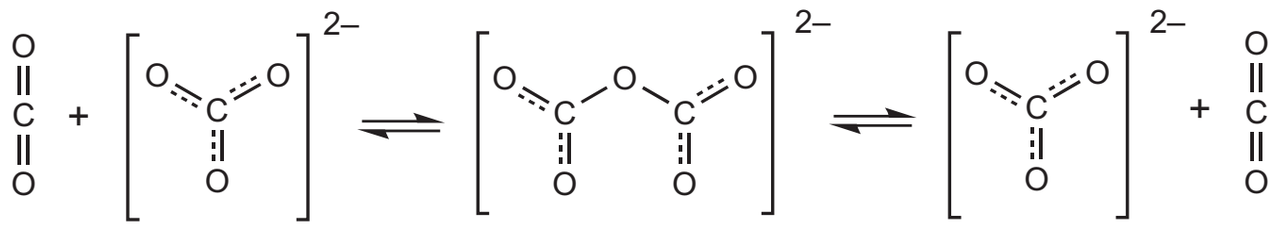
Na-RHO Constrained AIMD simulations using CP2K

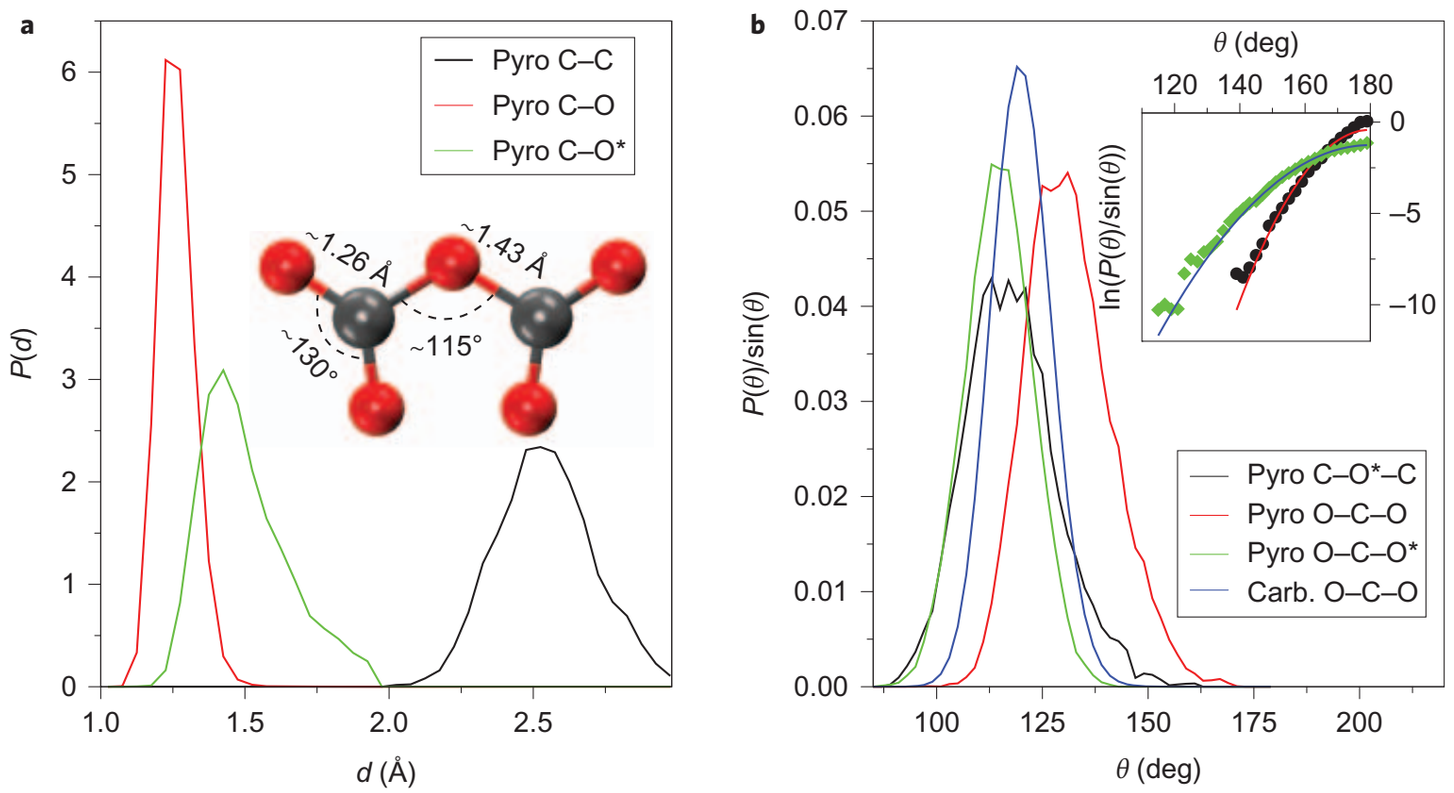




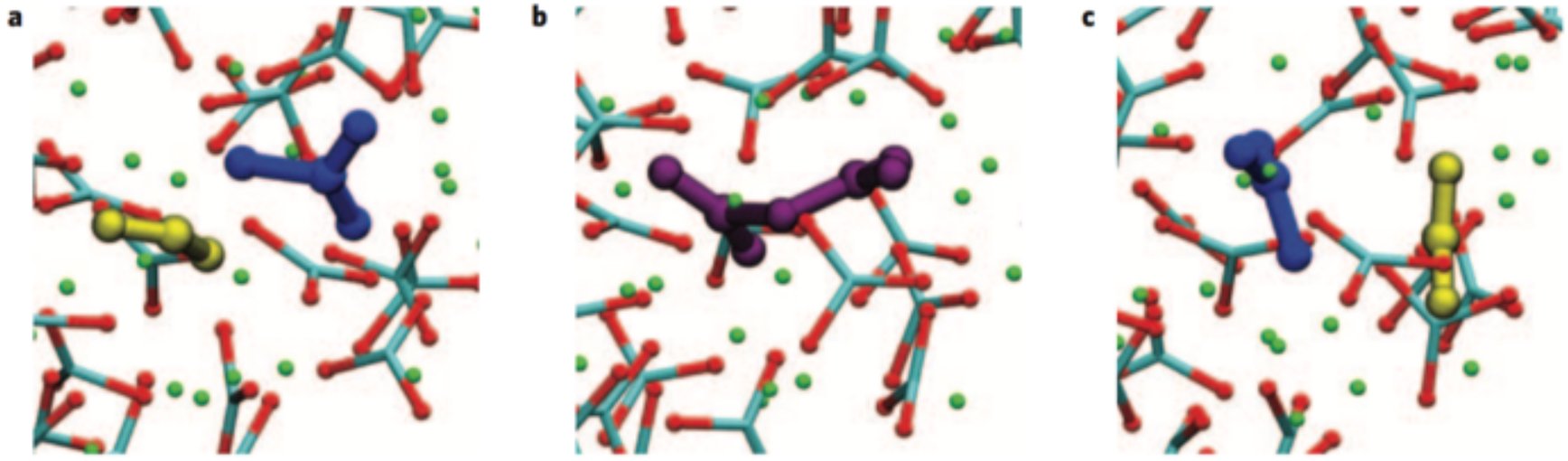
Solvation in carbonate melts

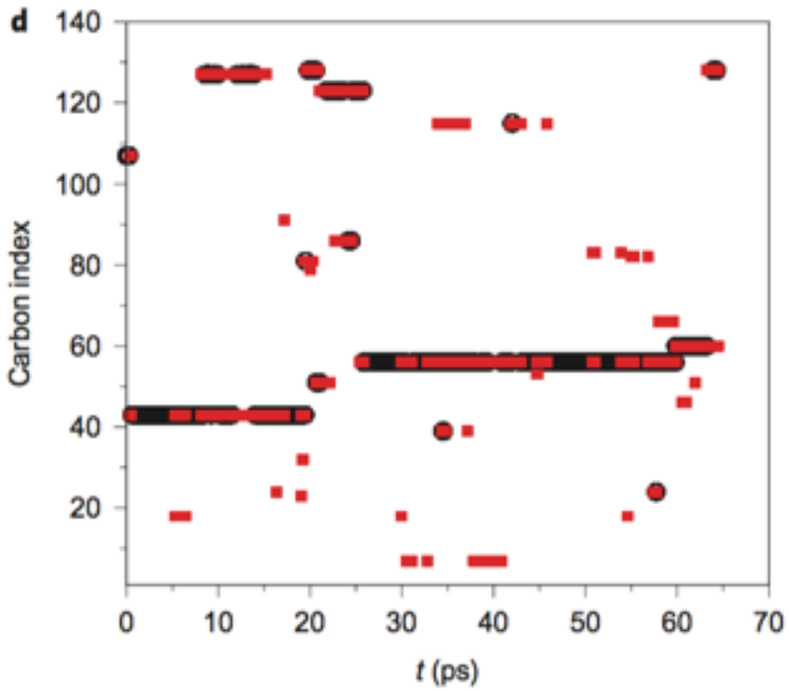
- Reactivity, speciation and solvation structure of CO_2 in carbonate melts
- Relevant for carbon in deep geological formations
- Relevant to CO_2 electroreduction to CO (to be used as fuel) when solvated in a molten carbonate electrolyte
- High solubility of CO2 (among other species) attributed to "pyrocarbonate" $C_2O_5^{2-}$
  - **No direct experimental evidence**
  - **No thermochemical data**

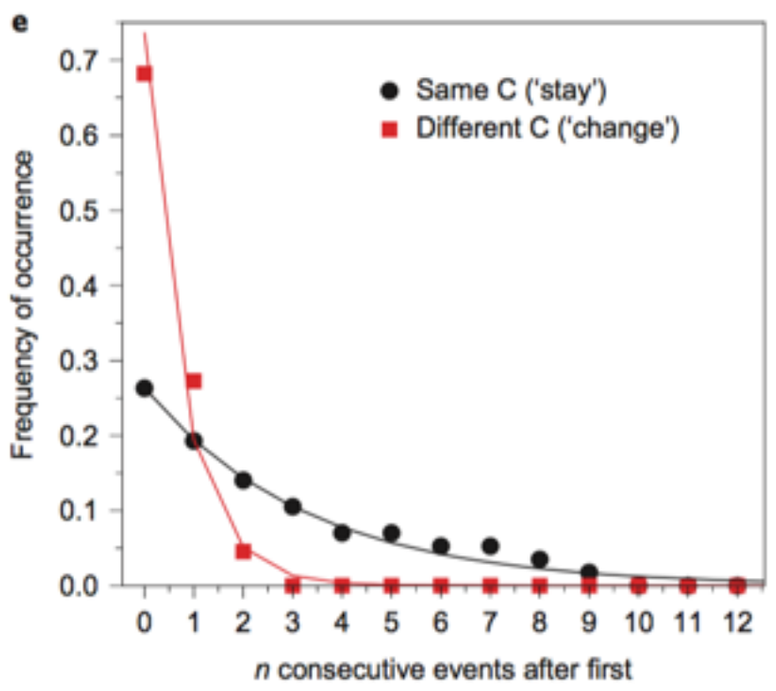




Solvation in carbonate melts







Solvation in carbonate melts

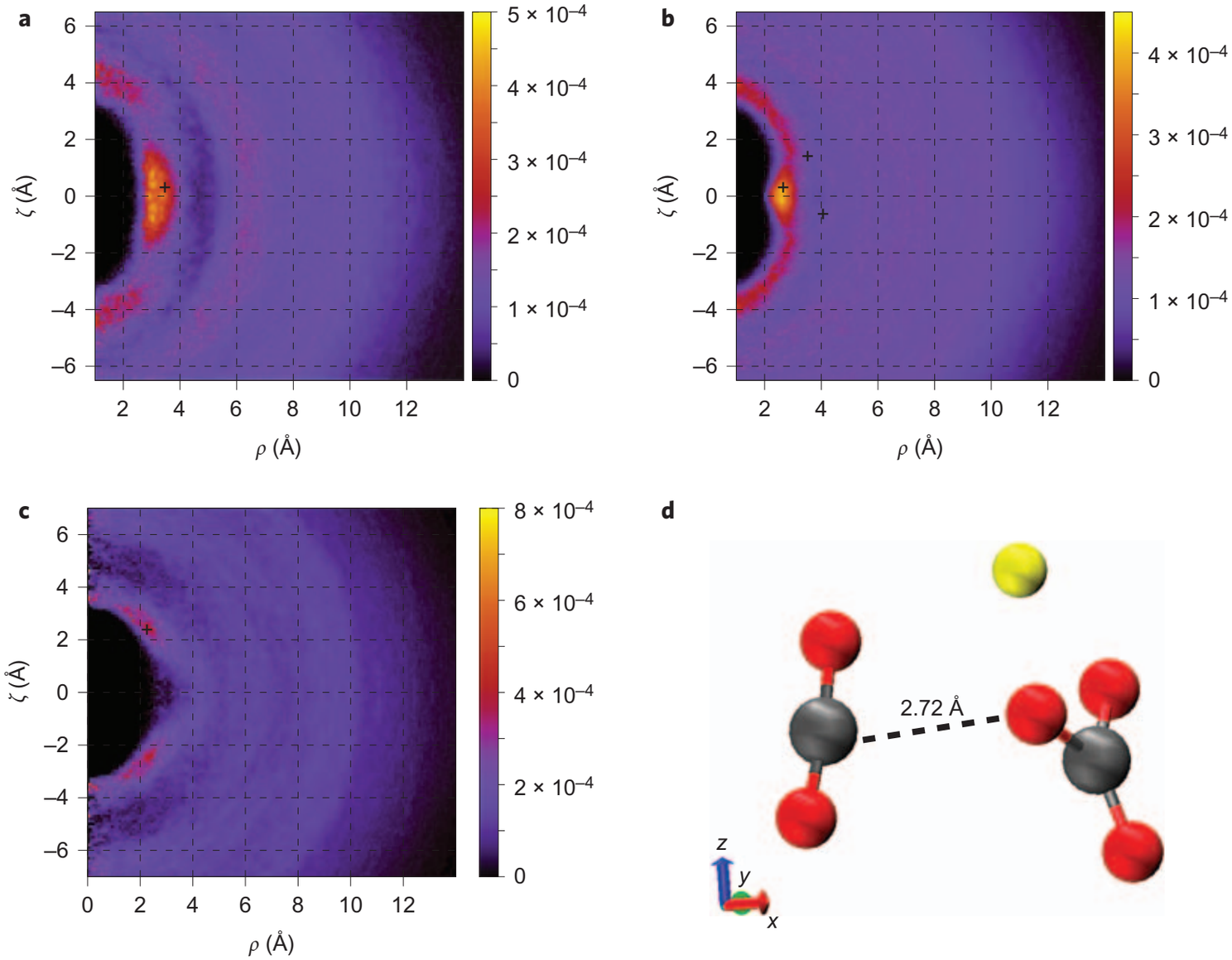


Figure 4 | Solvation structure around the CO_2 molecule. a–c, Two-dimensional colour charts (see Methods) around the CO_2 molecule for C atoms (**a**), O atoms (**b**) and Ca atoms (**c**). The CO_2 molecule is oriented with its O–O axis along the $\hat{\zeta}$ direction, where $\zeta = 0$ is the mid-point of the O–O distance. ζ is thus the projection of an atom position along the O–O axis, and ρ is its distance from the O–O axis. **d**, Gas-phase geometry obtained for a cluster composed of CO_2, CO_3^{2-} and Ca^{2+} (see Methods). Cartesian axes are shown at the bottom. C, grey; O, red; Ca, yellow. Positions of the atoms of carbonate and Ca in the gas phase are marked as + symbols in the respective plots for the condensed phase. Distances are measured in ångstroms.

Solvation in carbonate melts

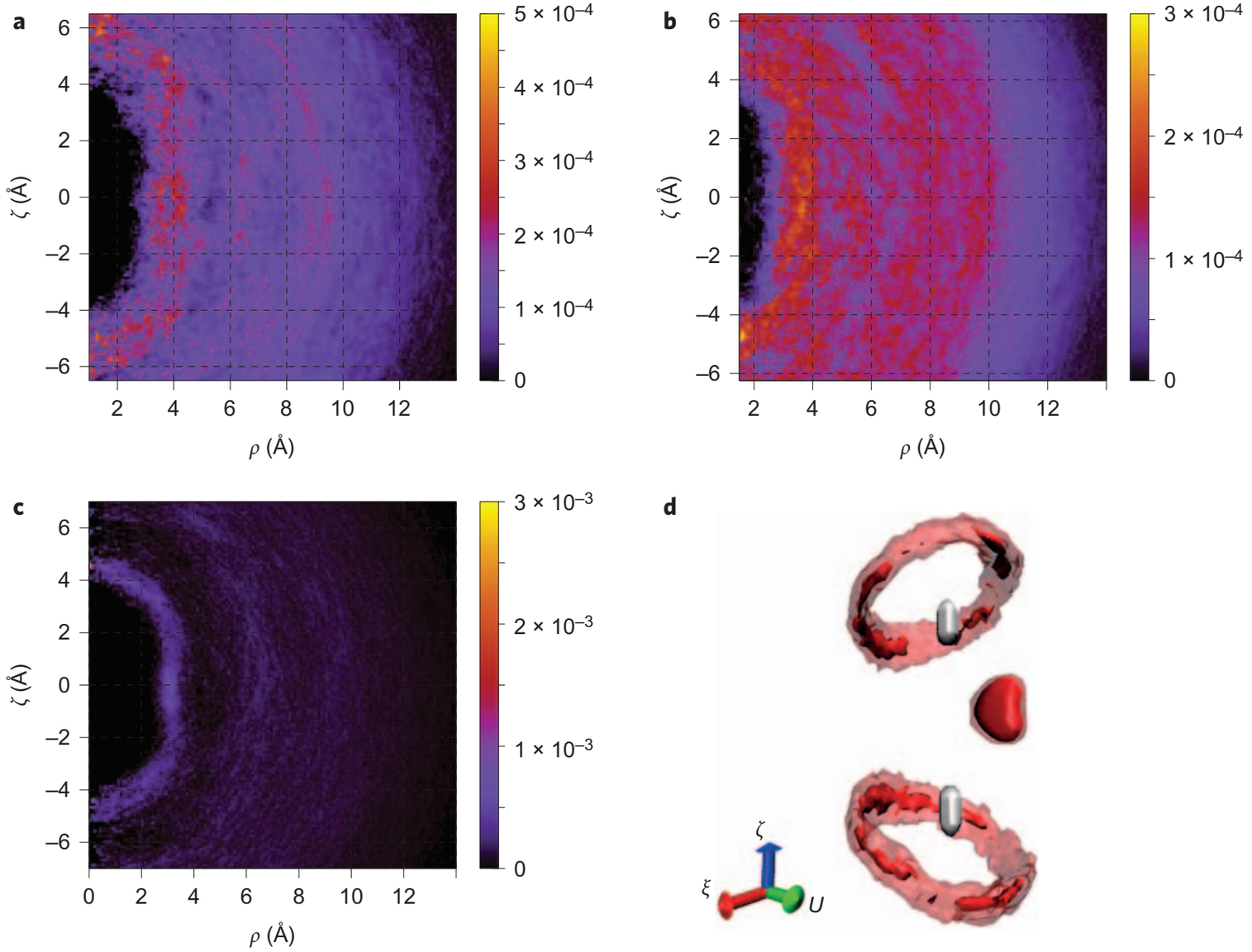


Figure 5 | Solvation structure around the pyrocarbonate ion. a–c, Two-dimensional colour charts (see Methods) around the pyrocarbonate molecule for C atoms (**a**), O atoms (**b**) and Ca atoms (**c**). The $C_2O_5^{2-}$ molecule is oriented with its C–C axis along the $\hat{\zeta}$ direction, where $\zeta = 0$ is the mid-point of the C–C vector. ζ is thus the projection of an atom position along the C–C axis, and ρ is its distance from the C–C axis. The former C of the CO_2 molecule is always placed in the negative ζ portion of the plots. **d**, Three-dimensional colour chart of the pyrocarbonate molecule (see Methods). The $\hat{\zeta}$ direction coincides with the C–C axis, the $\hat{\upsilon}$ direction is the perpendicular to $\hat{\zeta}$ passing by O* and $\hat{\xi} = \hat{\upsilon} \times \hat{\zeta}$. Iso-probability surfaces are plotted corresponding to $P = 0.005$ for C (grey), $P = 0.002$ for O (transparent red) and $P = 0.007$ for O (solid red). Distances are measured in ångstroms.

Acknowledgments

Experimental work

- Marie-Anne Springuel-Huet (Paris)
- Renaud Denoyel (Marseille)
- Joël Patarin, Gérald Chaplais (Mulhouse)
- Jean-Pierre Bellat (Dijon)
- Joeri Denayer, Gino Baron (Brussels)
- Jorge Gascon, Freek Kapteijn (Delft)
- Andrew Goodwin (Oxford)
- Abraham Clearfield, Kevin Gagnon (Texas A&M, Berkeley)
- Tony Cheetham (Cambridge)
- Satoshi Tominaka (NIMS)

... and you!

Simulation and theory

- Alain Fuchs (CNRS)
- Anne Boutin, Rodolphe Vuilleumier (École normale supérieure)
- Caroline Mellot-Draznieks (UCL, Collège de France)
- Alex Neimark (Rutgers University, USA)
- Kenneth Evans, Arnaud Marmier (Exeter)

CHEMISTRY OF MATERIALS

ACS AuthorChoice

Perspective

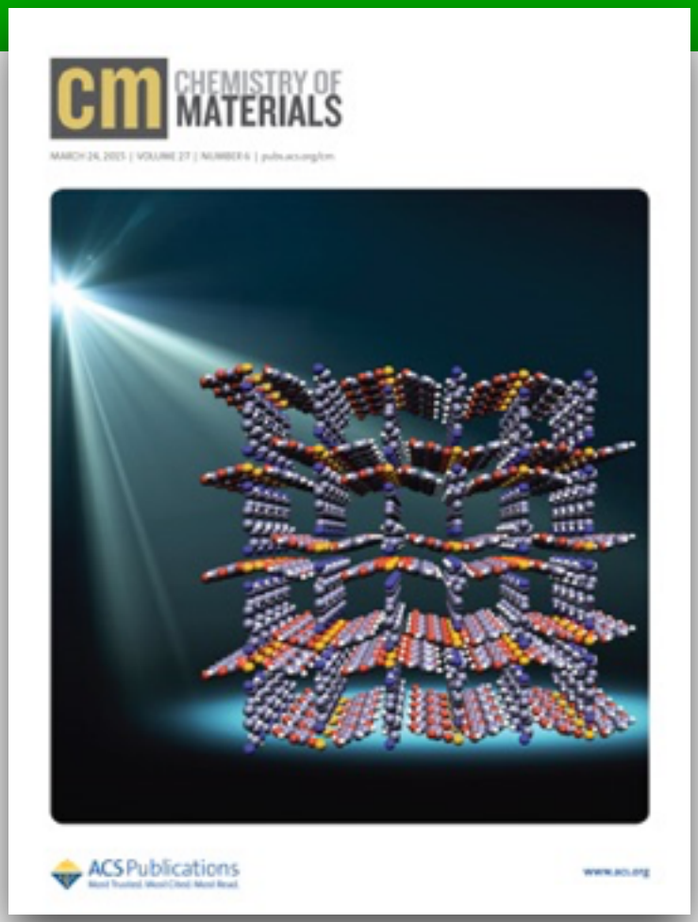
pubs.acs.org/cm

Responsive Metal–Organic Frameworks and Framework Materials: Under Pressure, Taking the Heat, in the Spotlight, with Friends†

François-Xavier Coudert*

PSL Research University, Chimie ParisTech – CNRS, Institut de Recherche de Chimie Paris, 75005 Paris, France

Chem. Mater. **2015**
March 24 issue

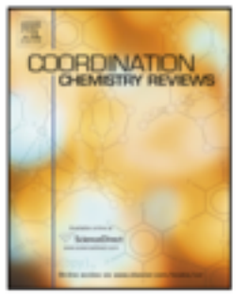


ELSEVIER

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Review

Computational characterization and prediction of metal–organic framework properties

François-Xavier Coudert*,[1], Alain H. Fuchs

PSL Research University, Chimie ParisTech – CNRS, Institut de Recherche de Chimie Paris, 75005 Paris, France