

# Flexible Nanoporous Graphenes for Gas Separation: An Effective Pore-Widening Mechanism

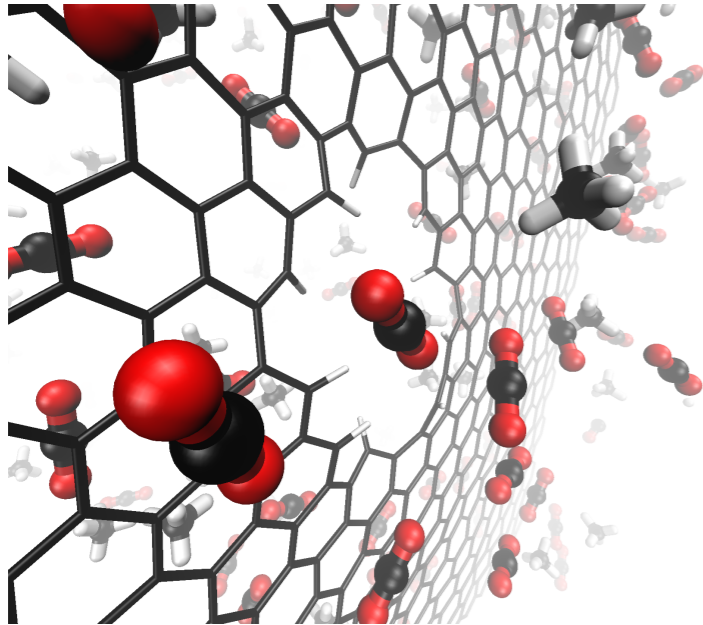
Juncheng Guo, Guillaume Galliero, Romain Vermorel

Laboratoire des Fluides Complexes et leurs Réservoirs, Pau

*INTERPORE2026 - 05/21/2026 , Nantes*

# 2D Nanoporous Graphene Membranes (NPG)

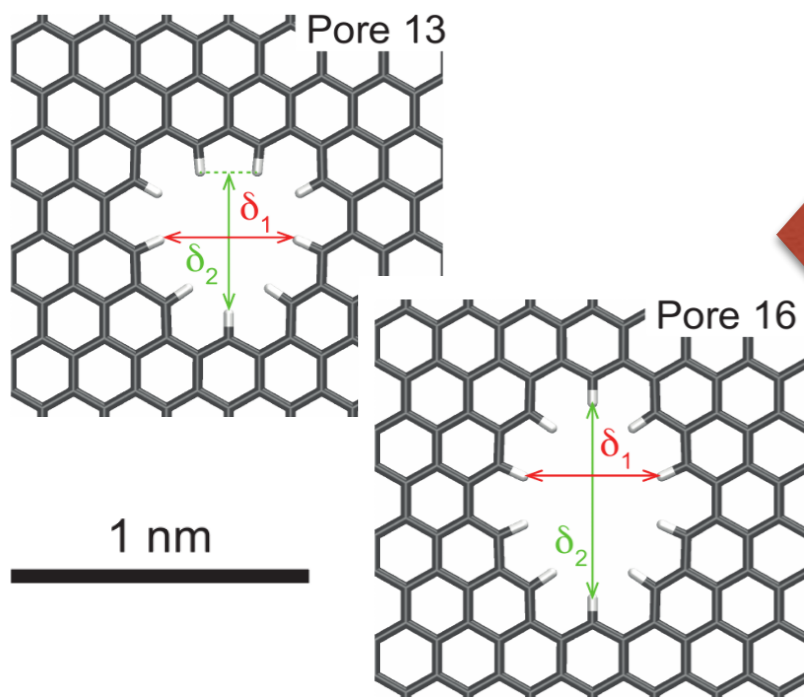
## Promising material for separation processes



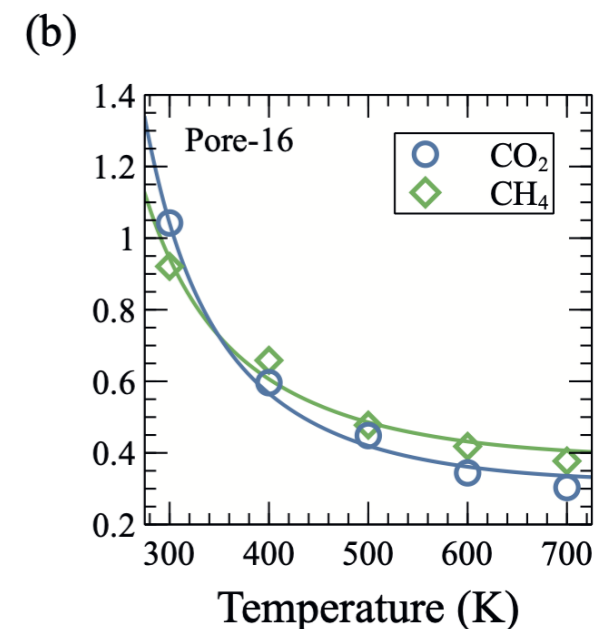
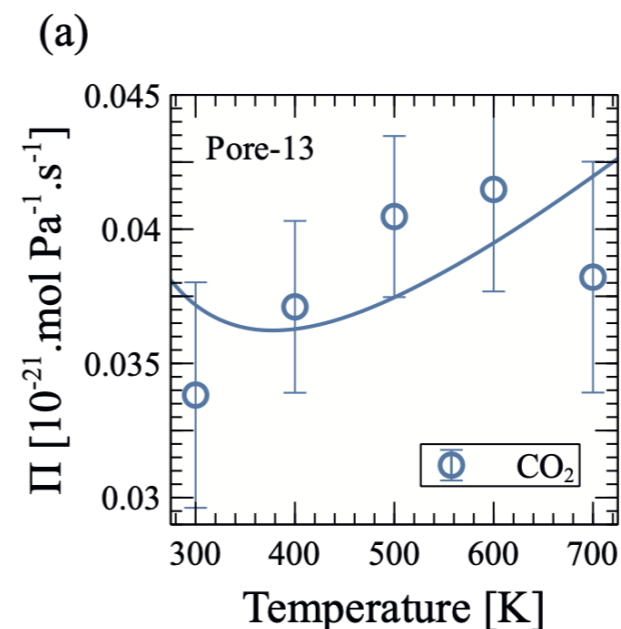
- Pore size  $\approx$  molecular diameter  $\Rightarrow$  **high selectivity**
- An atom thick  $\Rightarrow$  **low energy cost**

## Ideal toy systems to investigate activated gas permeation

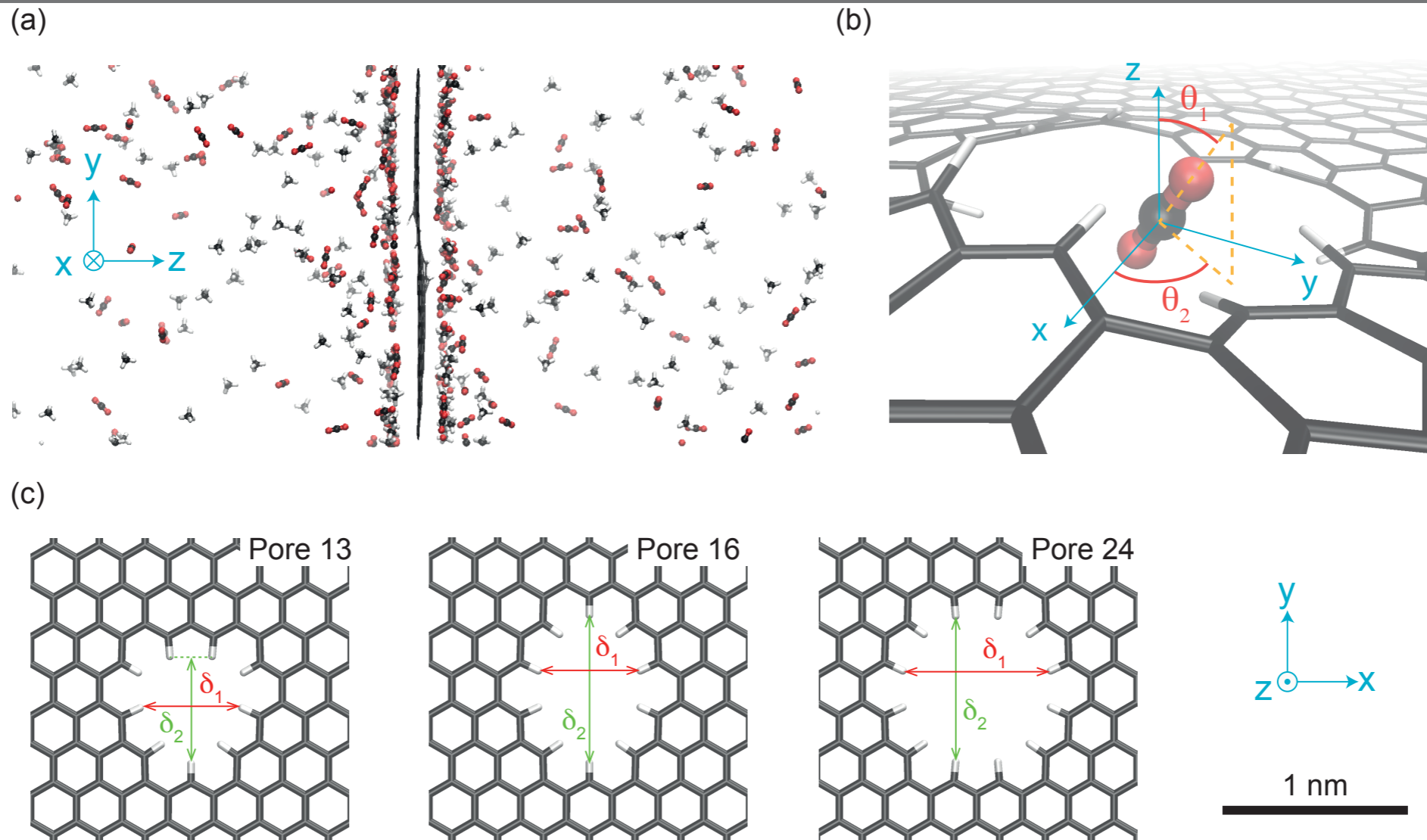
(inherent to other nanoporous materials)



Structure vs Permeance

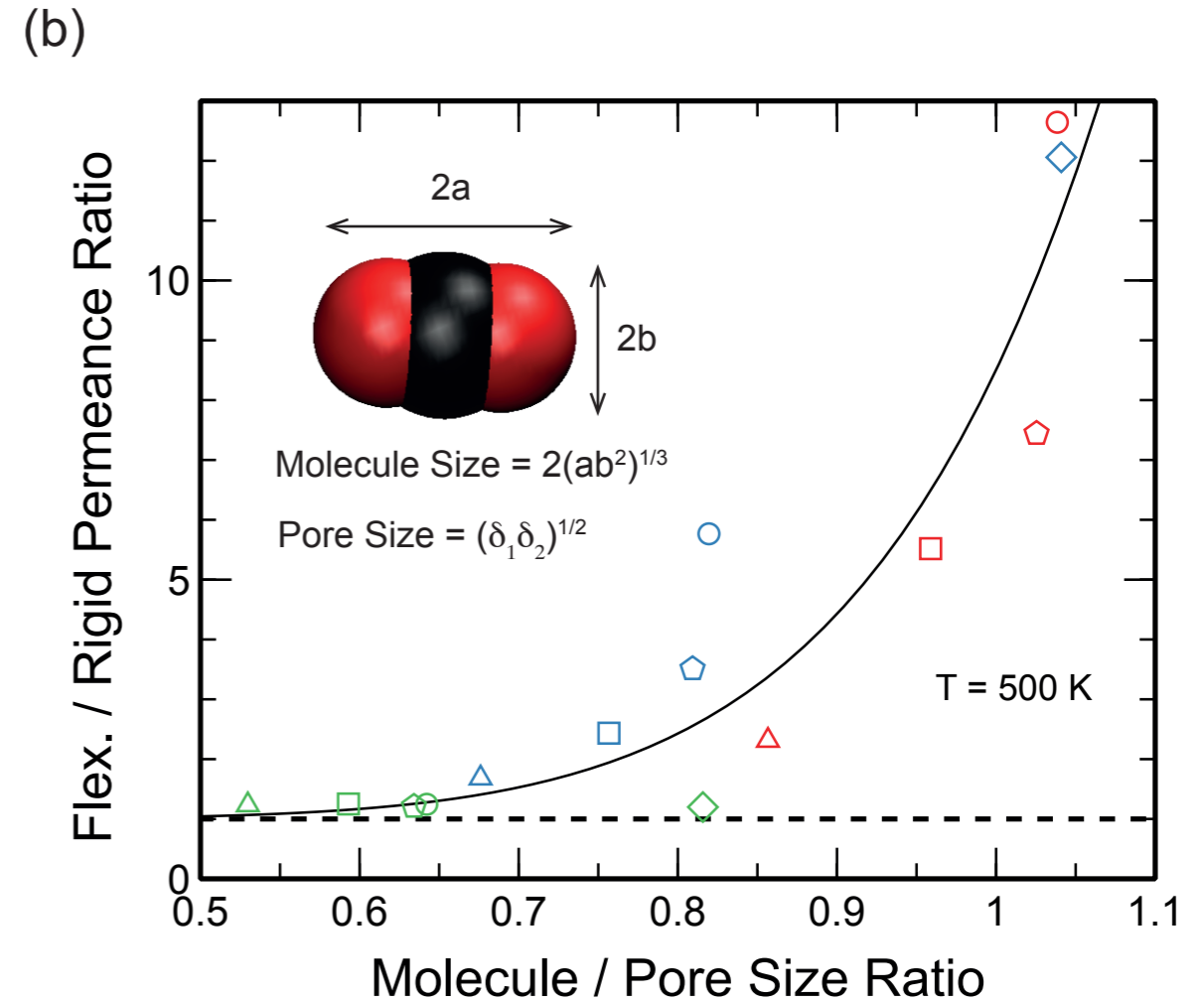
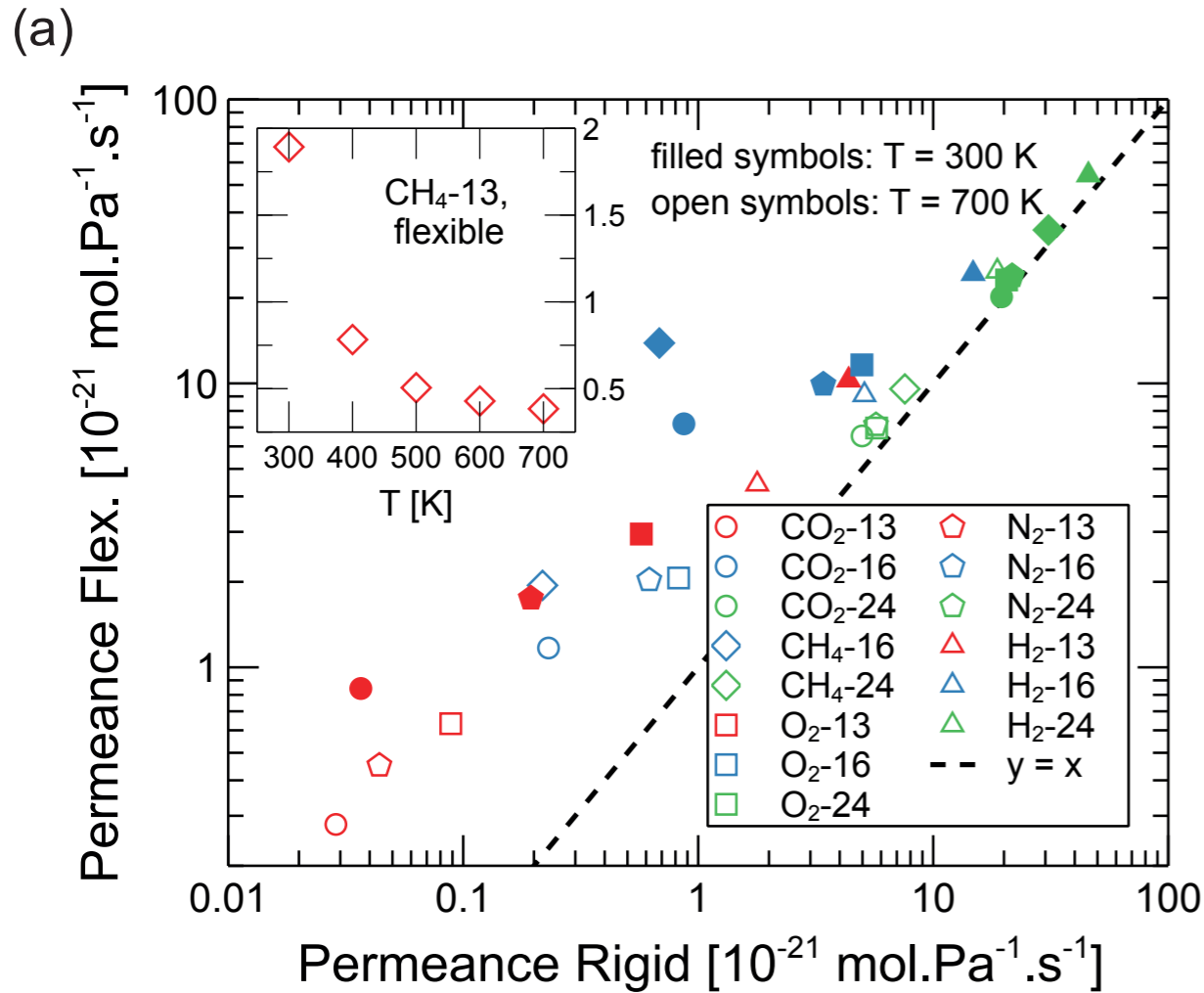


# Today's question: role of membrane flexibility ?



- **Question: influence of graphene flexibility ?**
- Fully rigid zero plane-stress **vs** Fully Flexible NPGs membrane models.
- Equilibrium MD for CO<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>
- Molecular sieving regime ( $3\text{\AA} < \delta_i < 6\text{\AA}$ )

# Effect of graphene flexibility on permeance



- Flexibility

- ➡ increases Permeance

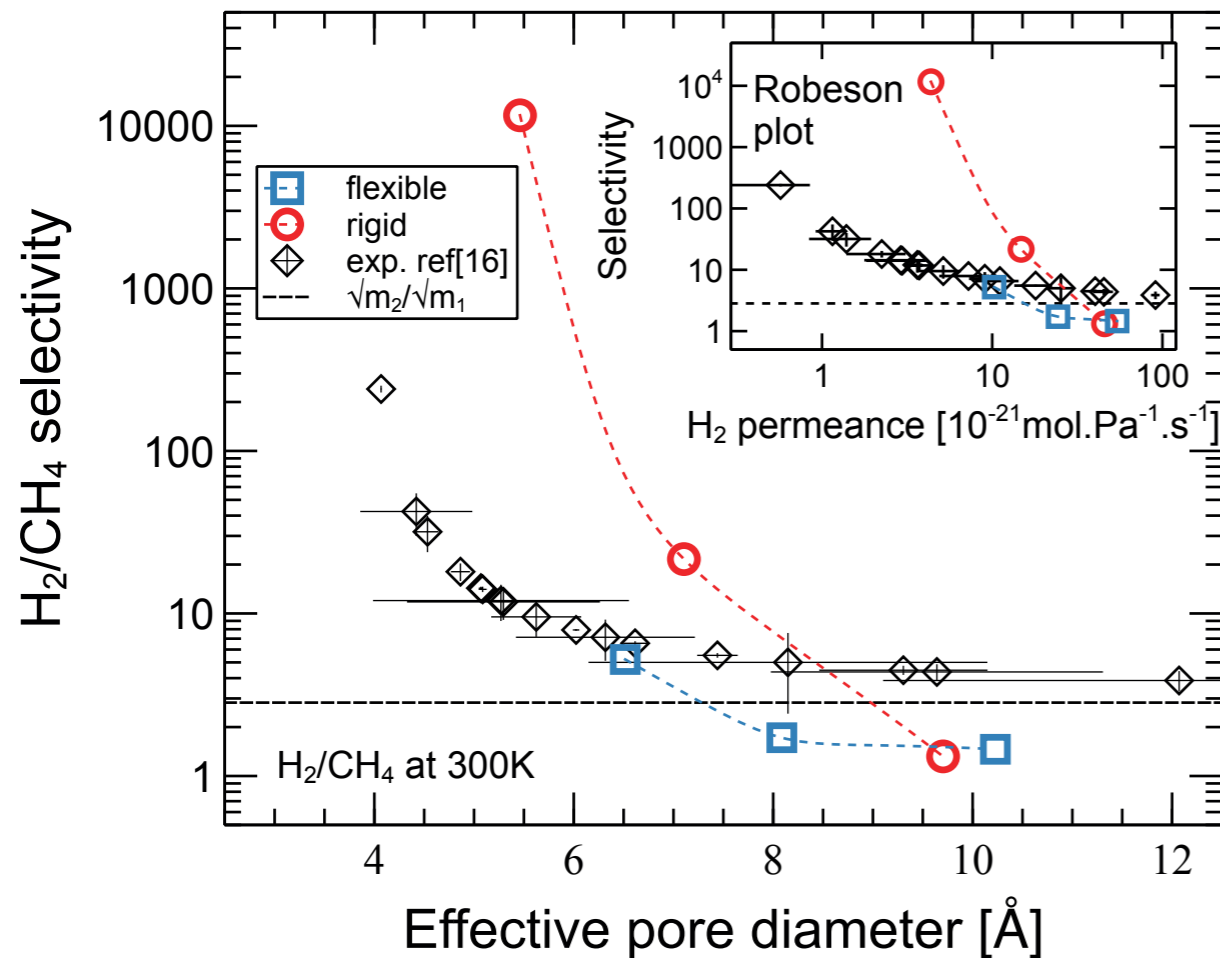
- ➡ decreases Selectivity

- Effect enhanced for high molecule/pore size ratio (molecular sieving).

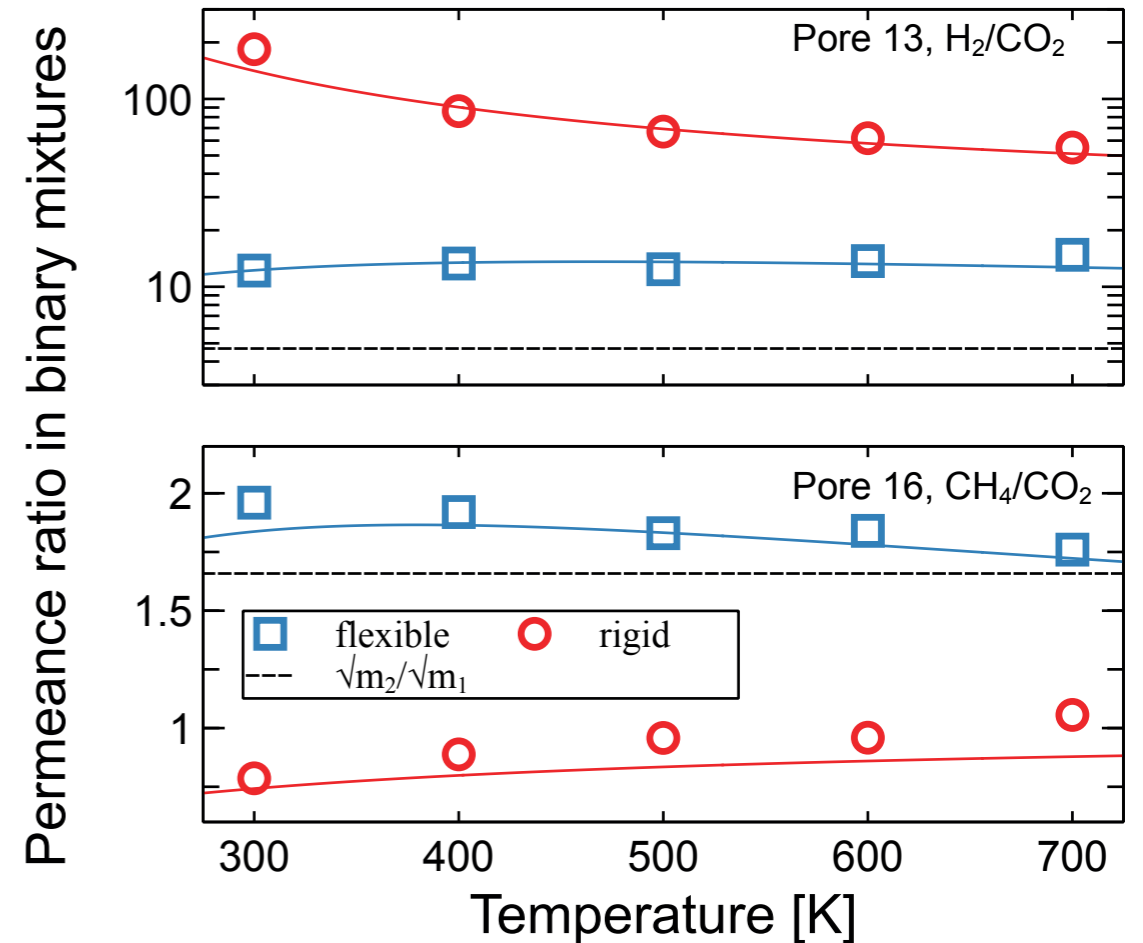
# Implications for gas separation

Exp. Data from Yuan et al., Adv. Mater., 2104308 (2021)

(a)



(b)

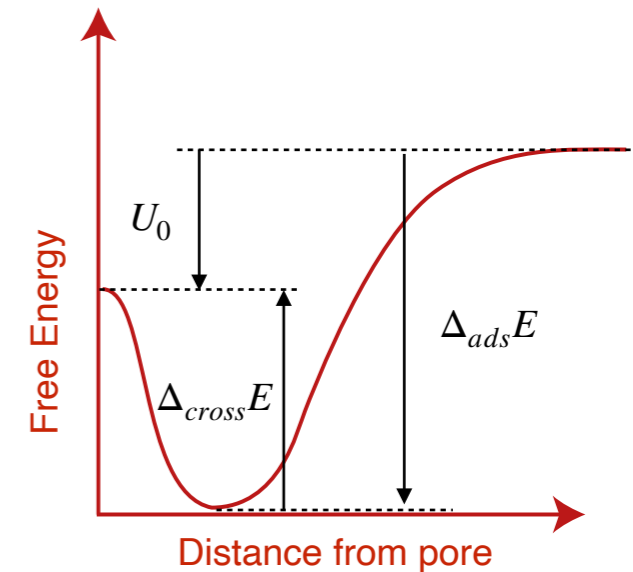
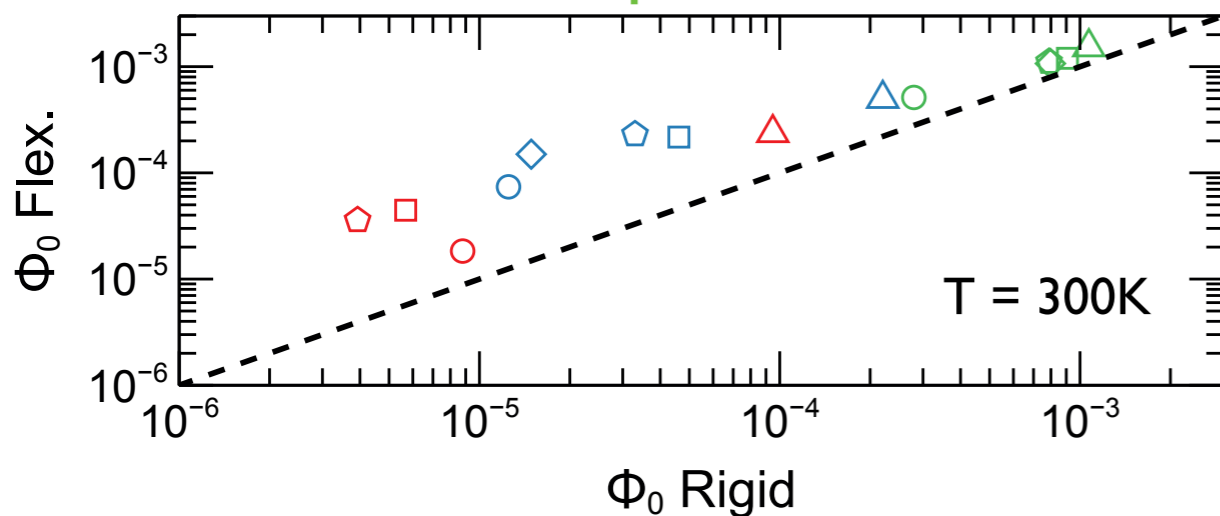


- For flexible models, the divergence of selectivity is shifted to smaller pore sizes, in better agreement with experiments.
- Flexibility may decrease selectivity by orders of magnitude (e.g. H<sub>2</sub>/CO<sub>2</sub>).
- Flexibility may reverse selectivity (e.g. CH<sub>4</sub>/CO<sub>2</sub>).

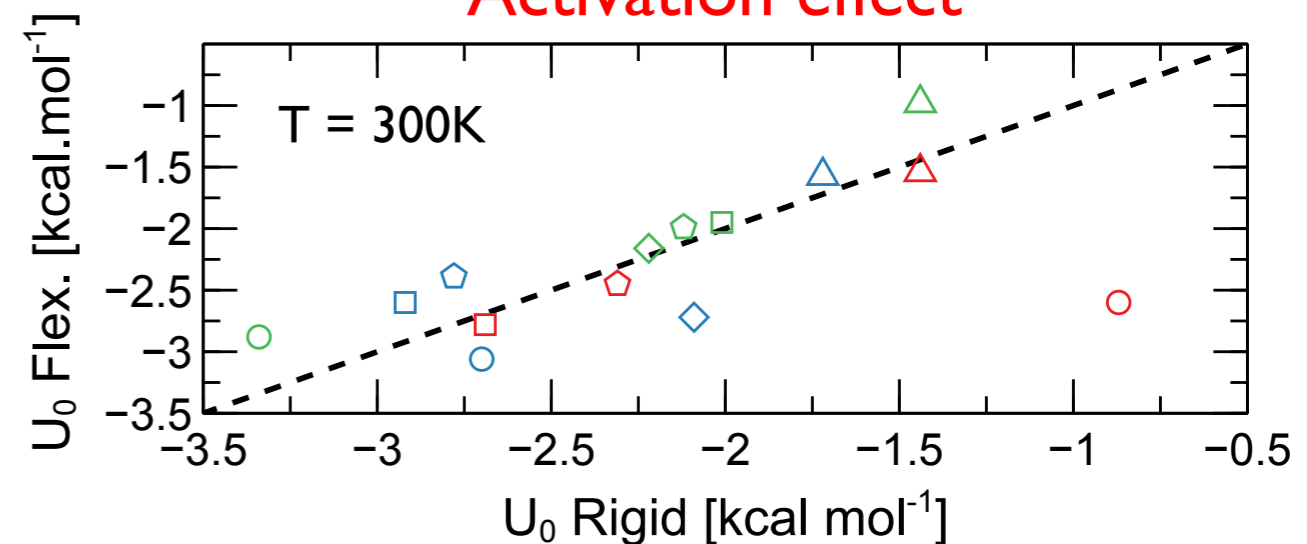
# Insights from an analytical permeance model

$$\text{Permeance} \propto \phi_0(T) \exp\left(-\frac{U_0}{kT}\right)$$

Entropic Effect

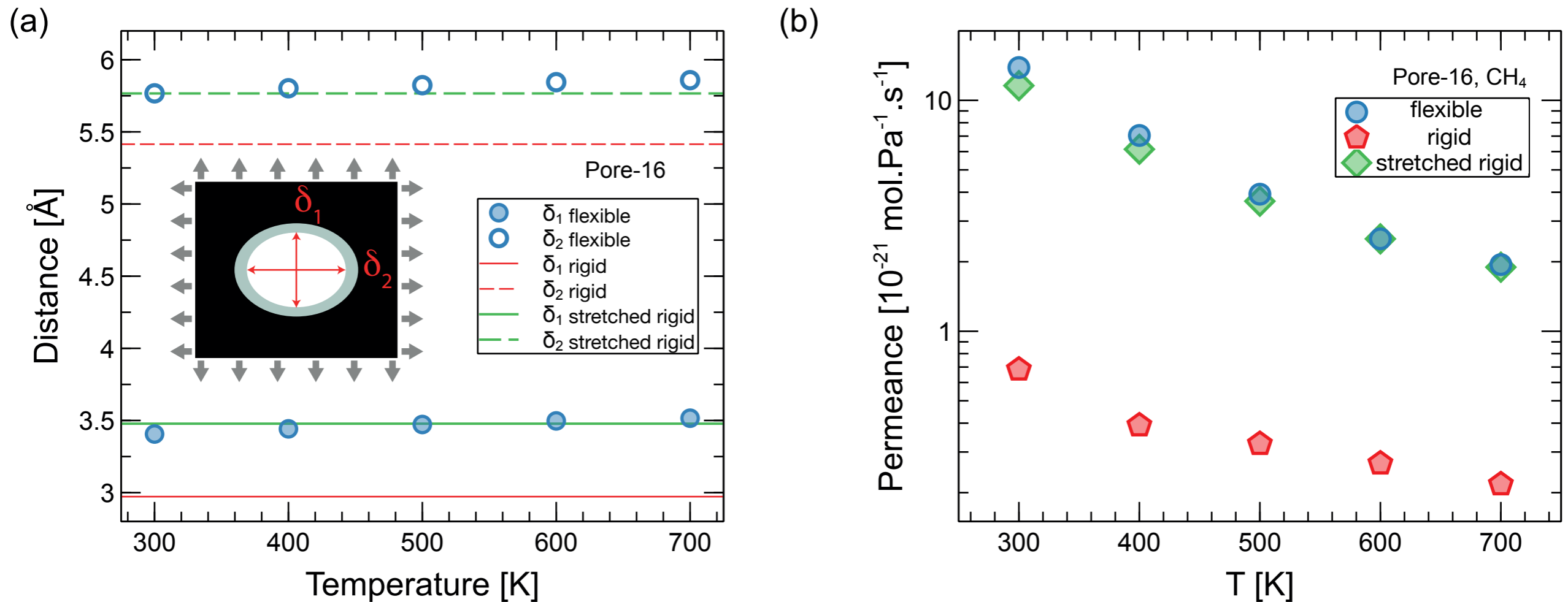


Activation effect



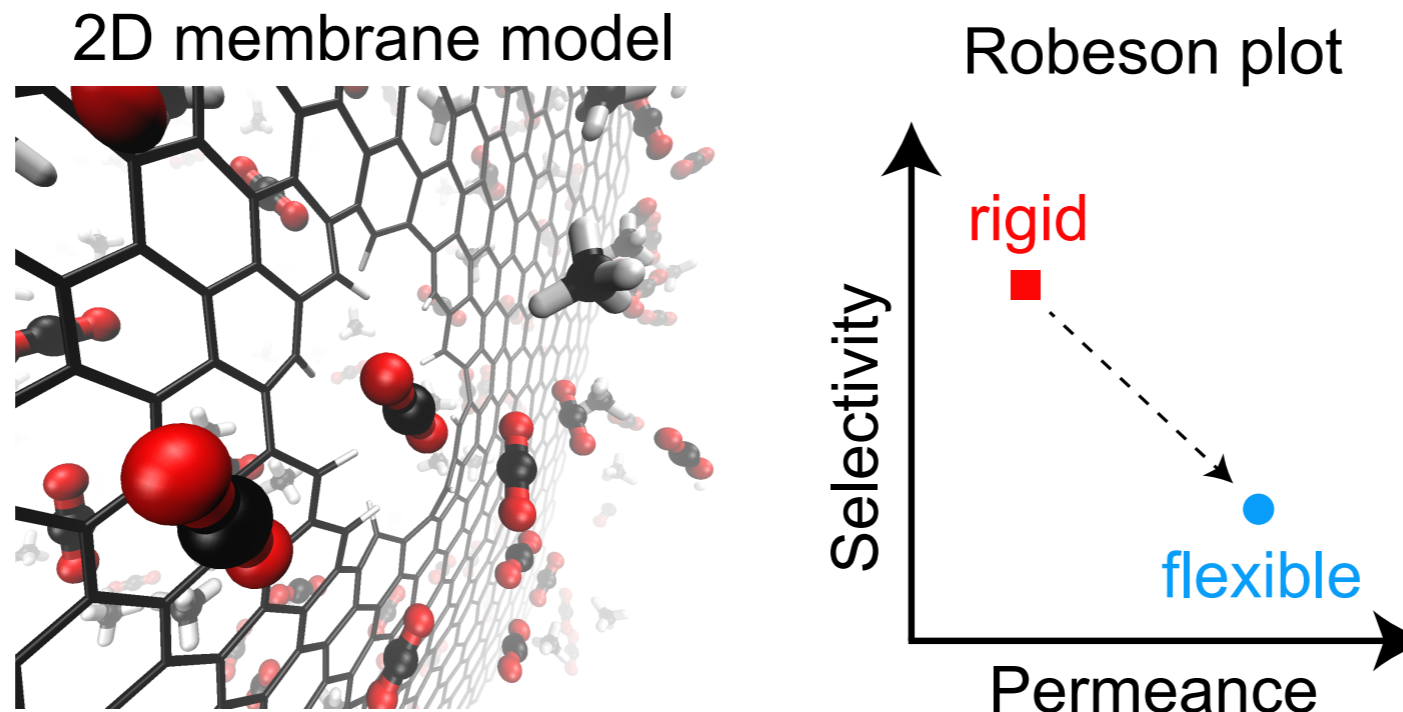
- Fitting of the model to simulation data
- Aside from extreme cases (e.g. CO<sub>2</sub> - pore I3), activation energy is barely affected
- Flexibility increases Entropy (Mobility) suggesting an **increased effective pore size**

# Effective pore size controls permeance



- Flexible and stretched rigid membranes exhibit similar permeances.
- Vibrational details play a secondary role.
- Flexibility can largely be captured through effective pore widening.

# Take home messages

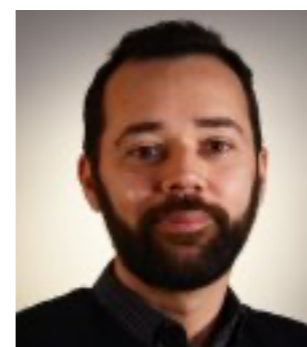


- Flexibility becomes critical in the molecular sieving regime
  - ➔ increases permeance.
  - ➔ decreases selectivity.
  - ➔ improves comparison with experimental data.
- The dominant effect is entropic. Flexibility acts as an effective pore-widening mechanism.
- Effective pore size may be more important than vibrational details.

**Thank you !**



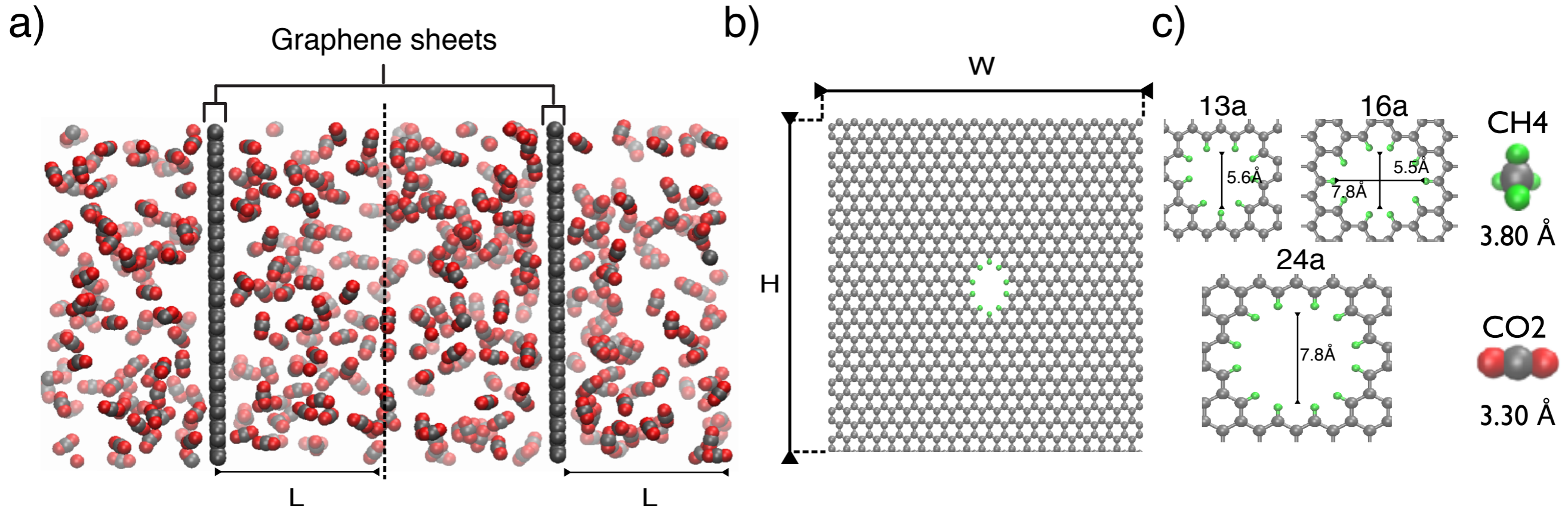
**Juncheng Guo**  
(now at Mines Paris, PSL University)



**Guillaume Galliéro**

# BONUS

# Classical MD simulations



## Simulation details

- MD simulations performed with LAMMPS (equilibrium MD and biased MD for PMF computations).
- The pores are hydrogen-terminated.
- We show results for several kinds of gas molecules: CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>
- Force fields: AIREBO (flexible Graphene), OPLS-AA (CH<sub>4</sub> and Graphene-Gas interactions), Modified TraPPE\* (CO<sub>2</sub>), 3-sites FF\*\* (H<sub>2</sub>), 2-sites FF\*\*\* (O<sub>2</sub>, N<sub>2</sub>)

\*M. Perez-Blanco et al, *J. Phys. Chem. B*, **114**, 36 (2010)

\*\*H. Liu et al, *Solid State Commun.*, **175-176**, 101-105 (2013)

\*\*\*M. Krishnamurthy et al, *Mol. Simul.*, **32** (1), 11-16 (2006)

## Parameters

- 5 temperatures  $300\text{K} \leq T \leq 700\text{K} \Rightarrow$  **supercritical conditions**
- 5 densities  $0.3\text{mol/L} \leq \rho \leq 2\text{mol/L} \Rightarrow$  **exp. conditions** (e.g. CH<sub>4</sub>:  $5\text{ bar} \leq P \leq 50\text{ bar}$ )
- Three types of pores  $5.5\text{Å} \leq \text{pore size} \leq 7.8\text{Å} \Rightarrow$  **sub-nanopores**

# Permeance Model

Permeance = molar flux / pressure jump      $\Pi = (jS)/(N_A\Delta p)$

Thermal velocity

$$j = \underbrace{\frac{\bar{v}S_{pore}}{4}\Delta\rho}_{\text{Kinetic theory}}, \quad \underbrace{\Delta p = kT\Delta\rho}_{\text{Ideal gas}}, \quad \phi = \frac{S_{pore}}{S}$$

$$\Pi = \frac{S}{4N_A} \frac{\bar{v}}{kT} \phi$$

Accessible surface porosity

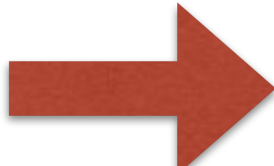
# Permeance Model

Potential of Mean Force in the plane of the pore:

$$U_{pmf}(x, y, z = 0, \theta_i) = U_0 + \frac{f_x}{2}x^2 + \frac{f_y}{2}y^2 + \sum_{i=1}^{n_a} \frac{f_{\theta_i}}{2}(\theta_i - \theta_{i0})^2$$

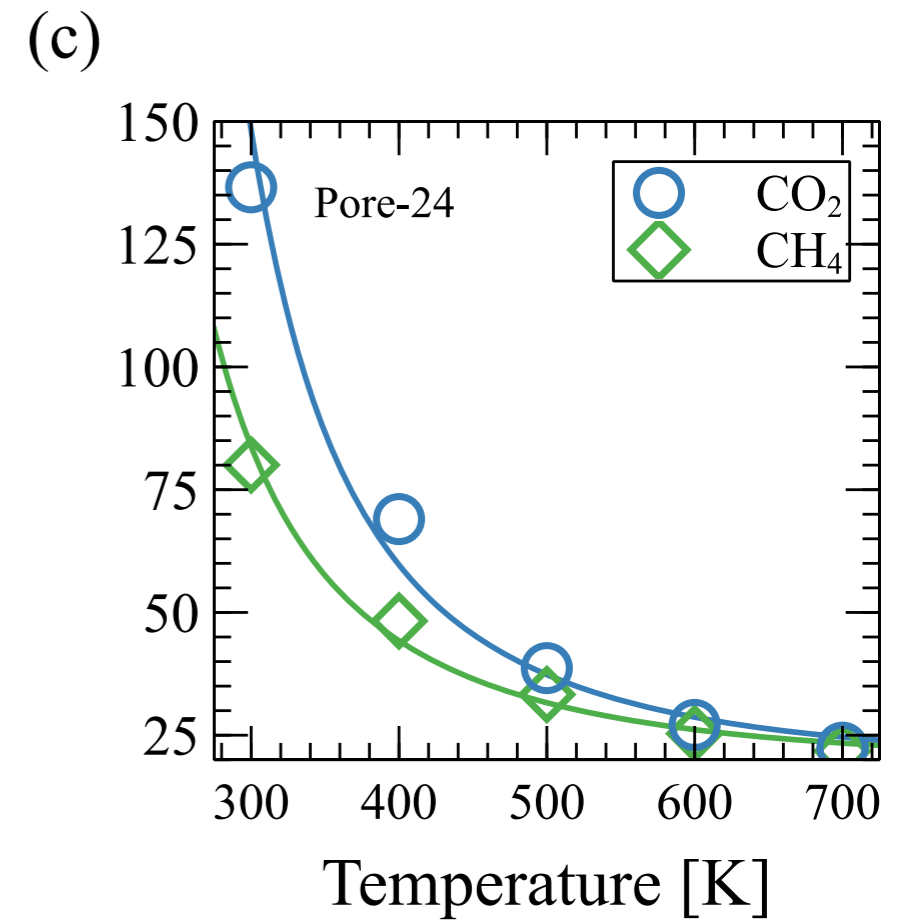
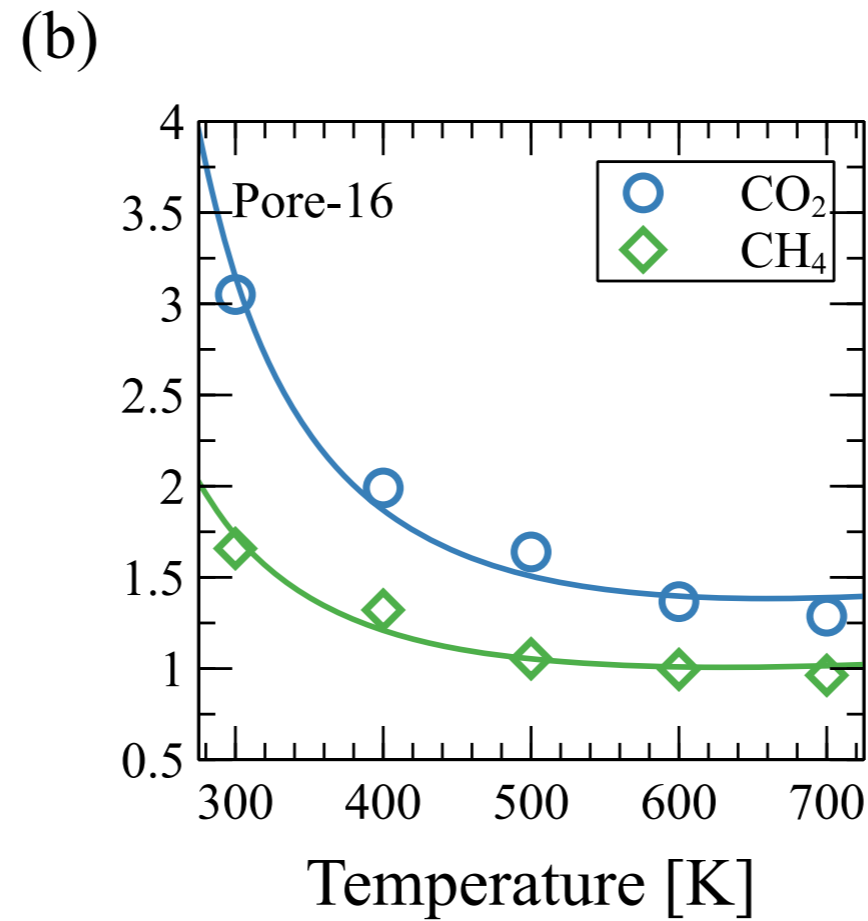
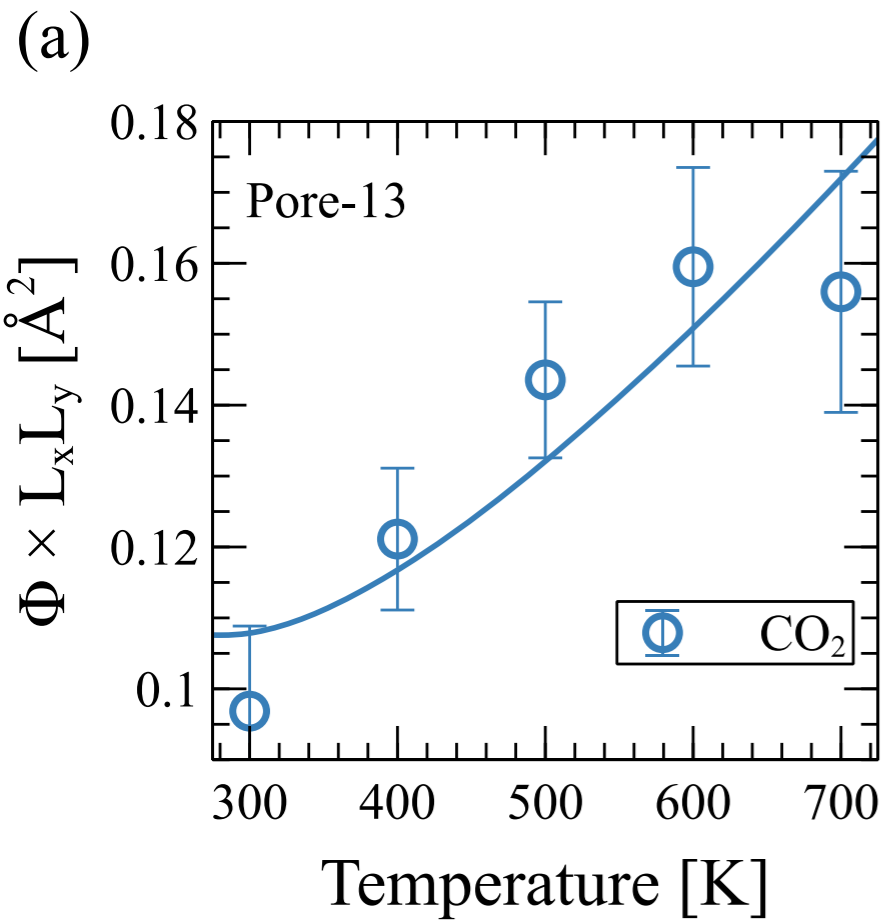
Surface porosity:

$$\phi = \prod_i^{n_a} \int \frac{d\theta_i}{\alpha_i \pi} \int \frac{dxdy}{L_x L_y} e^{-U_{pmf}/kT}$$


$$\phi = \frac{2\pi(2/\pi)^{\frac{n_a}{2}} (kT)^{1+\frac{n_a}{2}}}{L_x L_y \prod_{i=1}^{n_a} \alpha_i f} \exp\left(-\frac{U_0}{kT}\right)$$

Adjustable parameters:  $f = \sqrt{f_x f_y} \prod_{i=1}^{n_a} \sqrt{f_{\theta_i}}$  and  $U_0$

# Permeance Model



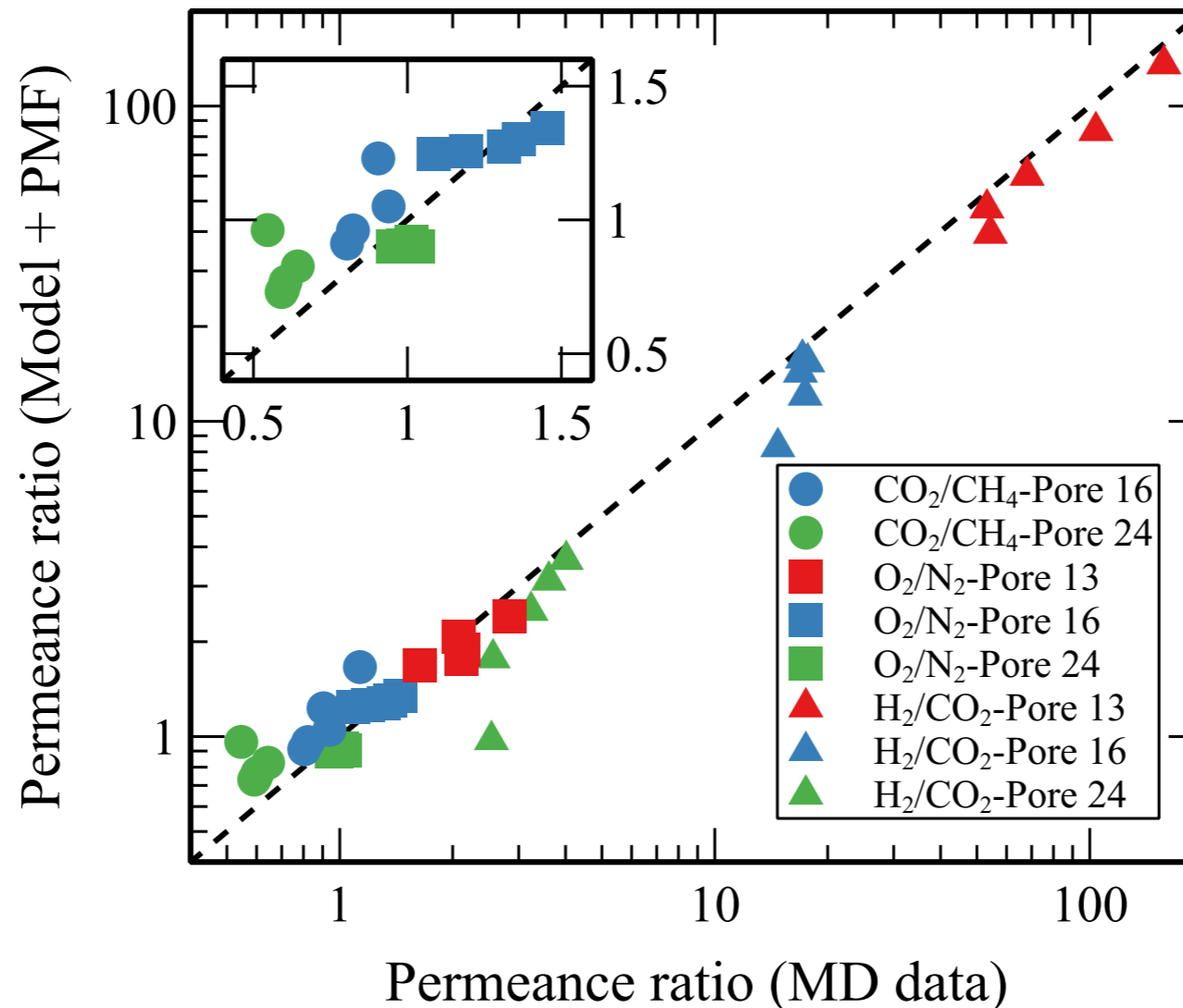
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$$\phi = \frac{2\pi(2/\pi)^{\frac{n_a}{2}}}{L_x L_y \prod_{i=1}^{n_a} \alpha_i} \frac{(kT)^{1+\frac{n_a}{2}}}{f} \exp\left(-\frac{U_0}{kT}\right)$$

Adjustable parameters:  $f = \sqrt{f_x f_y} \prod_{i=1}^{n_a} \sqrt{f_{\theta_i}}$  and  $U_0$

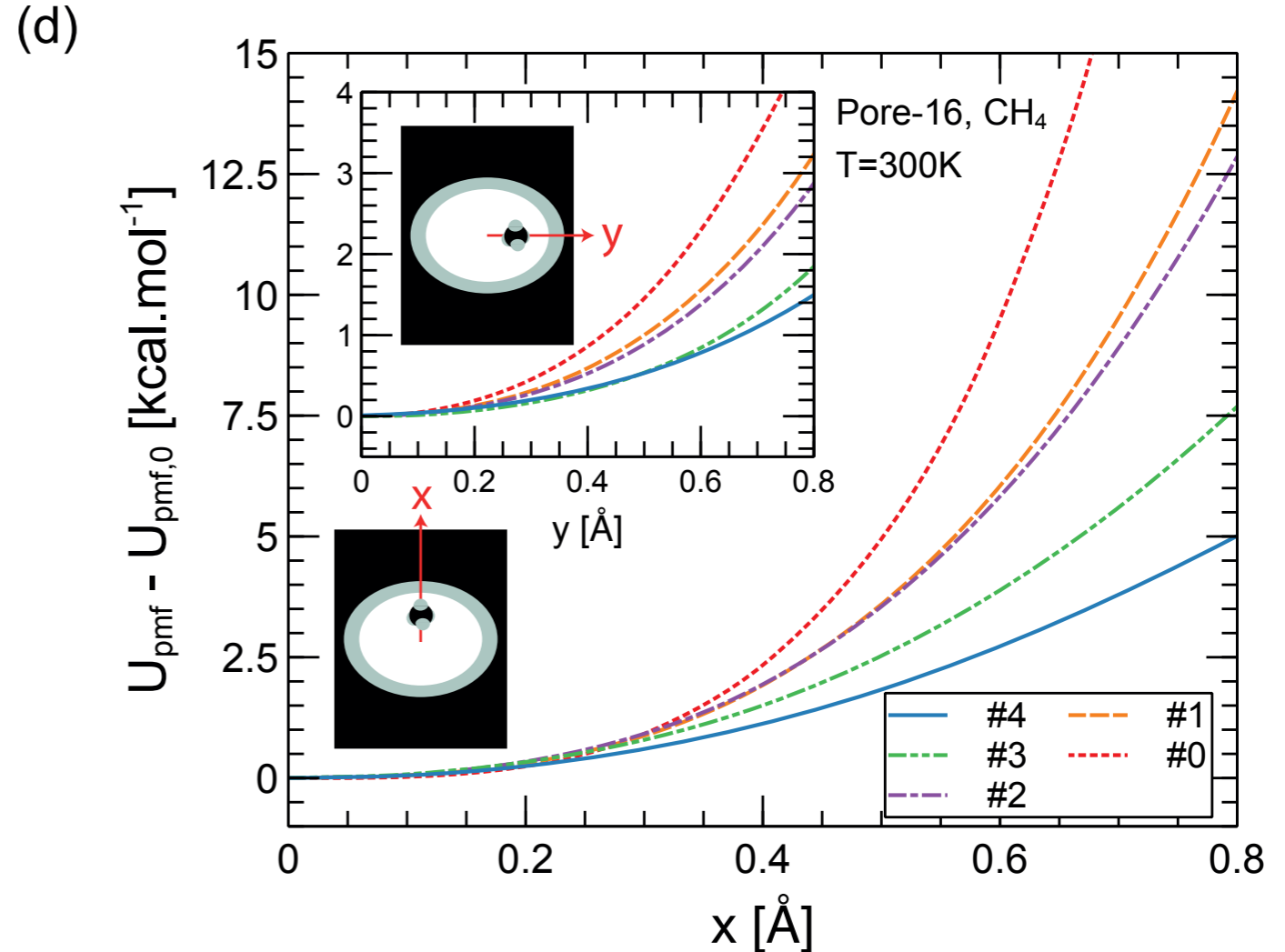
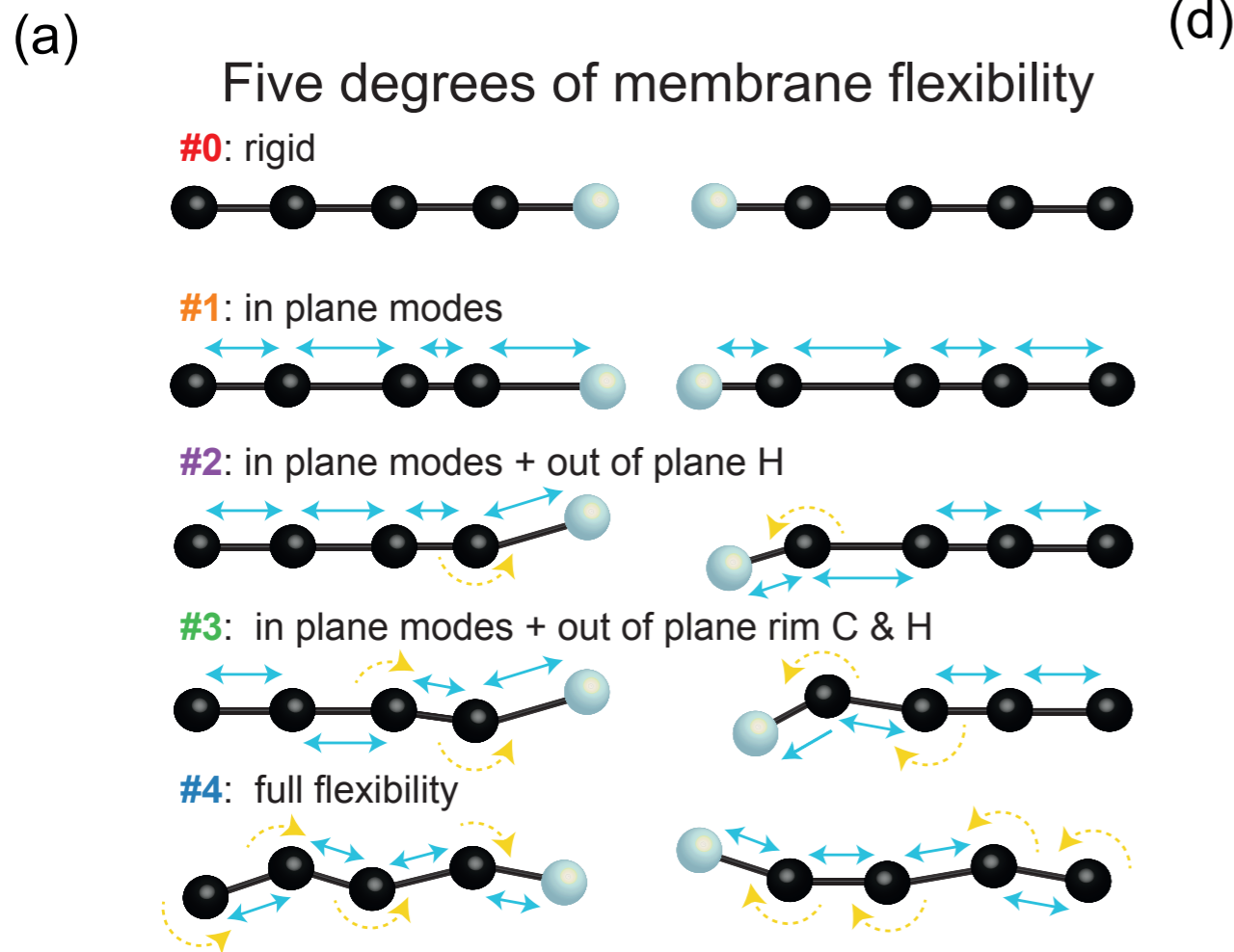
# Selectivity: direct estimation from the PMF

- Binary mixtures: Selectivity  $\propto \Pi_1/\Pi_2$



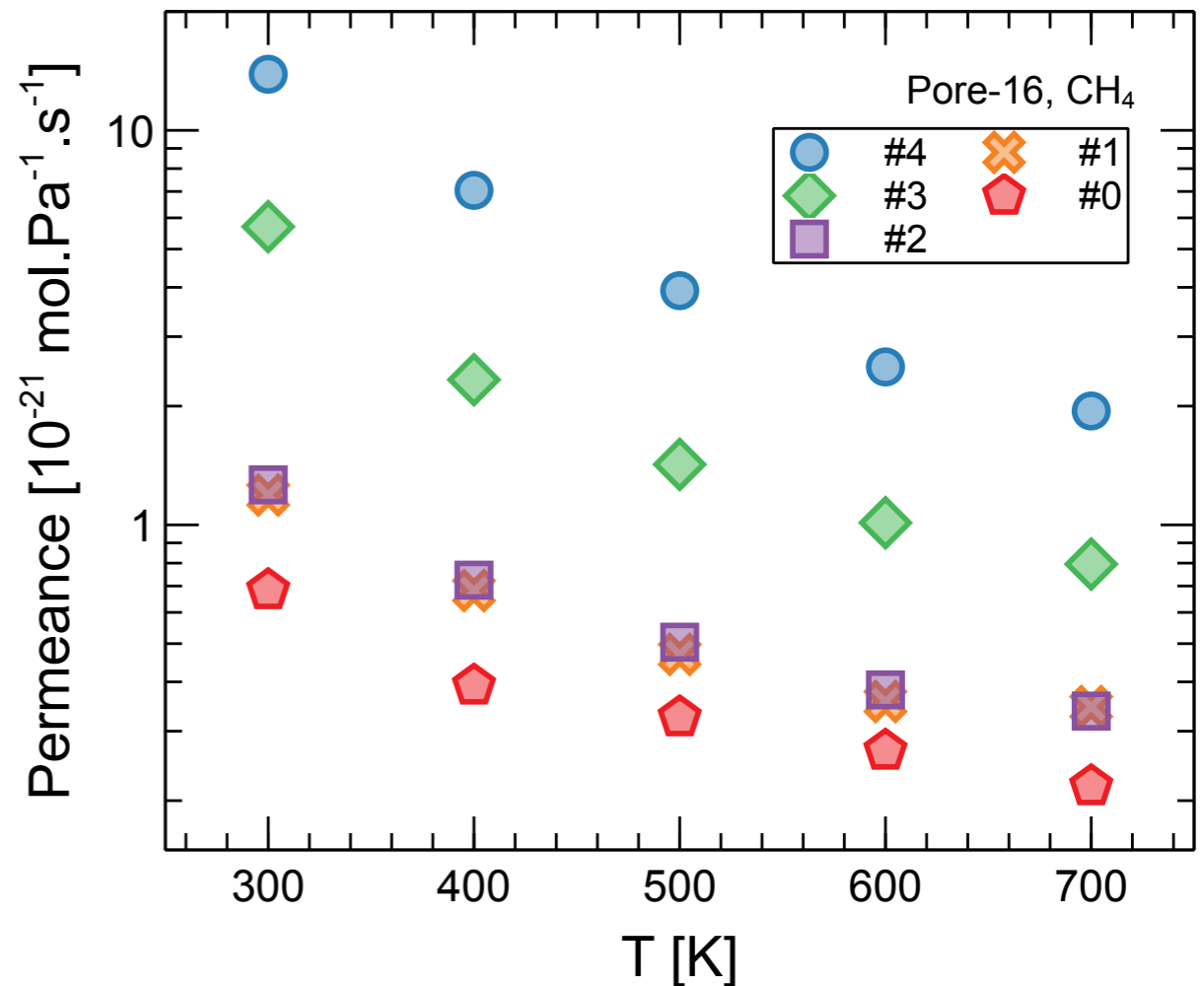
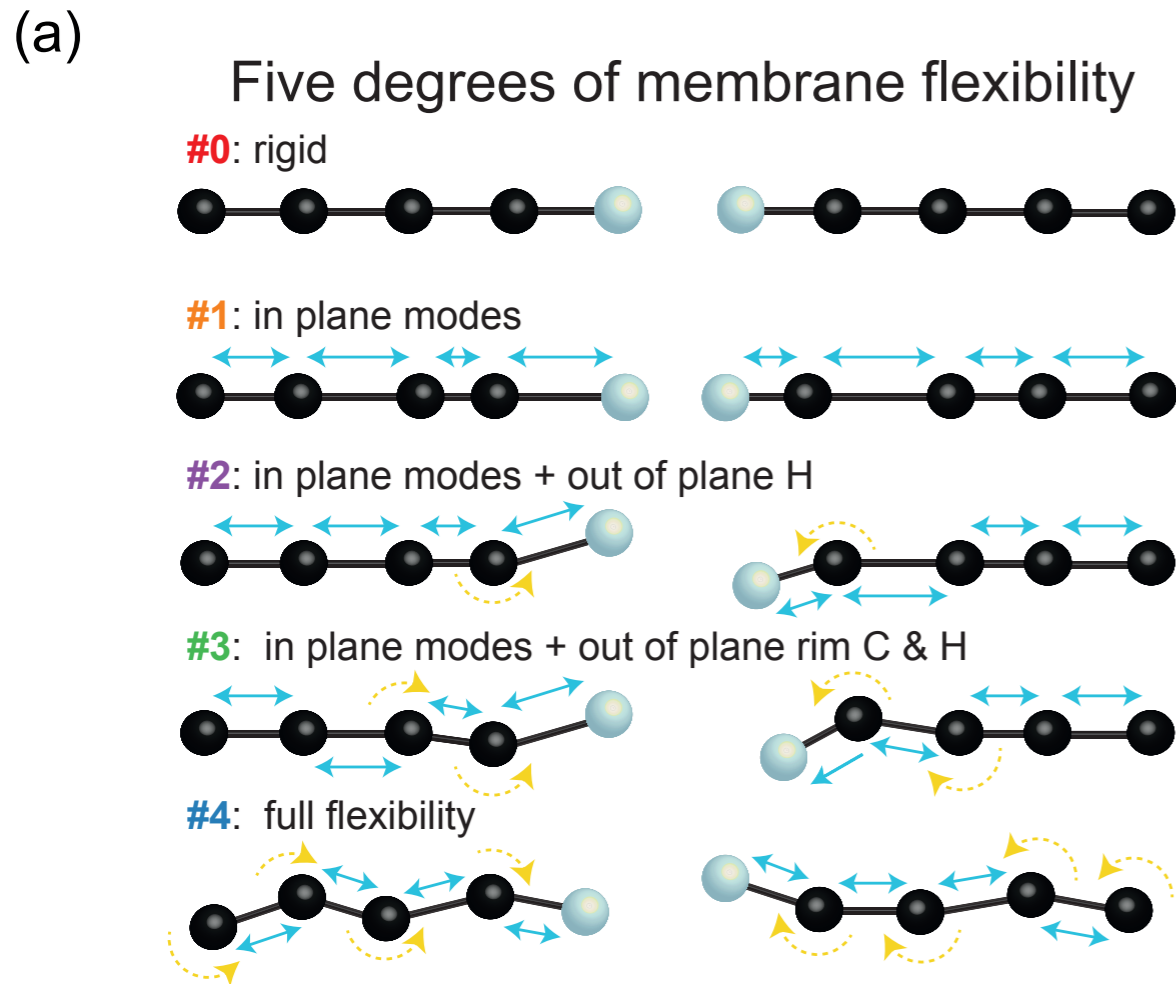
- The selectivities obtained by simulation are compared to those obtained by directly feeding the model with the parameters of the PMF.
- Selectivity deduced directly from the PMF. Valuable for the design of efficient membranes (chemical functions, pore sizes, etc.).

# Introducing flexibility step by step



- Progressive Softening of the PMF with increasing flexibility, **in agreement with the permeance model.**
- In the case of H-terminated pores, releasing the out of plane motion of H atoms does not affect the PMF significantly.

# Introducing flexibility step by step



- Progressive Softening of the PMF with increasing flexibility, **in agreement with the permeance model.**
- In the case of H-terminated pores, releasing the out of plane motion of H atoms does not affect the PMF significantly.
- **Permeance values are in line with the above observations.**