日本機械学会
熱工学コンファレンス2022

東京大学
THE UNIVERSITY OF TOKYO

Daiguji & Hsu Lab
Thermal Engineering
MECH
mechanical engineering

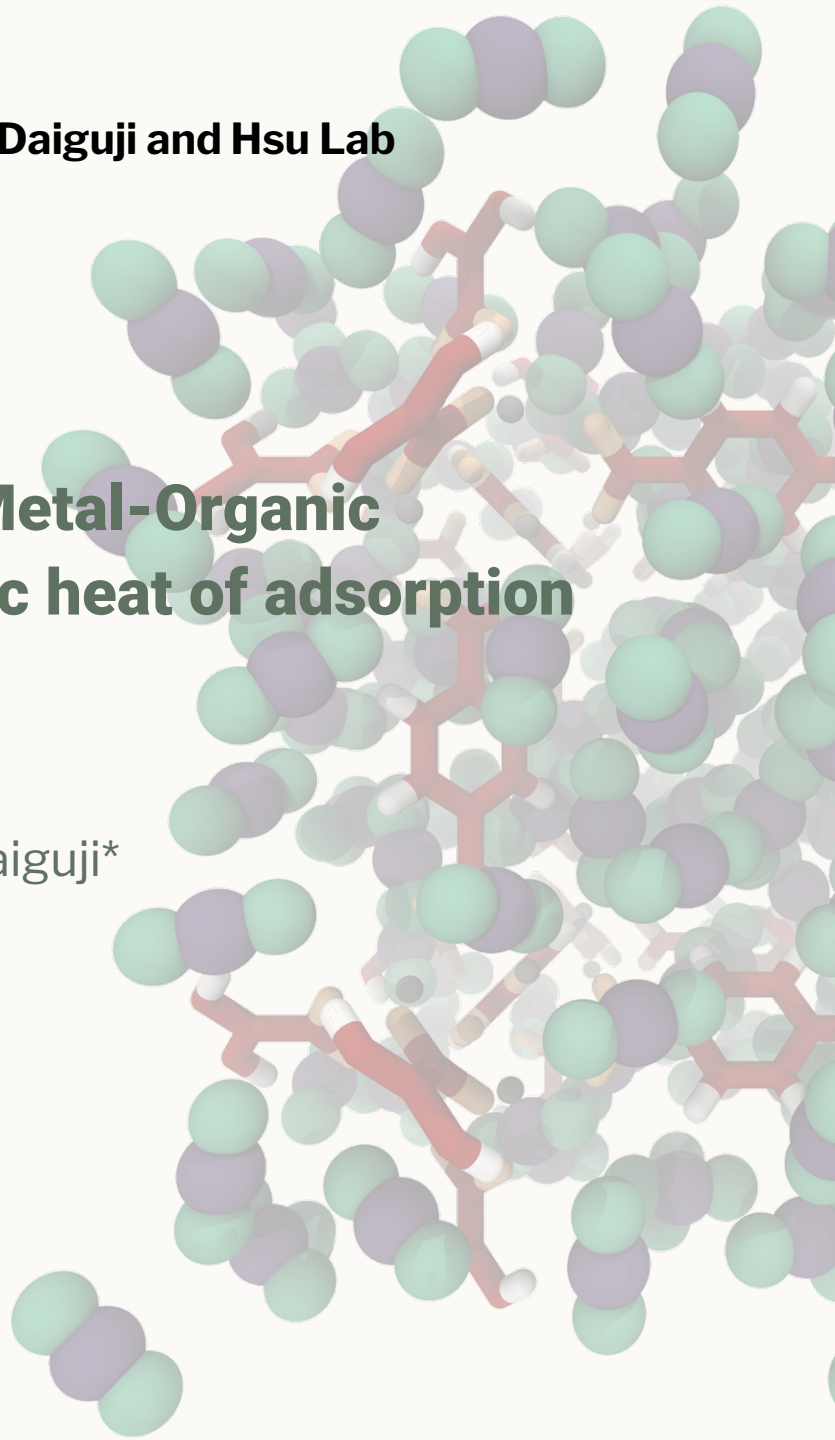
Daiguji and Hsu Lab

Study on Carbon Dioxide Adsorption Properties of Metal-Organic Frameworks (MOFs) : Relationship between isosteric heat of adsorption and MOF structure

Gunjan Auti, Shubo Fei, Hibiki Kimura, Wei-Lun Hsu, and Hirofumi Daiguji*

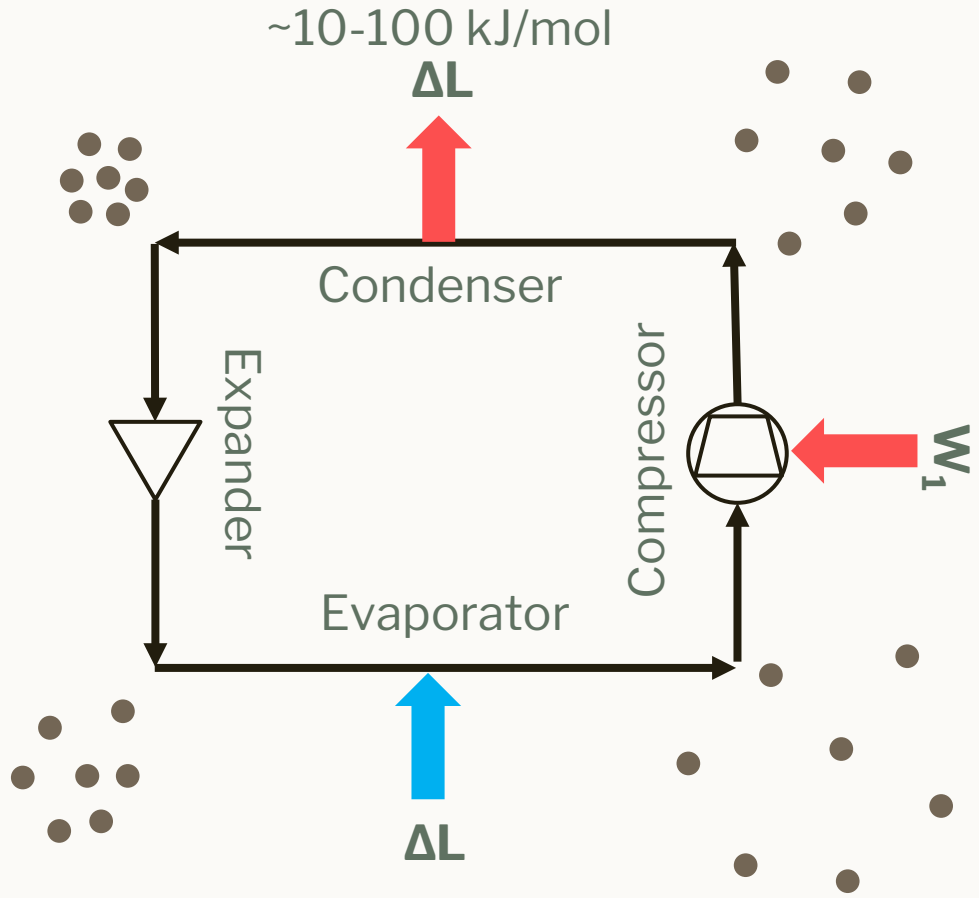
OS14 ナノスケール熱制御 (3)
8th October 2022
14:15~15:30

*daiguji@thml.t.u-tokyo.ac.jp

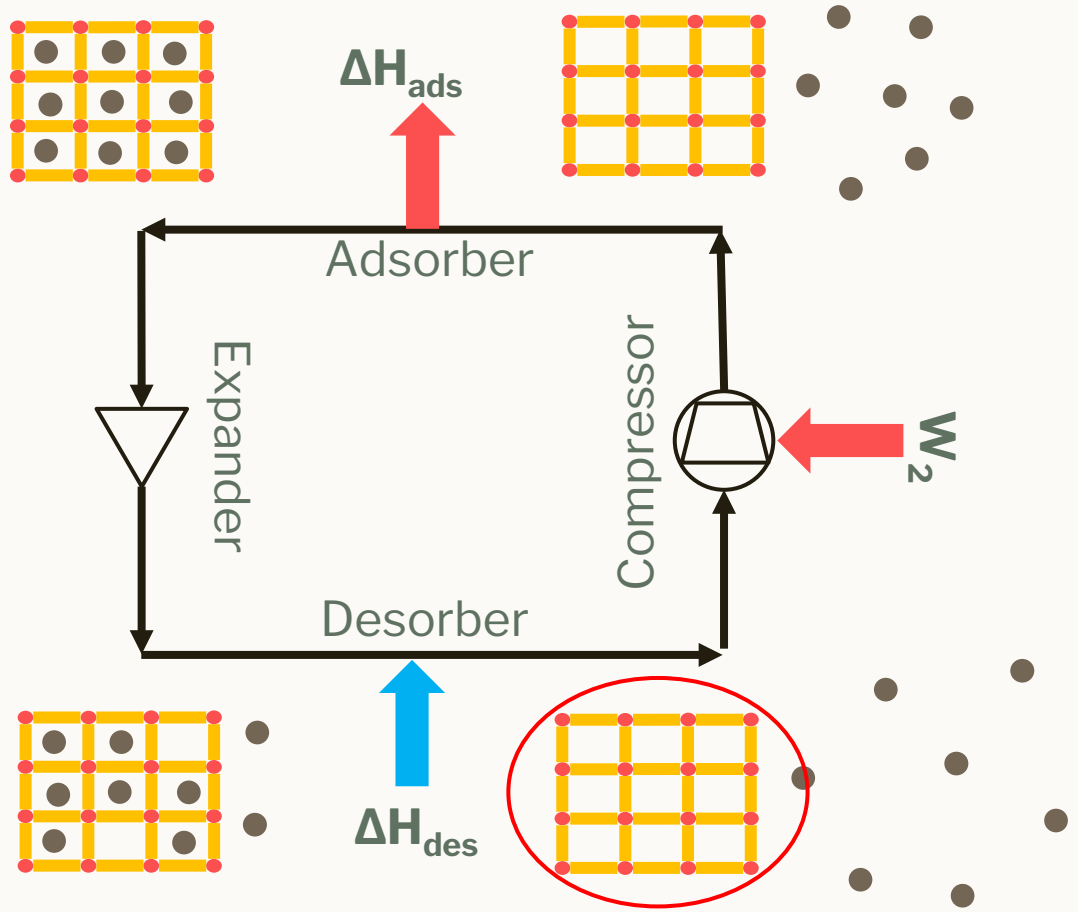


Adsorption Compression Heat Pump Cycle

Vapor compression Heat Pump



Proposed system



In the proposed system, due to capillary condensation, enthalpy of phase change as well as enthalpy of adsorption is released. Moreover, the maximum pressure in the proposed system will be lower than VCHP. This creates a twofold effect on the COP of the system.

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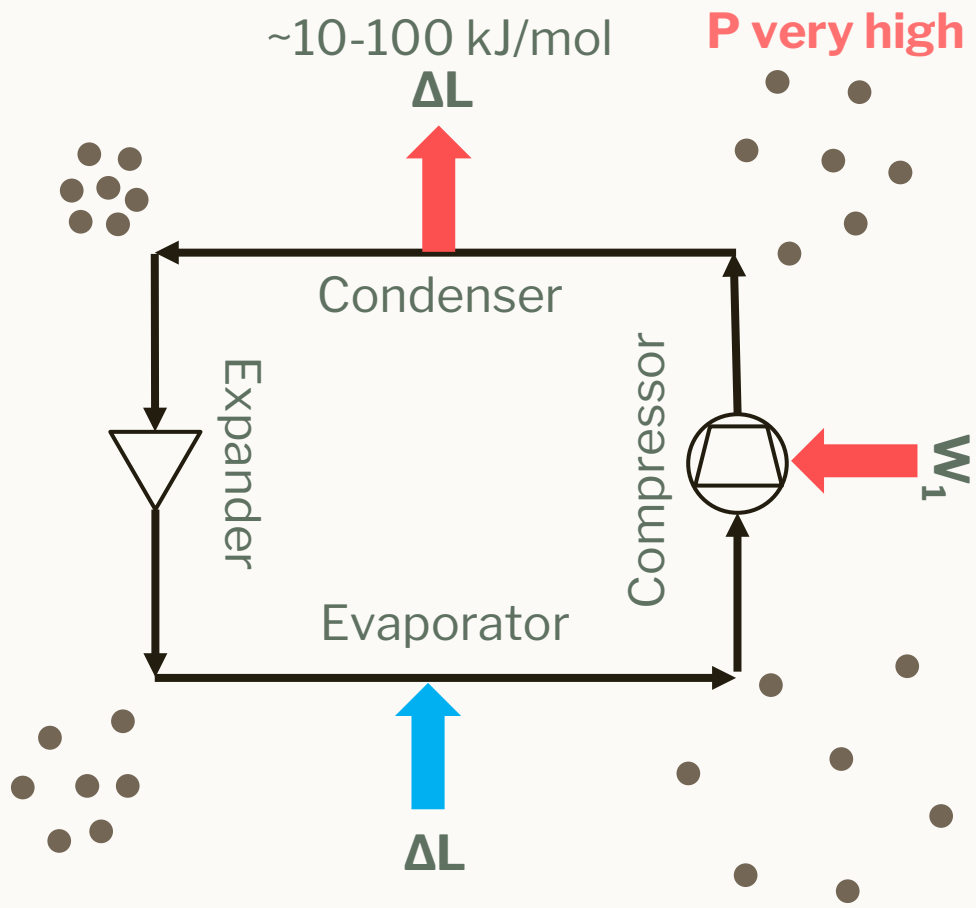

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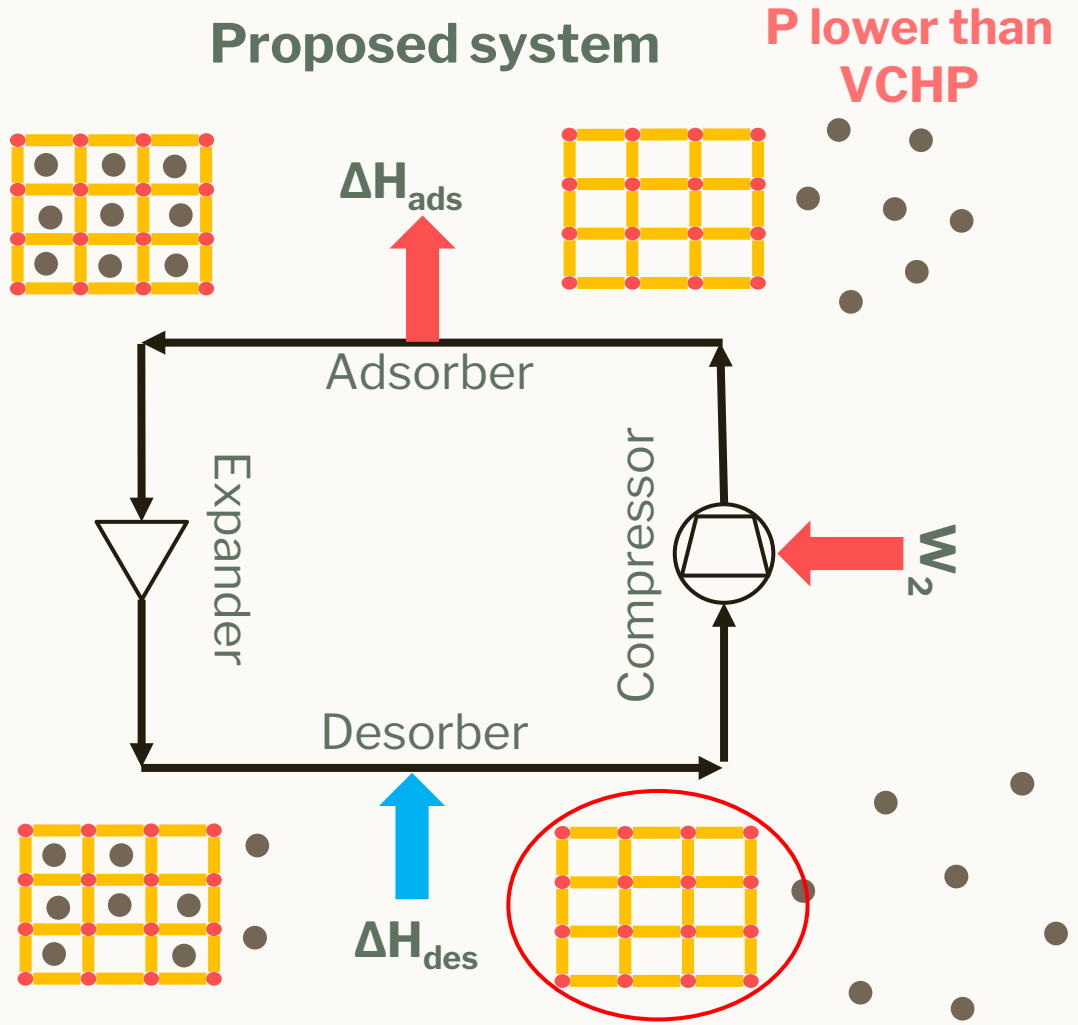

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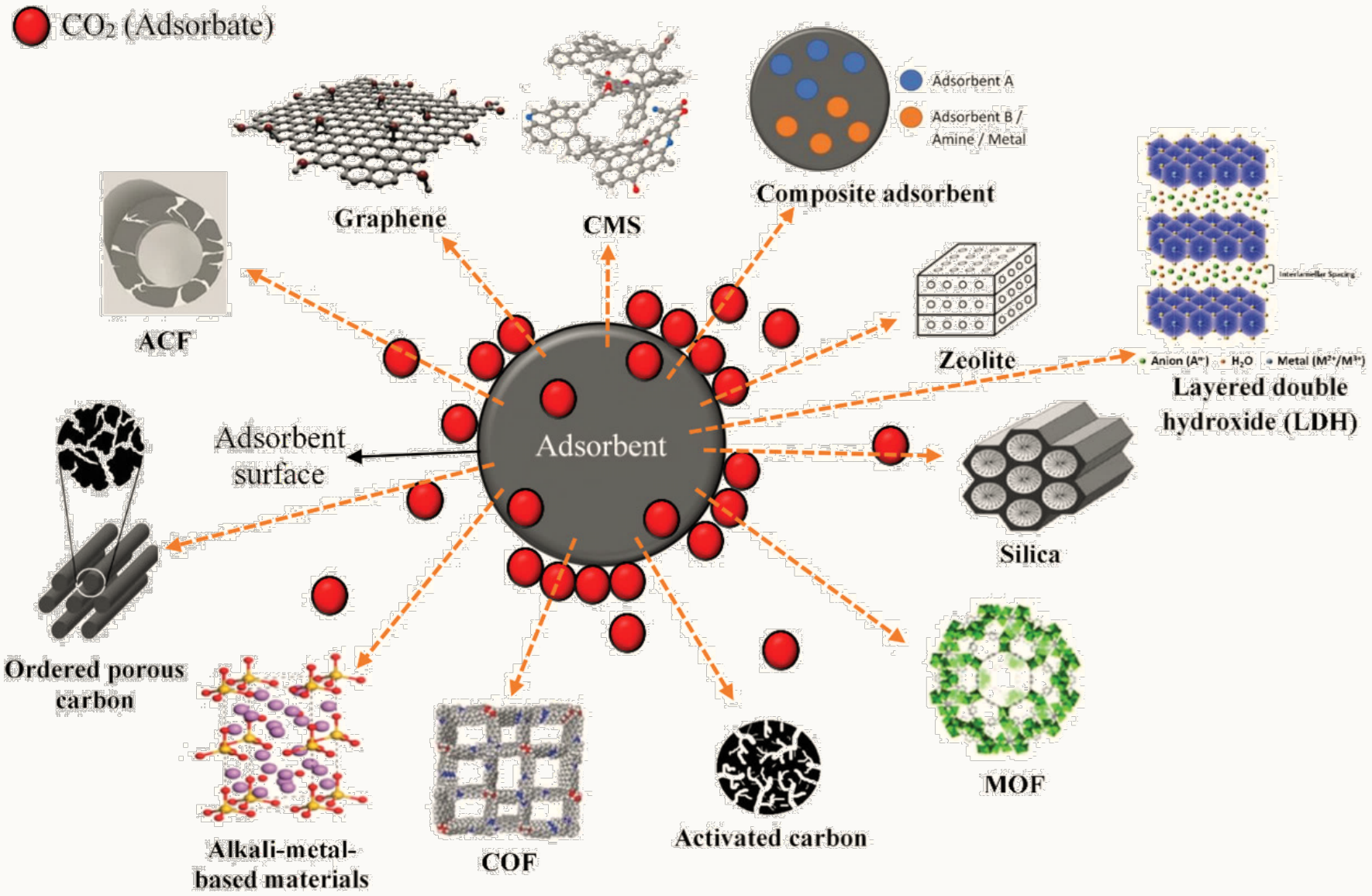
Adsorbents for CO_2 adsorption



Different types of adsorbents available for adsorption of CO_2
(Ref: Lai, J.Y., Ngu, L.H. and Hashim, S.S., Greenhouse Gas Sci. Technol., 11: 1076-1117, **2021**)

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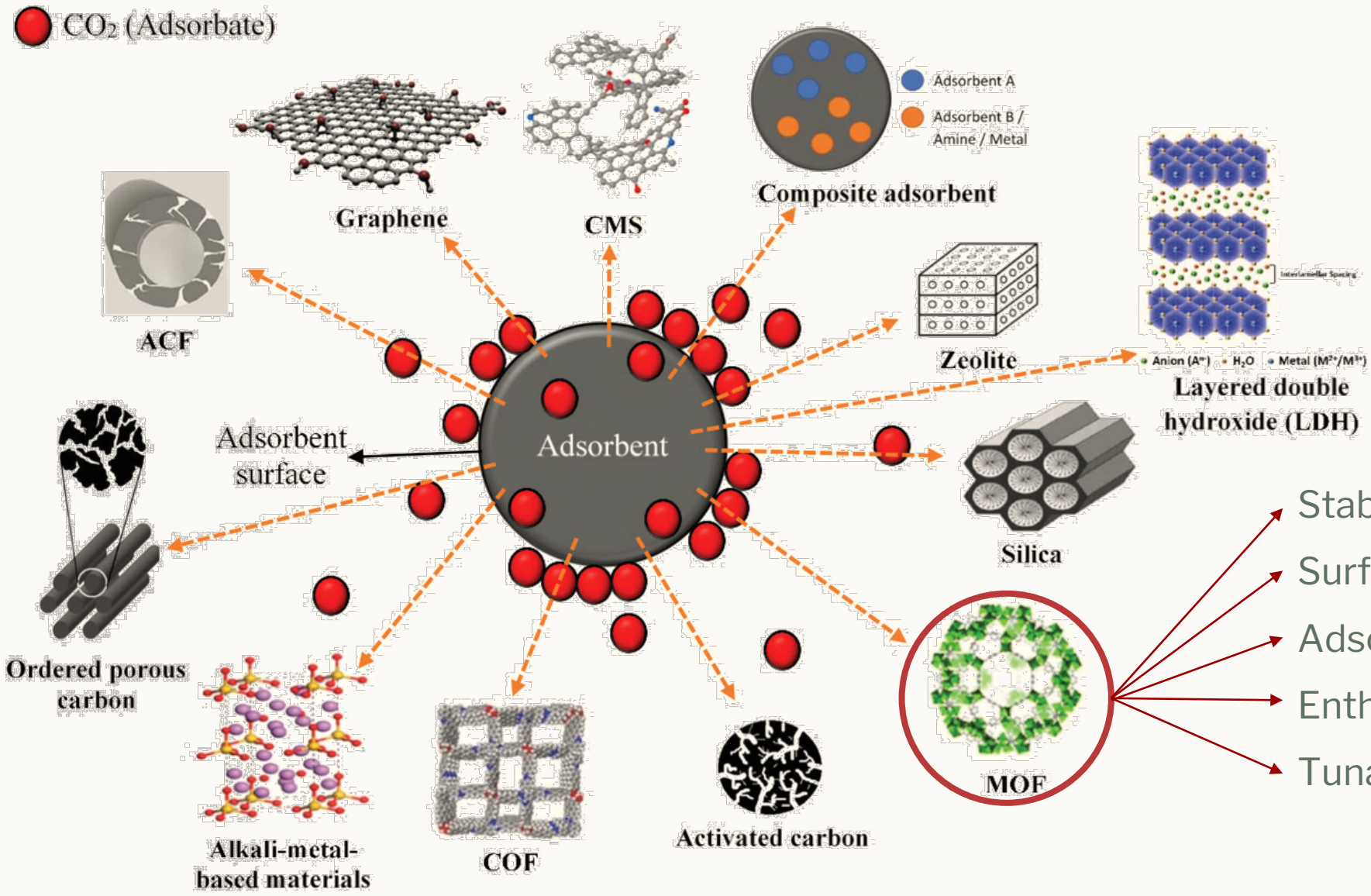

- Stability of the structure
- Surface areas
- Adsorption capacity
- Enthalpy of adsorption
- Tunability

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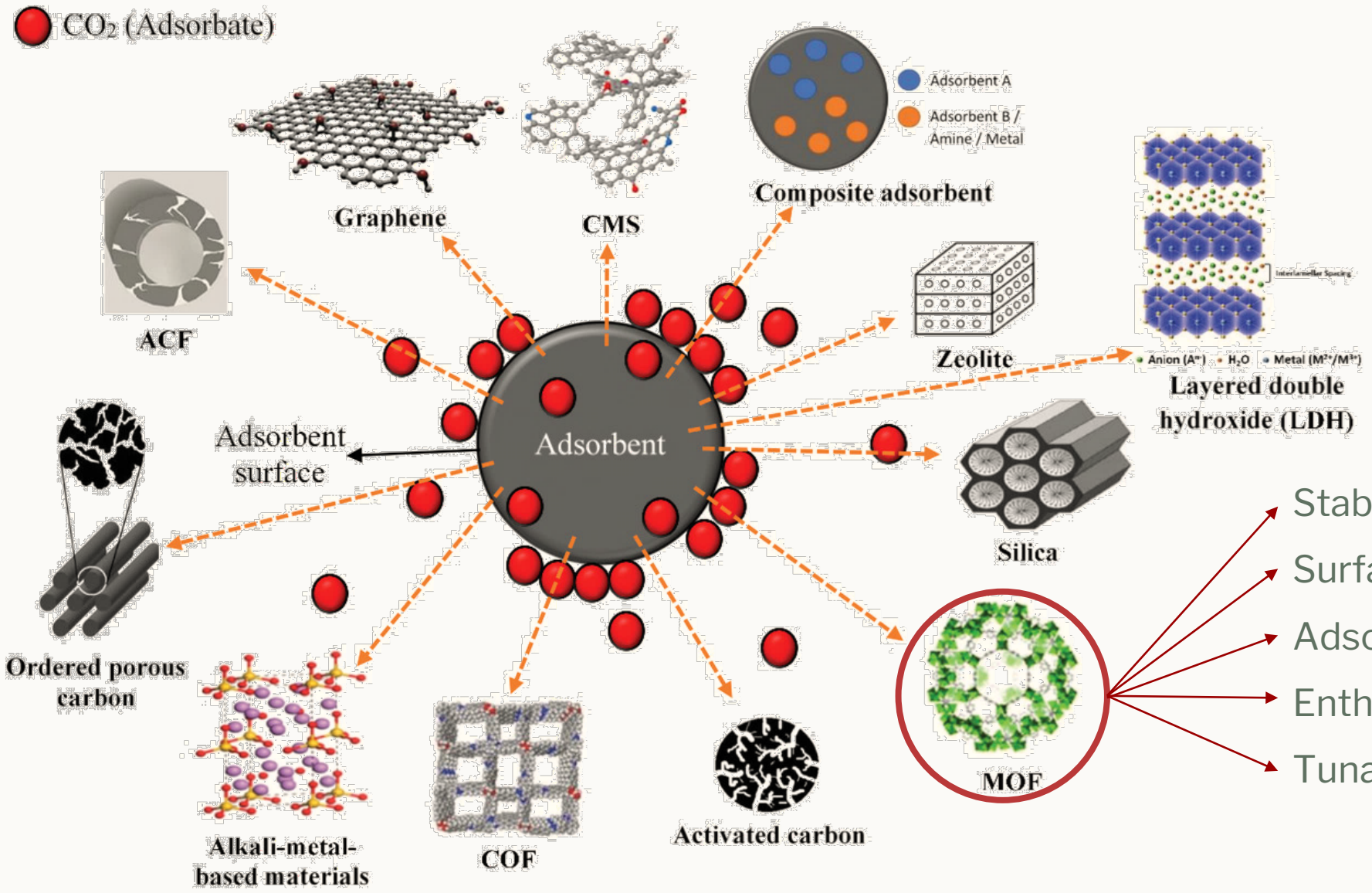

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MIL-101
MOF-177
UiO-66

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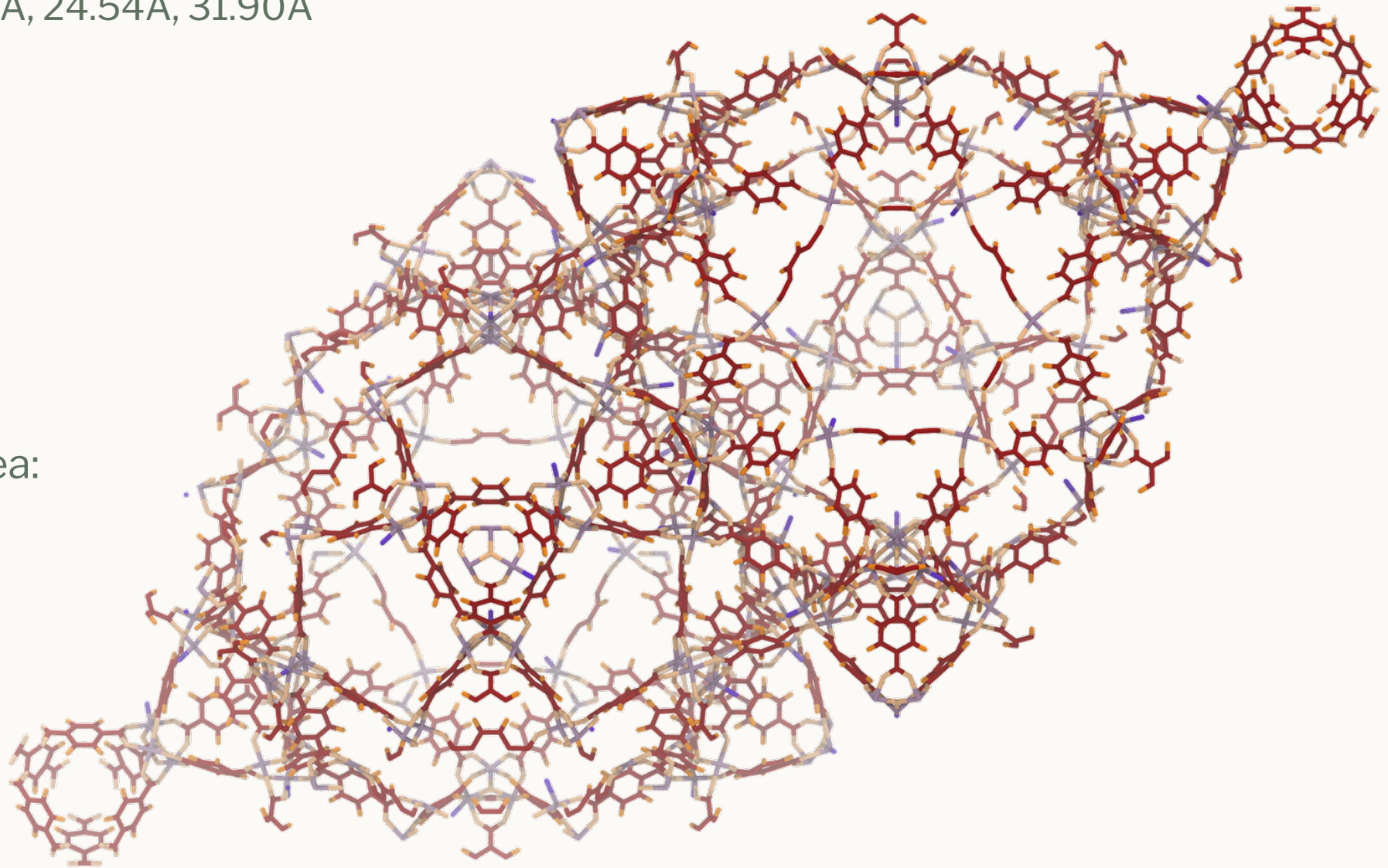
- Using the interaction energies and the radial distribution functions we explain the enthalpy of adsorption trends.
- In the end, we propose an optimum pore size of MOF for heat pump application.

MIL-101

Pore Sizes: 10.02Å, 24.54Å, 31.90Å

BET surface area:
5900m^2/g



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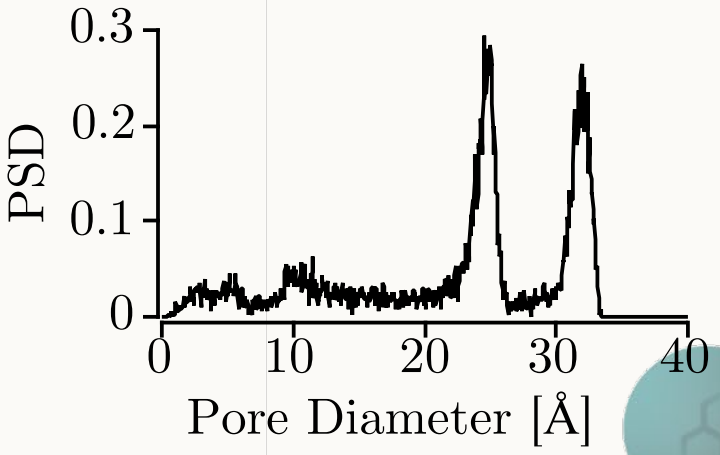

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MOF-177

BET surface area:
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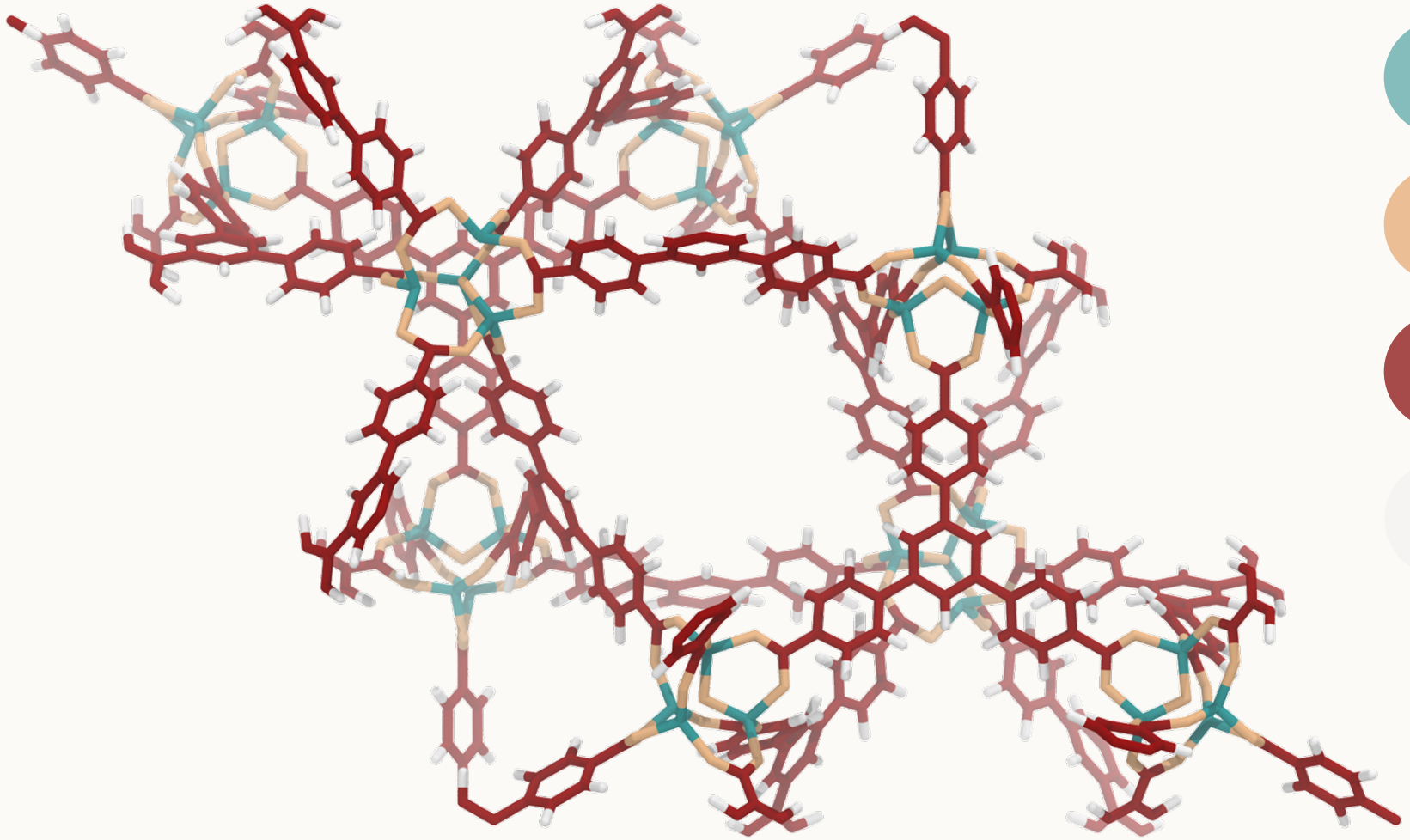
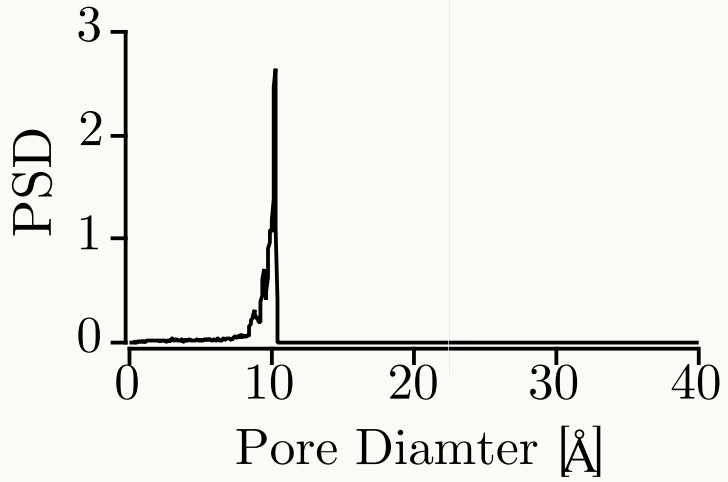
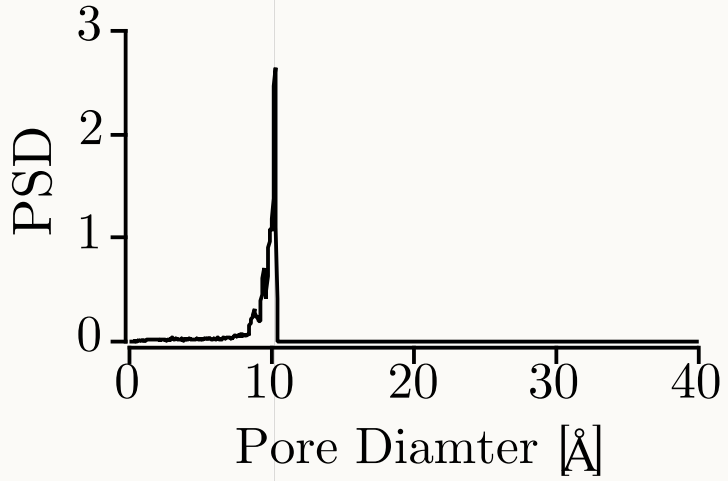




MOF-177

Pore Size: 10.22Å

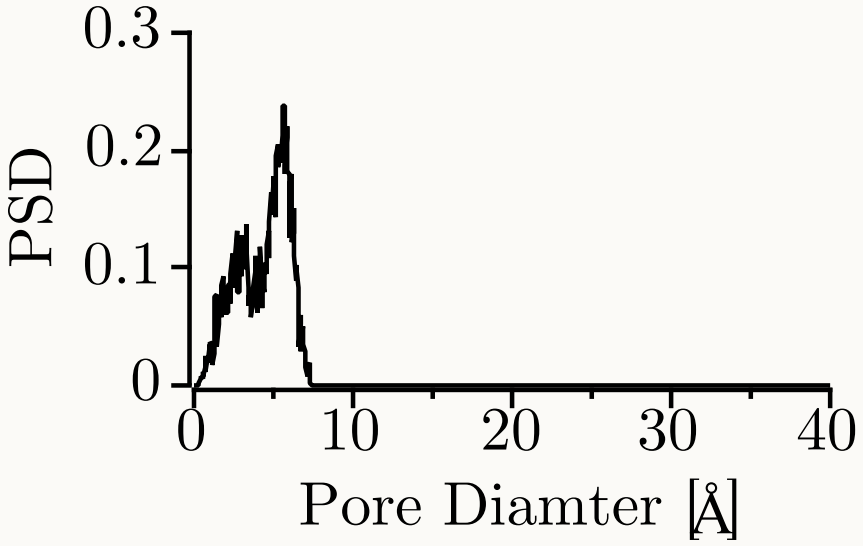
BET surface area:
4500 m^2/g



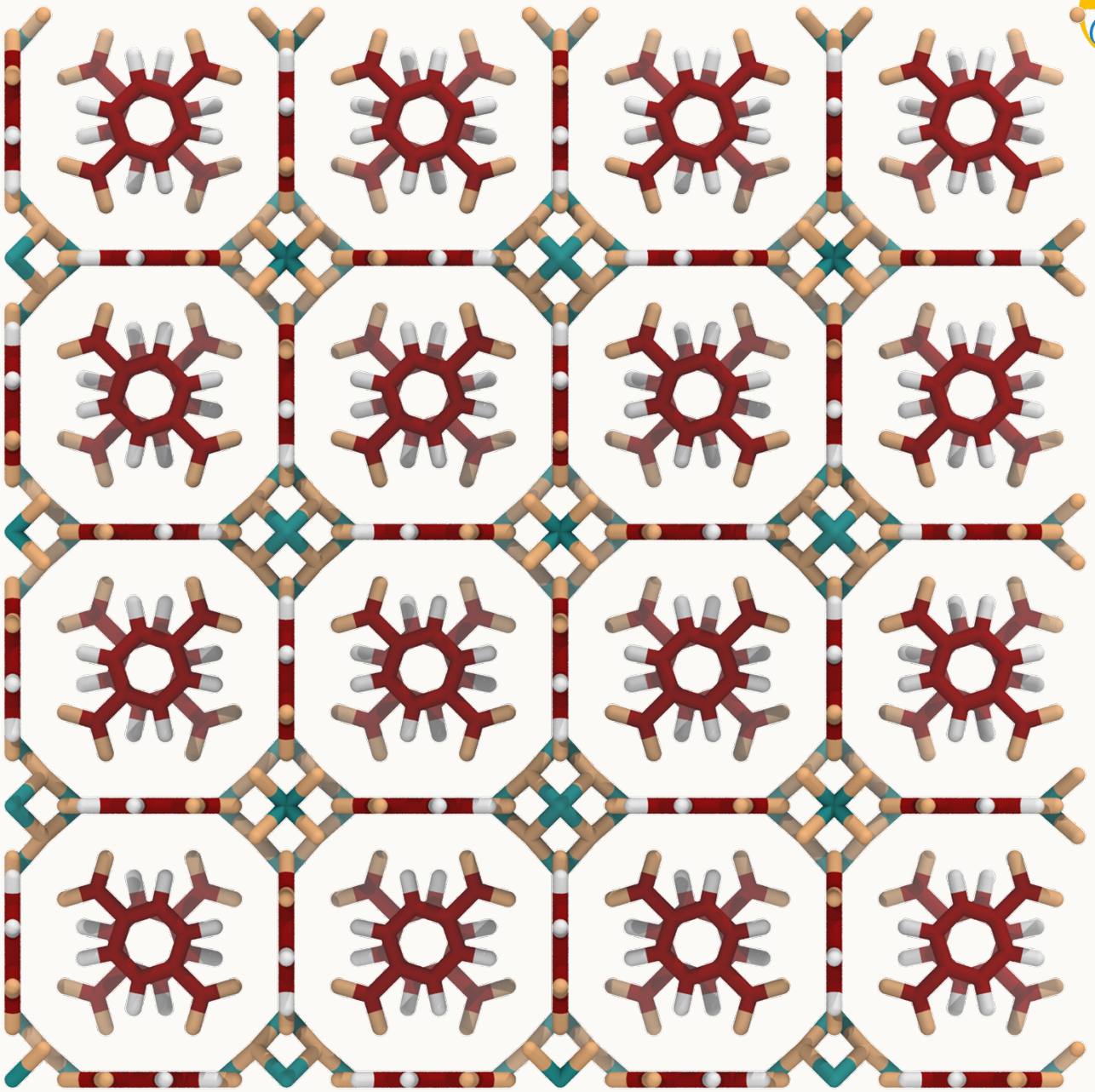
UiO-66

Pore Size: 5.45Å

BET surface area:
1390 m^2/g



Zr O C H



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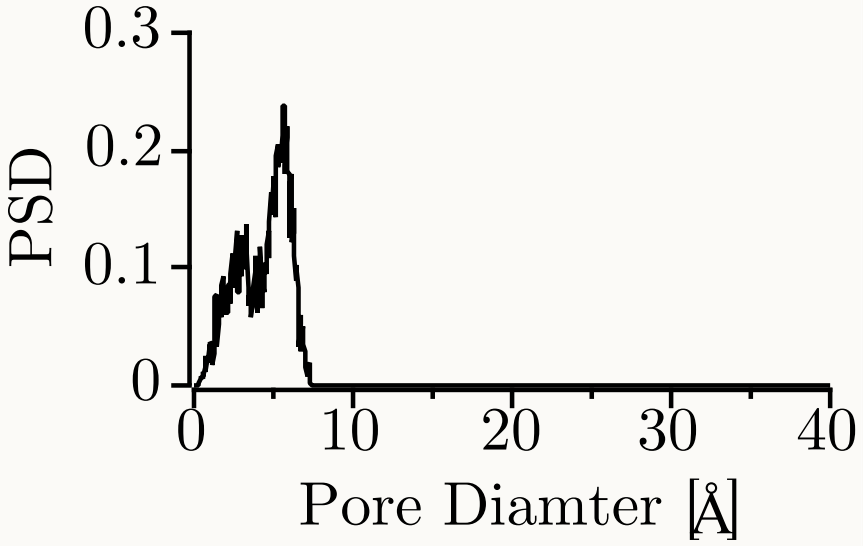

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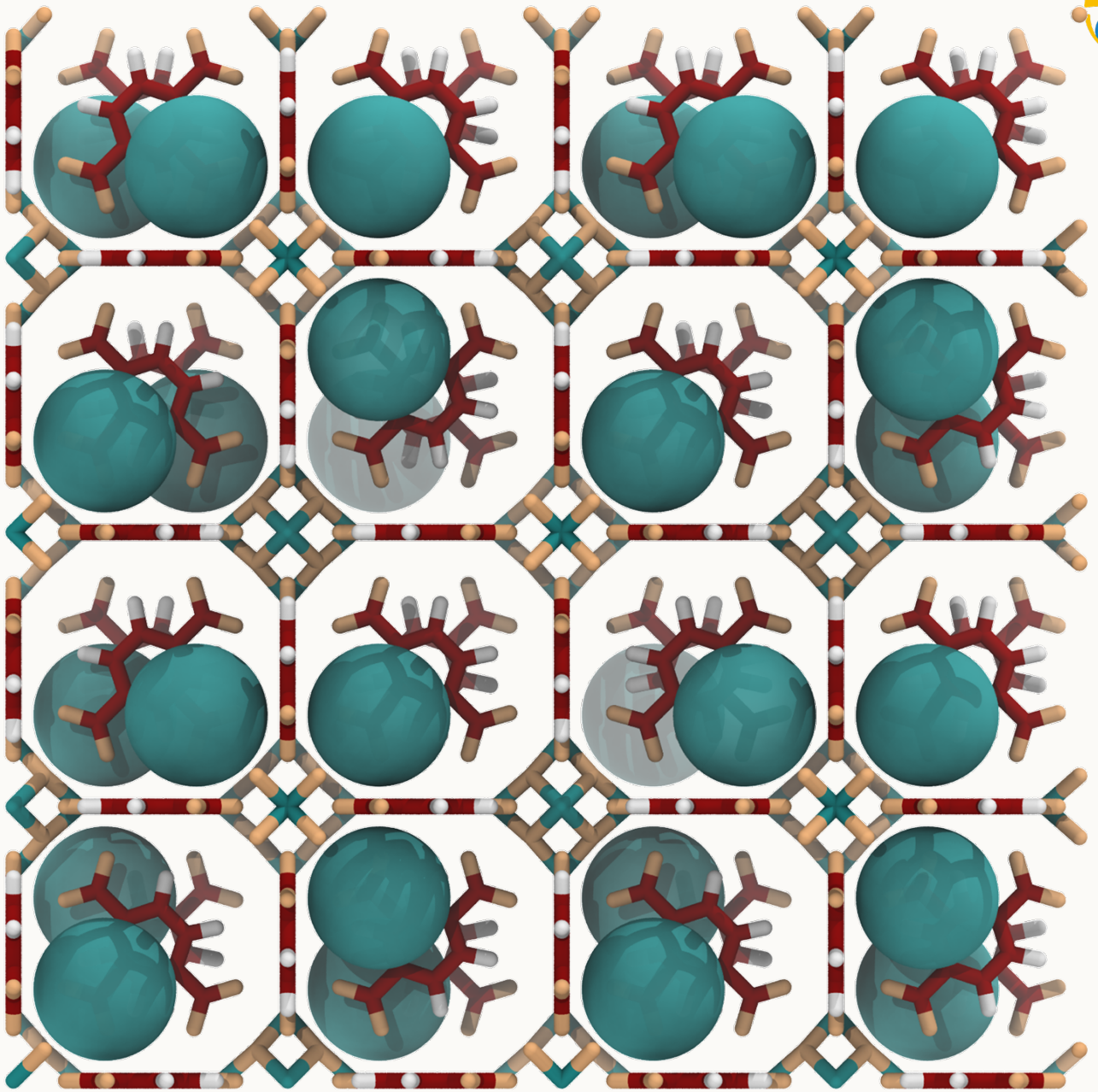
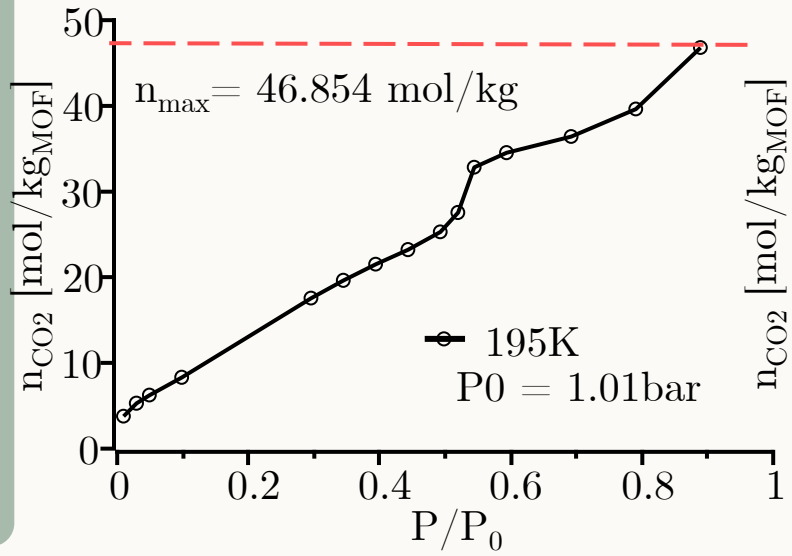


Adsorption Isotherm

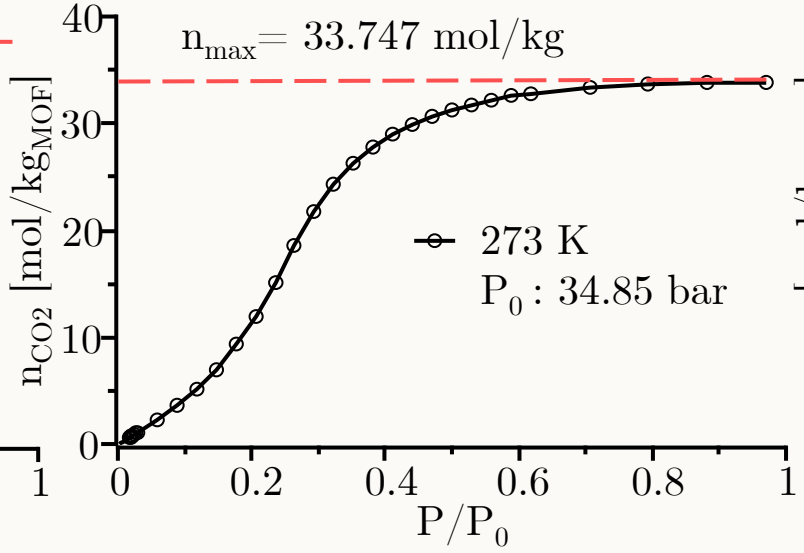
MIL-101

Pore Diameter: 31.90 Å



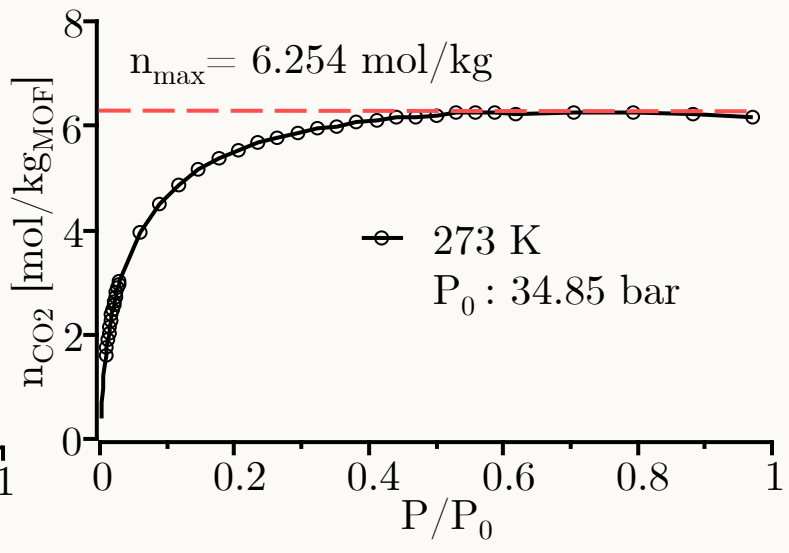
MOF-177

Pore Diameter: 10.22 Å



UiO-66

Pore Diameter: 5.54 Å



We can observe a trend, for MOFs with bigger pore diameter, amount of CO_2 adsorbed is more than for MOFs with smaller pores.

Adsorption Isotherm

CAPACITY

MIL-101 > **MOF-177** > **UiO-66**

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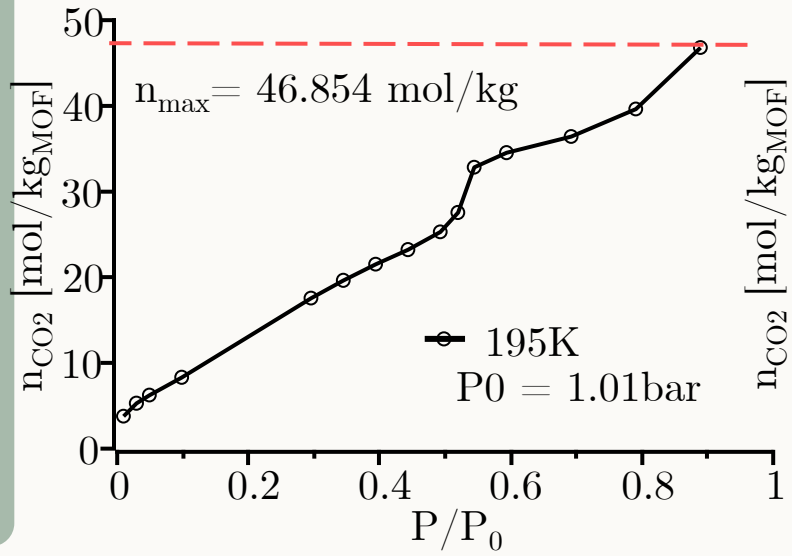

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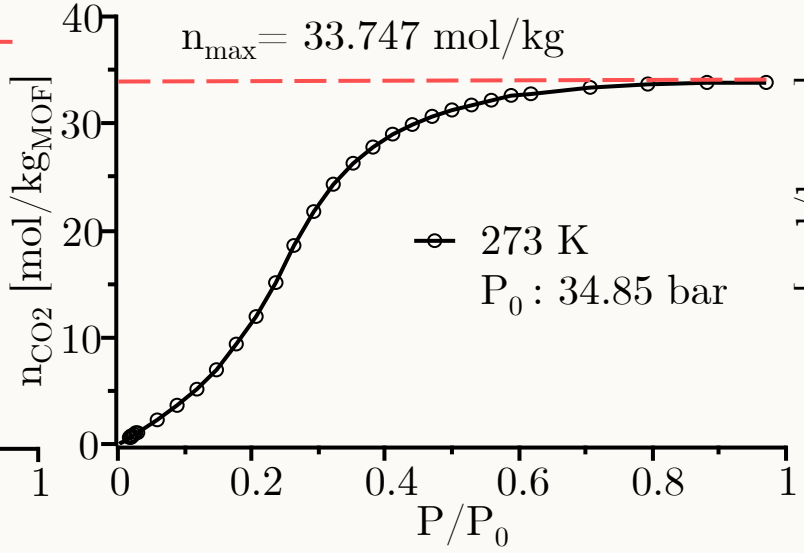

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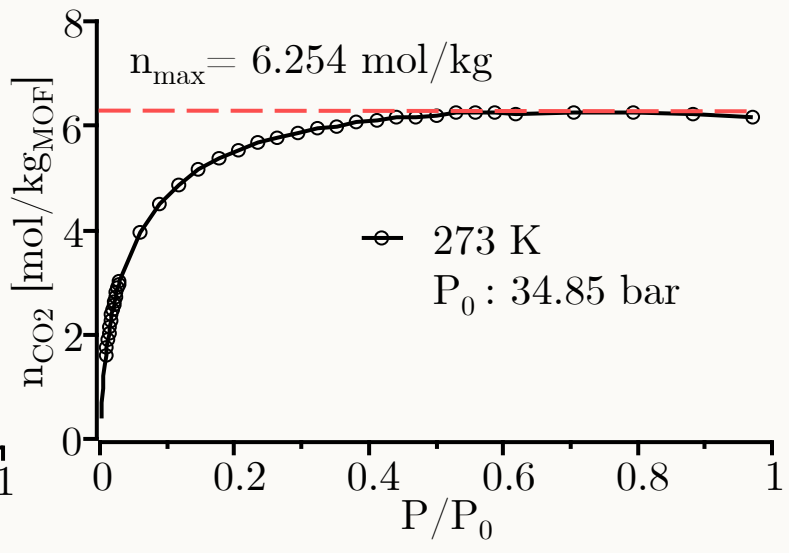

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Enthalpy of adsorption

MIL-101

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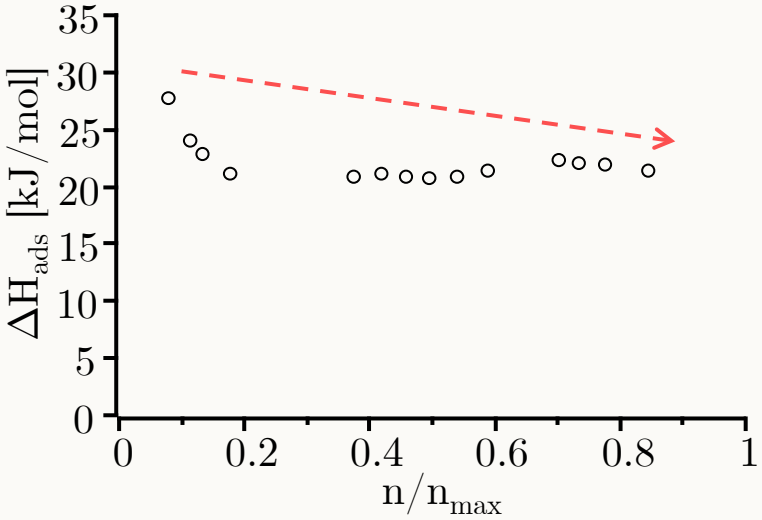

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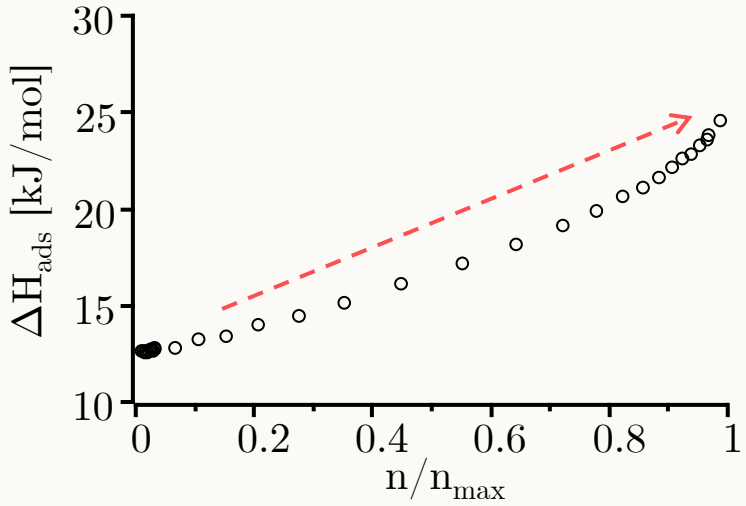

UiO-66

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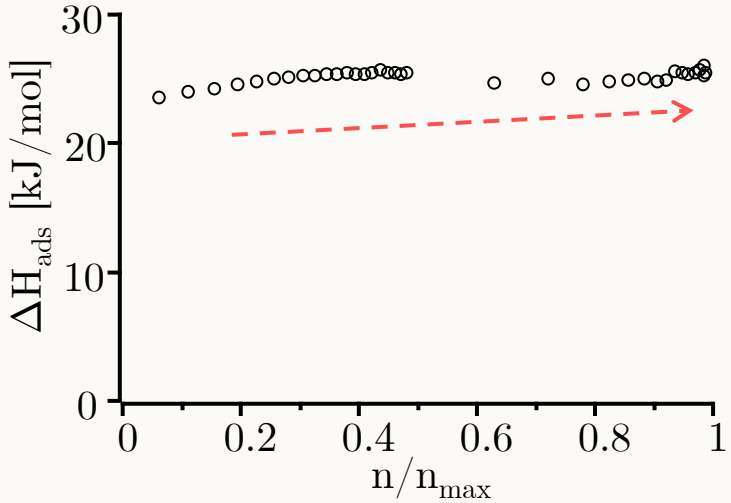

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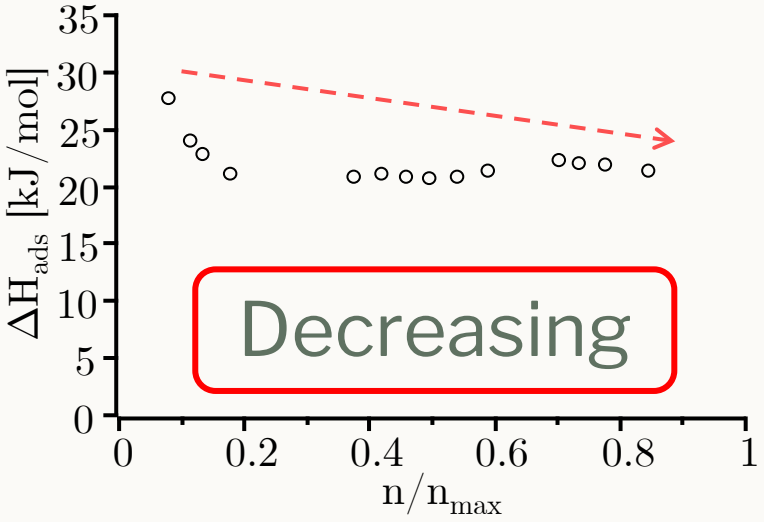

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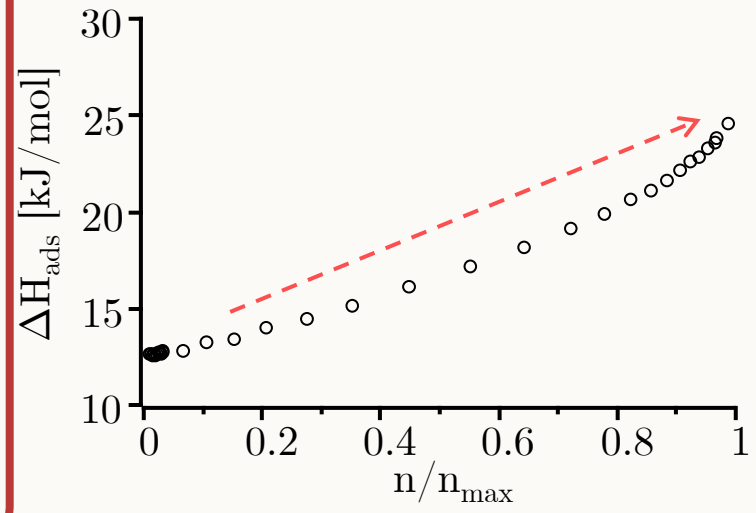

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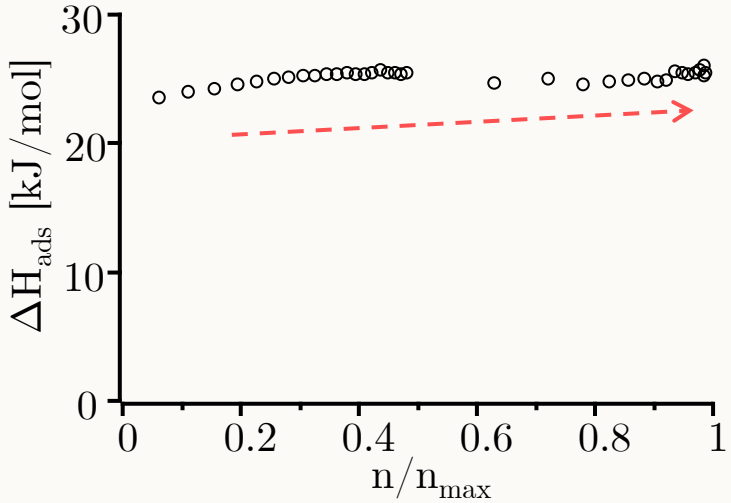

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Enthalpy of adsorption

Increasing

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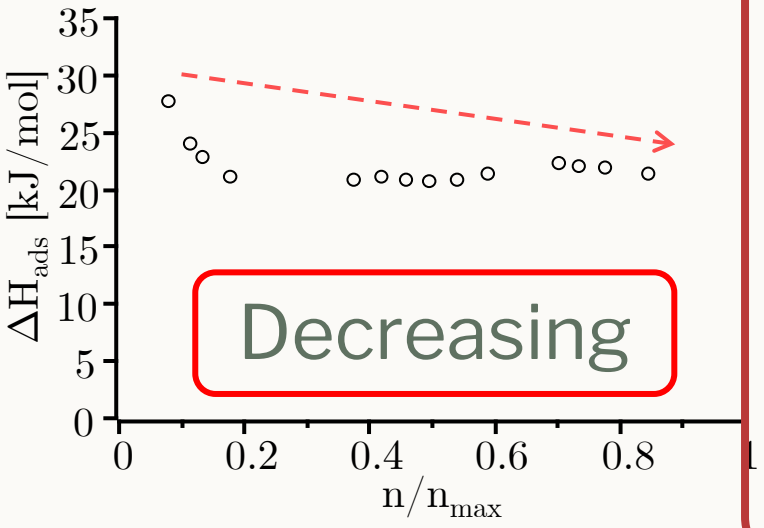
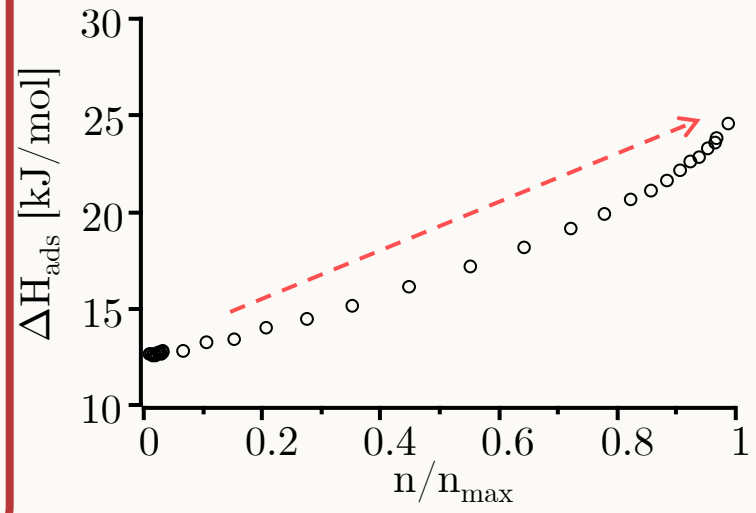


Decreasing

MOF-177

Pore Diameter: 10.22 Å



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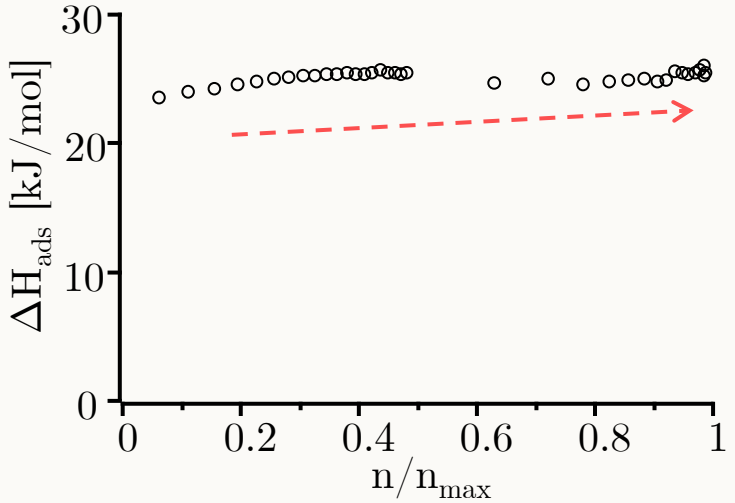

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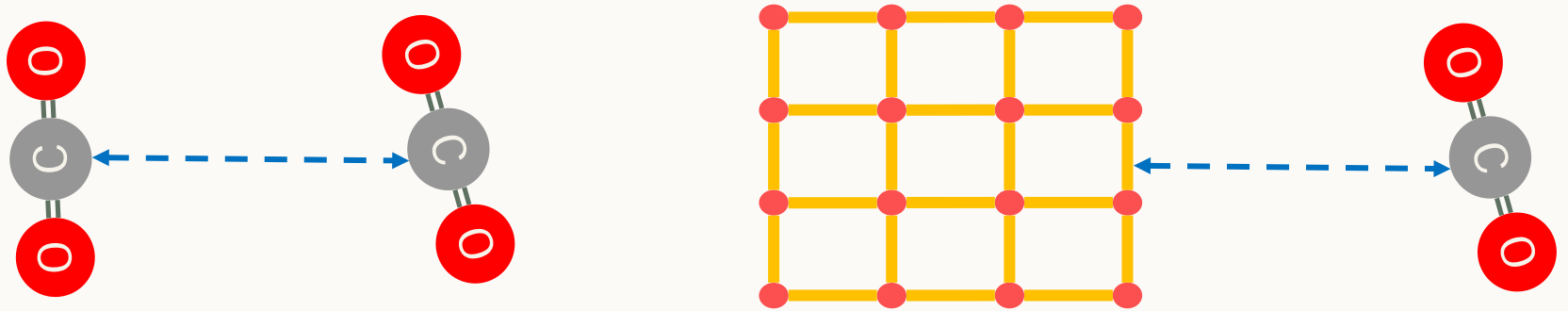
Interaction Energies



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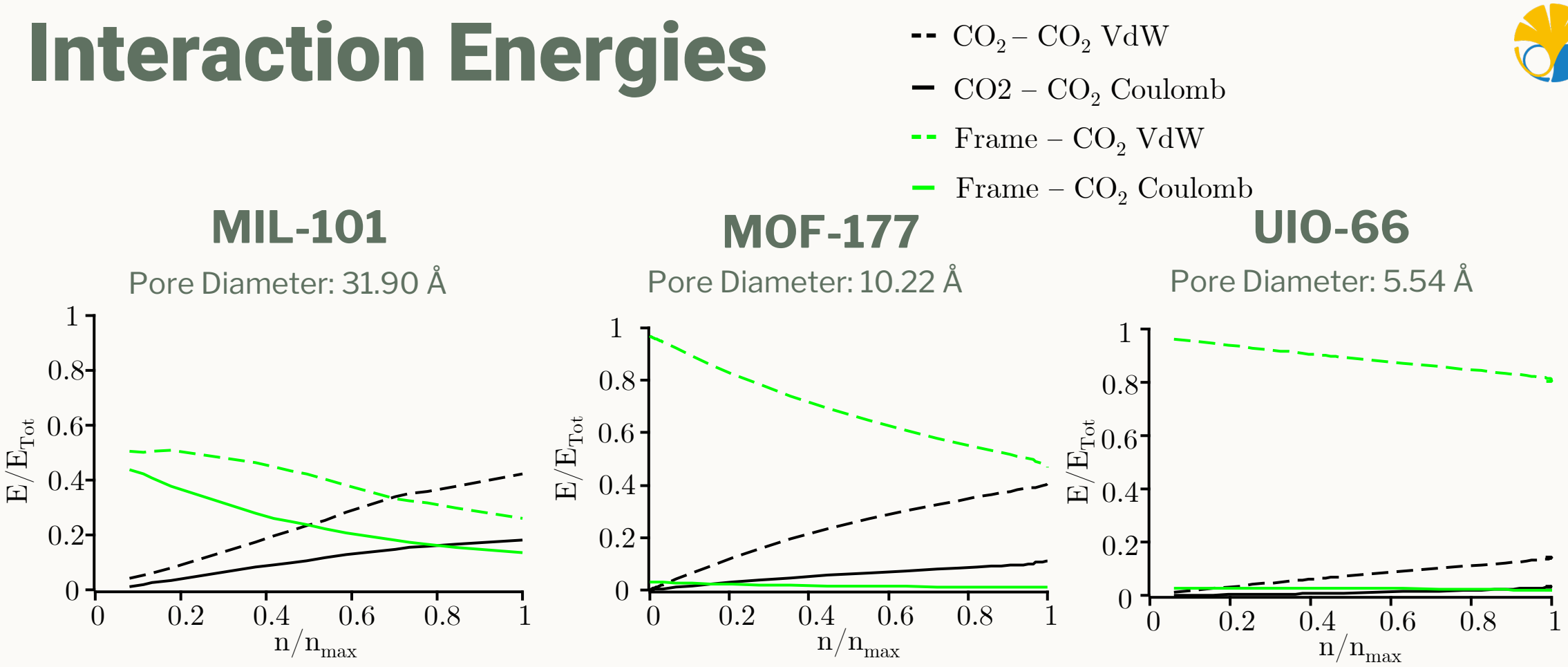
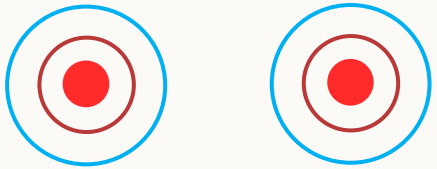


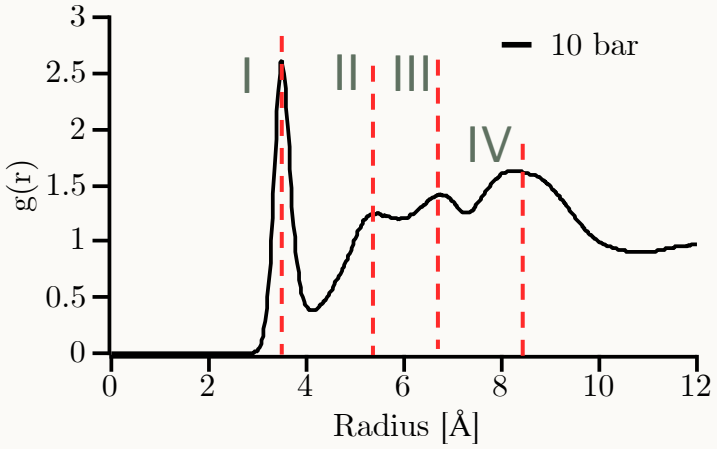
The interaction energies obtained from GCMC, may explain the trend observed in the earlier slide. Contribution of framework - adsorbent VdW interaction is much higher in case of smaller pore (UiO-66) which, in case of larger pore (MIL-101).

Adsorption sites

$$U_{VdW} = \frac{C_1}{r^6} - \frac{C_2}{r^{12}}$$

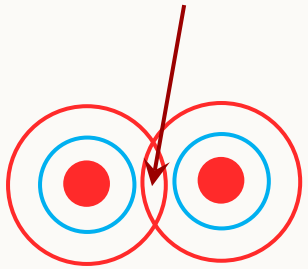


MIL-101

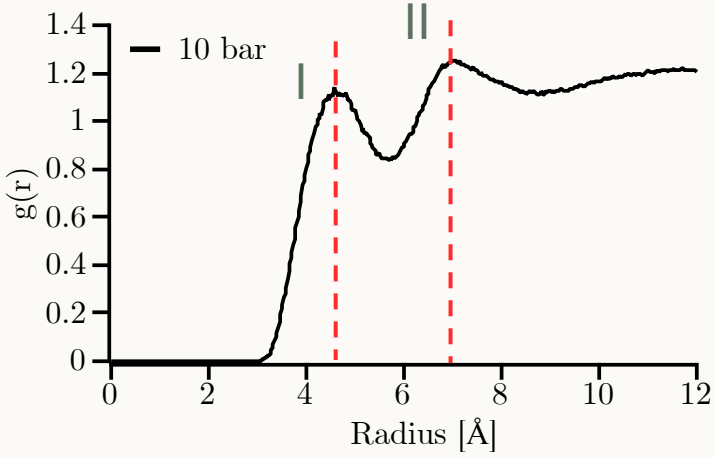


Adsorption site is mainly around the metal atom in the first co-ordination sphere

=> Only one metal atom is affecting the adsorption site

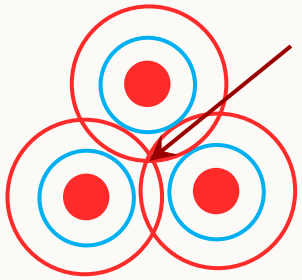


MOF-177

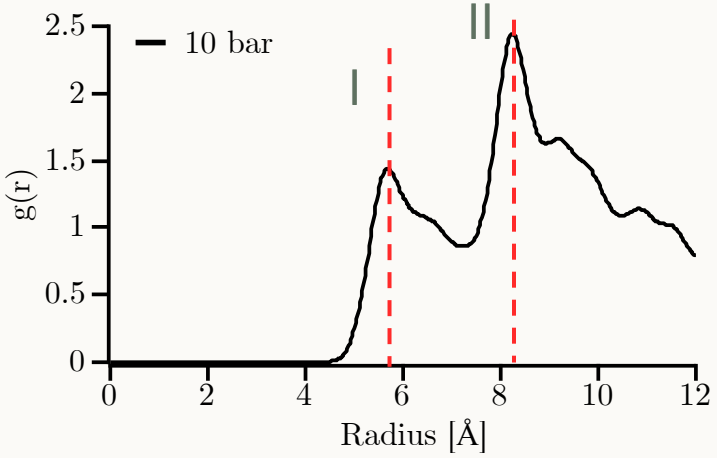


Peak II is higher, indicating that adsorption site is in the second co-ordination sphere around the metal atom

=> Multiple metal atoms are affecting the adsorption site



UIO-66



Peak II is significantly higher, indicating that adsorption site is in the second co-ordination sphere around the metal atom

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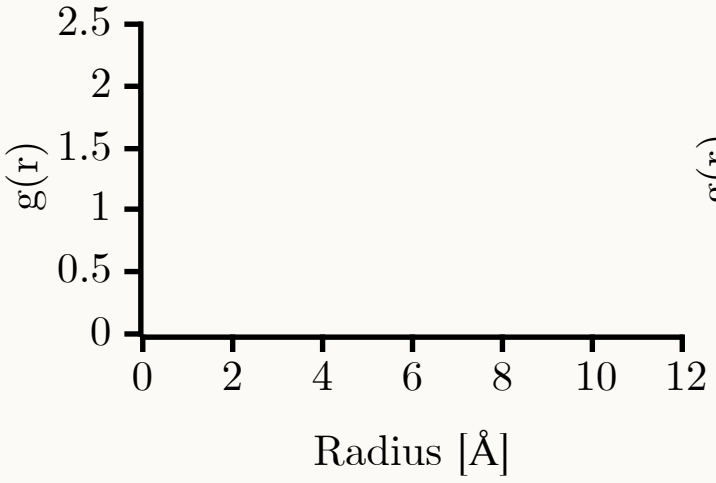
Adsorbed CO_2 Phase

MIL-101



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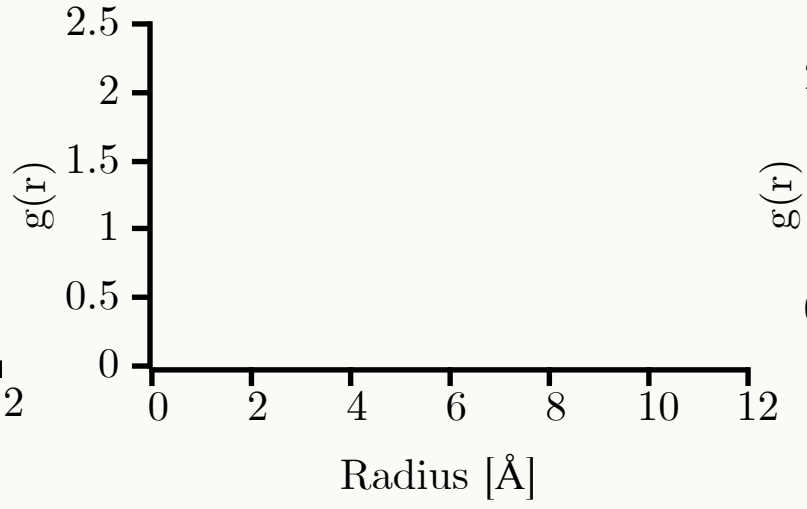

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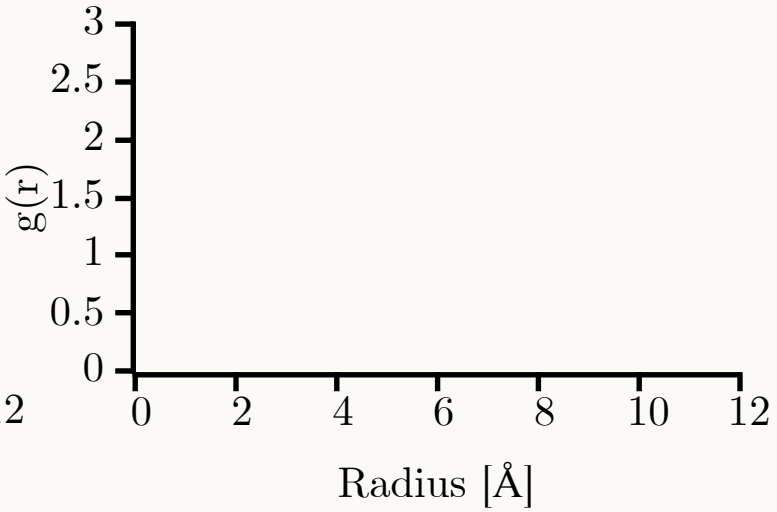

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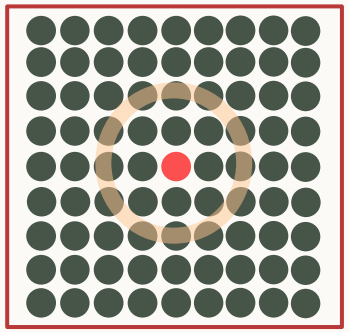
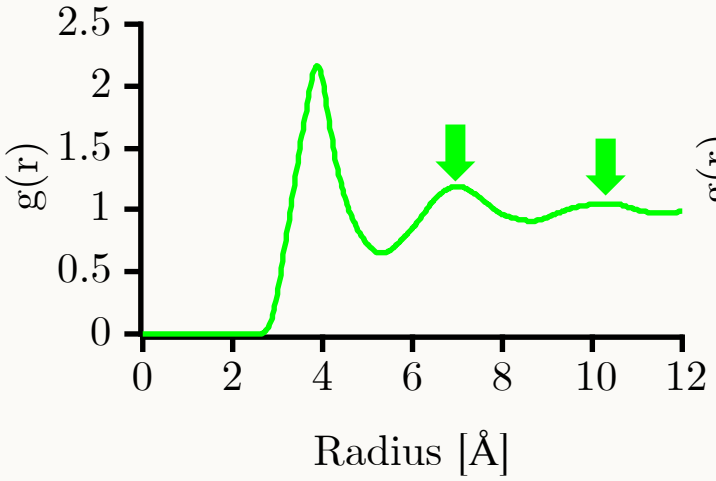


– Bulk solid

MIL-101



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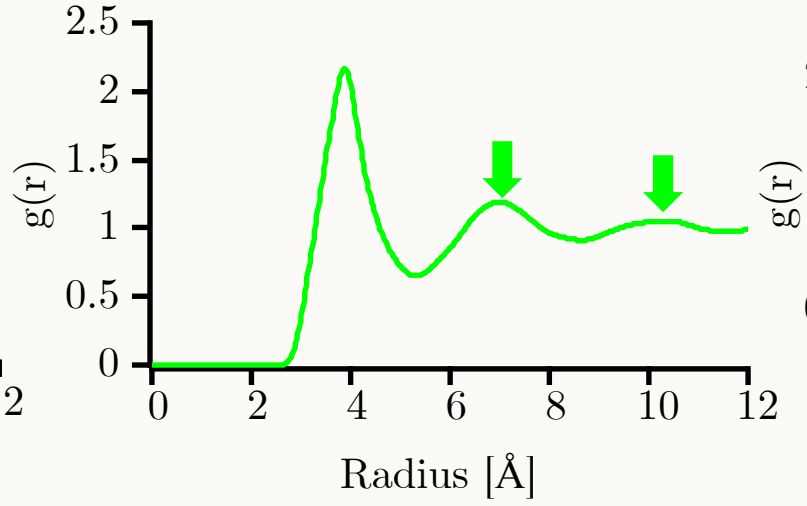

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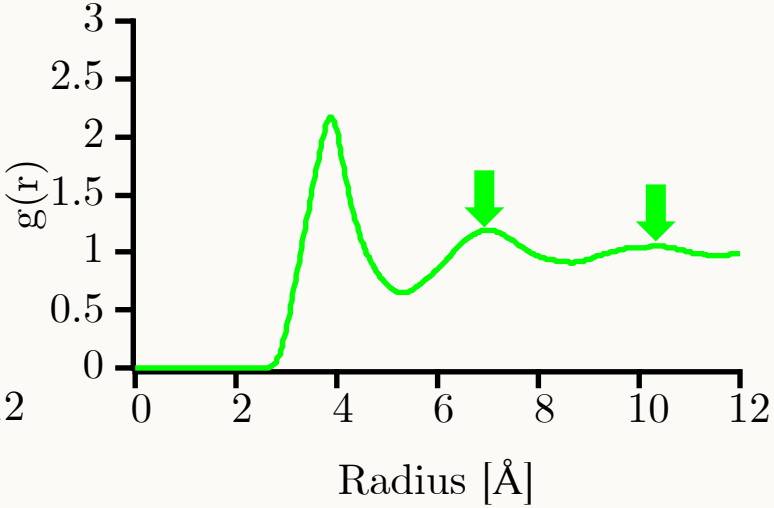
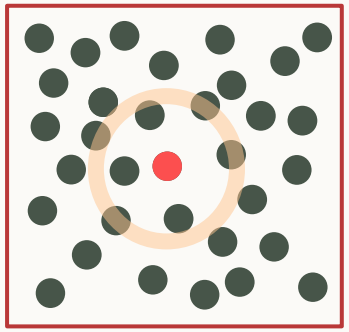
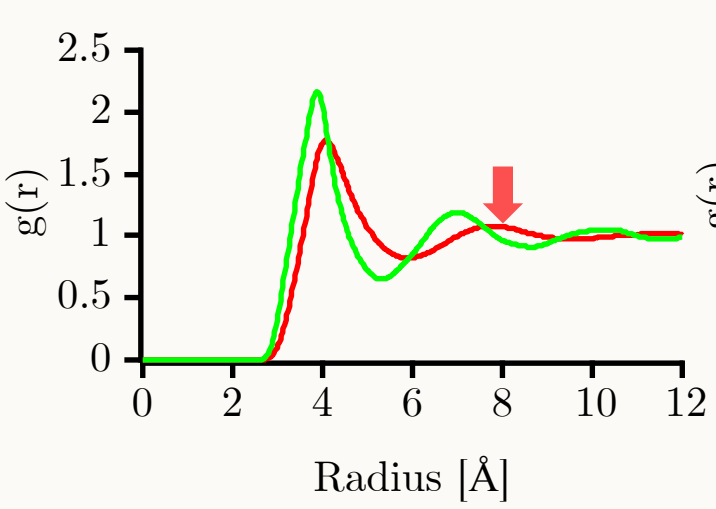


Adsorbed CO_2 Phase

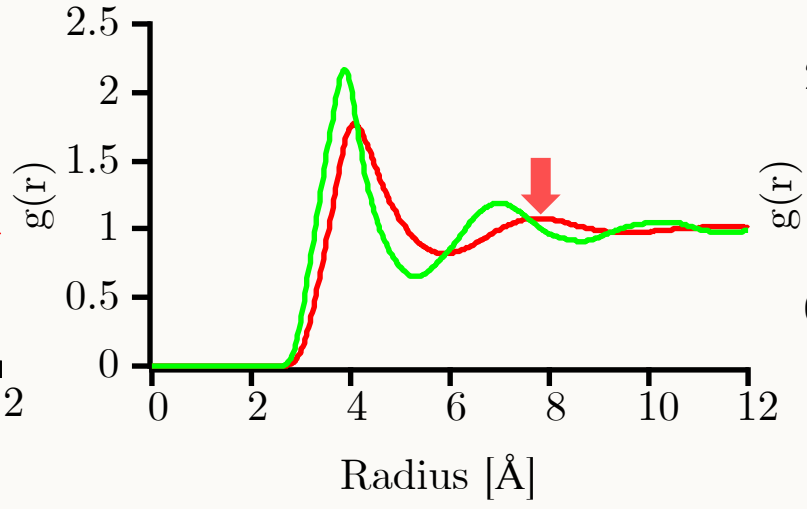


- Bulk solid
- Bulk liquid

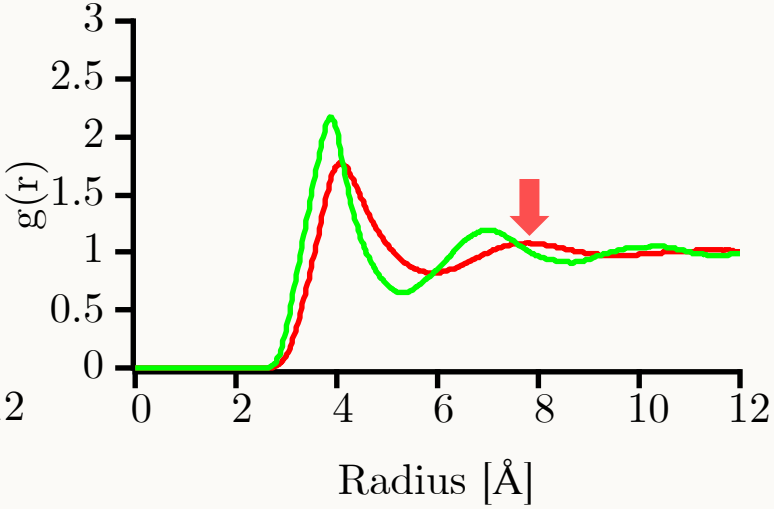
MIL-101



MOF-177



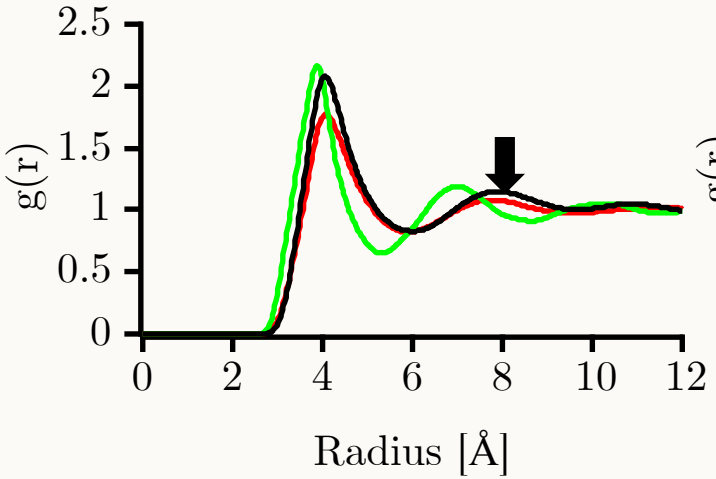
UIO-66

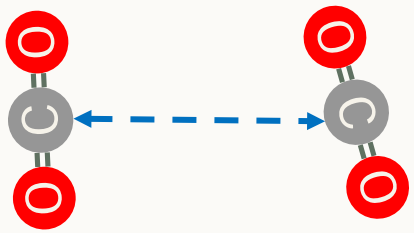


Adsorbed CO_2 Phase

- Bulk solid
- Bulk liquid
- 10 bar / 273 K

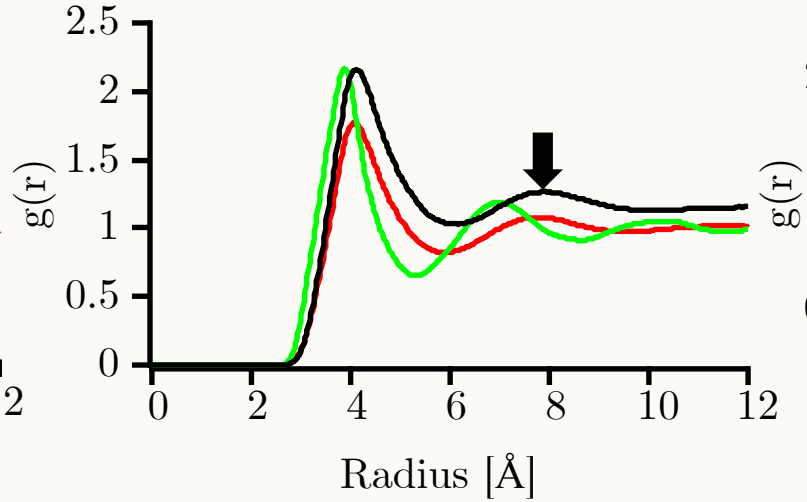
MIL-101

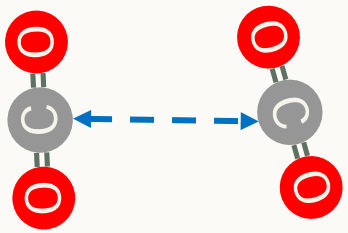




"Liquid Like"

MOF-177





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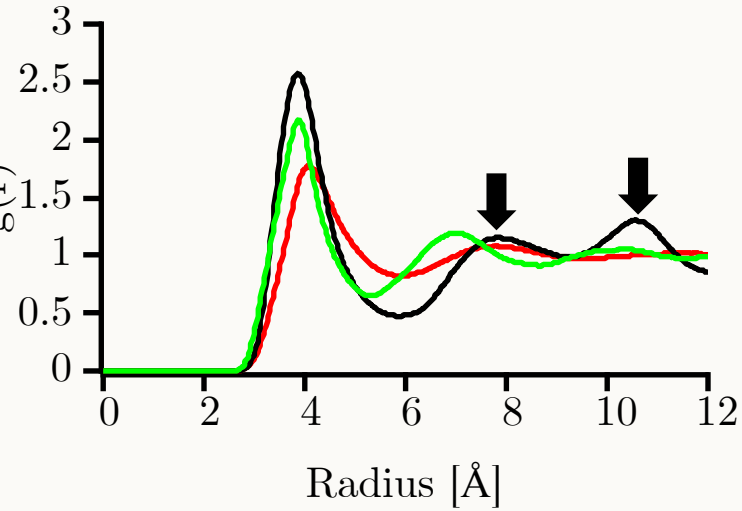
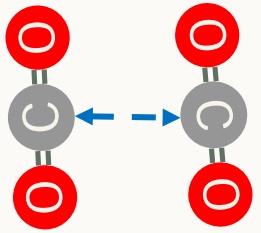
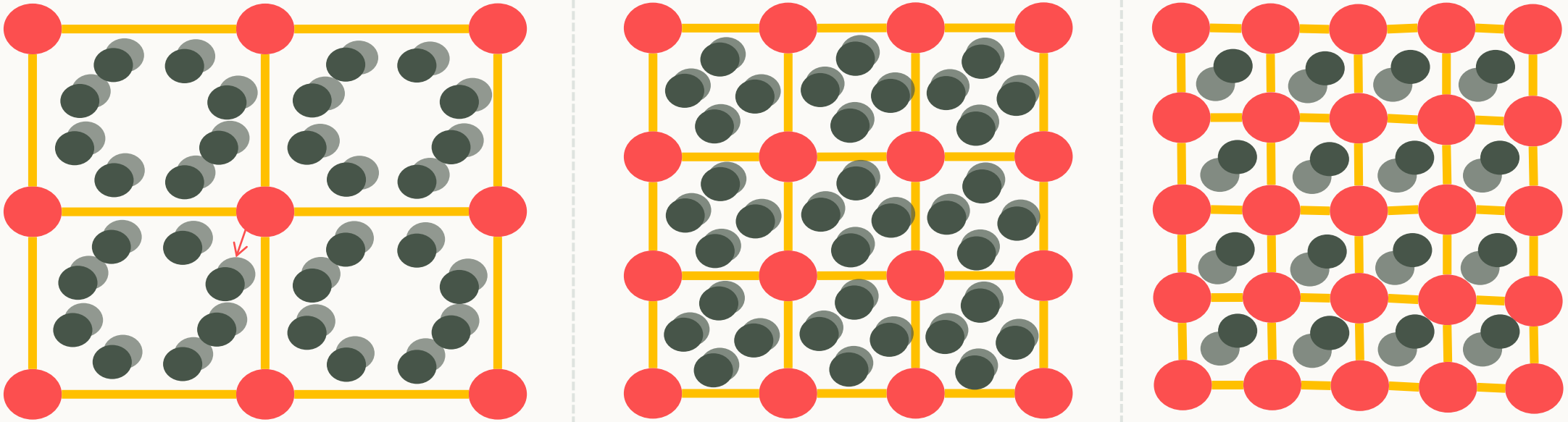




"Solid Like"

Effect of pore size on packing of CO_2

d_1 > d_2 > d_3



~ MIL-101
(~34Å)

~ MOF-5 / MOF-177
(~10-15Å)

~ UiO-66
(~6Å)

Effect of pore size on packing of CO_2

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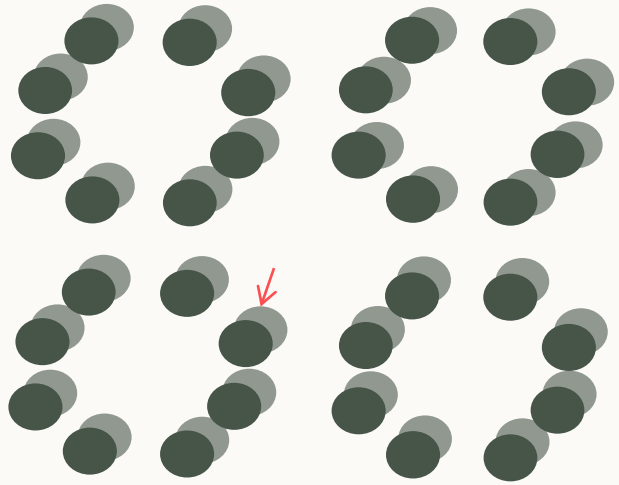

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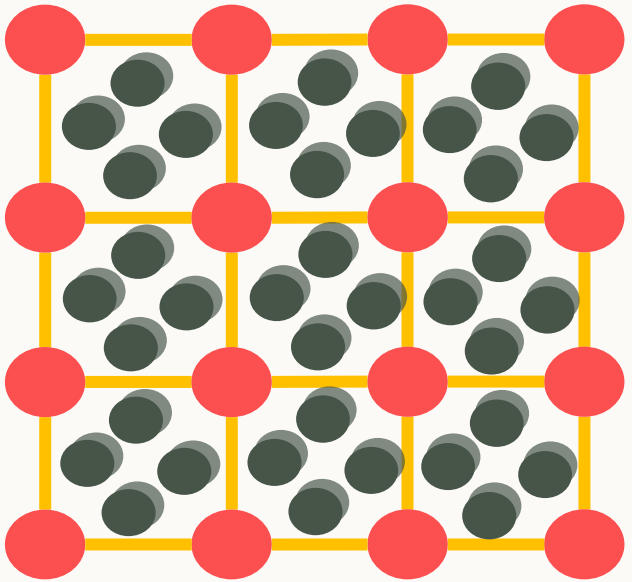

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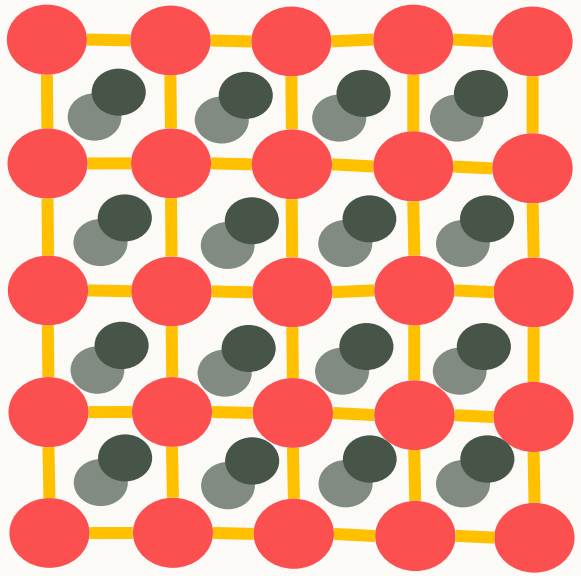


~ UiO-66
(~6Å)

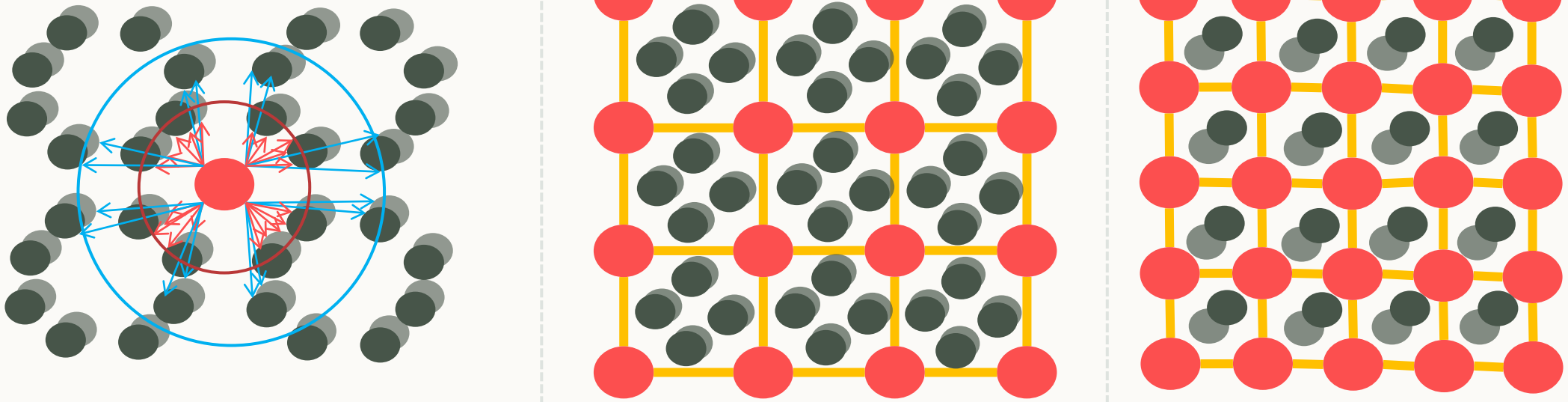
Effect of pore size on packing of CO_2

Arrows indicate the interaction between metal and CO_2 molecules

Weak interaction

Strong interaction

d_1 > d_2 > d_3



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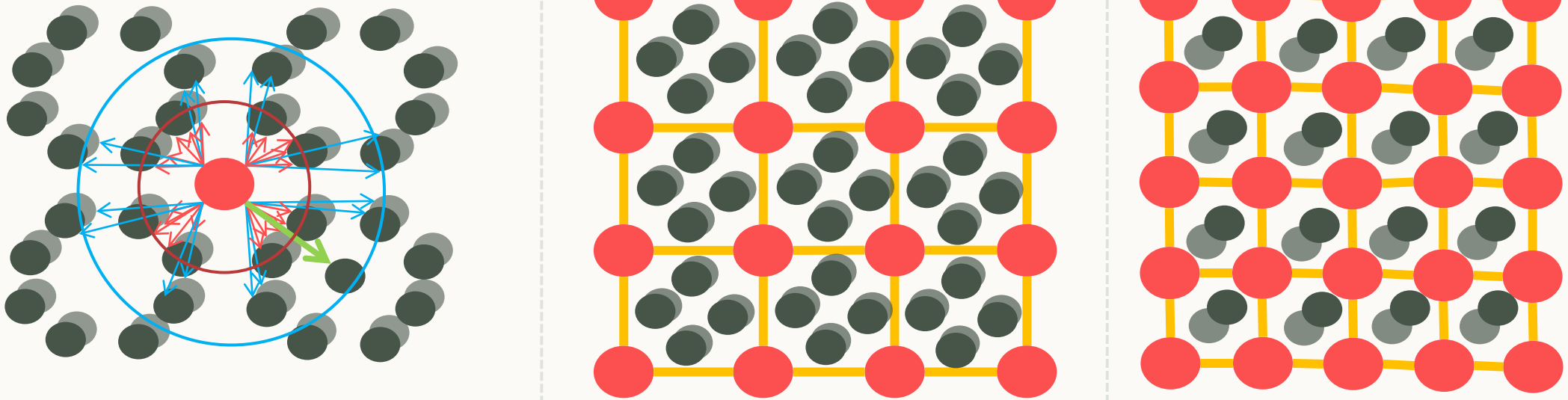

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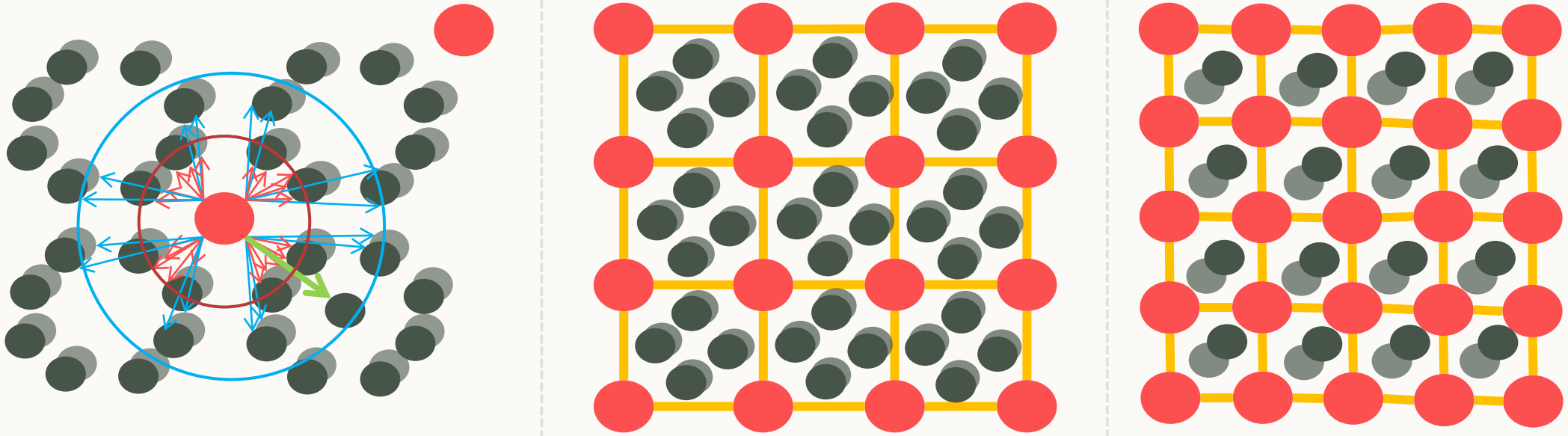

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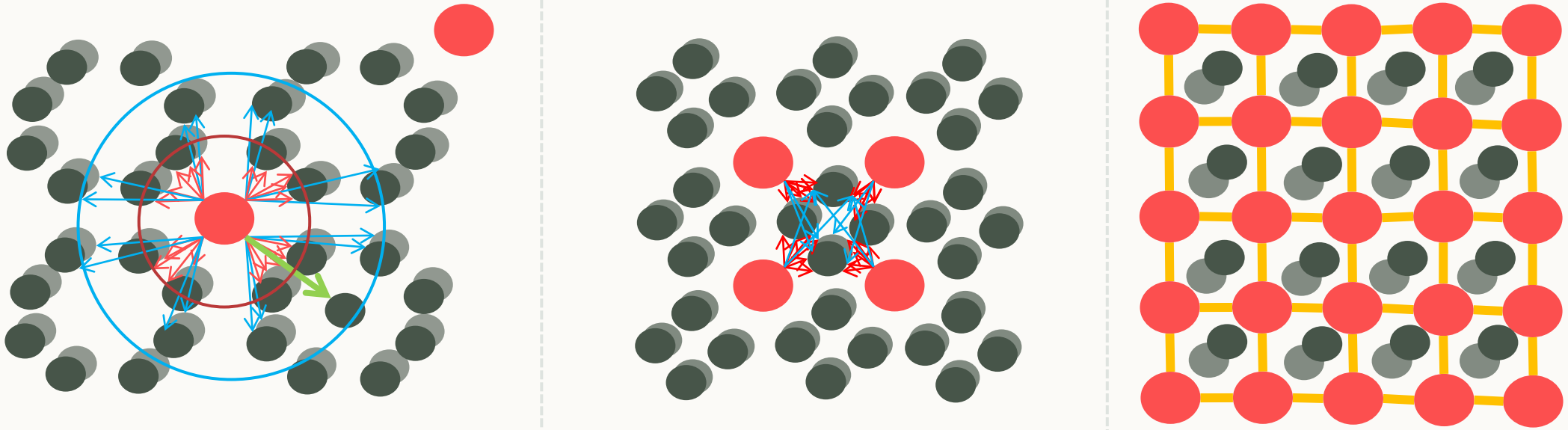

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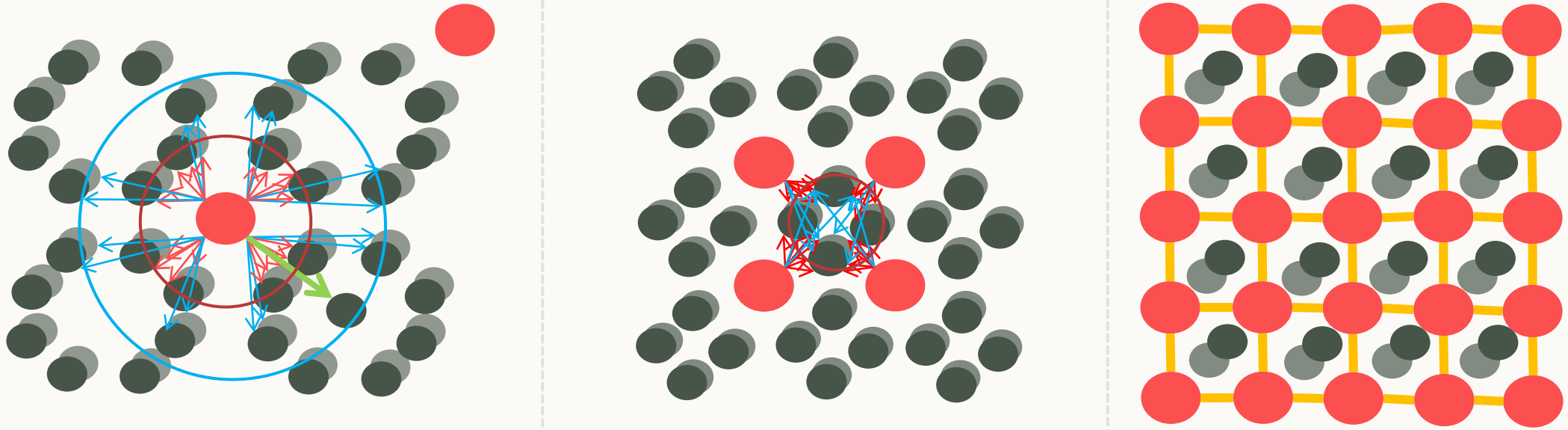

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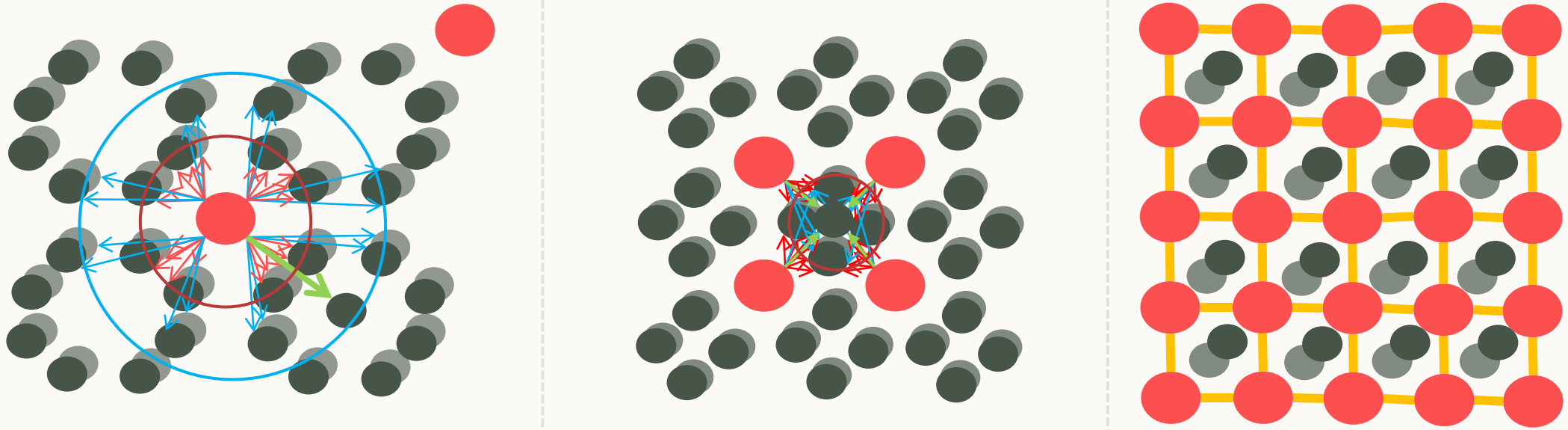

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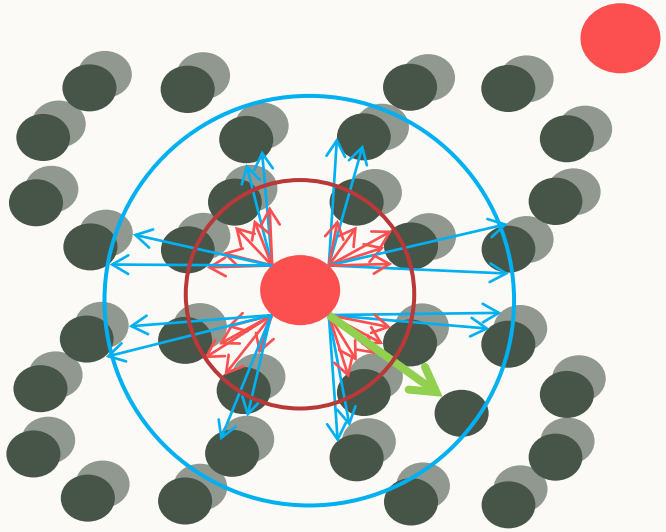

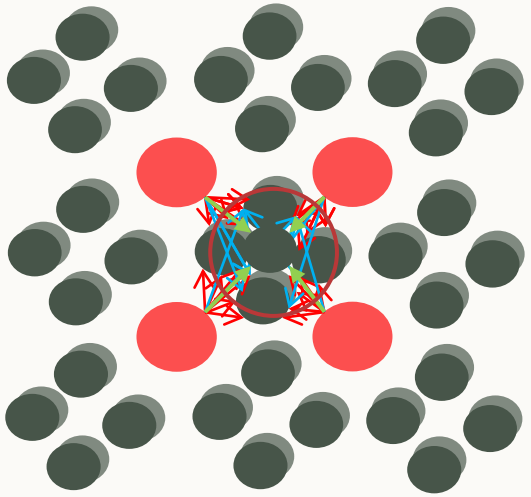

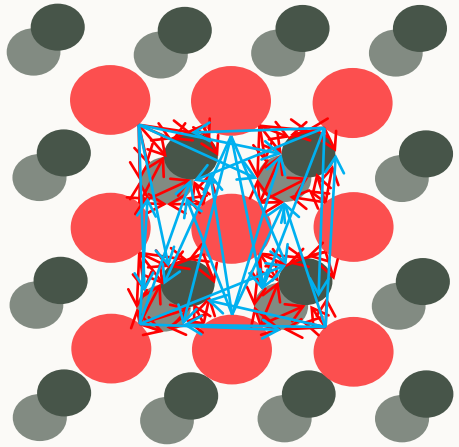

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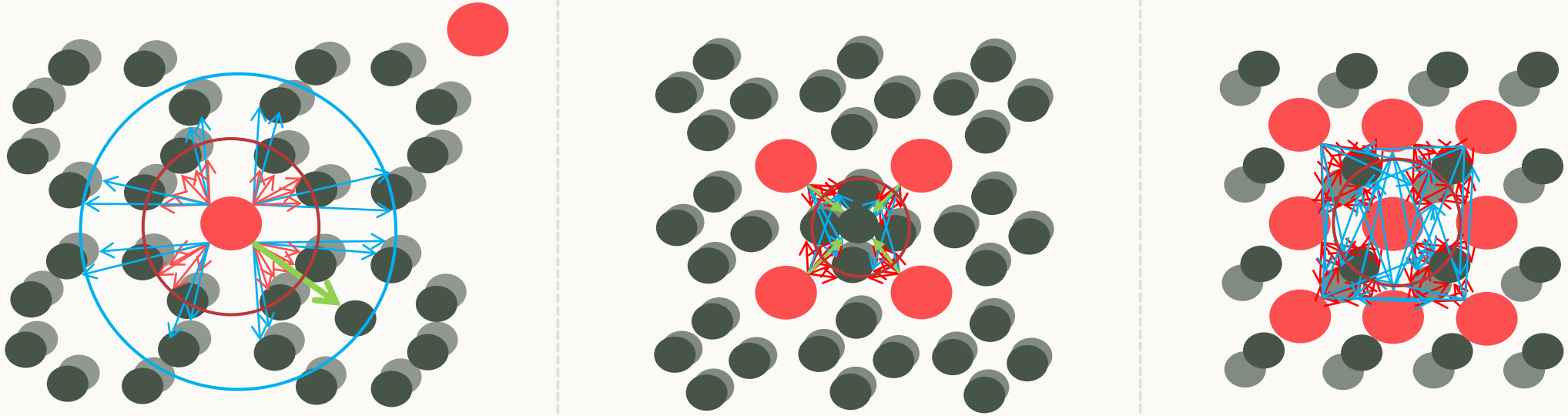

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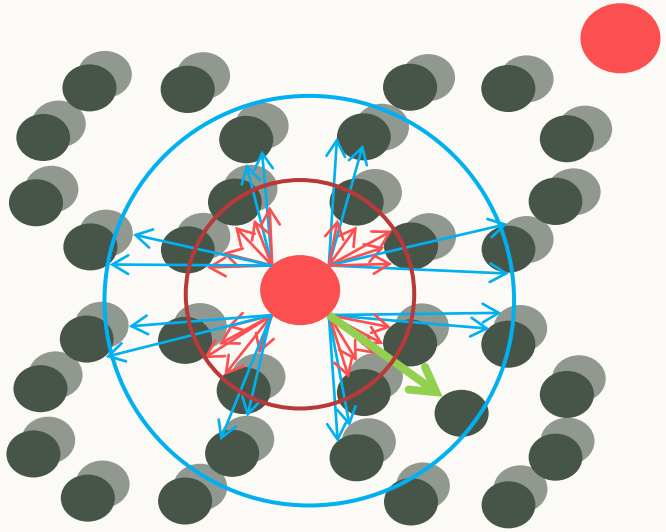

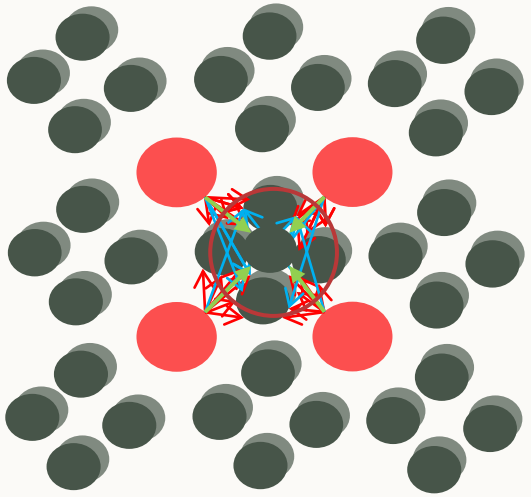

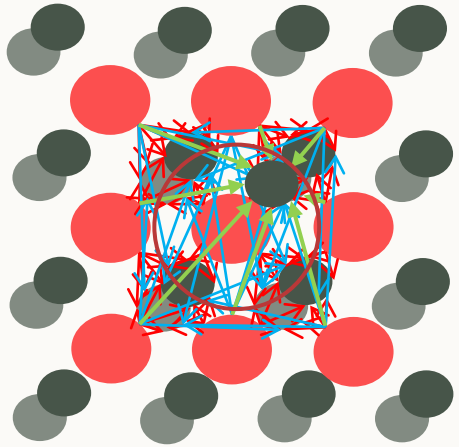

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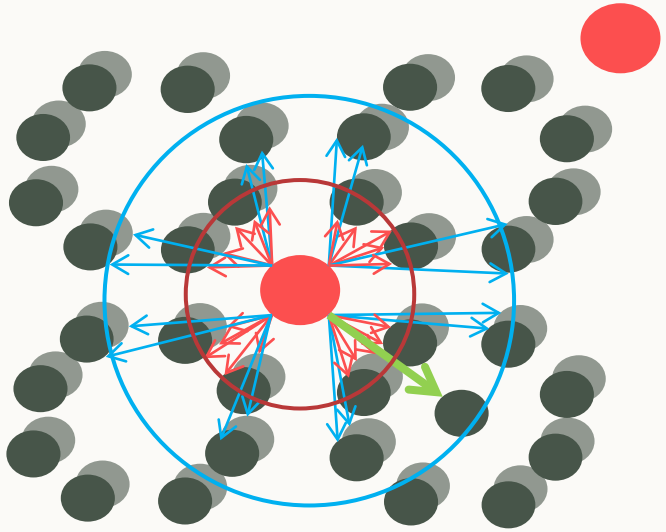

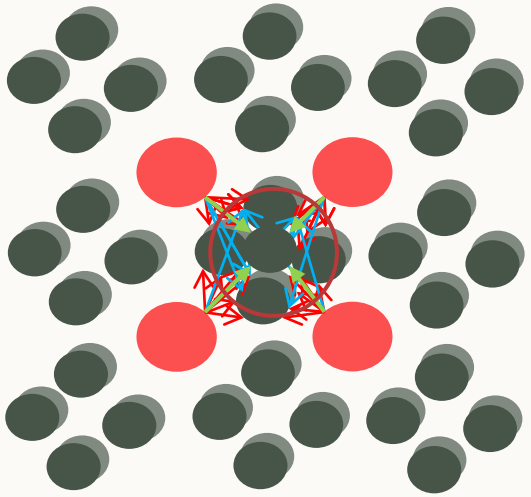

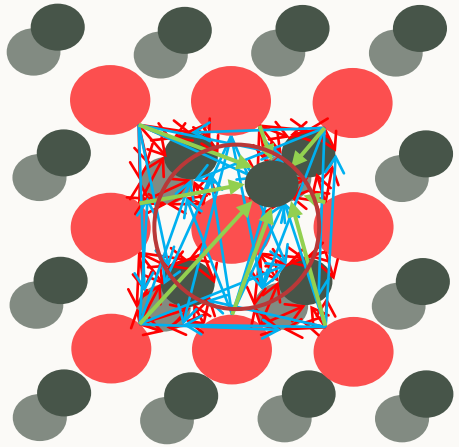

~ MIL-101
(~34Å)

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(~10-15Å)

~ UiO-66
(~6Å)

High capacity

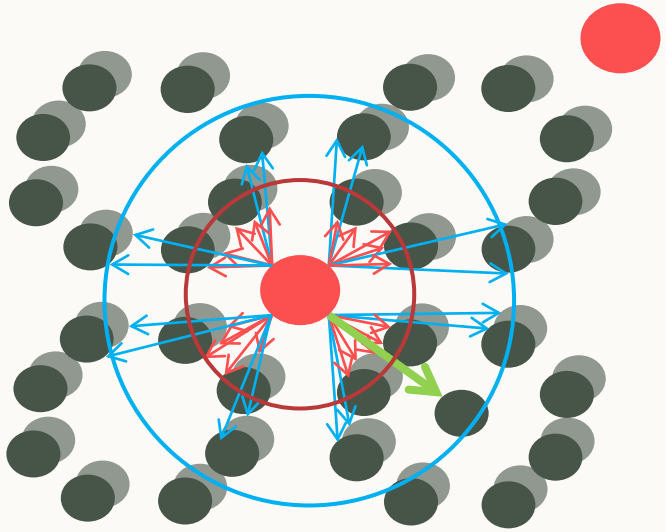
Effect of pore size on packing of CO_2

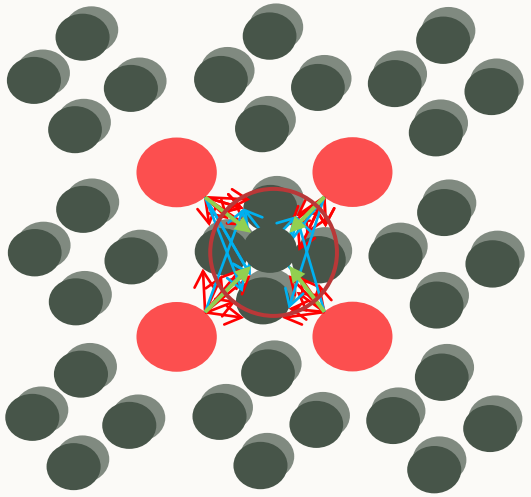
Arrows indicate the interaction between metal and CO_2 molecules

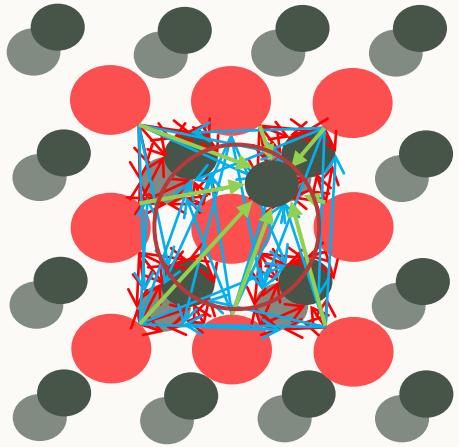
Weak interaction

Strong interaction

d_1 > d_2 > d_3







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(~6Å)

High capacity

High enthalpy of adsorption

Summary and Conclusions

- For **smaller pore diameter of MOF**, differential **enthalpy of adsorption increases with increase in amount of CO_2 adsorbed**
- **Higher Van der Waal interaction energy** is released in case of MOF with a **smaller pore size**
- Radial distribution functions for inter CO_2 molecules show that, adsorbed phase resembles '**solid like**' phase in case of **smaller pores** whereas, for **larger pores** it resembles the '**liquid like**' phase
- For **larger pores**, **single metal atom** affects the adsorption site, while in **smaller pores**, **multiple metal atoms interact** with a single adsorption site releasing more energy per CO_2 molecule adsorbed
- The **optimum pore size** of MOF for heat pump application is **around 10Å** (Not too small, not too large)

Thank You!