Nitrogen and oxygen adsorption in metal-organic frameworks for gas separations

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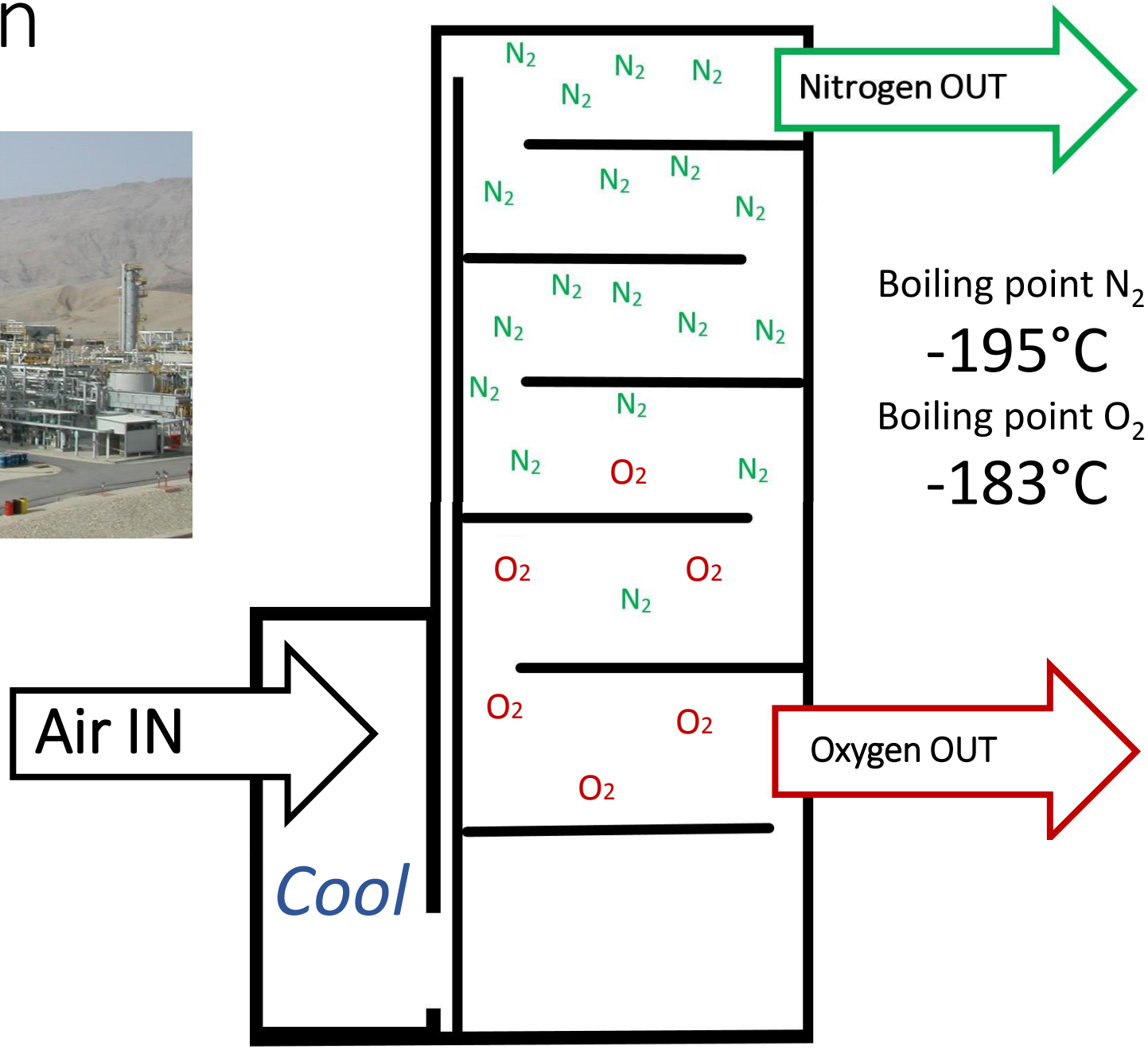
Overview

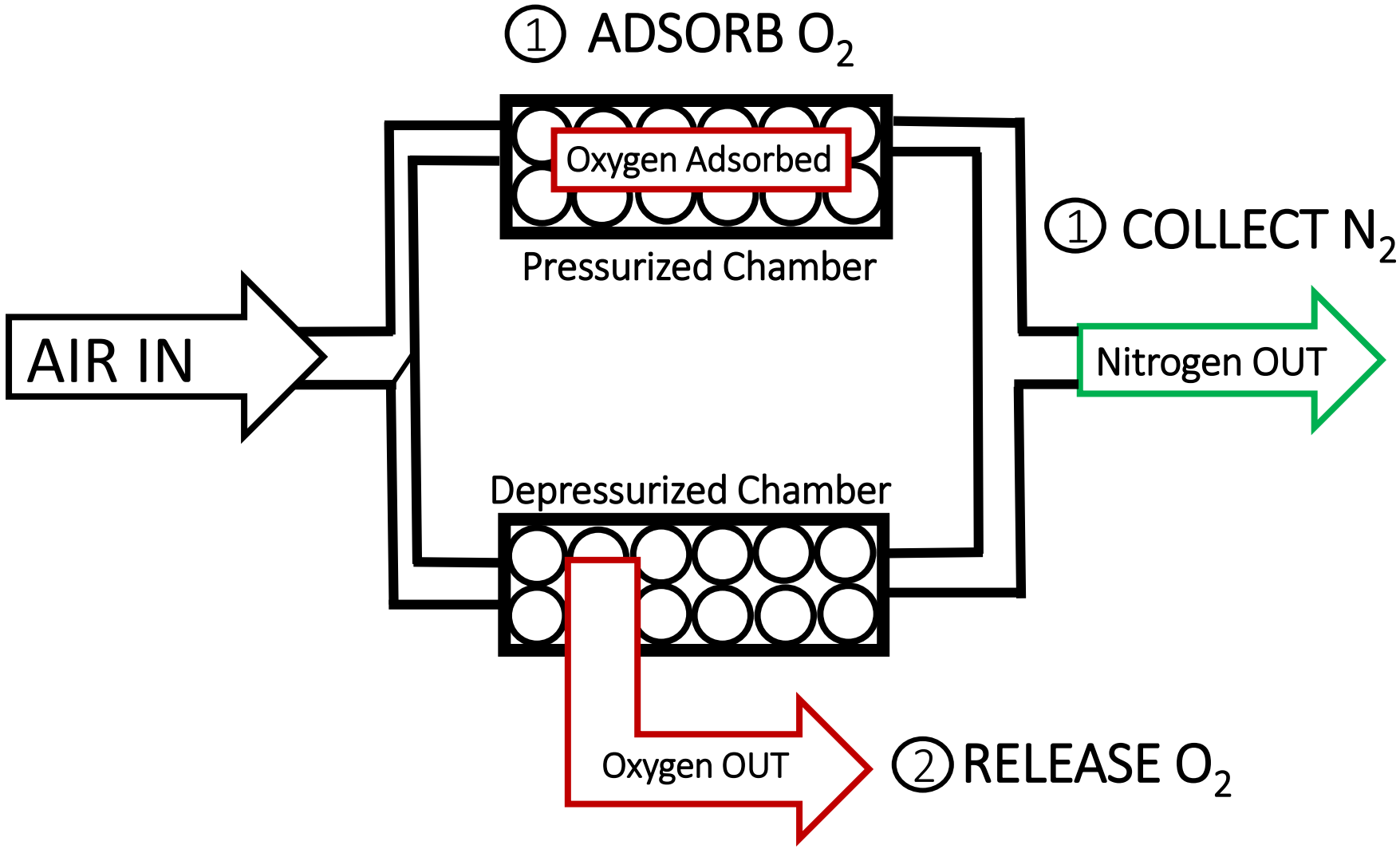
- Industrial N_2/O_2 gas separation
- Metal-Organic Frameworks
- Neutron Powder Diffraction
- Preliminary gas mixture studies

Cryogenic Distillation

Expensive, energy-intensive process

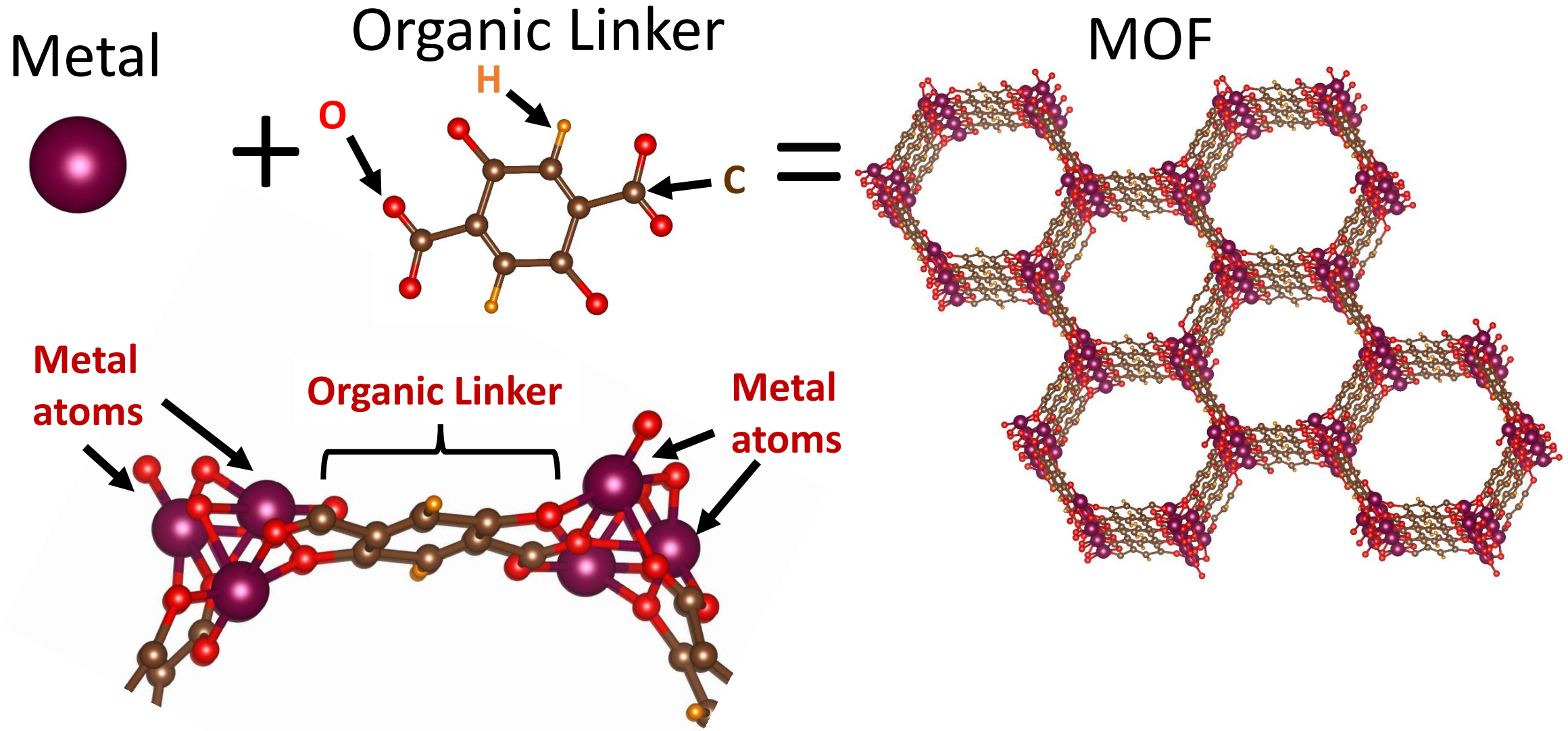


Pressure Swing Adsorption (N_2/O_2 example)



- Looking for better adsorption material:
  - Porous, crystalline powder
  - Higher selectivity for O_2 over N_2 for more ambient operating conditions

Metal-Organic Frameworks (MOFs)

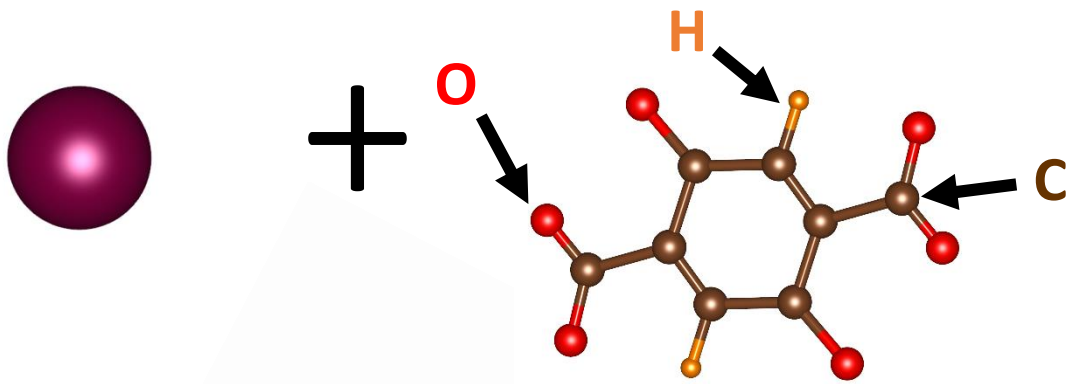


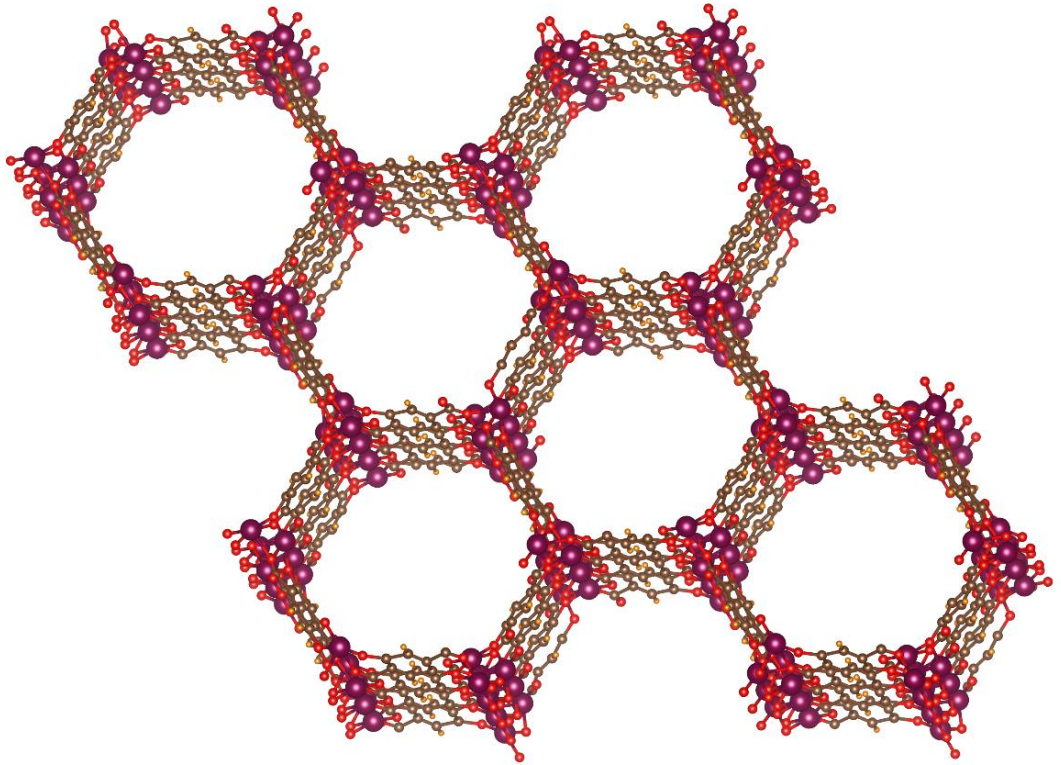
MOF-74

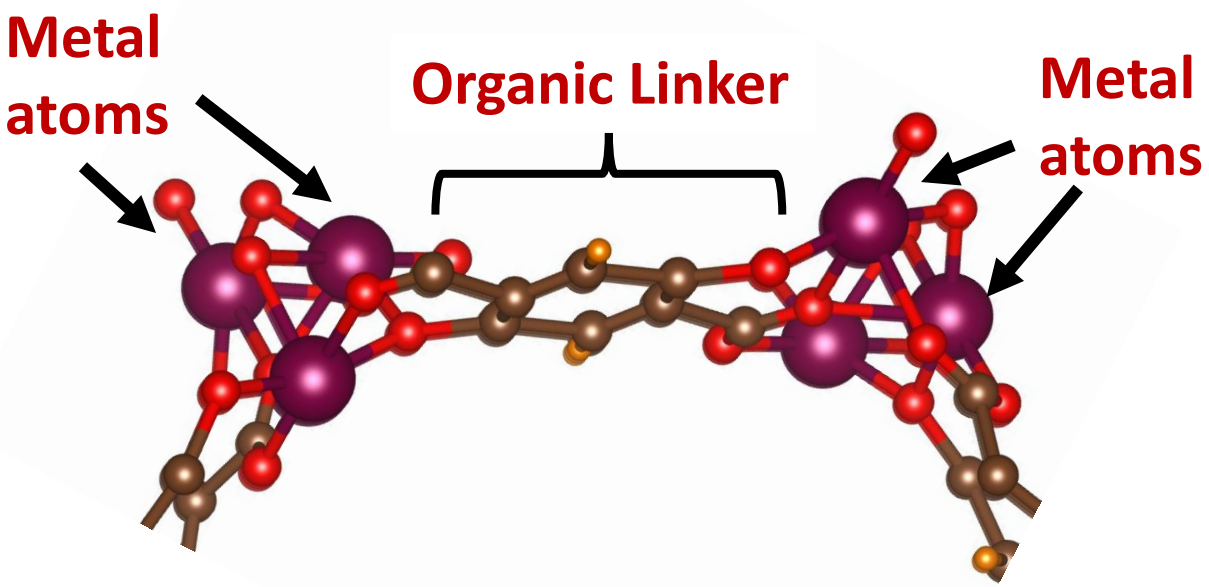
Metal= **Mg**, **Ni**, Mn, Fe, Co, Cu, Zn

dobdc = 2,5-dioxido-1,4-benzenedicarboxylate

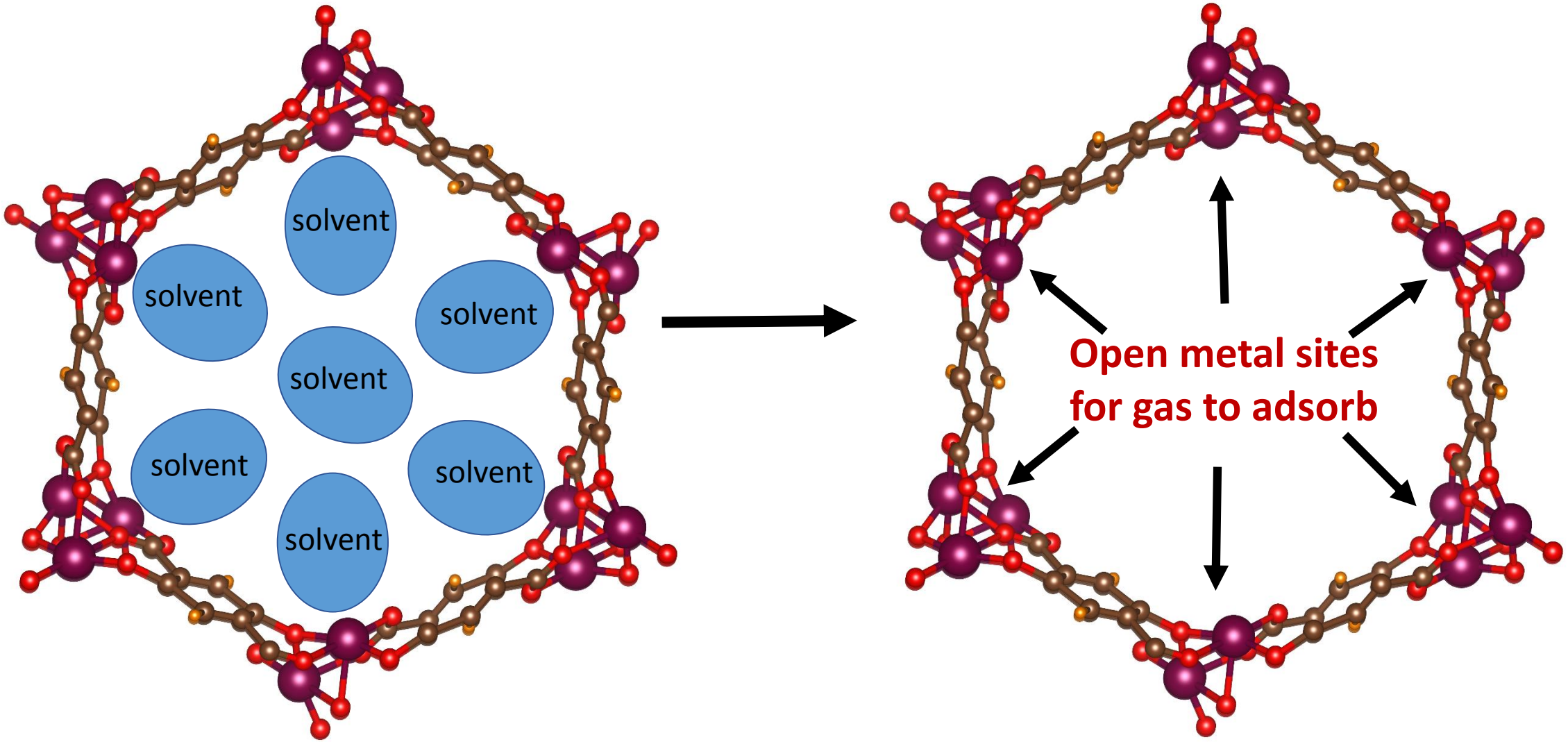
M2-2,5-dioxido-1,4-benzenedicarboxylate







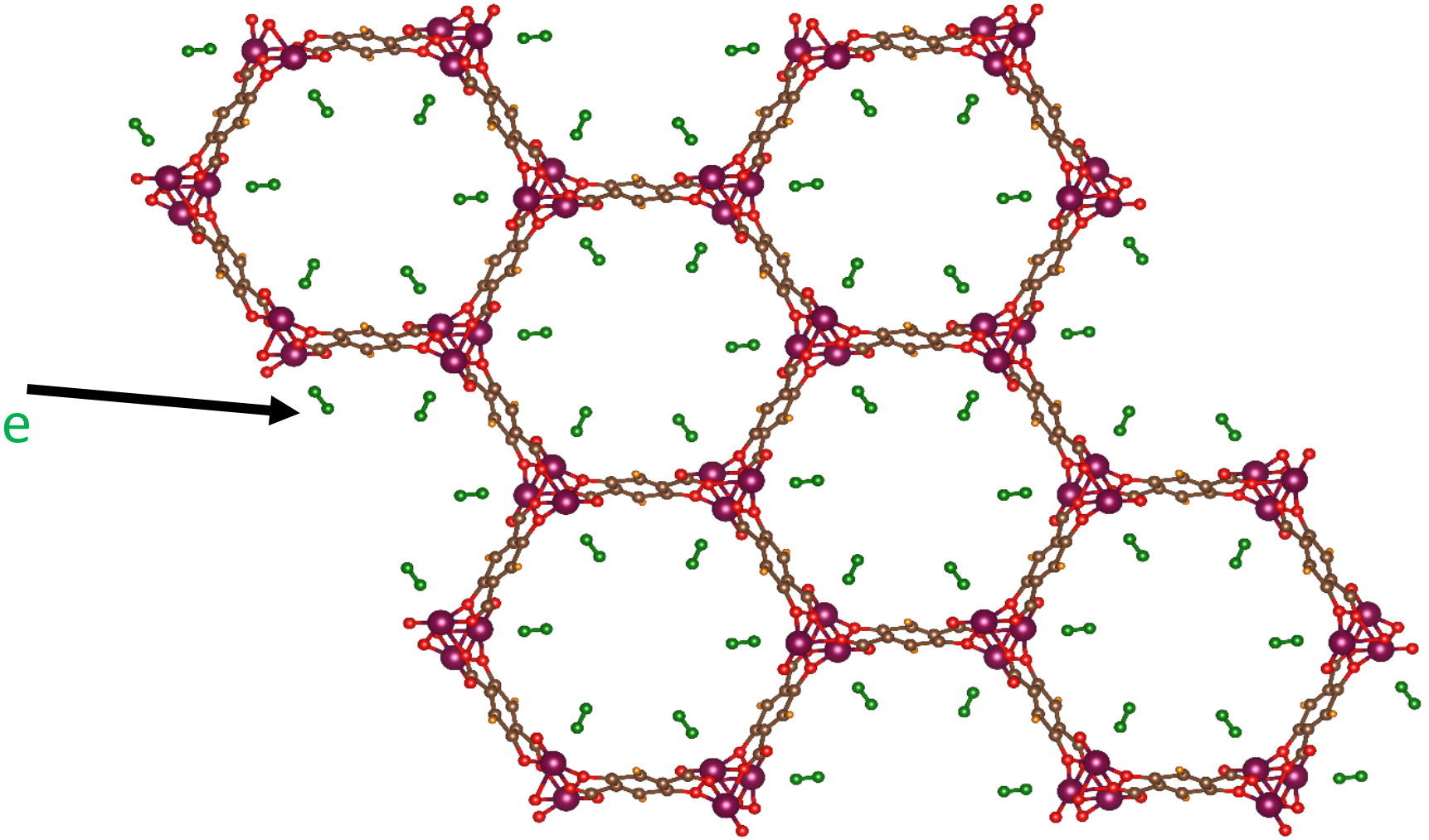
Open metal sites in MOF-74



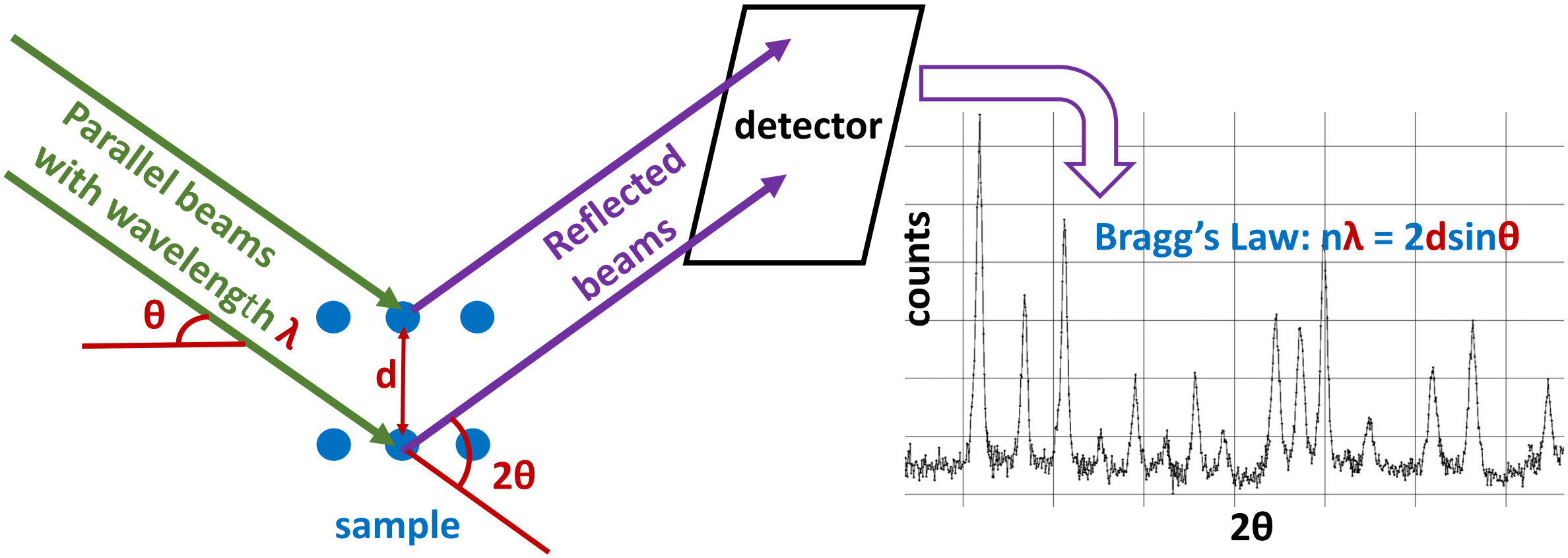
MOF-74 materials have a high concentration of open metal sites = adsorption enhancement

Gas molecules adsorb at the open metal site

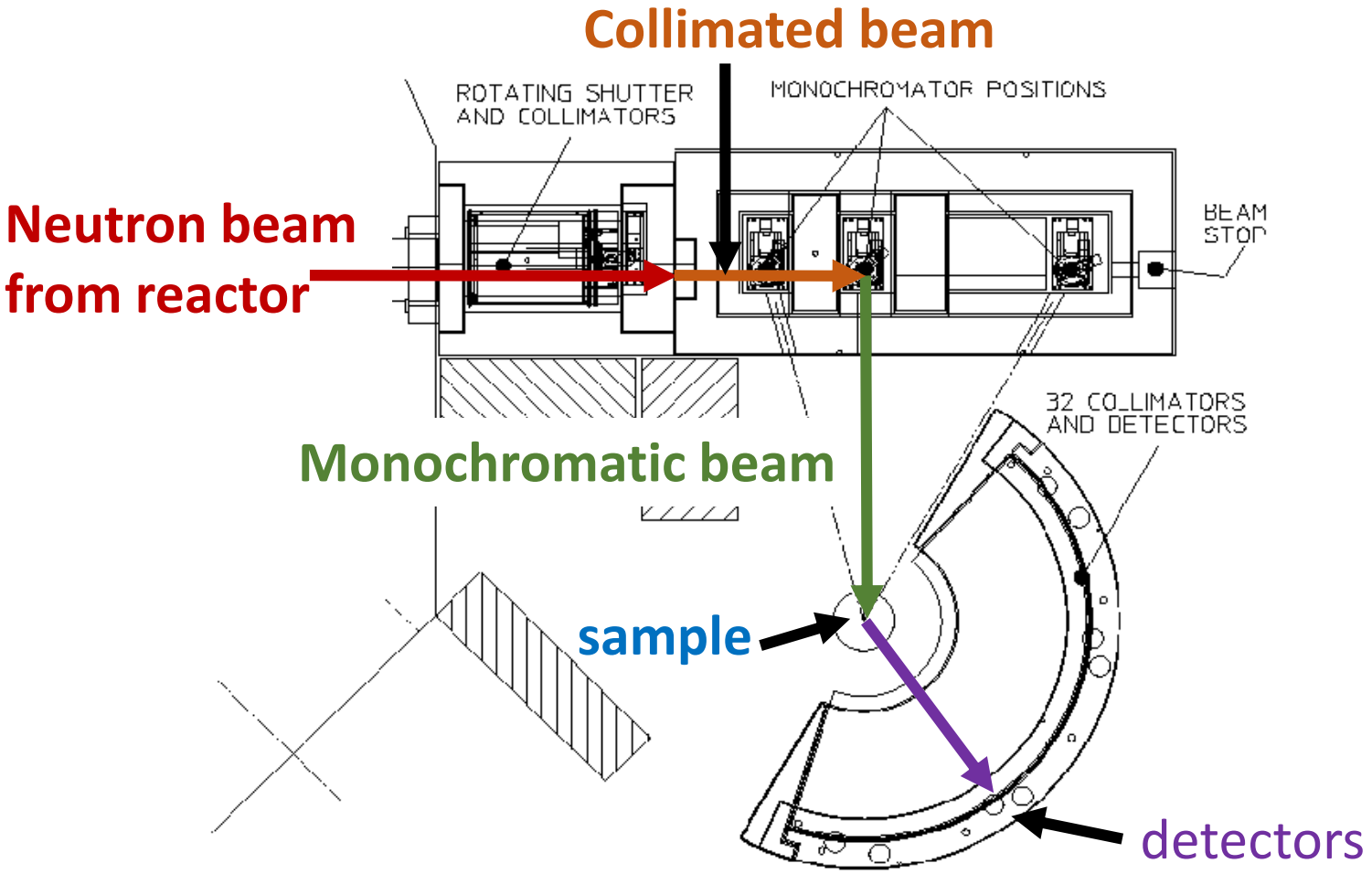
Example: N_2 adsorbed to the framework



Powder diffraction

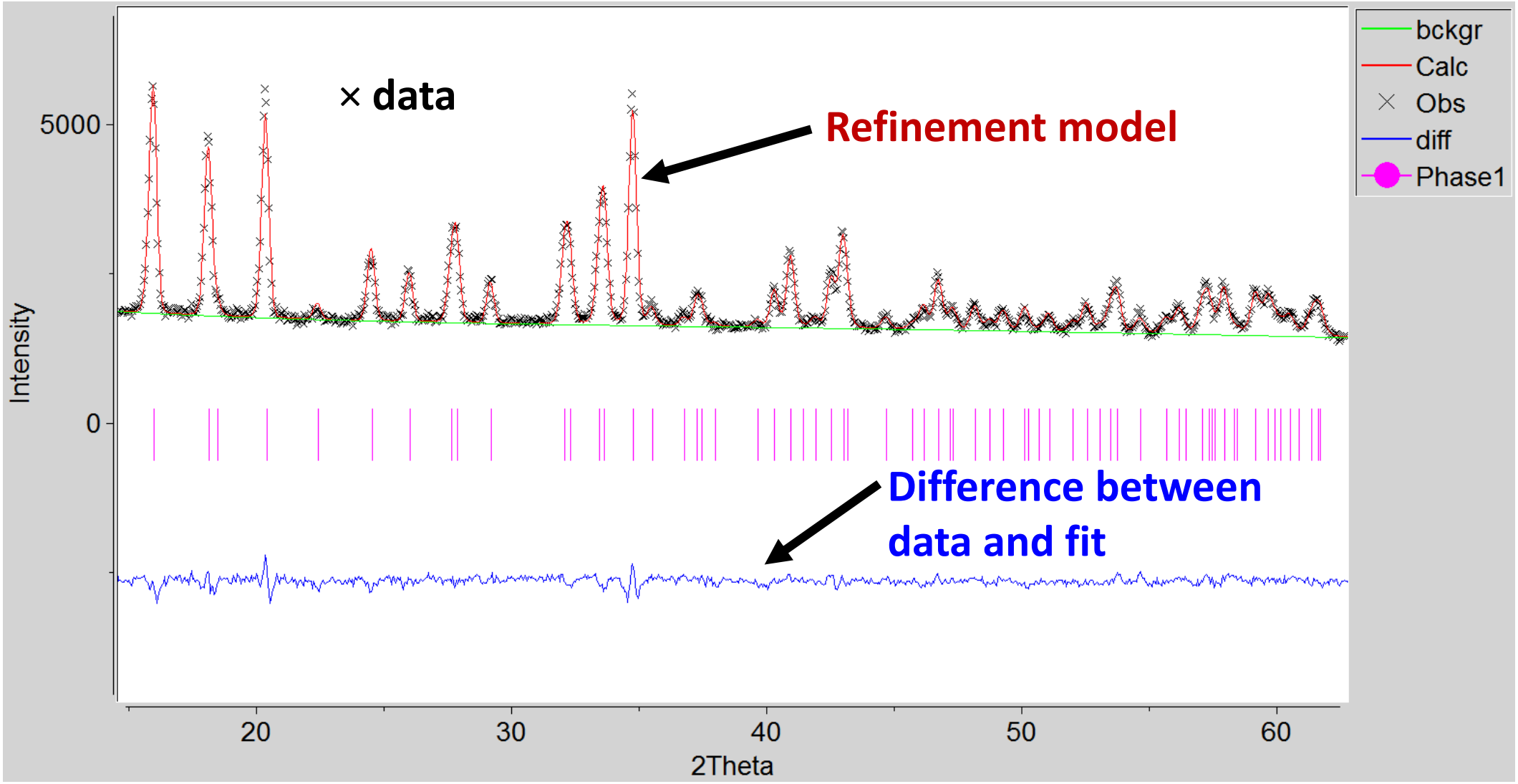


Powder neutron diffractometer (BT-1)

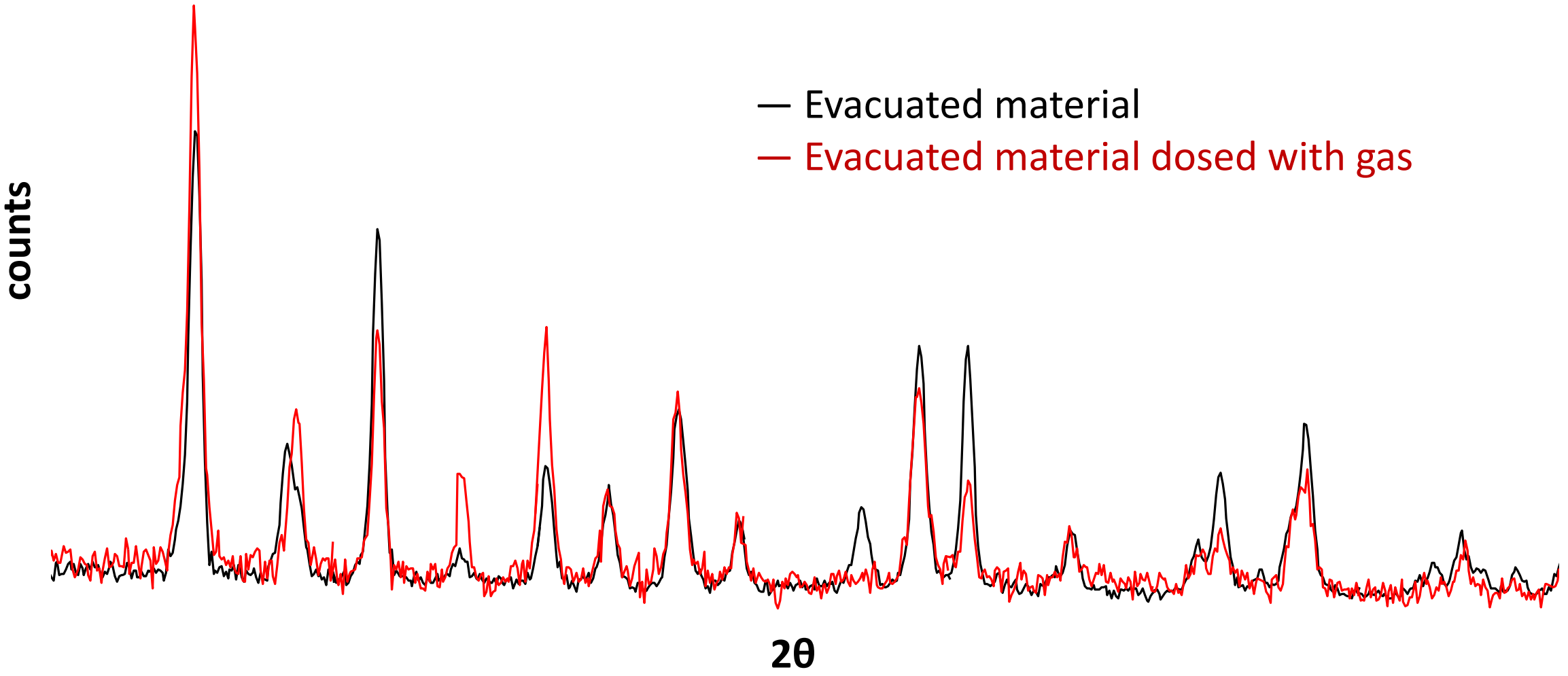


Ge(311) monochromator → λ = 2.078 Å

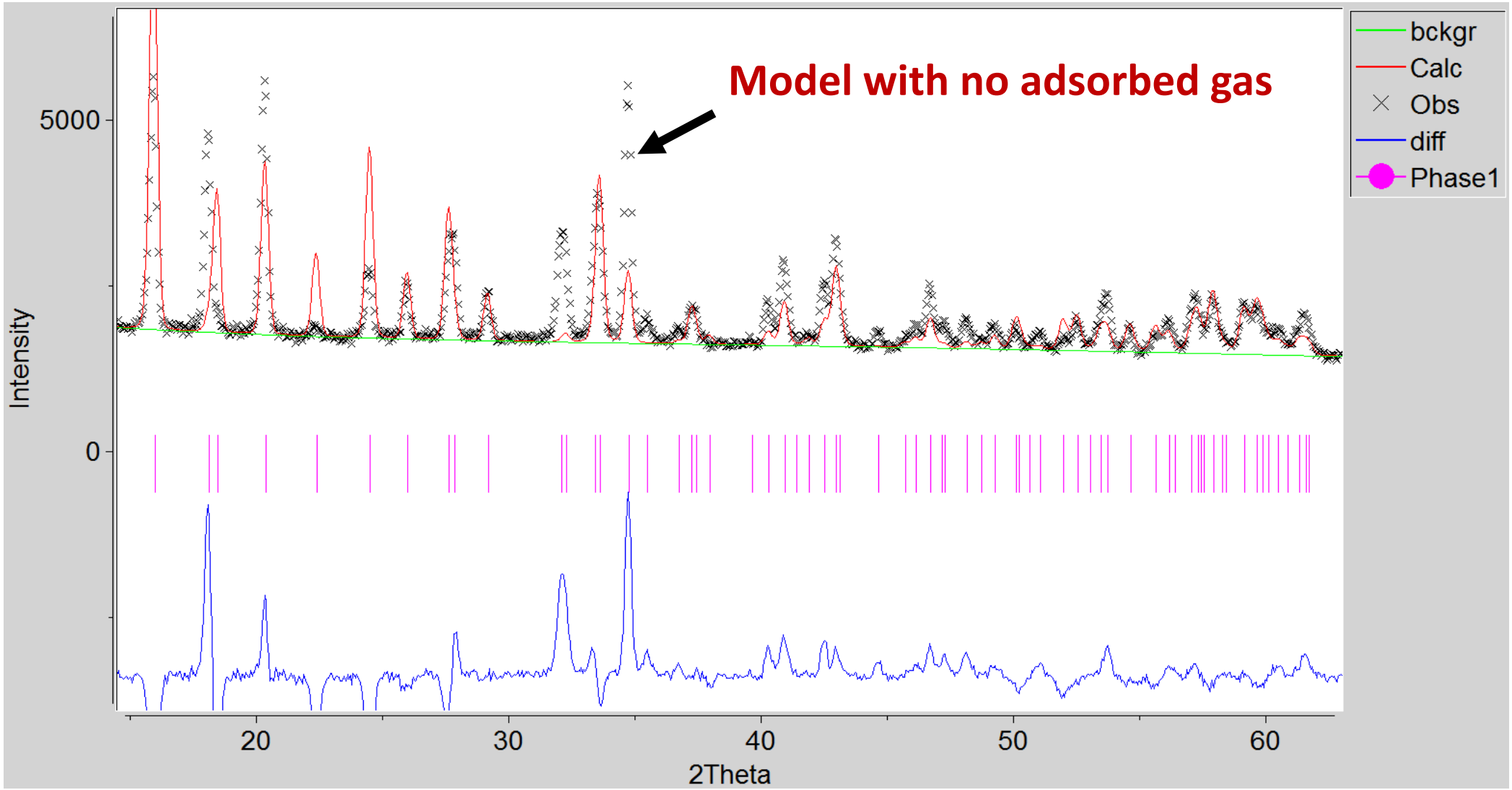
Rietveld Refinement



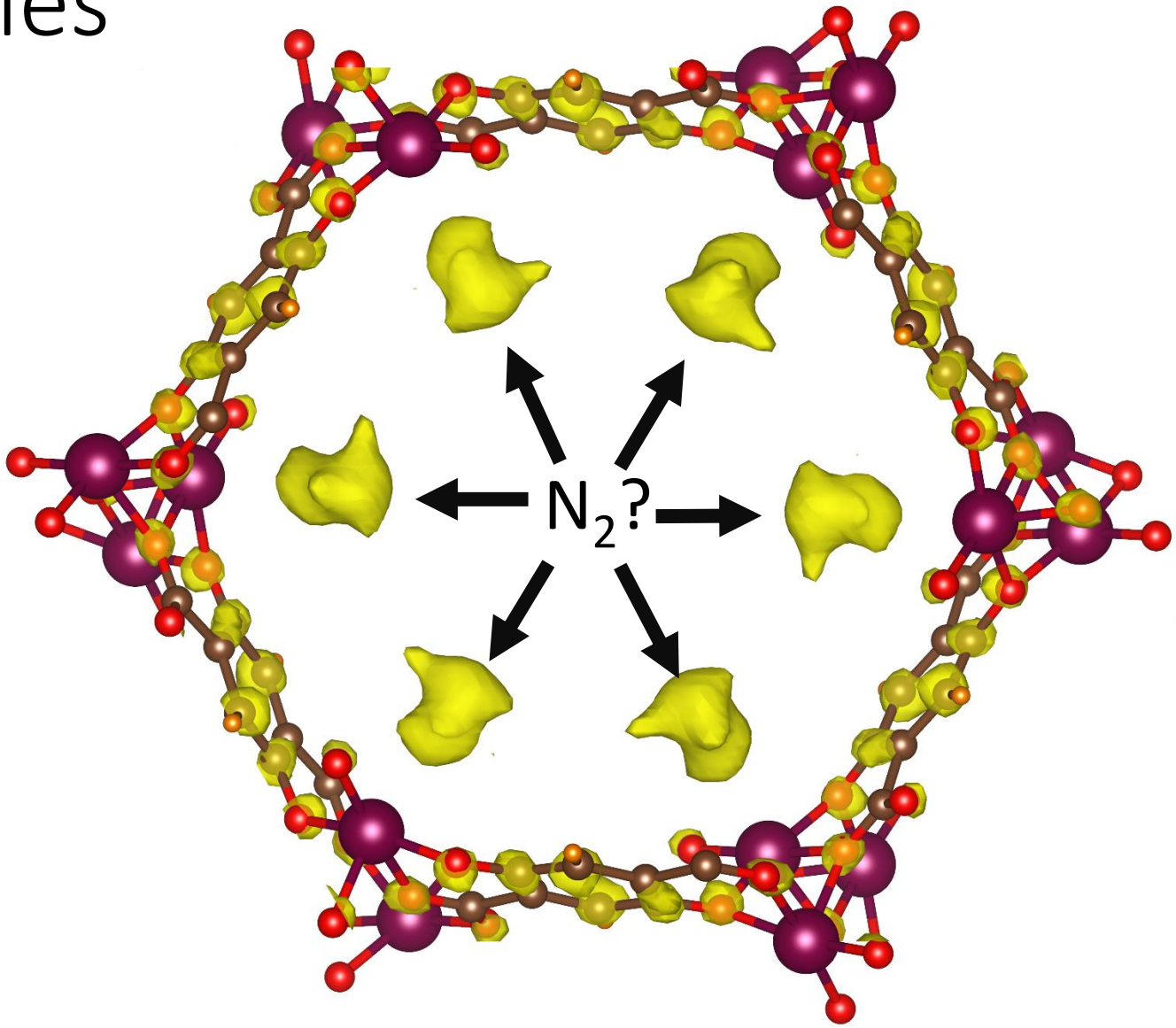
Powder diffraction pattern with and without gas



Rietveld Refinement



Fourier Difference Techniques - to find the gas molecules



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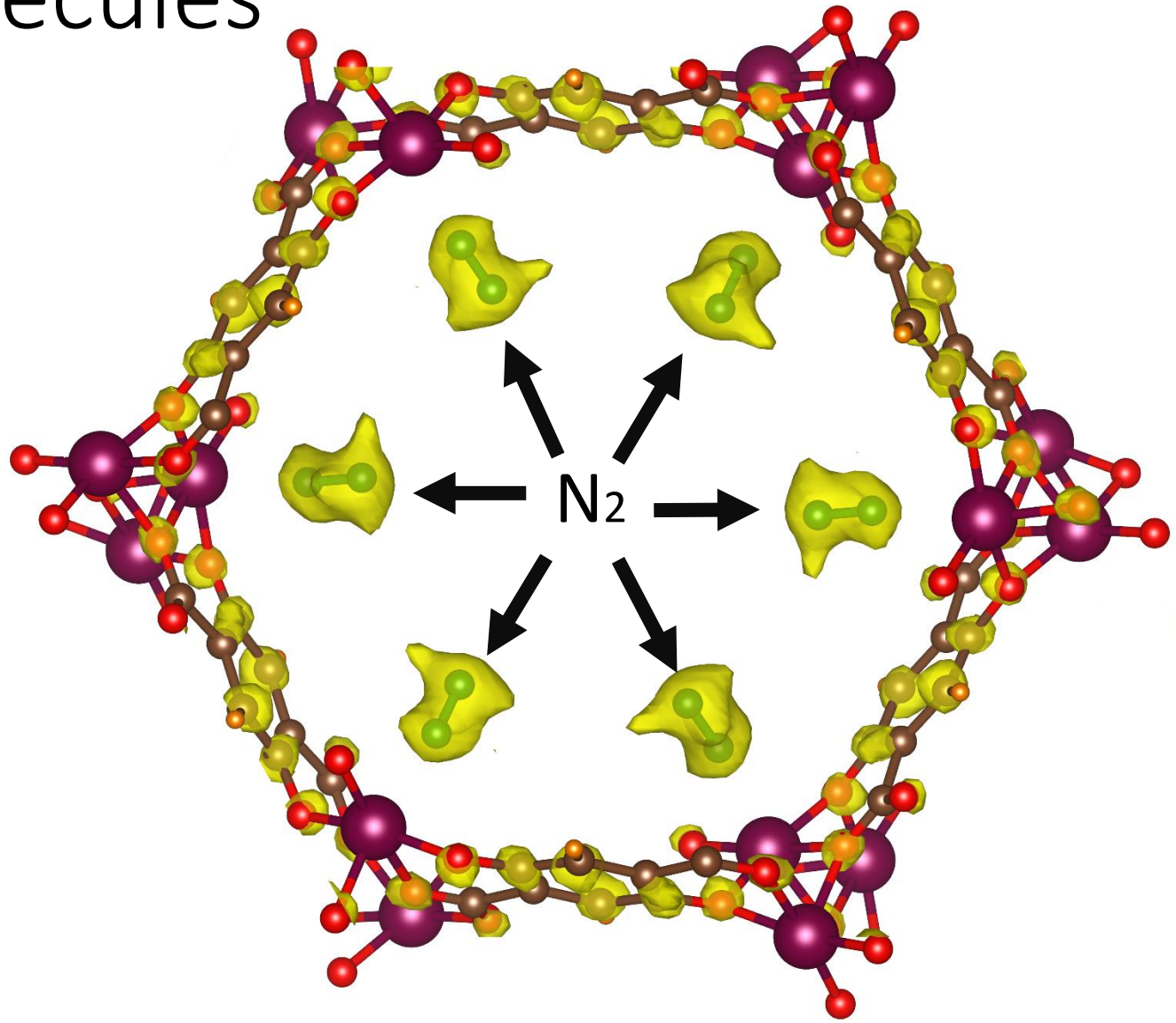

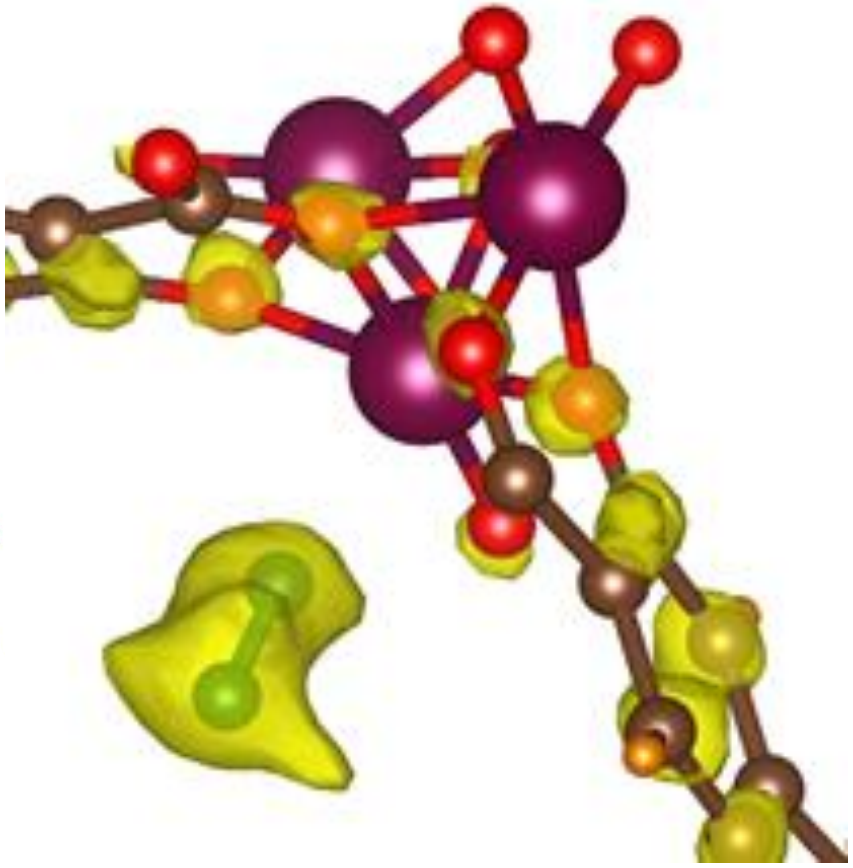

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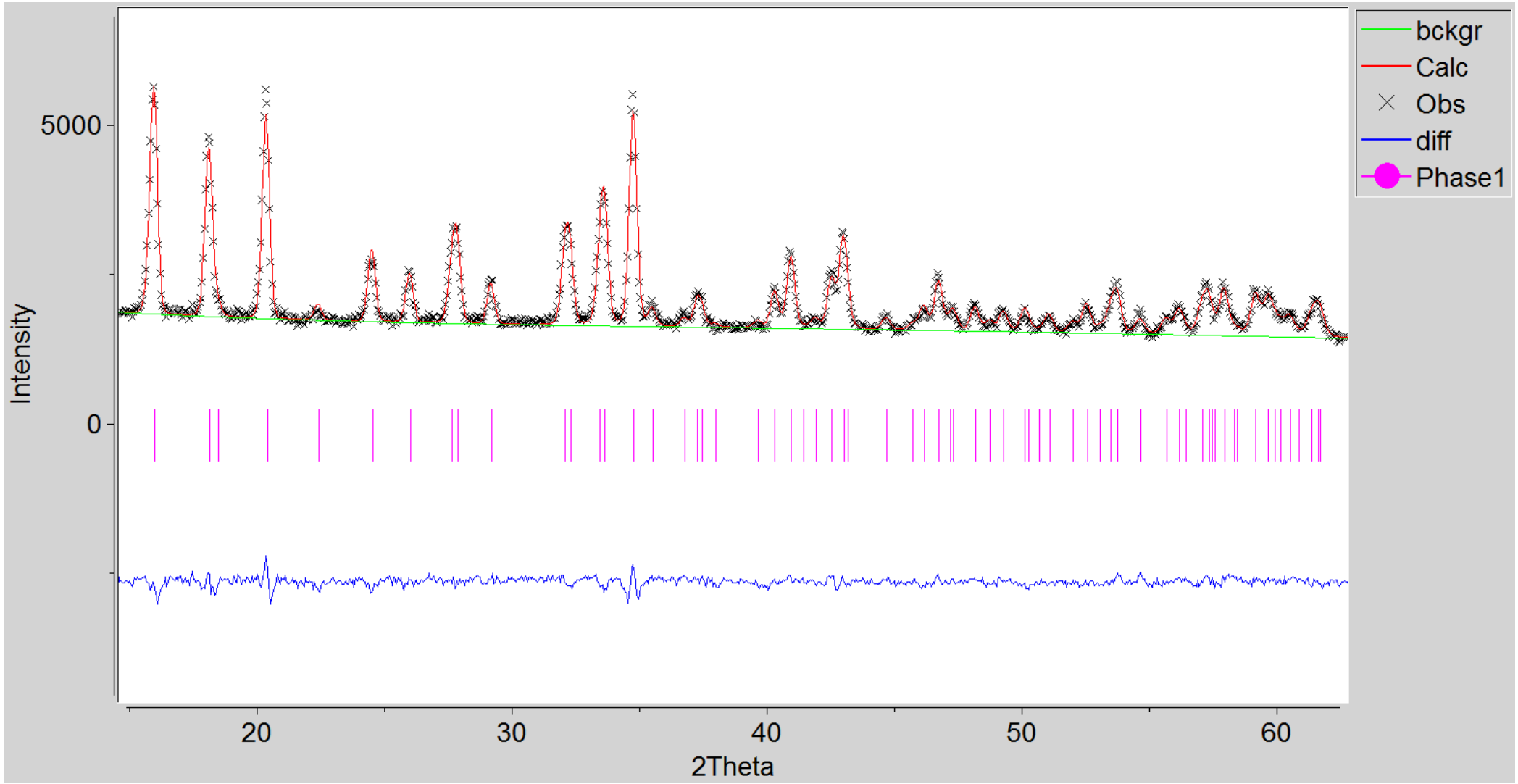
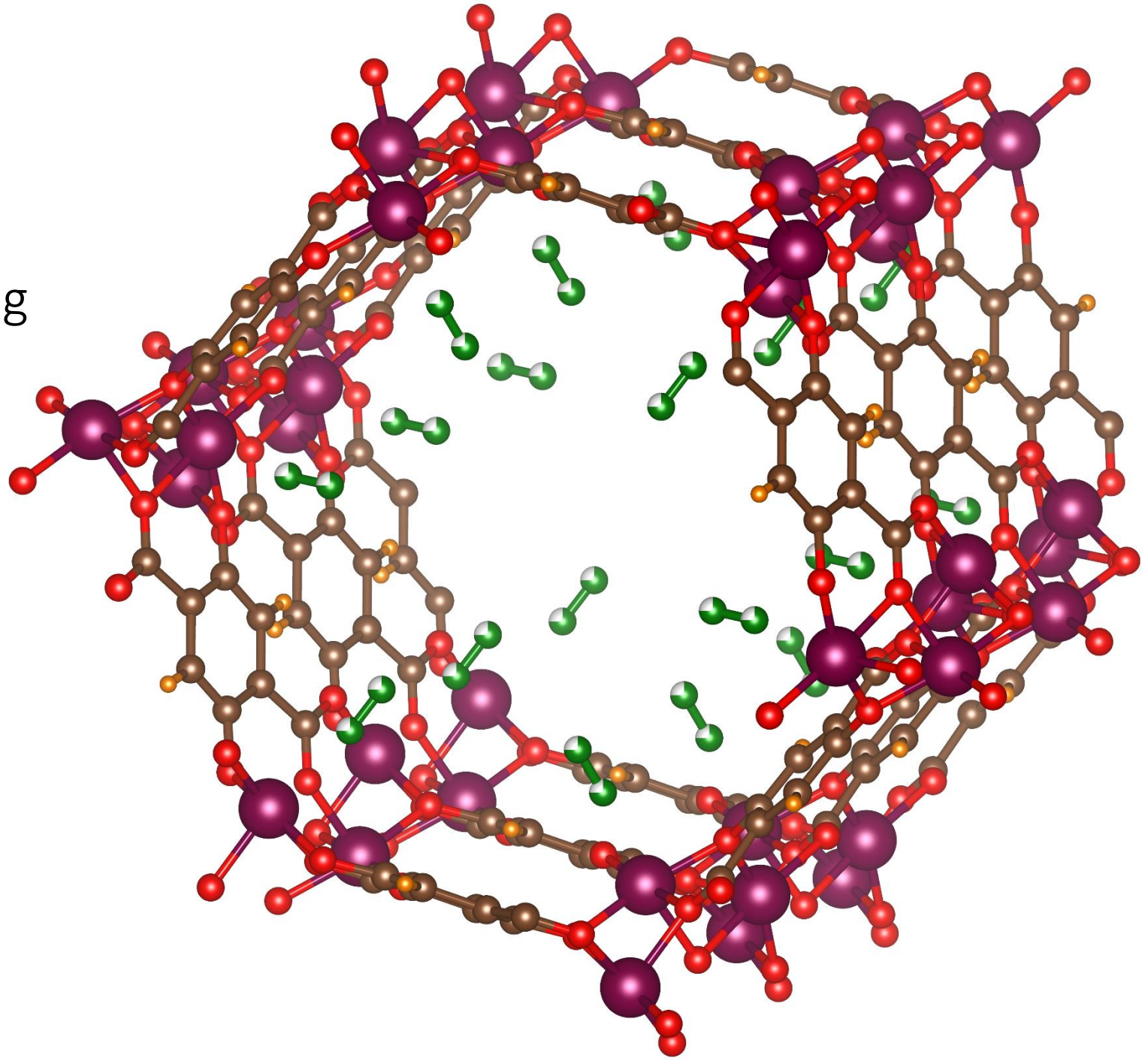


Our Project

- Extensive experience using this method on single-component adsorption, but…
- Can we extend this to mixtures to learn more about selectivity in these materials?



MOF-74 Synthesis

$$M(NO_3)_2 \bullet 6H_2O + H_4dobdc \xrightarrow[100°C,\ DMF]{} M_2dobdc \bullet xDMF$$ synthesis

$$M_2dobdc \bullet xDMF \underset{60°C,\ MeOH}{\longleftrightarrow} M_2dobdc \bullet xMeOH$$ solvent exchange

$$M_2dobdc \bullet xMeOH \underset{180°C,\ vacuum}{\longleftrightarrow} M_2dobdc$$ activation

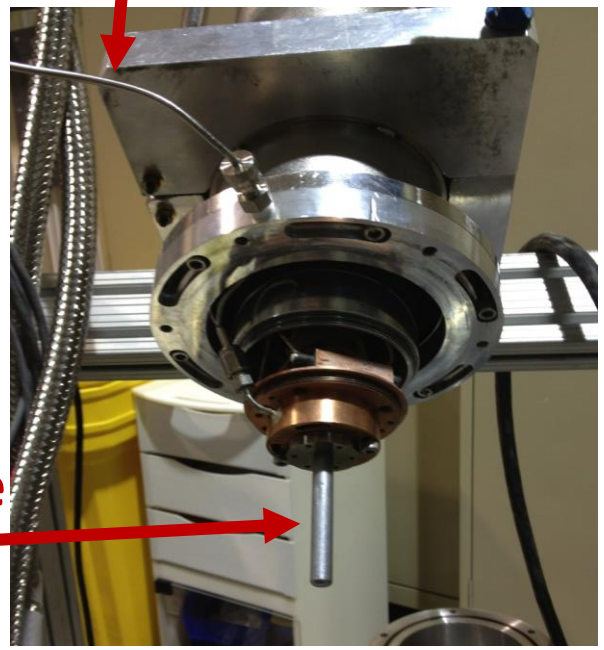
$$M = Ni, Mg$$

Preparing the sample for data collection

Crystalline, powder product

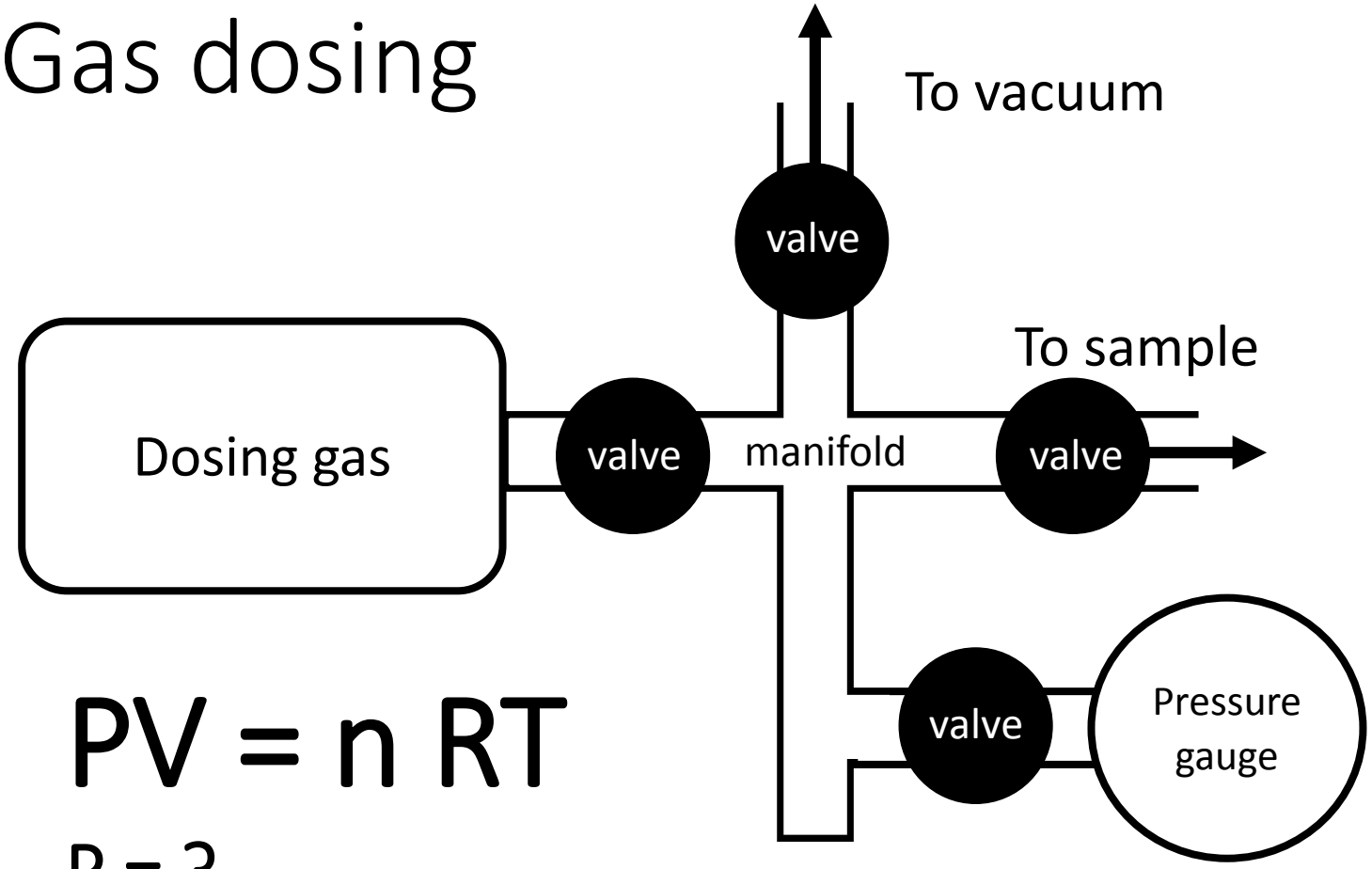
Gas line

Sample can



CCR

Gas dosing



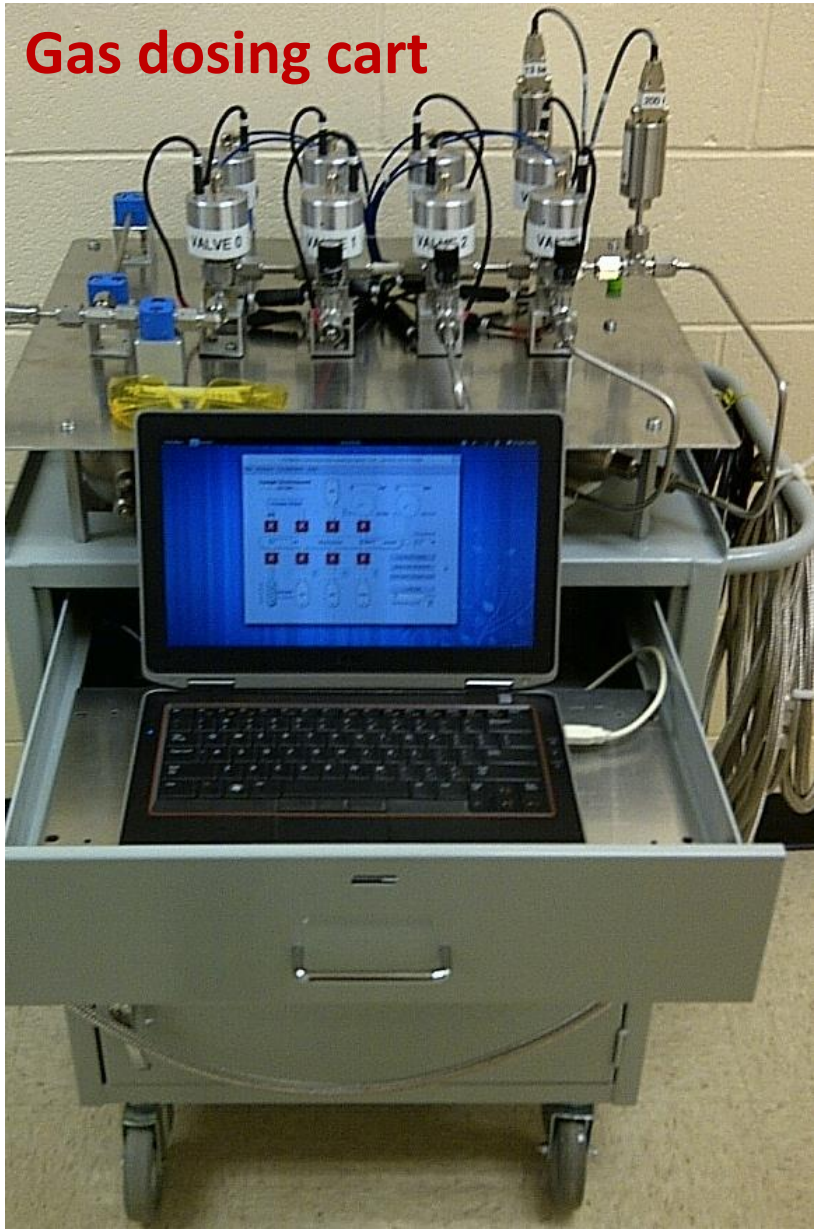
$$PV = n\,RT$$

P = ?

V = known volume of manifold

n = e.g. 1 gas molecule: metal site

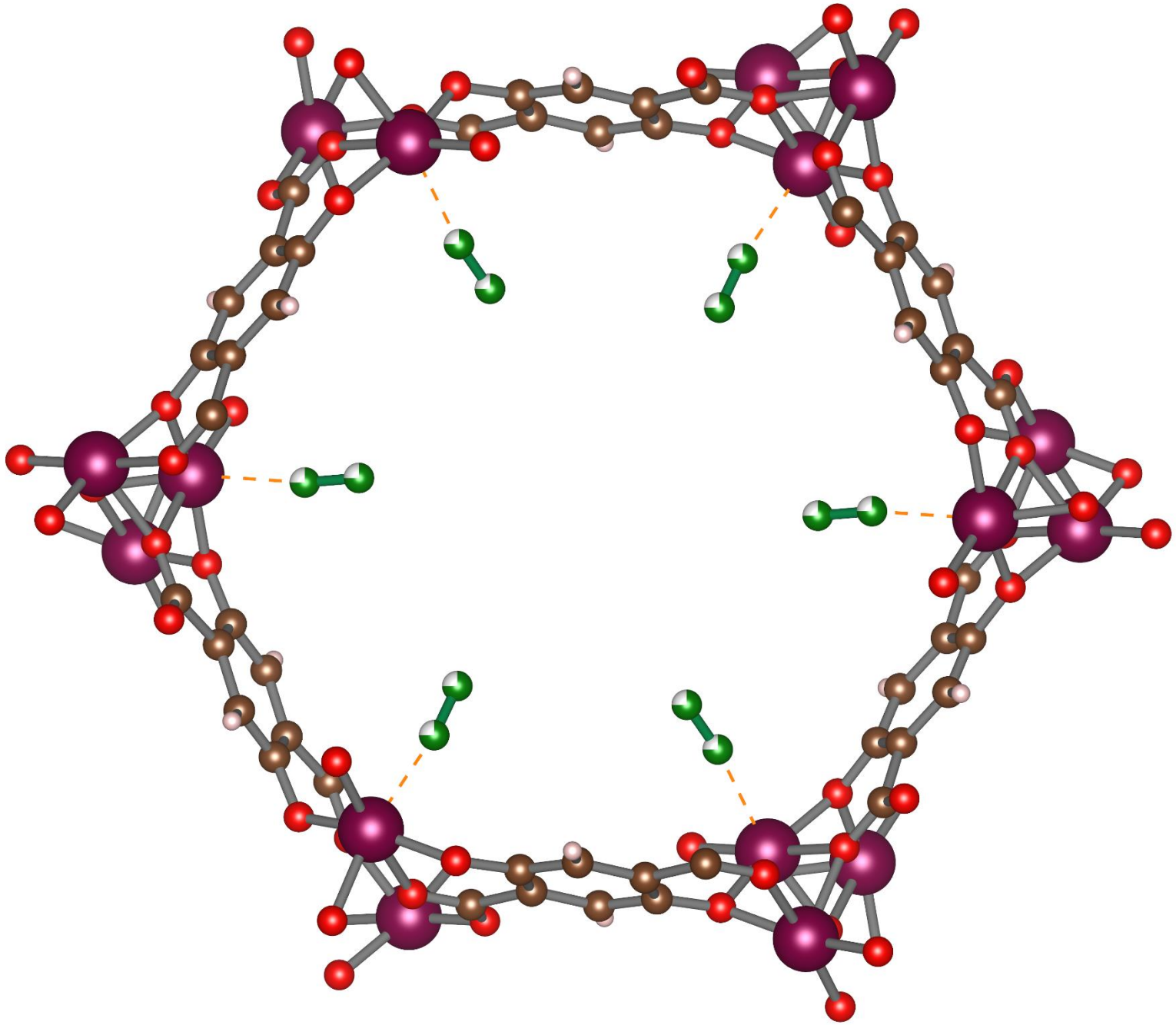
RT = constants



Nitrogen

Dosing Level:
0.75 N_2 : Mg site

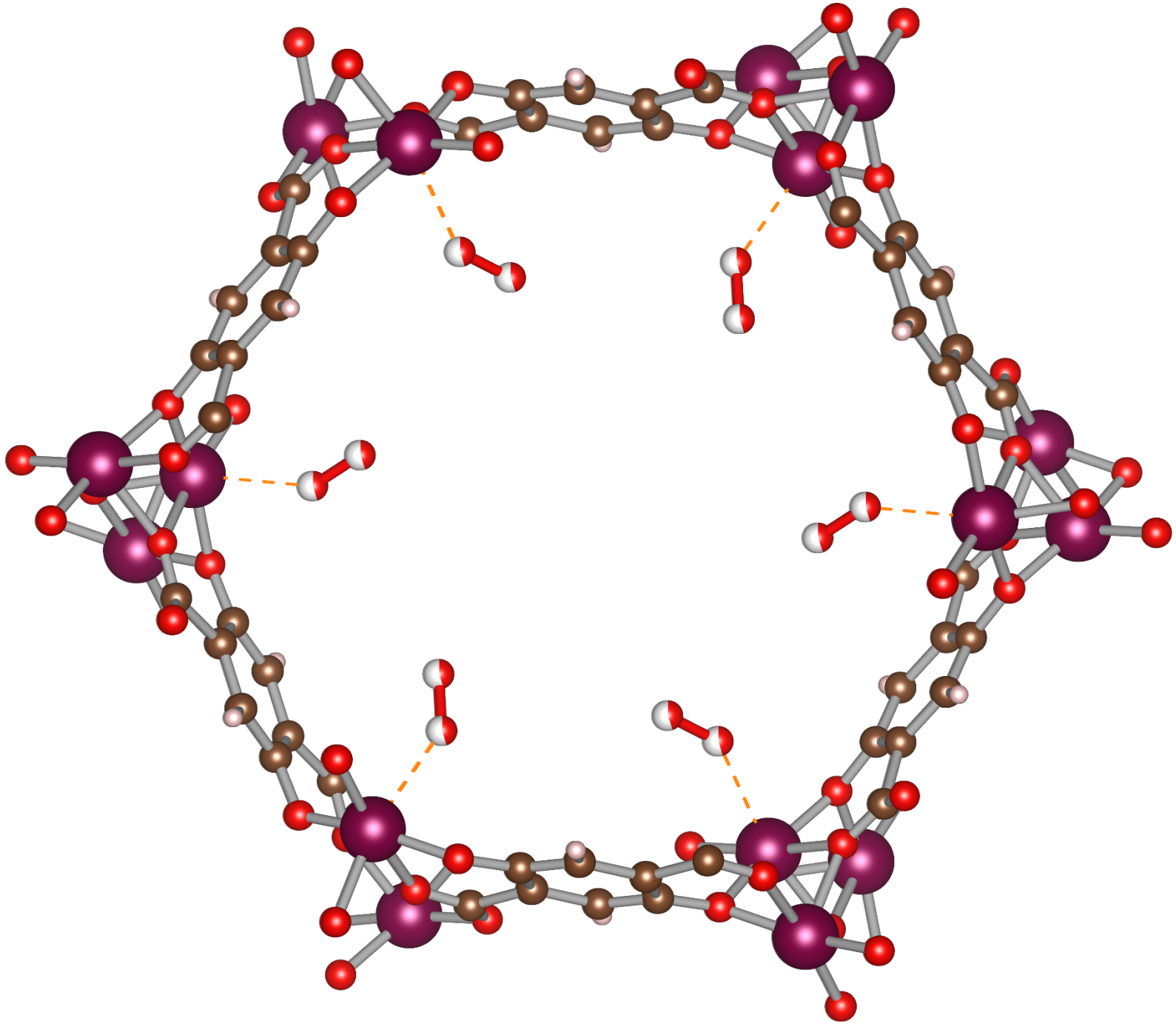
Refined occupancy:
0.7505



Oxygen

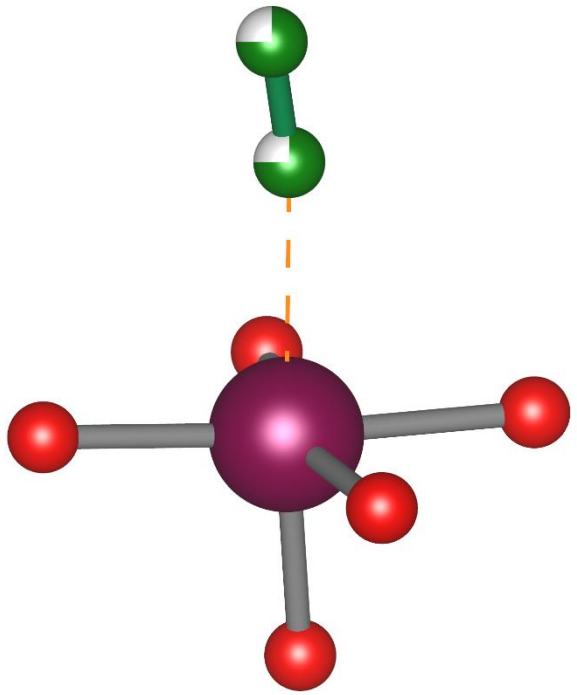
Dosing Level:
0.75 O_2 : Mg site

Refined occupancy:
0.7718



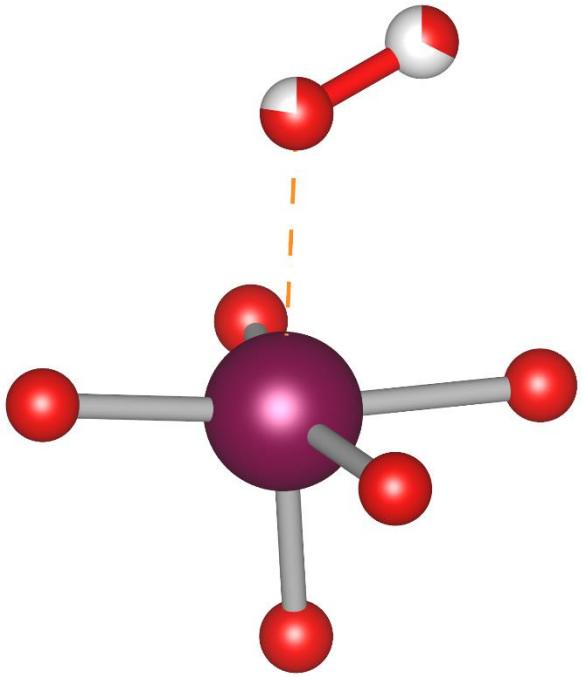
Can we find both molecules if dosed with a mixture of the two?

N_2



+

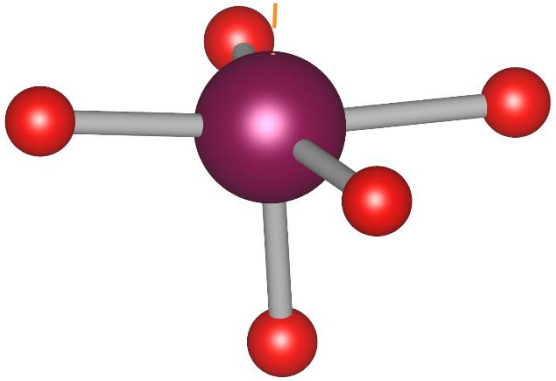
O_2



=

79%N_2/ 21% O_2 mixture (to simulate air)

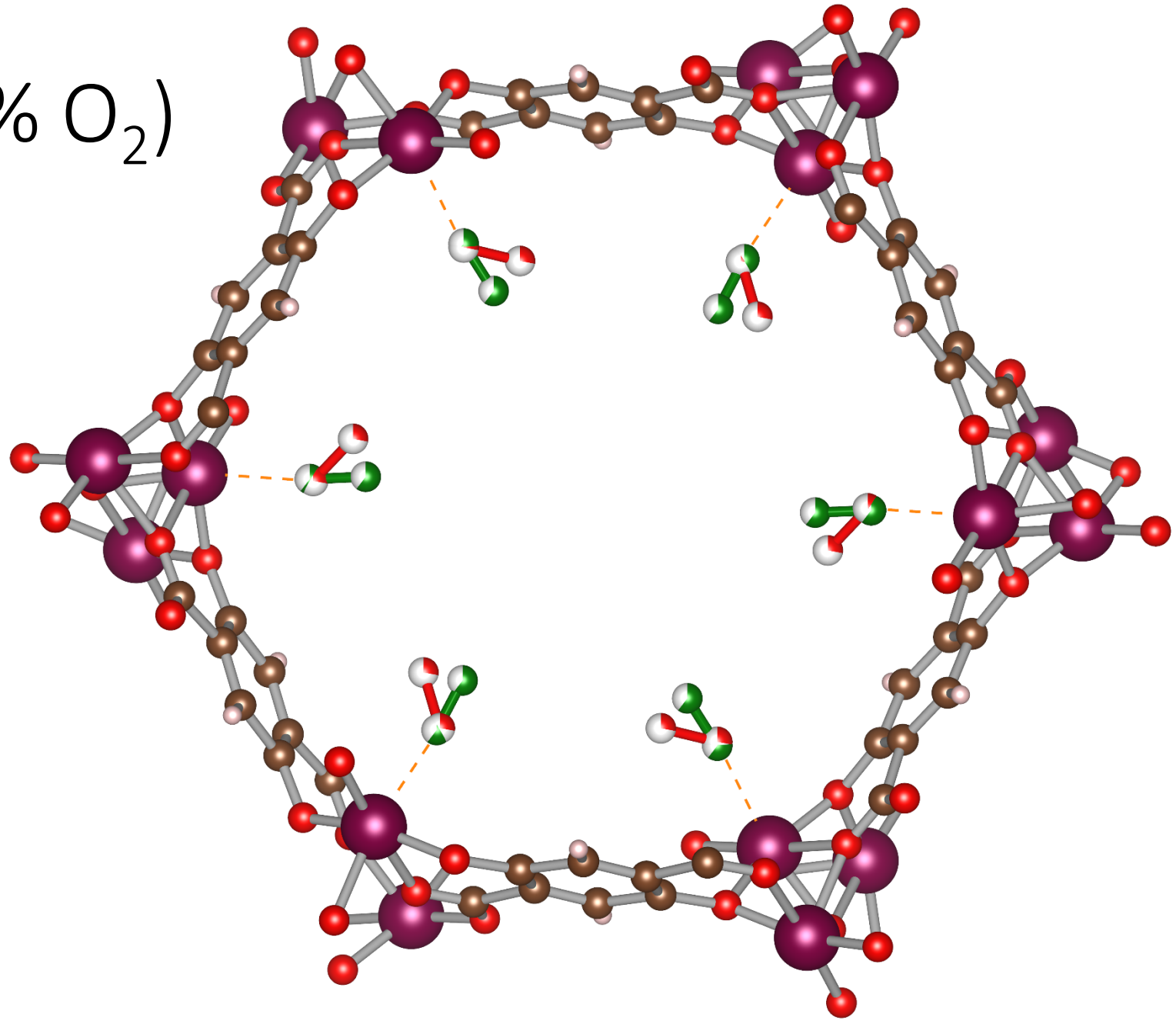
N_2 and O_2?



Mixture (79% N_2/21% O_2)

Dosing Level:
1 molecule: Mg site
Effectively 0.79 N_2:Mg
0.21 O_2:Mg

Refined occupancy:
N_2 0.6026
O_2 0.2773
(occupancy of N_2 at a secondary site is 0.1975)
Total: 1.0774



Mixture experiments using Ni-MOF-74…

- Objective—Directly observe selectivity for O_2 over N_2 indicated by higher occupancies of O_2 at the metal site

- Higher dosing—3 molecules: Ni site
- Range of temperatures—90K to 300K

Data analysis in progress

Conclusions

- Determined N_2 and O_2 binding orientations at metal site
- Were able to refine dosings of mixture with both molecules at the same adsorption site

- Future work
  - Continue refinement work on Ni-mixture data
  - Extend technique to other mixtures and MOFs

Acknowledgements

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