Increasing the hydrogen storage capacity of IRMOF-1 via applied electric fields

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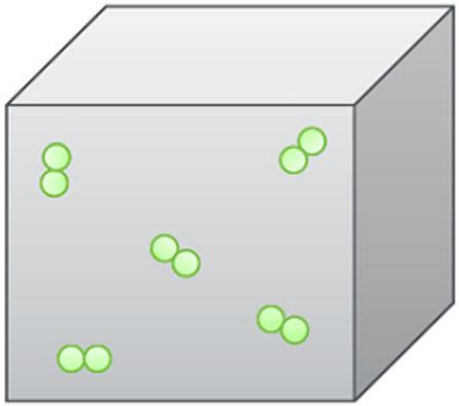
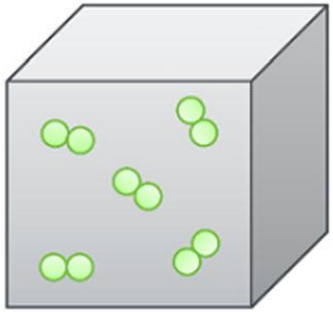
Physical vs Solid State Storage

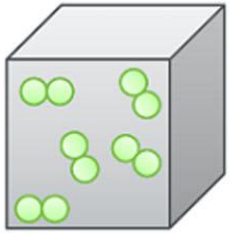
Physical Storage



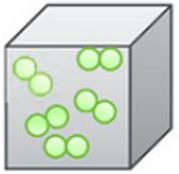
1 bar
normal
0.3 g/L



150 bar
lab cylinders
10 g/L



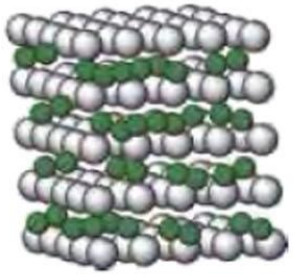
350 bar
Gen 1 vehicles
28 g/L



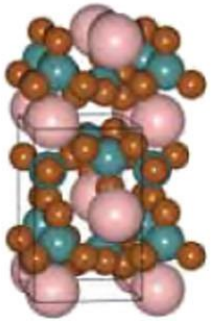
700 bar
Gen 2 vehicles
40g/L

liquid H_2
71 g H_2/L
@ 20 K

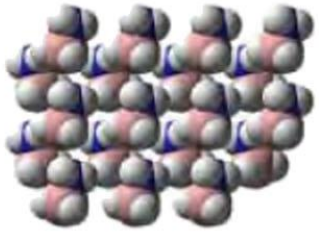
Materials -based Storage



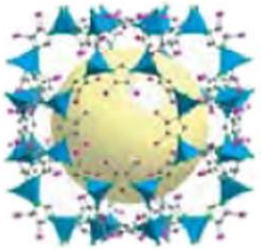
interstitial hydrides
~100-150 g H_2/L



complex hydrides
~70-150 g H_2/L



chemical storage
~70-150 g H_2/L



sorbents
≤ 70 g H_2/L

Reference

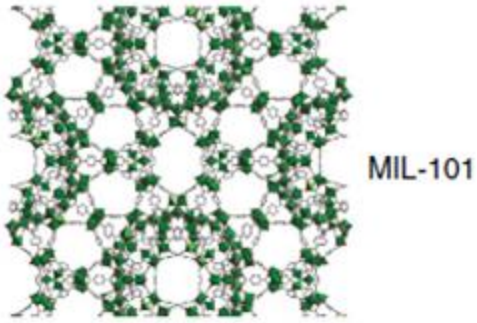
water
111 g H_2/L

Stetson N. An overview of U.S. DOE's activities for hydrogen fuel cell technologies. Clearwater, Florida, America, 2/27/2012.

H_2 Storage in Metal-Organic Frameworks (MOFs)

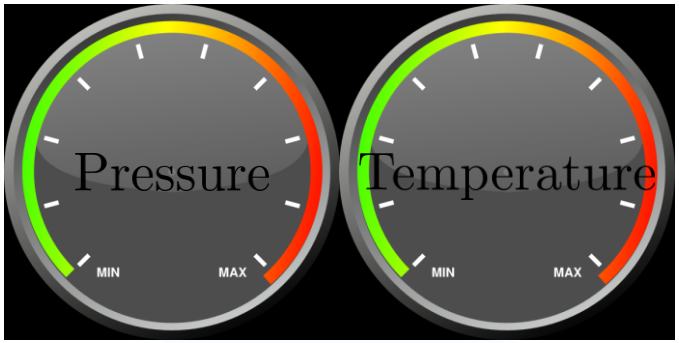
MOF	BET m^2/g	Langmuir m^2/g	P(bar)	T(K)	wt%	g/l	Q_{st} (kJ/mol)
MIL-101		5500	80	298	0.43	1.84	10
			80	77	6.1	26.1	
HKUST-1	1154	1958	50	77	3.6		4.5
			65	298	0.35		
IRMOF-6	2804	3305	45	77	4.63	31.7	

Chem. Soc. Rev. **38**, 1294 (2009)

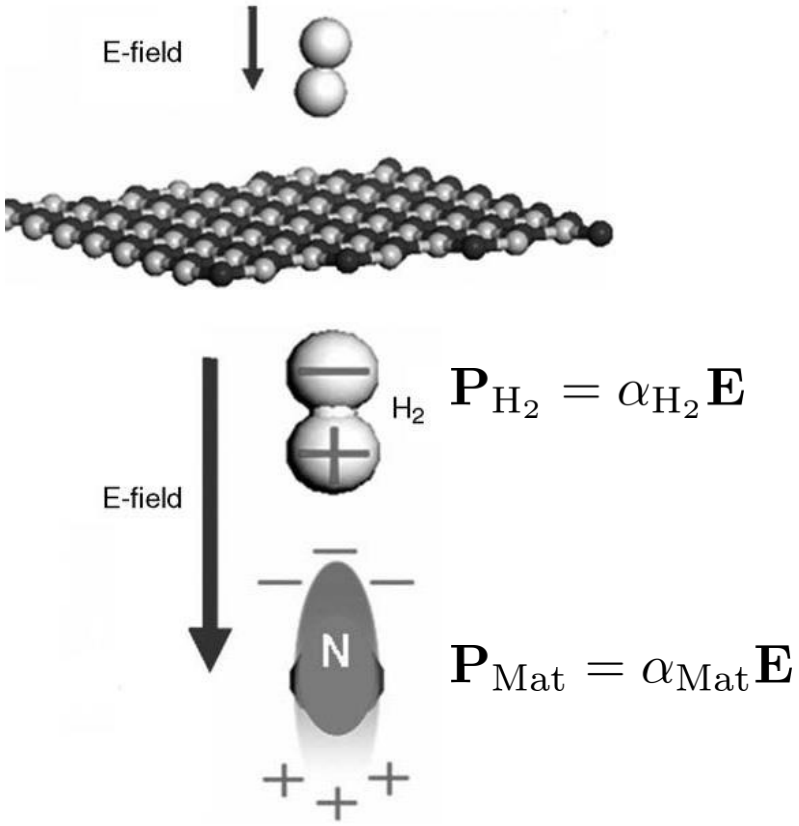


- DOE: 40g/L, 5.5wt% (2020)
  70g/L, 7.5wt% (final)
- Need Q_{st}~15-20kJ/mol
- How to increase binding?

Electric Field Controlled Physisorption



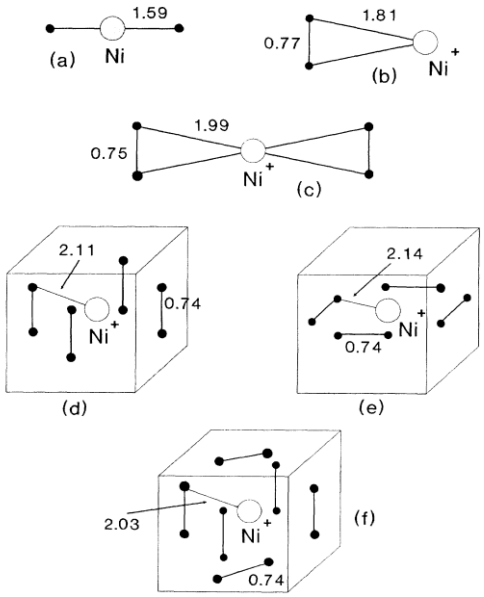
$$E = \frac{\mathbf{p}_1 \cdot \mathbf{p}_2 - 3(\mathbf{p}_1 \cdot \hat{r})(\mathbf{p}_2 \cdot \hat{r})}{4\pi\epsilon_0 r^3}$$



PNAS **107**, 2801 (2010)

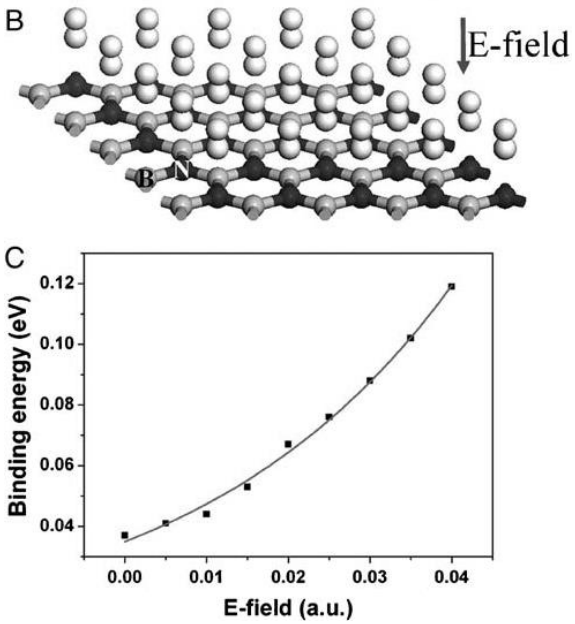
Enhancing H_2 Adsorption via Electric Fields

Polarization mediated binding



PRL **68**, 2277 (1992)

2D sheets: graphene, BN, AlN, B/C/N

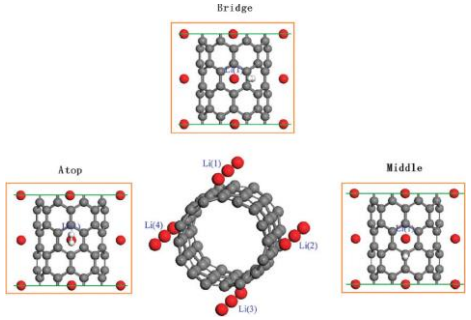


PNAS **107**, 2801 (2010),
CARBON **47**, 3452 (2009),
Struct Chem 22, 1039 (2011),
J. Nanopart. Res. **14**, 1256 (2012),
Int. J. Hy. En. **37**, 11842 (2012).

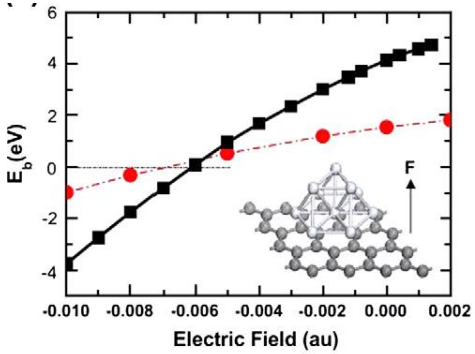
- Induced dipole-dipole interactions →improved binding energies.
- For fields > 0.01a.u. ~5GV/m. DOE storage limits can be reached.
- E=0.045 →Optimal binding energy.

Enhancing H_2 Adsorption via Electric Fields

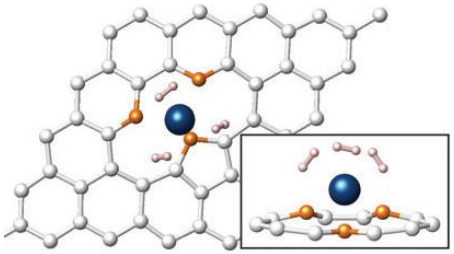
Metal-doped nanostructures



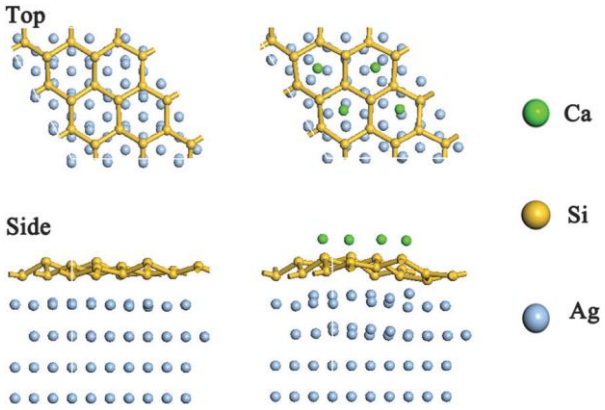
Phys. Chem. Chem. Phys., **11**, 9233–9240 (2009)



Computational Materials Science **68**, 61 (2013)

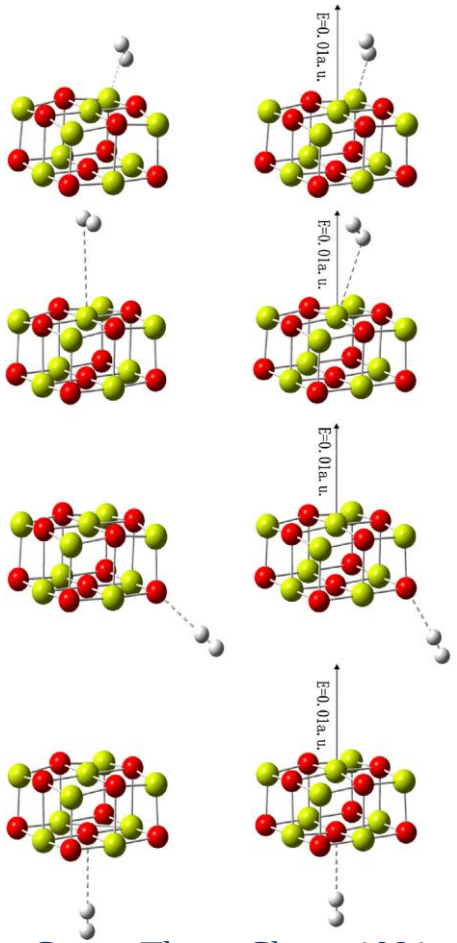


Phys.Chem. Chem. Phys., **15**, 3243 (2013)



Phys. Chem. Chem. Phys. **16**, 23985 (2014)

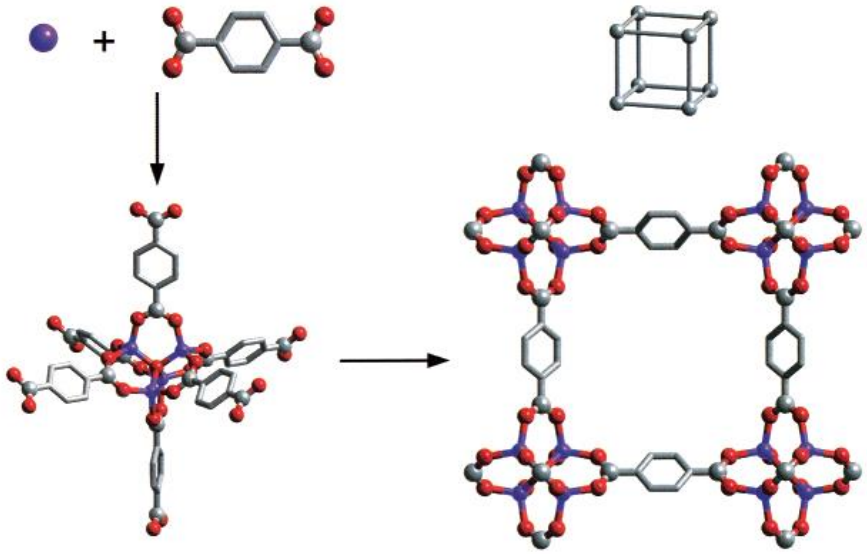
Oxide clusters

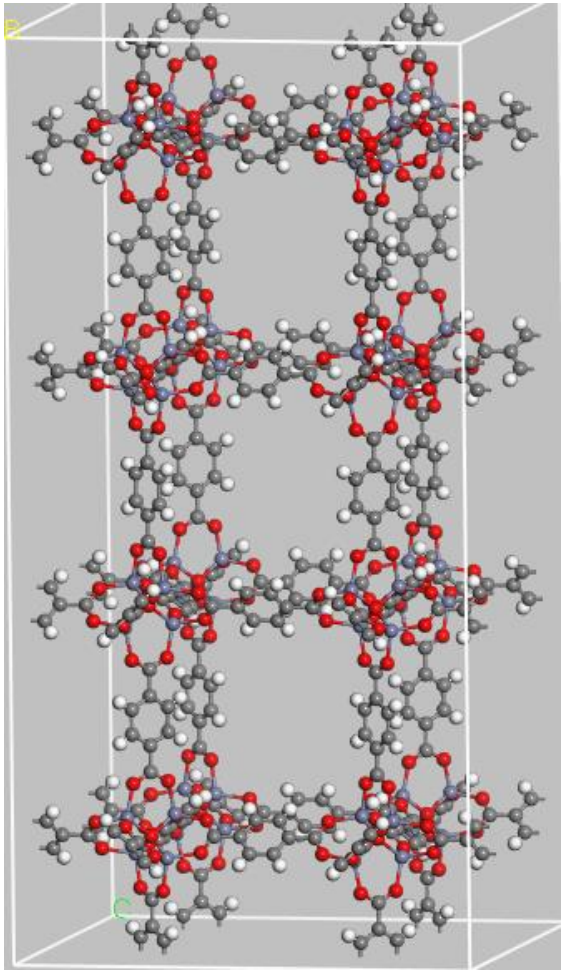


Comp. Theor. Chem. **1081**, 1 (2016)

Metal-Organic Frameworks as Storage Media

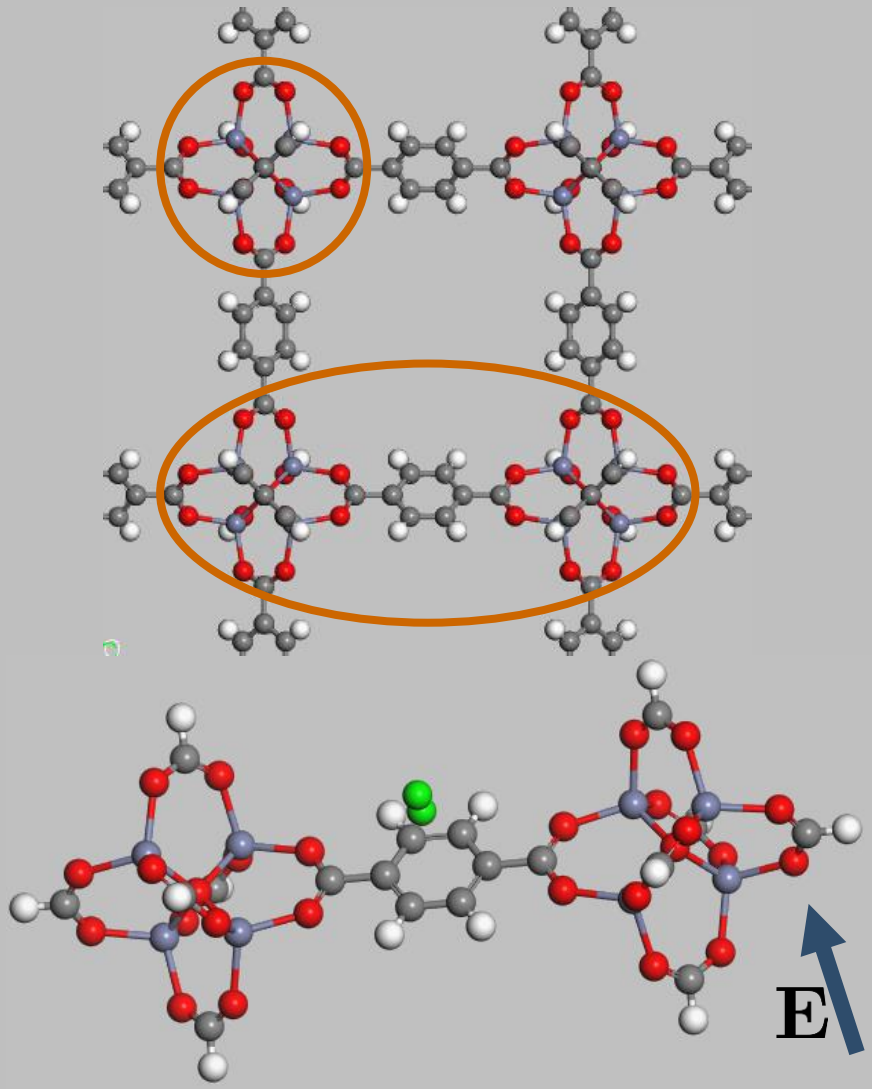
$$ZnO_4 + BDC = IRMOF-1$$



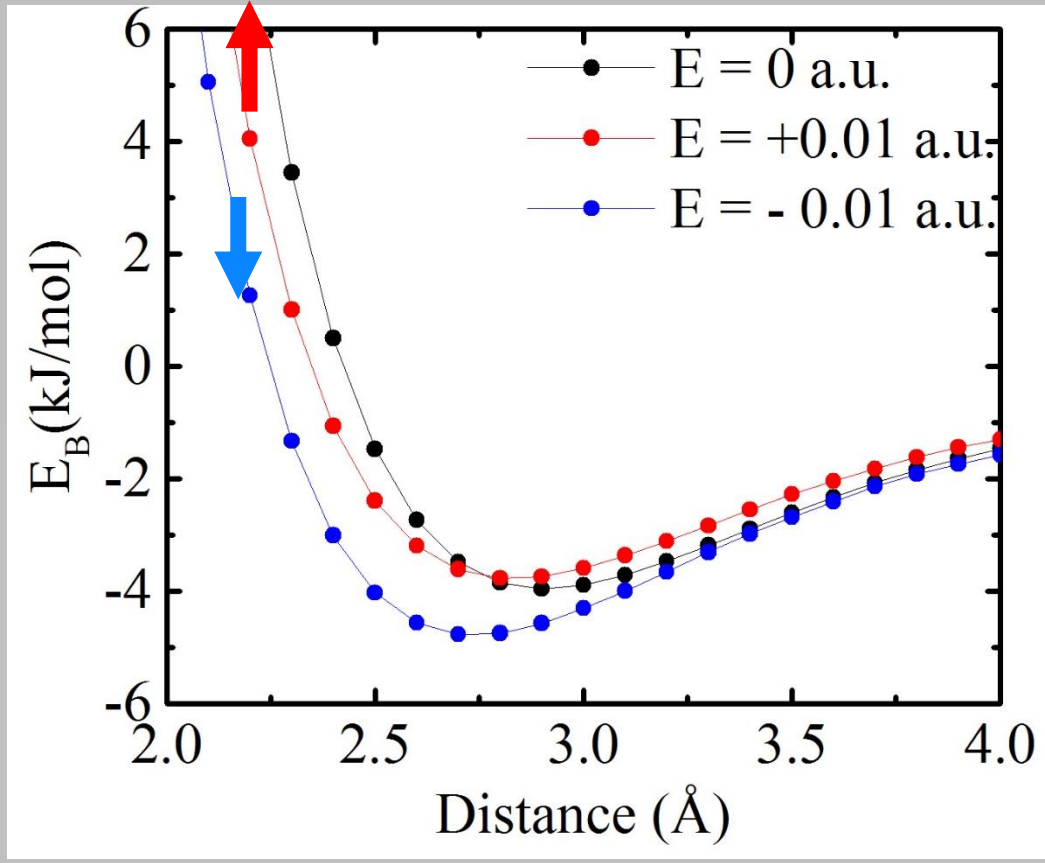


- ~5000m²/g pore surface
- nm-size communicating pores.
- Small adsorption enthalpies (3-7kJ/mol).

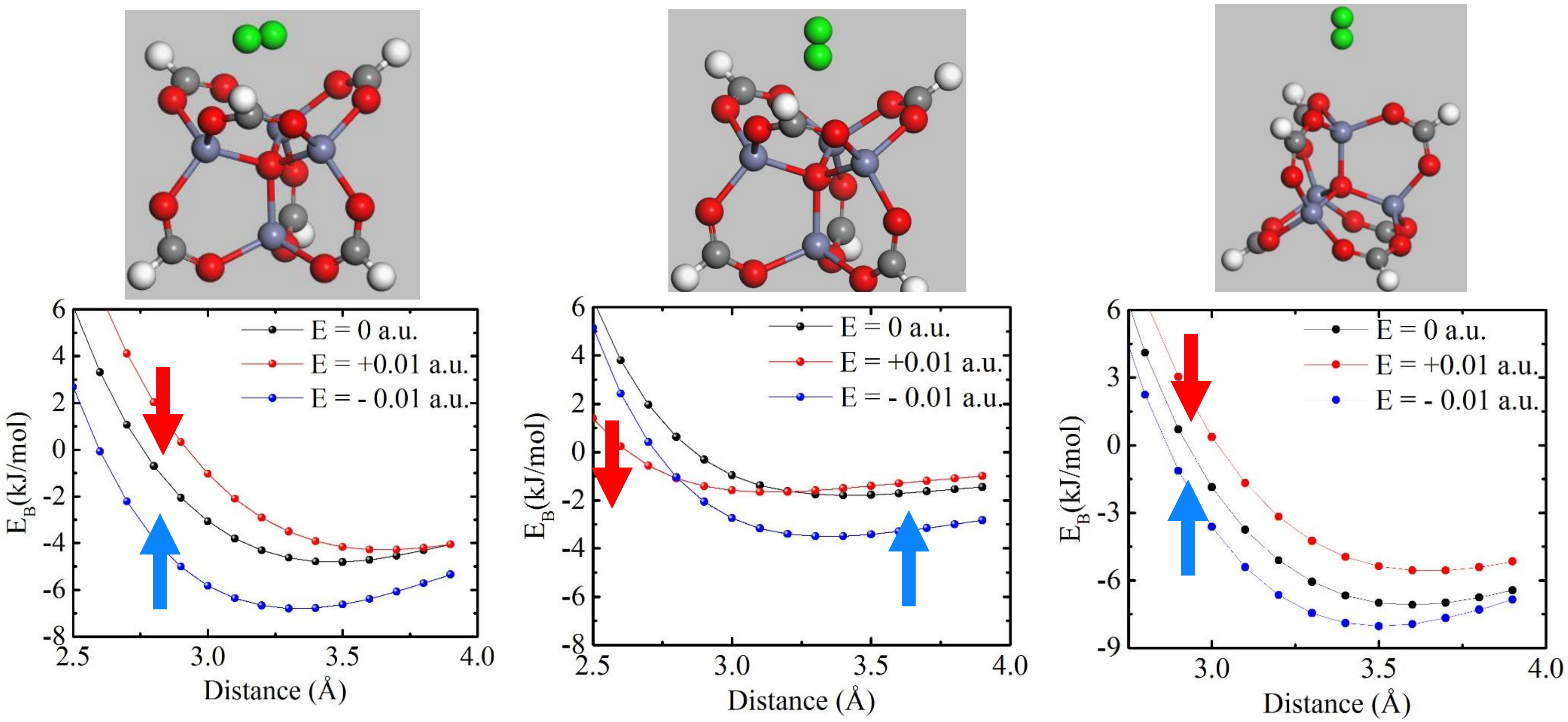
Binding Energies in Electric Field: Linker



$$E = 0.01\text{a.u.} \approx 5\text{GV/m}$$

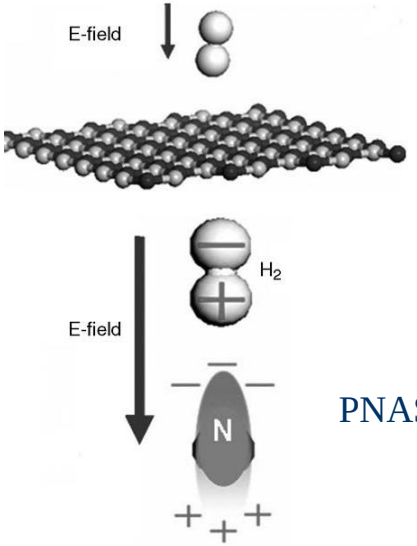


Binding Energies in Electric Field: SBU

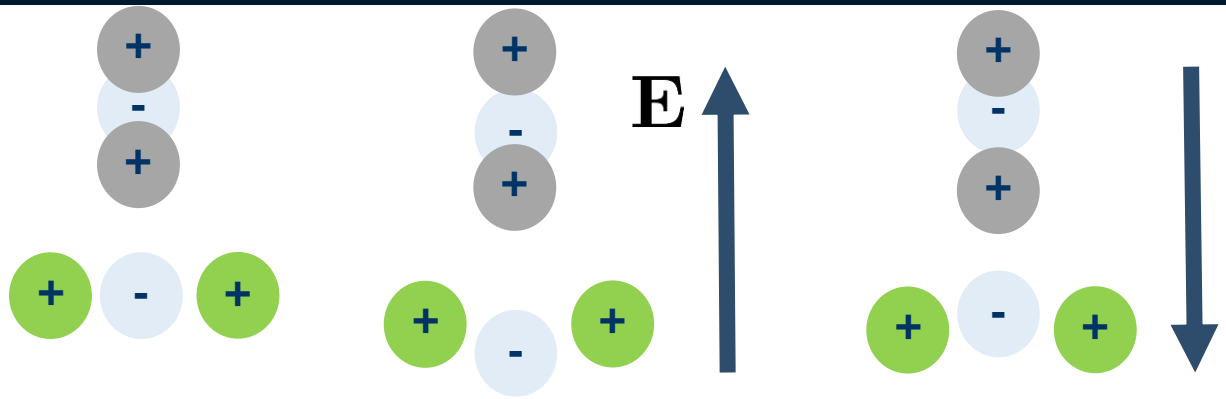


- E both enhance and decrease binding.
- $E_B \sim H_2$ orientation
- E=0.01a.u. ~ 20% change of E_B.

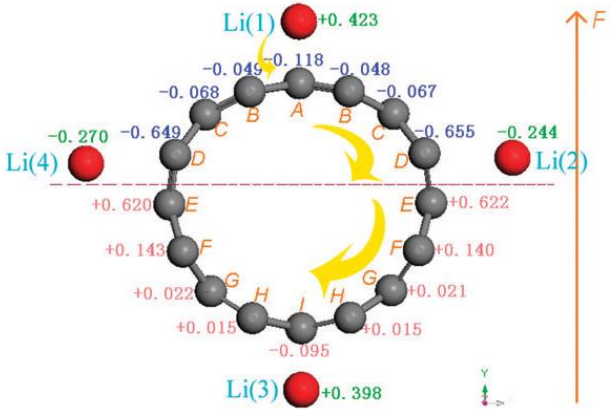
Extra: Simple Electrostatic Picture



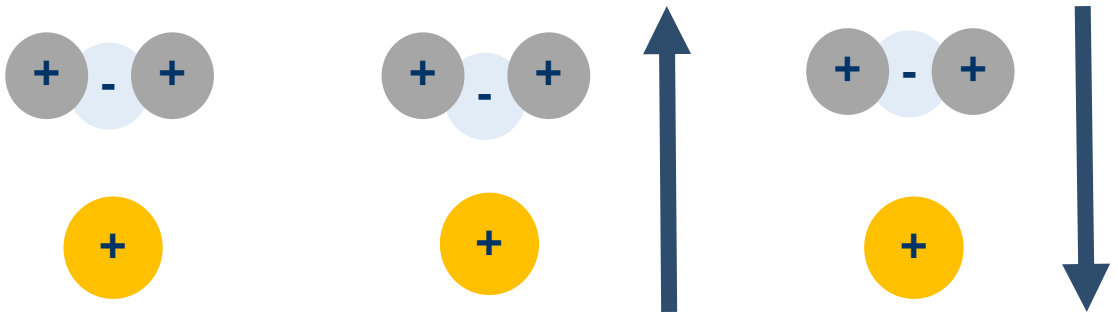
PNAS **107**, 2801 (2010)



$$E_{\mathrm{B}}(-E) > E_{\mathrm{B}}(0) > E_{\mathrm{B}}(E)$$

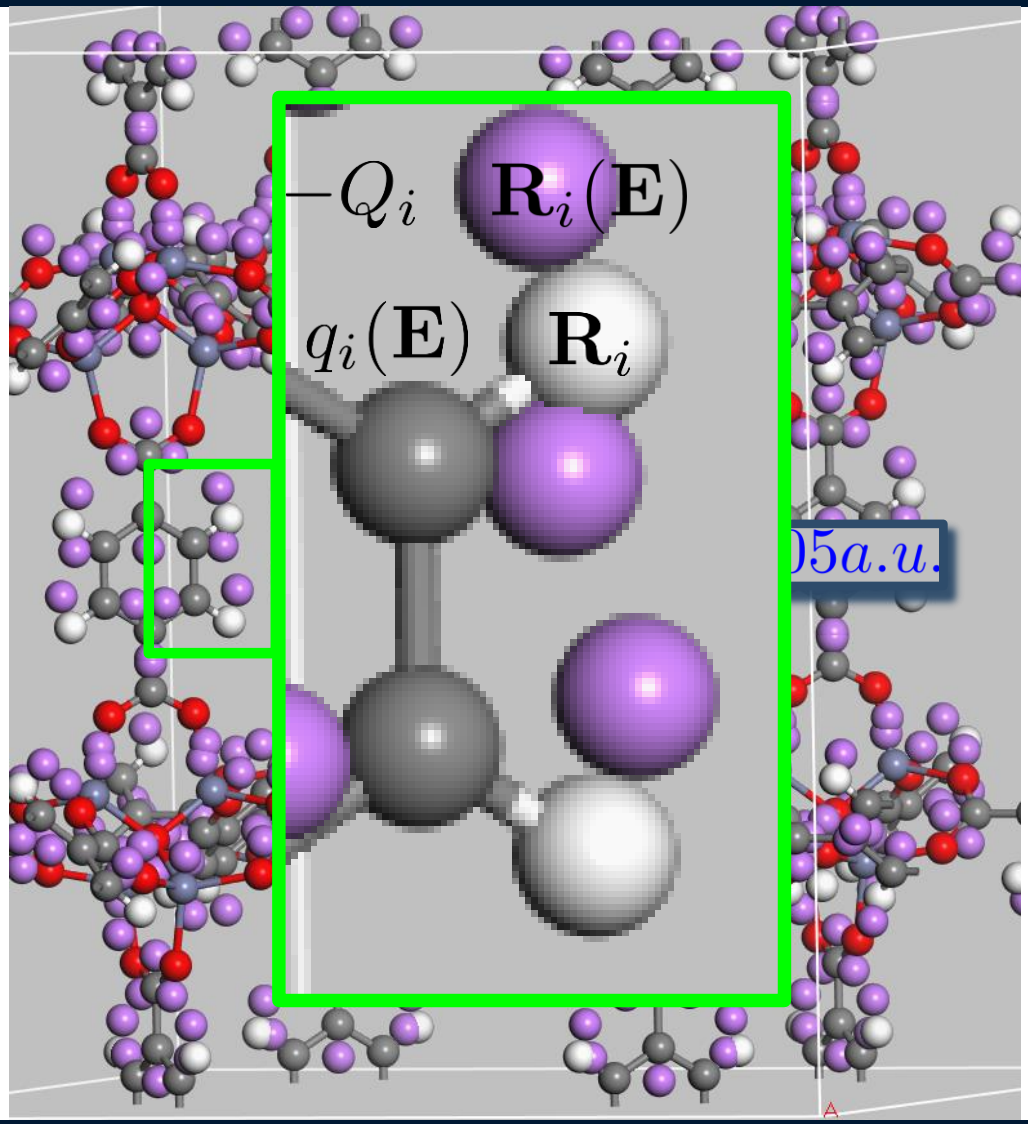


Phys. Chem. Chem. Phys., **11**, 9233 (2009)



$$E_{\mathrm{B}}(E) > E_{\mathrm{B}}(0) > E_{\mathrm{B}}(-E)$$

Relaxation of the Structure in Electric Field



- MOF atoms get polarized:

$$\delta \mathbf{r}_i = \mathbf{R}_i(\mathbf{E}) - \mathbf{R}_i$$

$$\delta \mathbf{p}_i = Z_i^* \delta \mathbf{r}_i$$

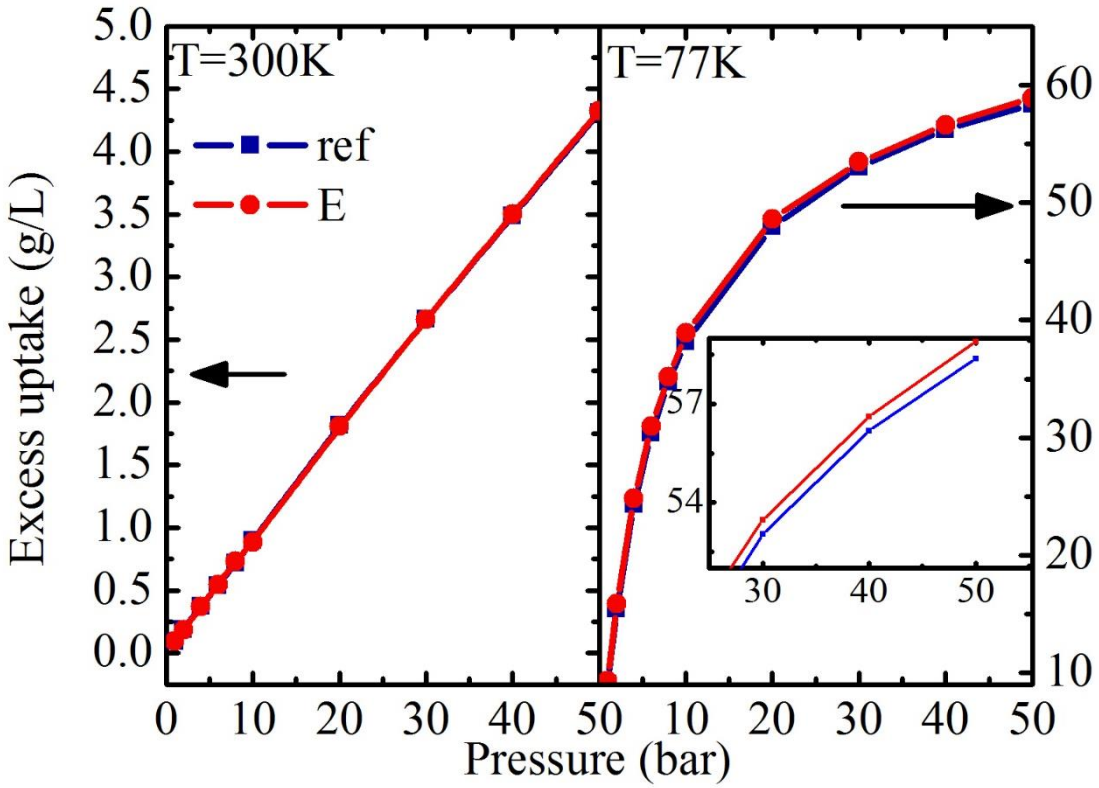
- **Shell model:**

atom i: $q_i(\mathbf{E}) = q_i + Q_i$

dummy charge: $-Q_i$

$$Q_i = \frac{\delta |\mathbf{p}_i|}{d}$$

Adsorption Simulations



- Dipole-dipole interaction:

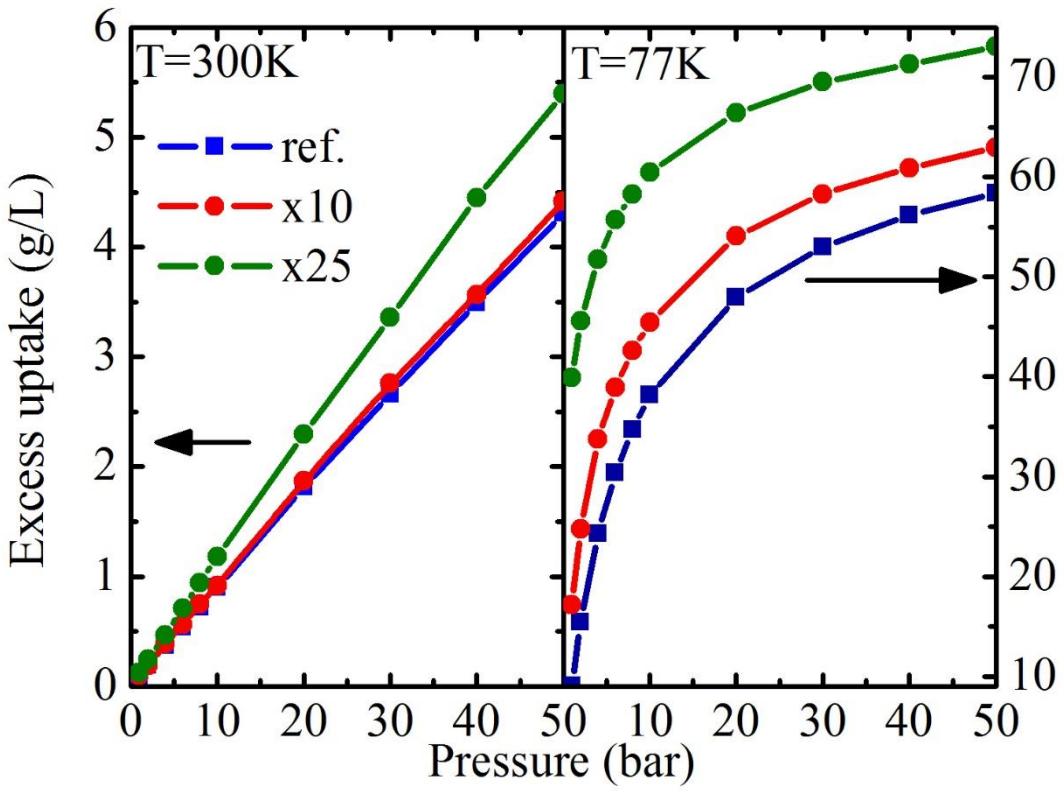
$$E = \frac{\mathbf{p}_1 \cdot \mathbf{p}_2 - 3(\mathbf{p}_1 \cdot \hat{r})(\mathbf{p}_2 \cdot \hat{r})}{4\pi\epsilon_0 r^3}$$

- Our field is 9x smaller than 0.045a.u (PNAS **107**, 2801 (2010))

$$\begin{aligned} \mathrm{H_2}: &\quad p_1/9 \\ \mathrm{MOF}: &\quad p_2/9 \end{aligned}$$

- →80 times less binding expected!

Larger Polarizability?

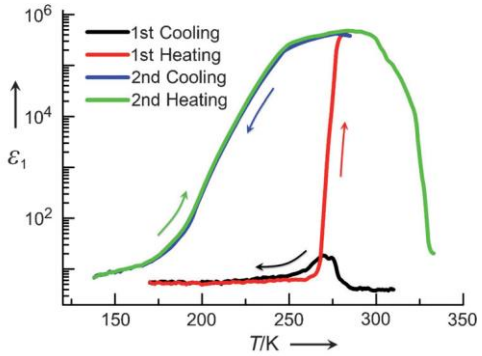


- We cannot increase E too much (Zener breakdown).
- Choose a more **polarizable** material?
- Larger pore field?

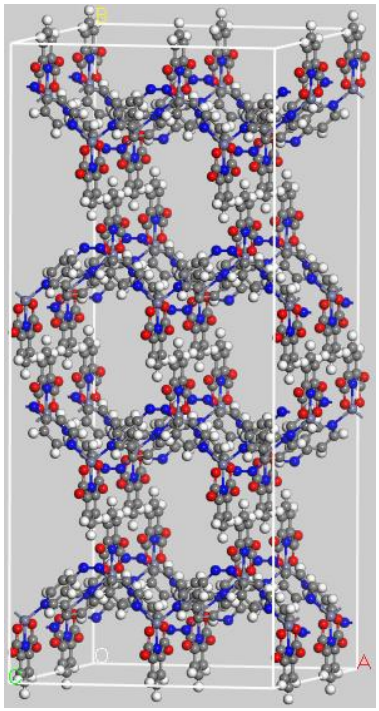
$$E_0 = 0.005$$

$$E \approx E_0 - \frac{4\pi}{3}\frac{P}{V} \approx 0.0045$$

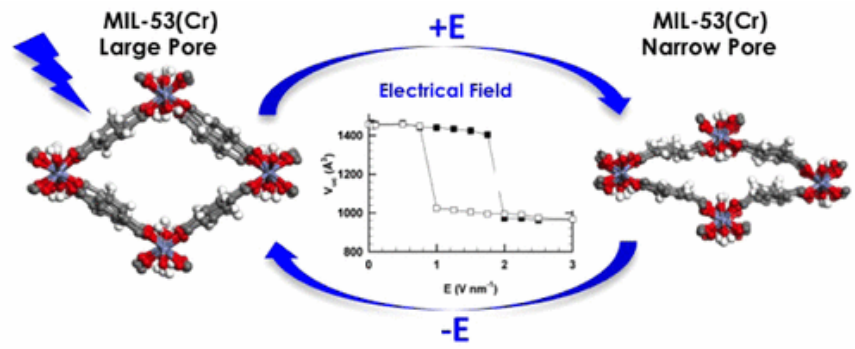
Conclusions and Further Questions



Angew. Chem., **123**, 11643 (2011).



Microporous and Mesoporous Materials, 159, 100, 2012



ACS Cent. Sci., 3 (5), 394 (2017)

- **E** cannot be too large:
  - Zener breakdown (material bandgap)
- Look for **large polarizability**:
  - Ferroelectric MOFs
  - Breathing MOFs?
  - Polarizable linker functions.