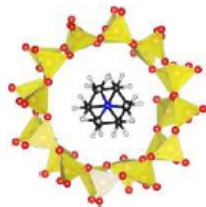


Locating organic guest molecules in zeolite channels by advanced crystallographic analysis

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Colloque Zéolithes Host-Guest

Montpellier 17 sept. 2024

(Amphithéâtre Balard, Campus CNRS Montpellier)

With: Marco Fabbiani, Shadi Al-Nahari, Laura Piveteau, Eddy Dib, Vasyl Veremeienko, Arnold Gaje, Dan G. Dumitrescu, Philippe Gaveau, Tzonka Mineva, Dominique Massiot, Julien Haines, and Bruno Alonso

Chem. Mater. 2022, 34, 366–387

Do not forget to stay for:

- Tzonka Mineva (11h40):
"Organization at the atomic scale of interfaces between organic structure directing agents and silicate frameworks"
- Bruno Alonso (17h20)
"Geometrical order/disorder in Host-Guest Zeolites through solid-state NMR approaches"

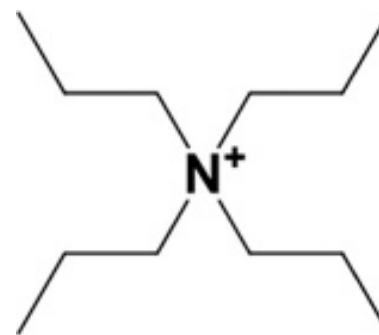
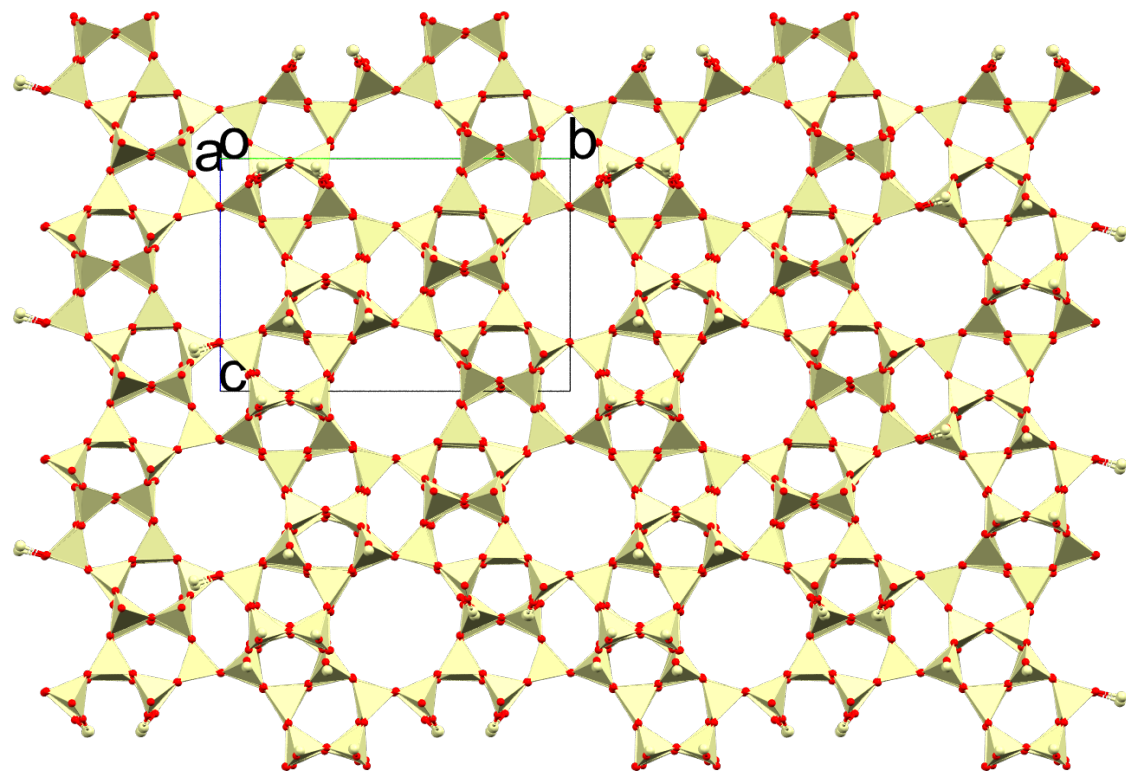
How does disorder (of different nature) affect the properties of a zeolite?

Synthesis of zeolites and OSDA's

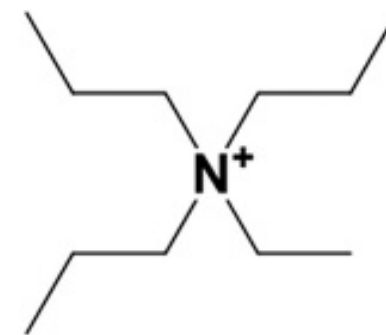
- OSDA: Organic Structure Directing Agent
- Different effects during synthesis:
 - Charge balancing
 - Space filling
 - Lock-and-key relationship between guest and host

Question:
where and how is the OSDA located in the pores of the zeolite?

ZSM-5 and OSDA's



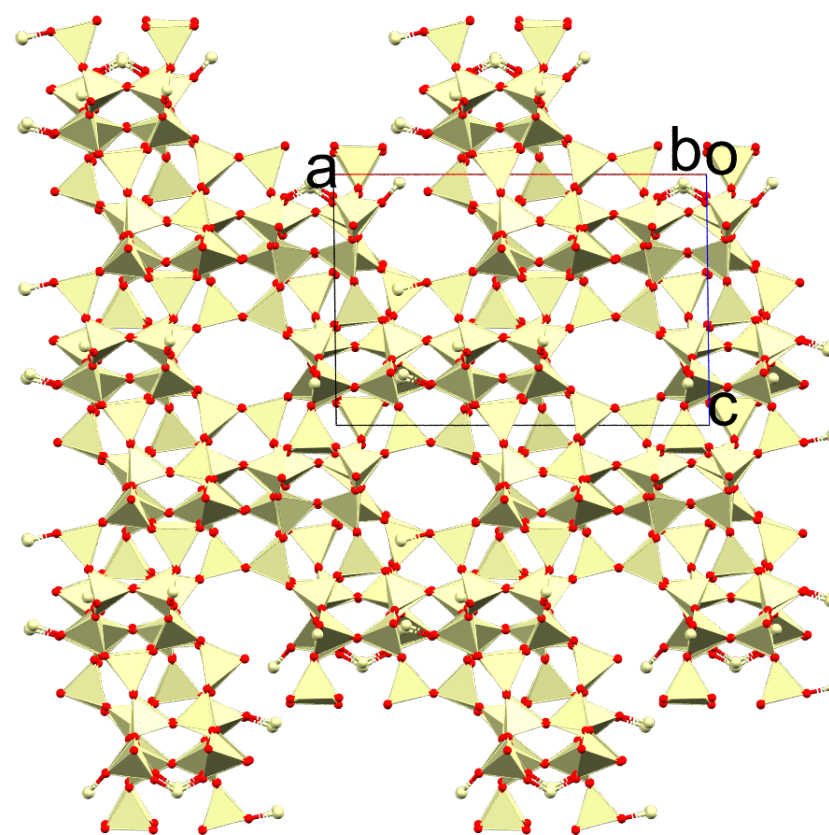
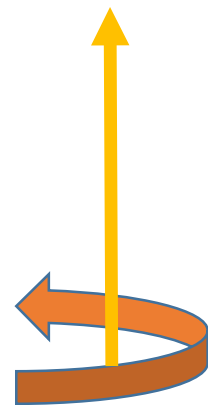
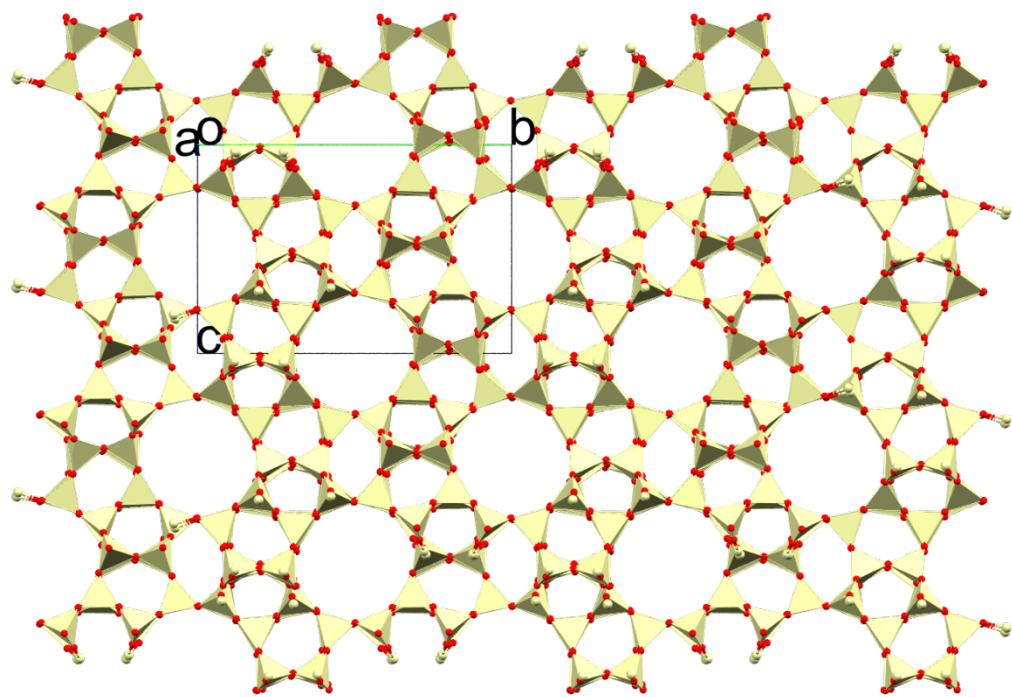
TPA



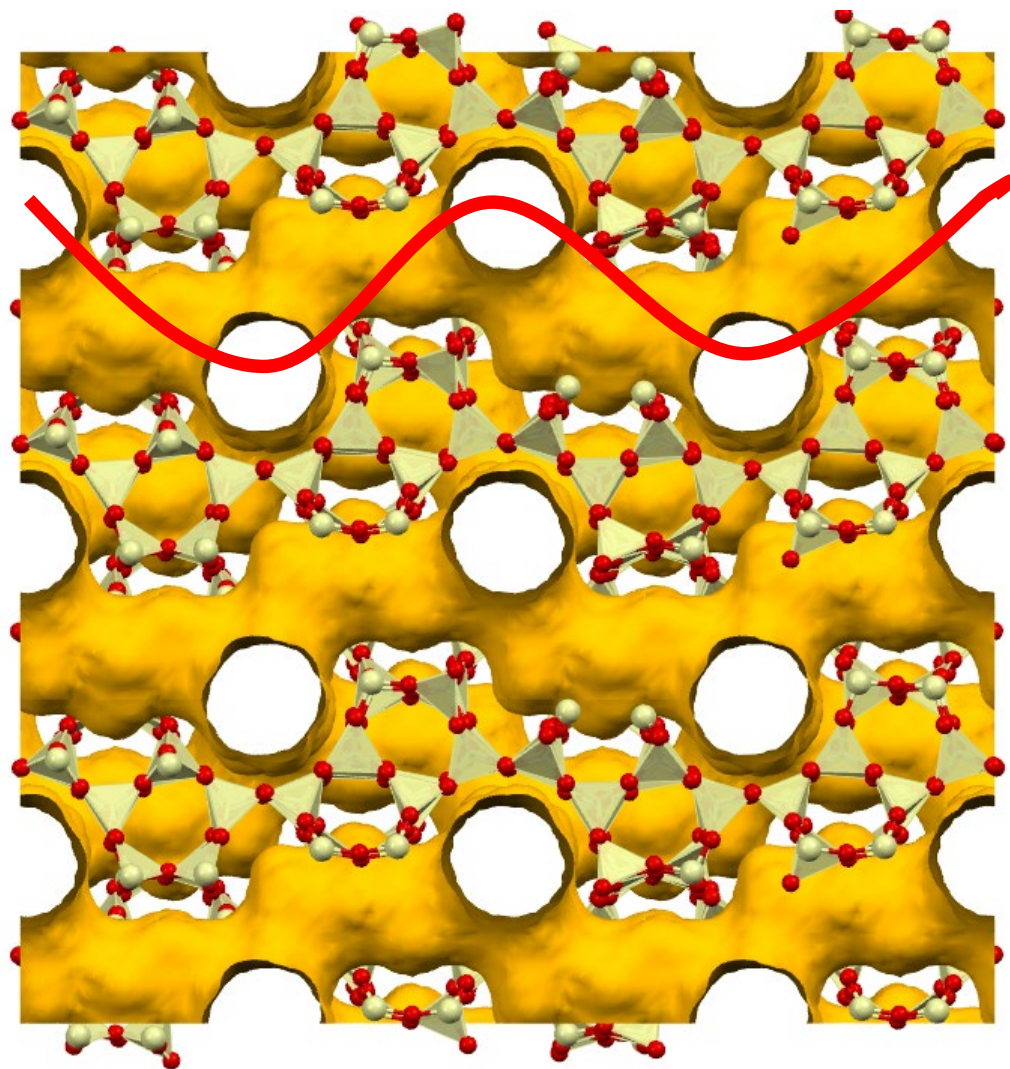
TPEA

OSDA: Organic Structure-Directing Agent

The channels in ZSM-5

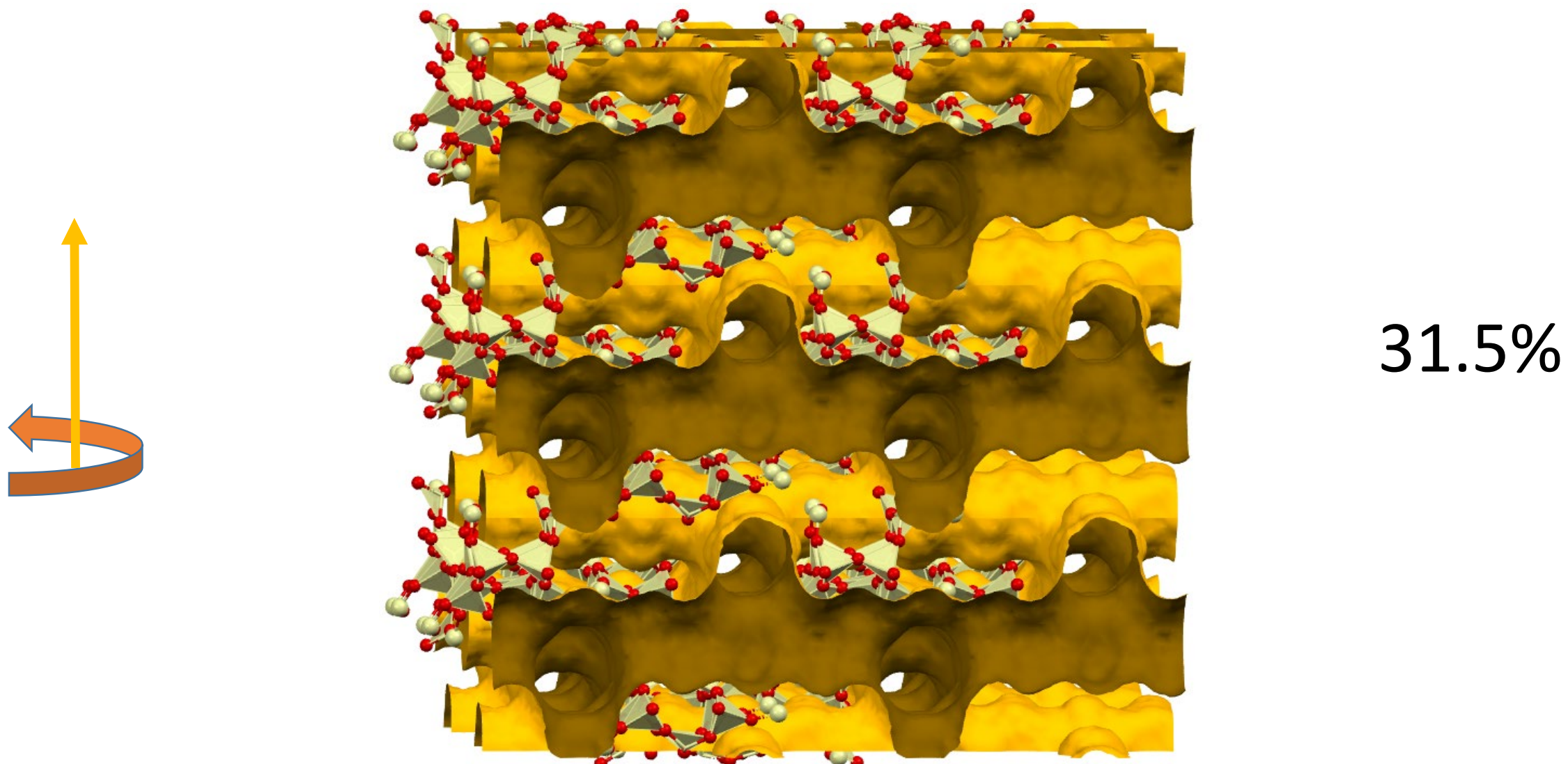


Solvent accessible volumes in ZSM-5

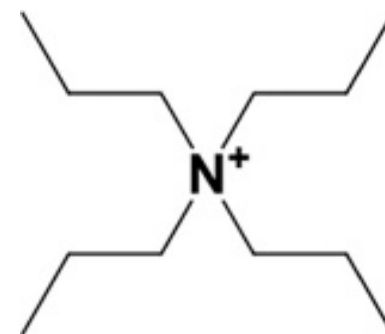
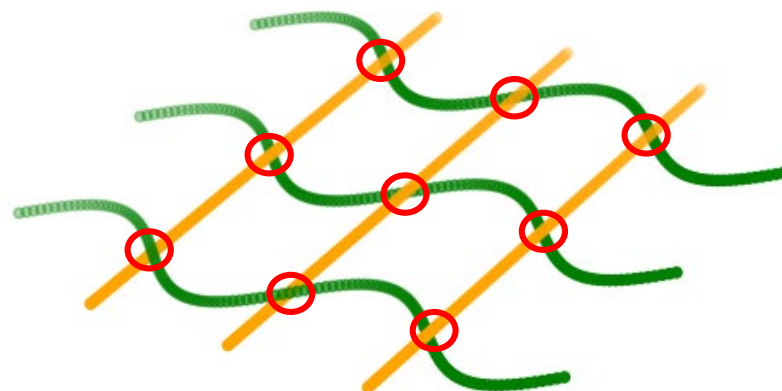


31.5%

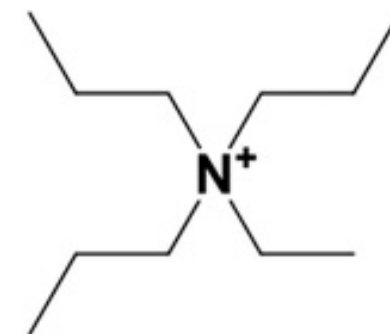
Solvent accessible volumes in ZSM-5



Straight and sinusoidal channels in ZSM-5



TPA



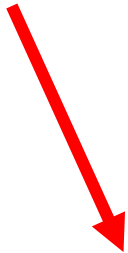
TPEA

X-ray diffraction: how to get the structural model

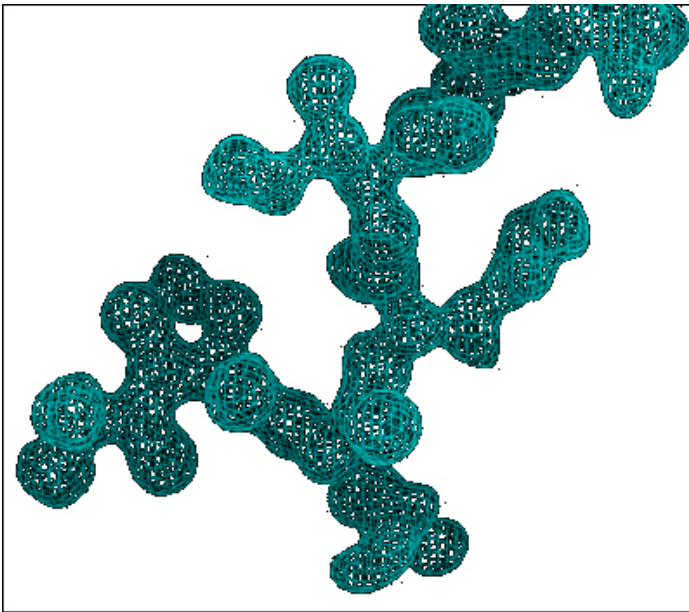
- What we want is to obtain the atomic positions in the unit cell
- X-rays interact with the electron clouds of the atoms
 - -> we determine an *electron density*
 - -> from this we build an *atomic model*
- We measure the intensities of the diffracted beam in different directions
- Mathematical relation exists between the intensities and the electronic density within the crystalline matter
- *Fourier transform*

X-ray diffraction: how to get the structural model

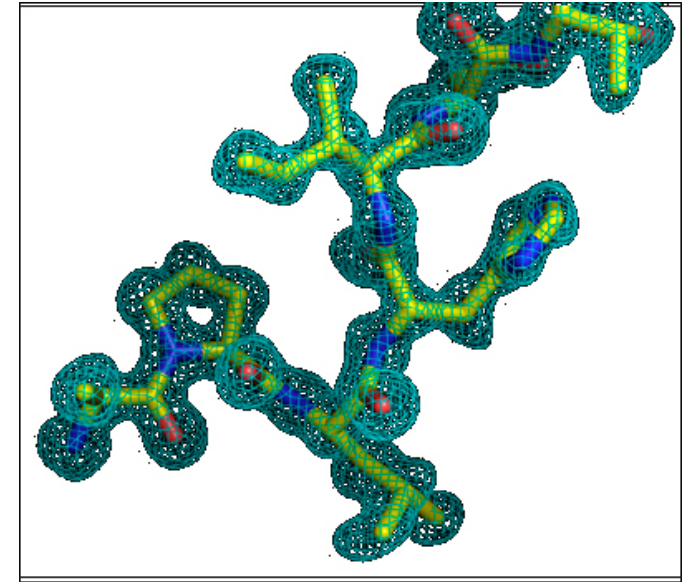
$$I_{obs}(hkl) \sim ||F_{obs}(hkl)|e^{2\pi i\varphi_{obs}(hkl)}|^2$$


$$\rho(x, y, z) = \frac{1}{V} \sum_{hkl=-\infty}^{\infty} |F_{obs}(hkl)| e^{-2\pi i(hx+ky+lz-\varphi_{obs}(hkl))}$$

X-ray diffraction: how to get the structural model



Model building



X-ray diffraction: how to know that the model is correct

Model (positions x, y, z) ->

$$|F_{calc}(hkl)|e^{\varphi_{calc}(hkl)} = V \sum_{xyz=-\infty}^{\infty} \rho(x, y, z)e^{2\pi i(hx+ky+lz)}$$

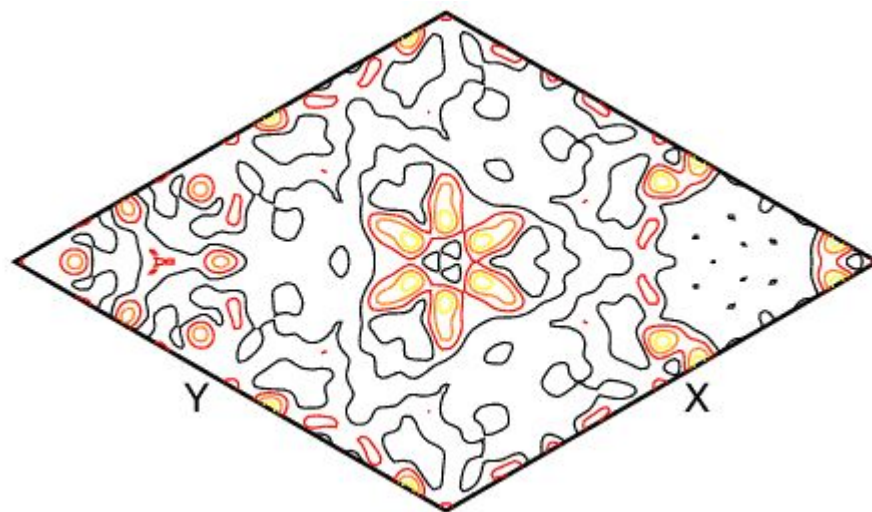
R should be as small as possible

$$R = \frac{\sum ||F_{obs}| - |F_{calc}||}{\sum |F_{obs}(hkl)|}$$

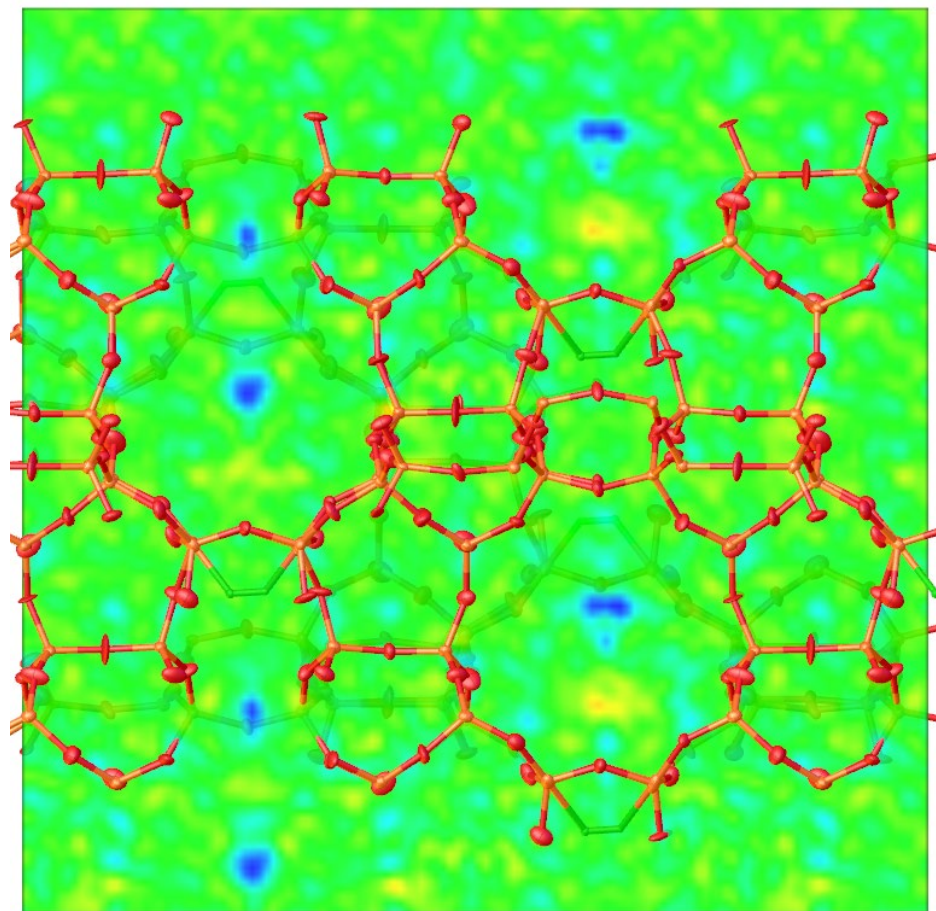
X-ray diffraction: how to find tiny details in the structure

The difference Fourier map:

$$\Delta\rho(x, y, z) = \frac{1}{V} \sum_{hkl=-\infty}^{\infty} [|F_{obs}(hkl)| - |F_{calc}(hkl)|] e^{-2\pi i(hx+ky+lz-\varphi_{calc}(hkl))}$$

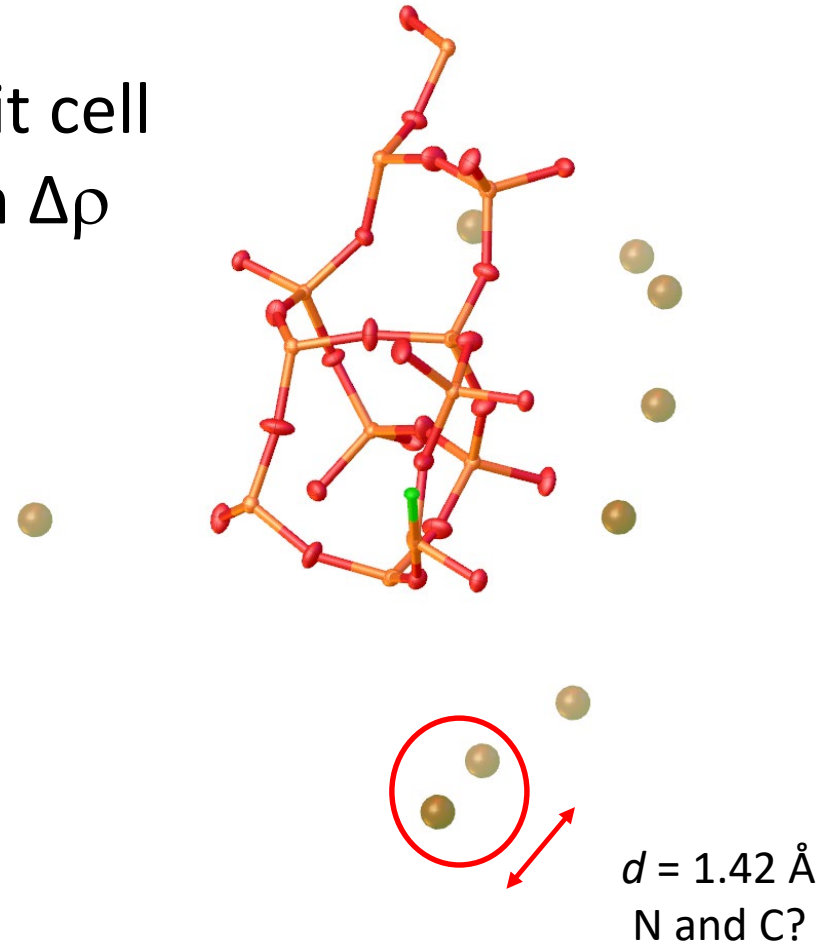


Finding TPA and TPEA in ZSM-5

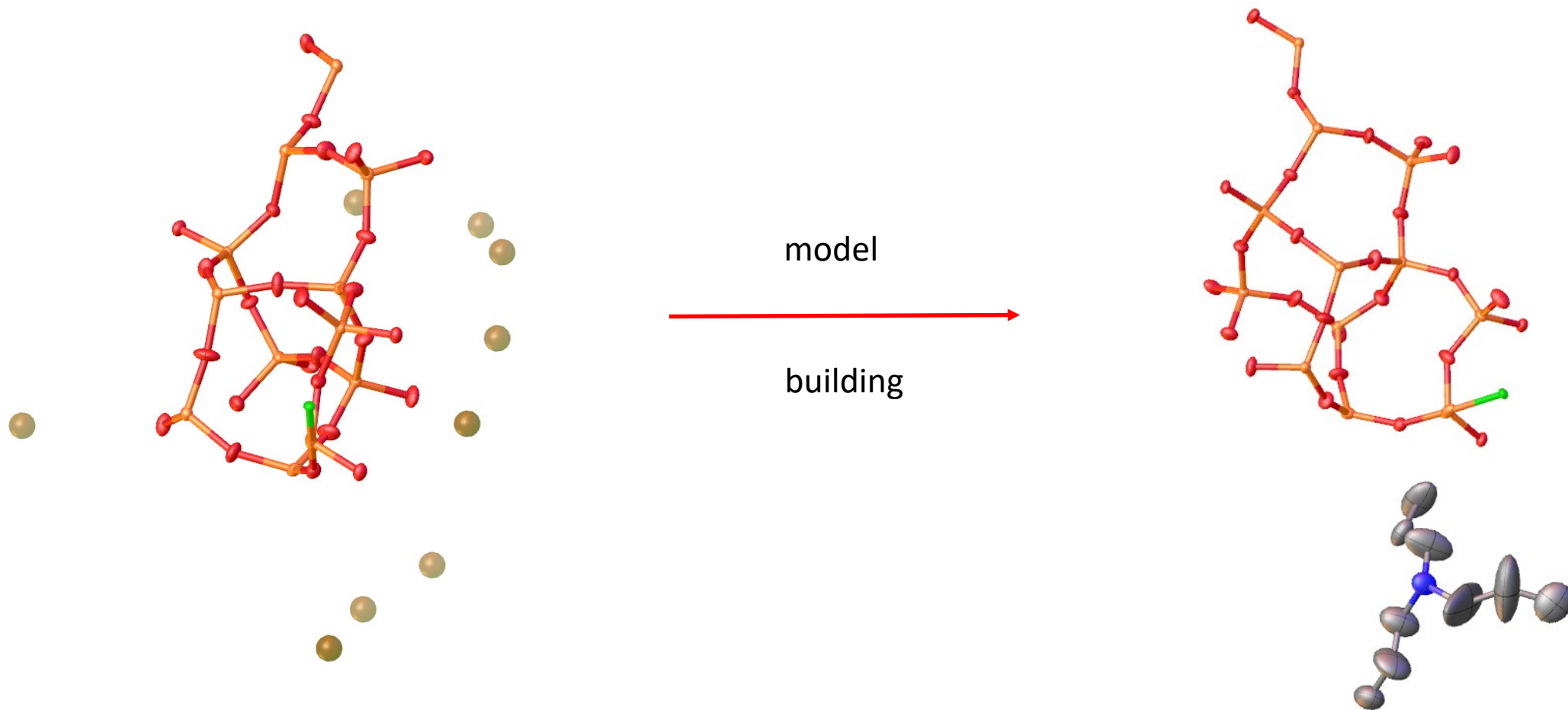


Finding TPA and TPEA in ZSM-5

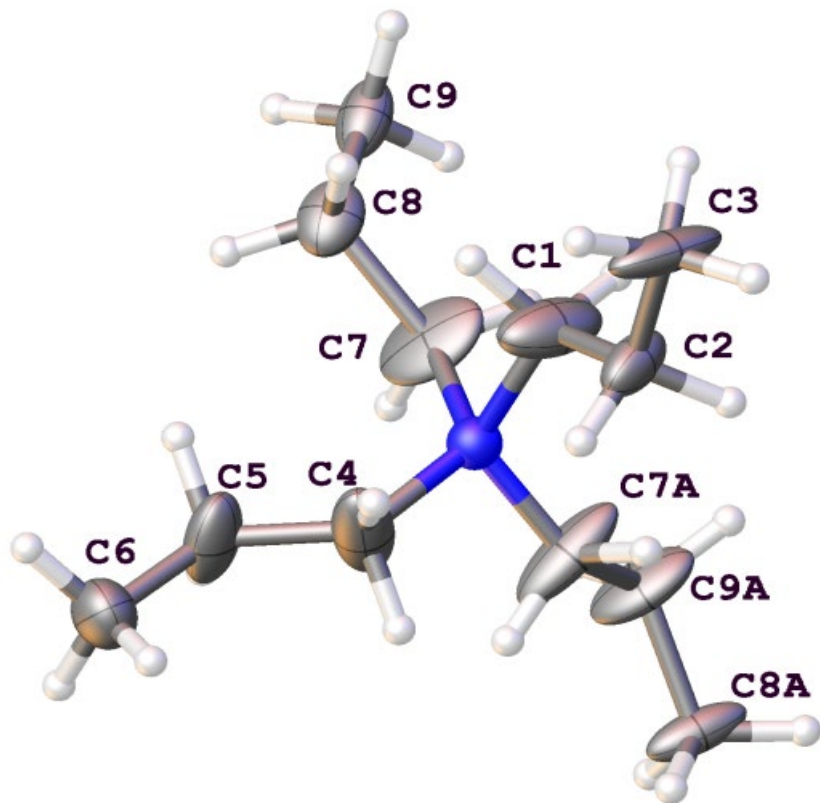
- Use only symmetry-independent part of unit cell
- Start model building with strongest peaks in $\Delta\rho$



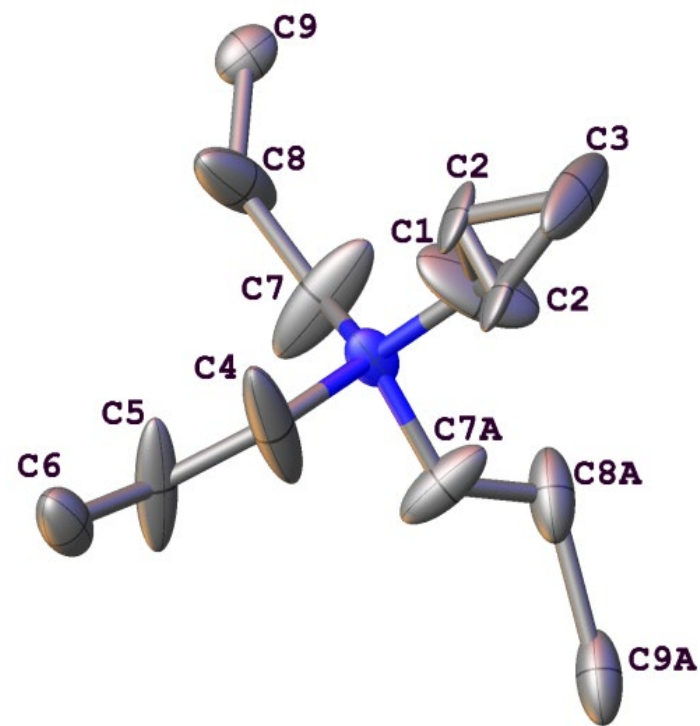
Finding TPA and TPEA in ZSM-5



Finding TPA and TPEA in ZSM-5



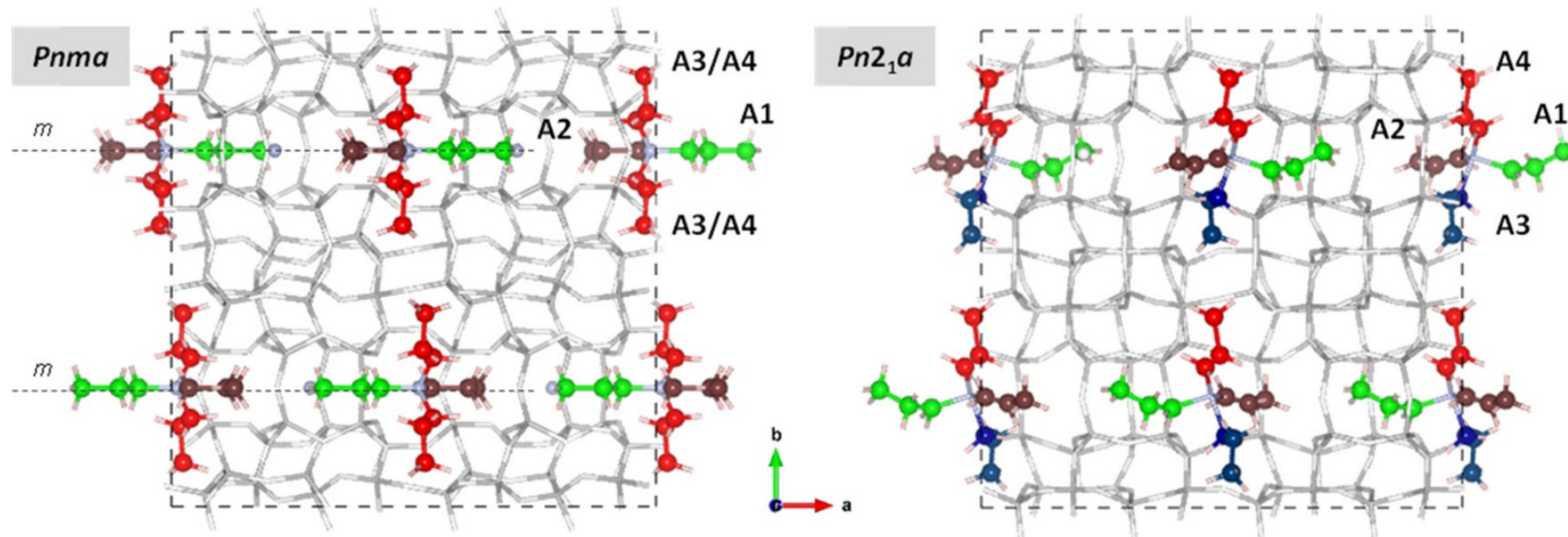
TPA



TPEA

Pitfalls

- Complicated twinning
 - TPA-ZSM-5 is monoclinic at low temperatures -> double twin
- Pseudo mirror-plane, difficult distinction between $Pnma$ and $Pn2_1a$
- Due to disorder no clear distinction between ethyl and propyl arm (TPEA)
 - Refinement of occupancies designates one arm to be the ethyl chain located in the straight channel



Conclusions

- Synchrotron (Elettra) X-ray data necessary to obtain these results; 3D electron diffraction will probably not give better results*
- Careful model building using successive difference Fourier maps remains the best choice (MEM techniques could be an alternative)
- Cross-validation with spectroscopic data, especially NMR, is absolutely necessary to obtain a full structural picture of zeolites and silicates containing OSDA's

*See for instance: Cho *et al.* – *Chem. Mater.* 2021, 33, 11, 4146–4153