PSI Center for Photon Science

CO-induced dynamic behaviour of supported Pd nanoparticles

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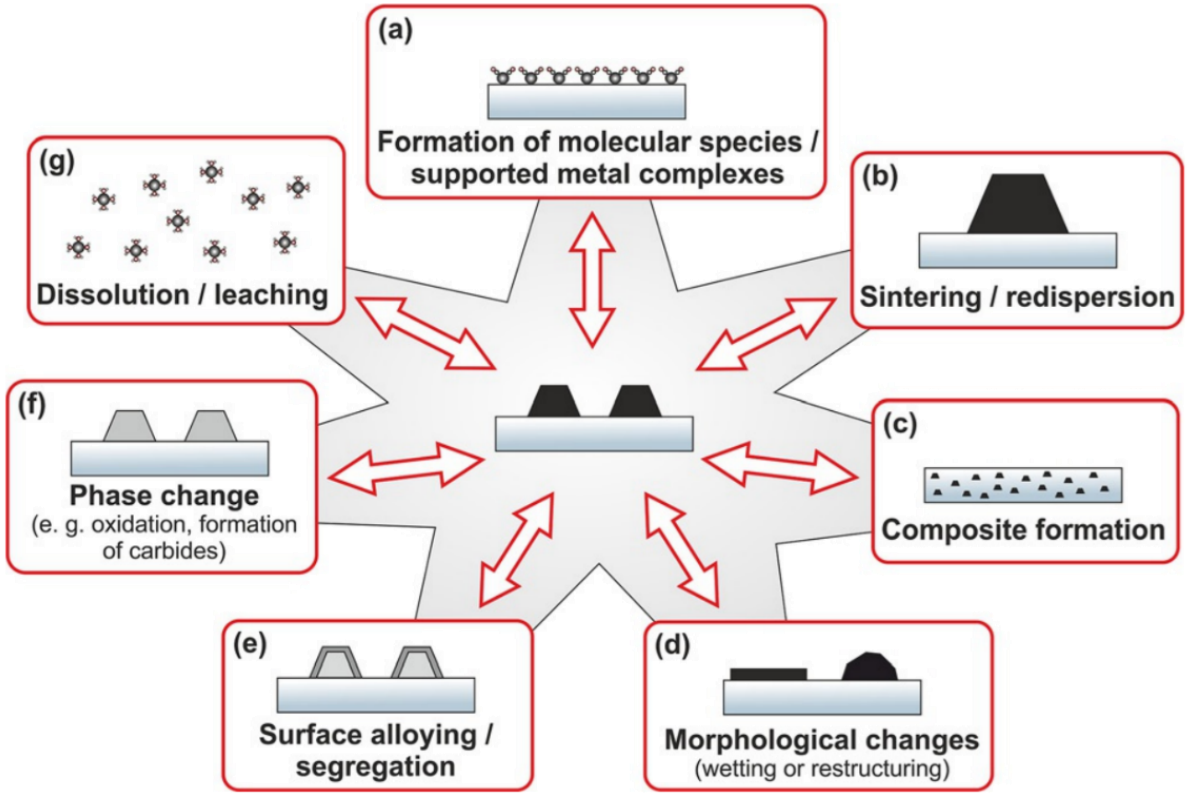
Grenoble, 15.01.2026

Introduction

The interaction between **Pd nanoparticles** and **CO** is of extensive importance in catalysis and materials science

- CO oxidation
- Synthesis of hydrocarbons
- Chemisorption methods

Many possible interactions!



Kalz K. F. et al., ChemCatChem. 2017, 9, 17 – 29

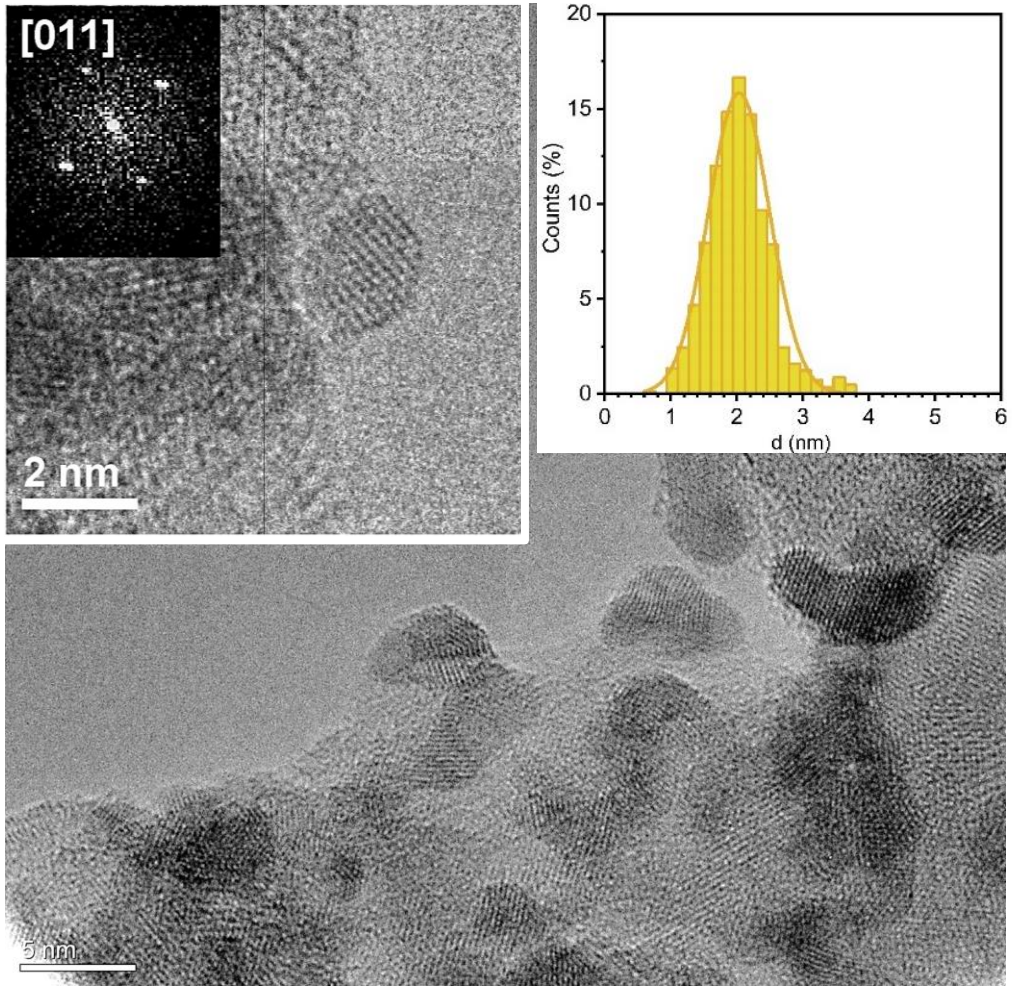
The catalyst: Pd/Al_2O_3

Synthesis

- 5 wt% Pd
- Mixed phase Al_2O_3
- Deposition-precipitation synthesis
- Precious metal recovered from industrial waste

Preliminary characterization

- Pd average size: **2.0 ± 0.5 nm** (HR-TEM)
- Dispersion: 36% (CO chemisorption)



Kinetics and dynamics of
CO adsorption on Pd nanoparticles

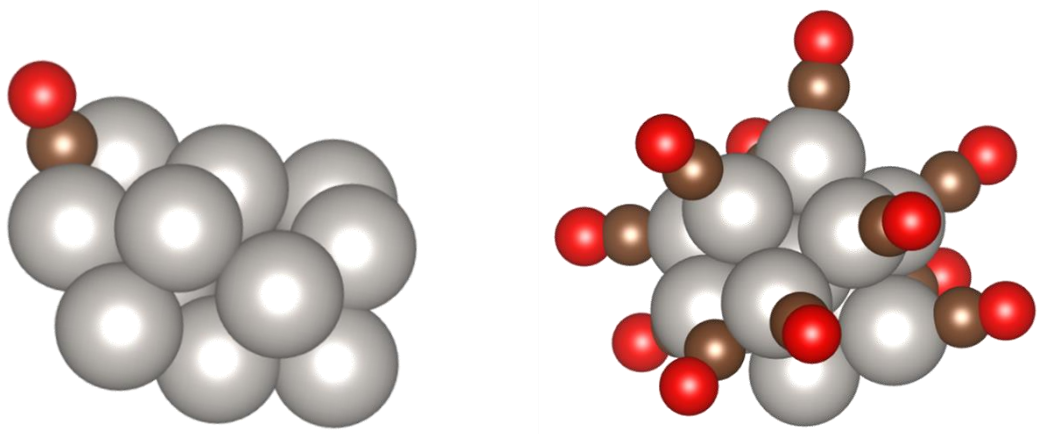
The challenges

Detect small NPs

Monitor their changes in reaction conditions

Evaluate their interaction with the support

Track surface phenomena



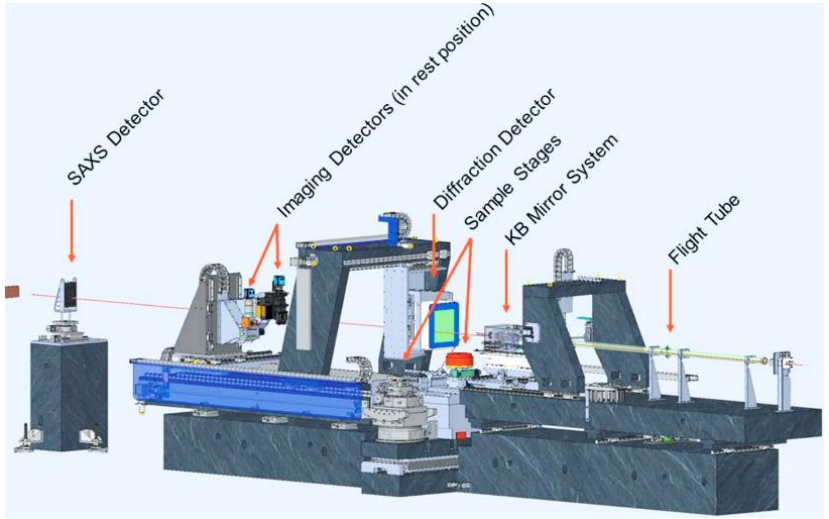
The approach

High energy beamline (ID15A)

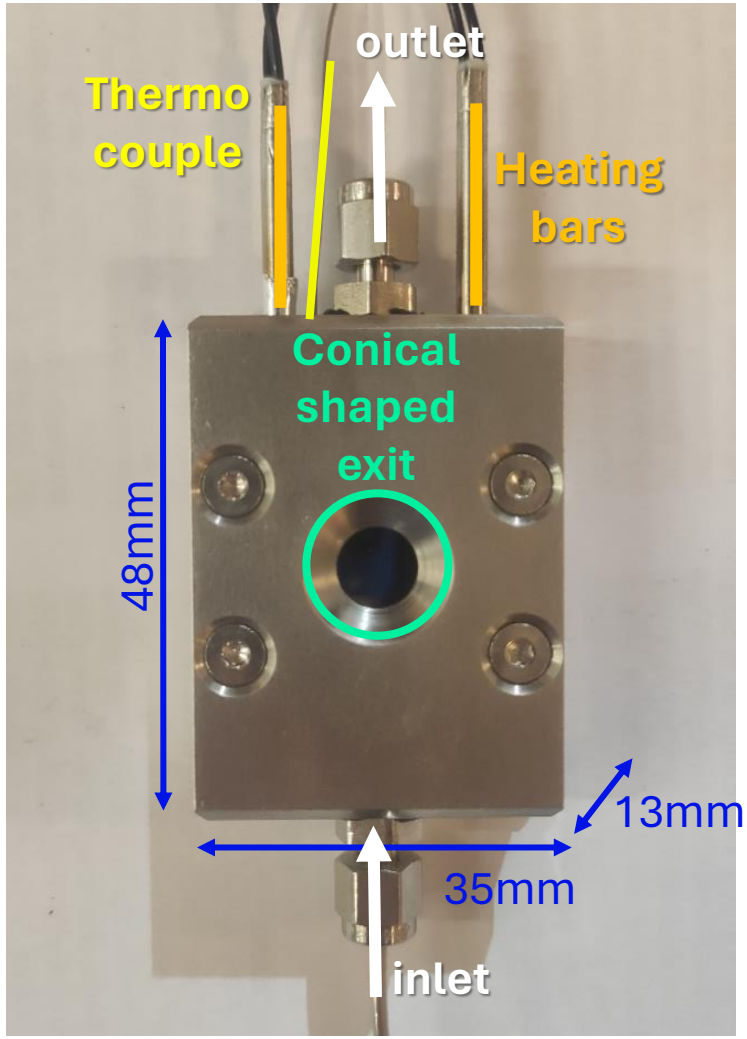
High time resolution (Pilatus3)

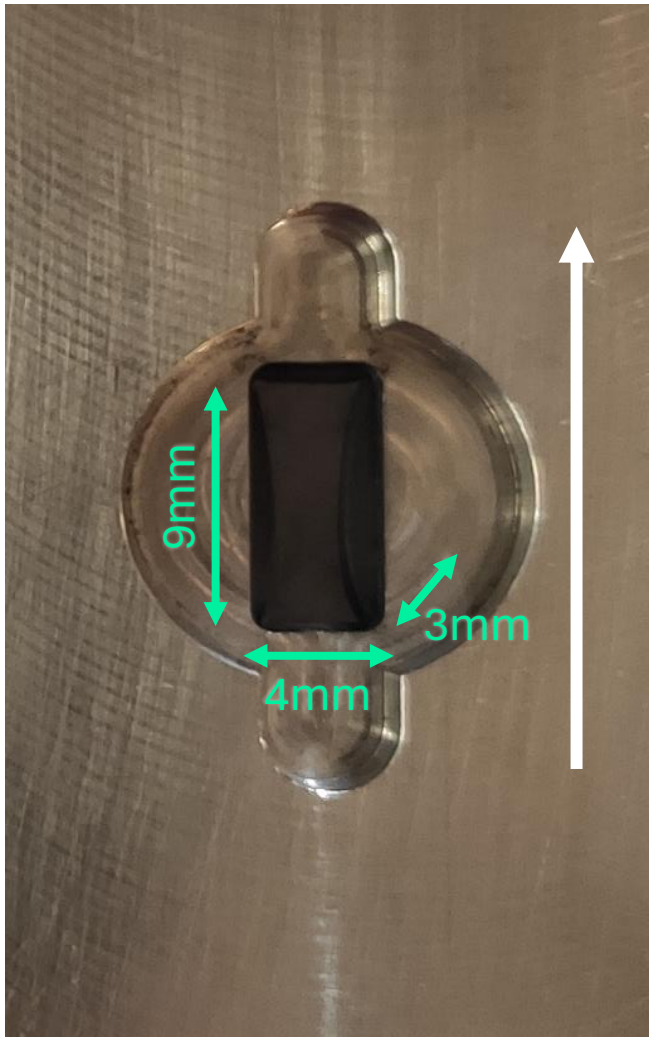
Design a PDF-optimized *operando* cell

Combine Modulated Excitation and model-free analysis

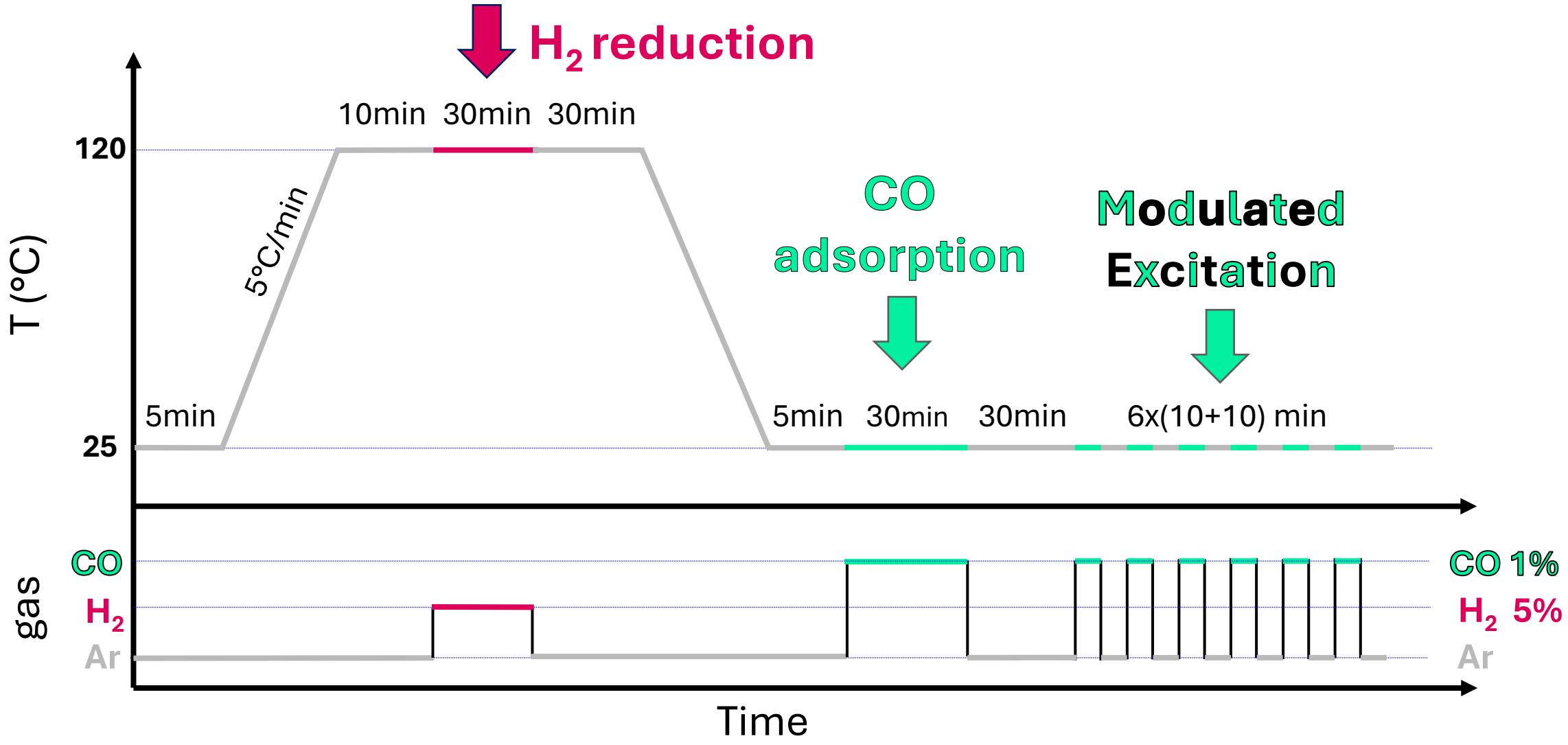


A cell for *operando* liquid and gas phase measurements

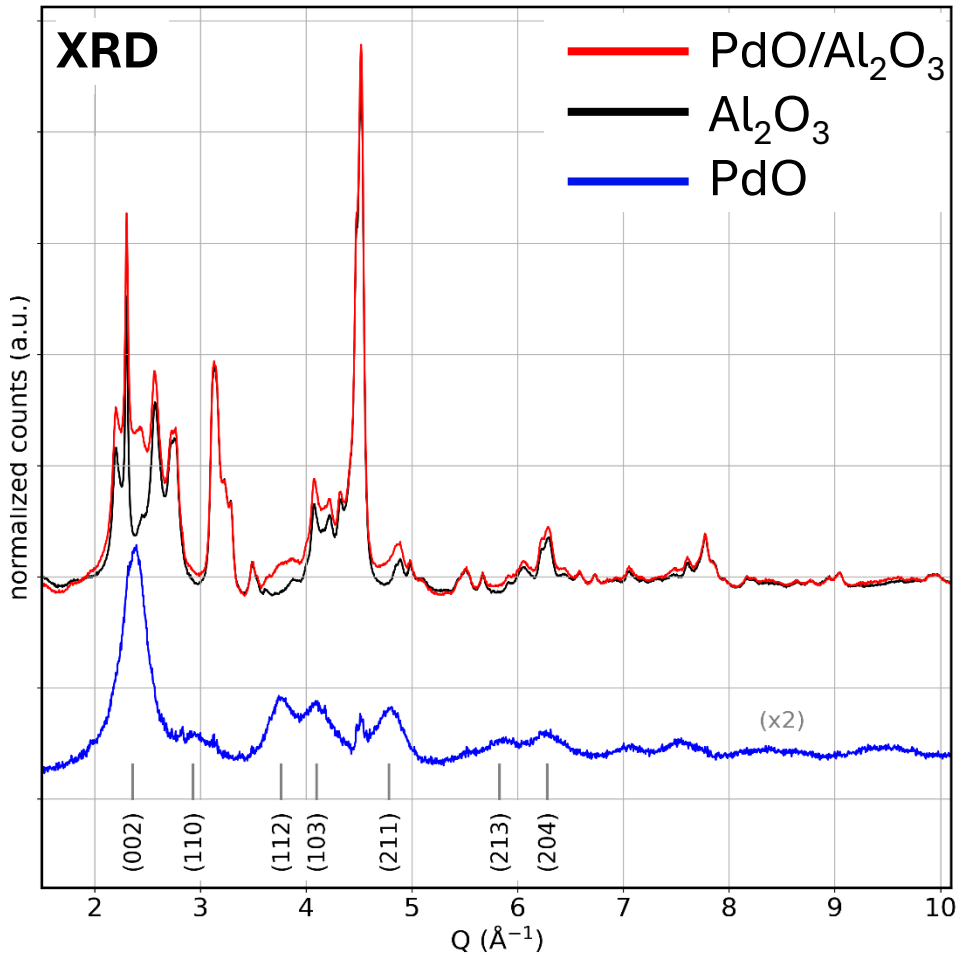


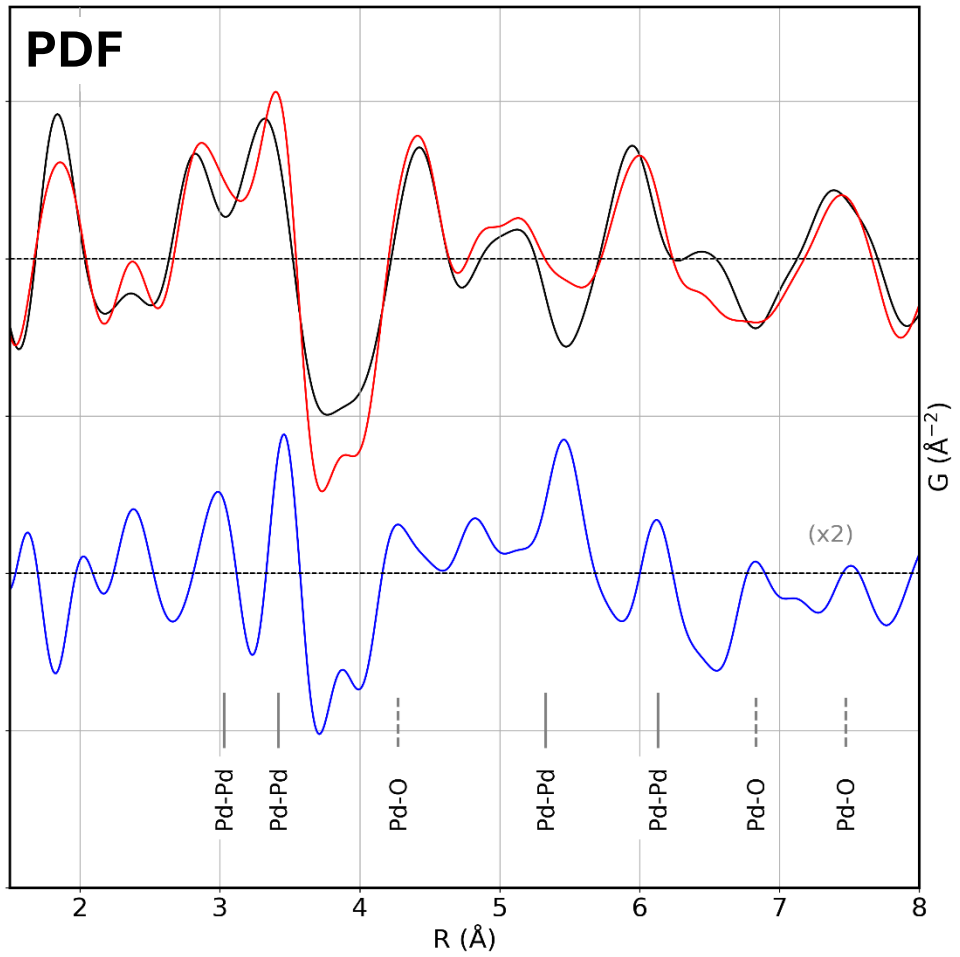


Experimental protocol



Starting state





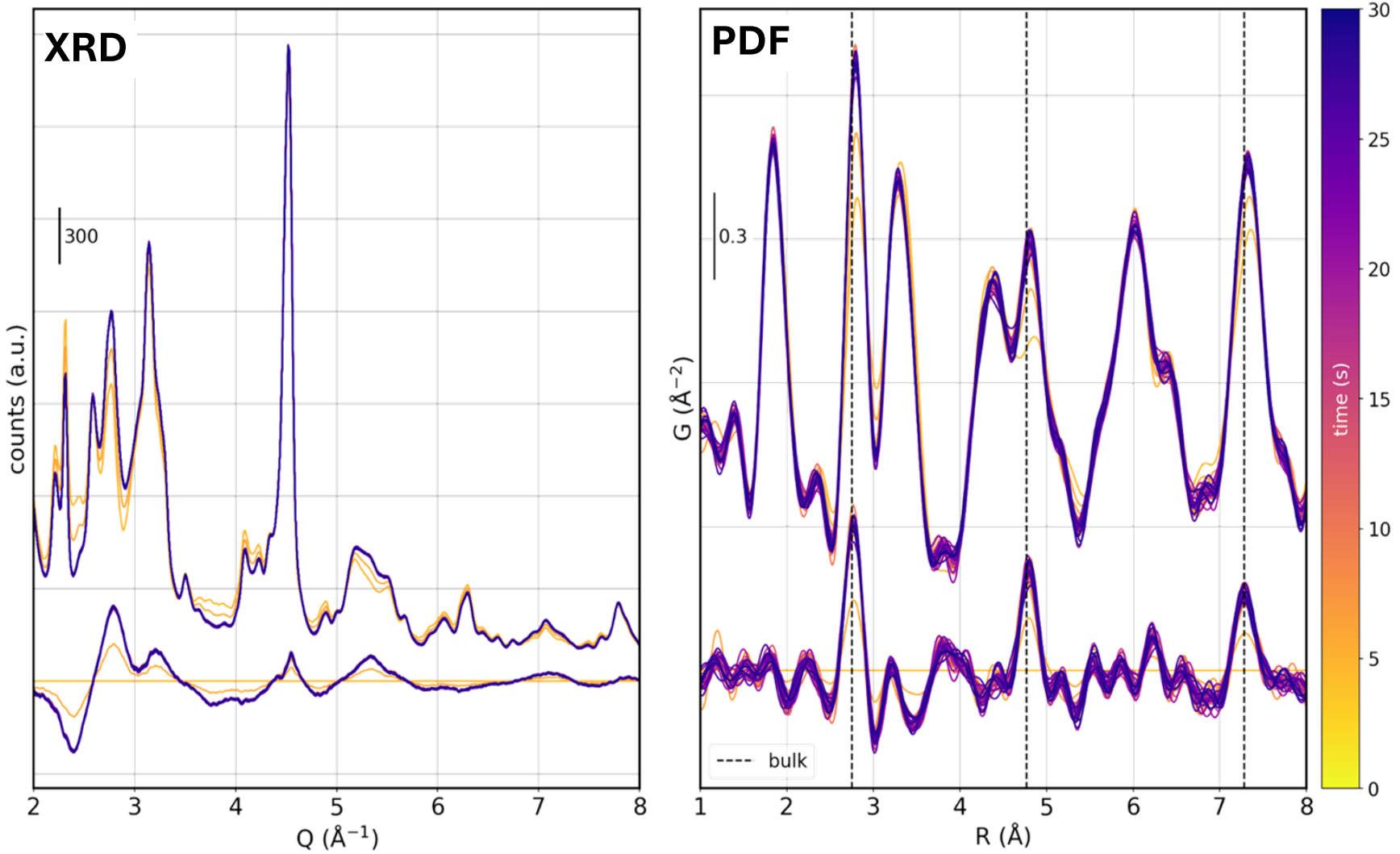
Q_{max} = 24 Å^{-1}

Energy = 98 keV

25 °C, Ar

PdO NPs are detected regardless of the complex background and the loading

Operando reduction

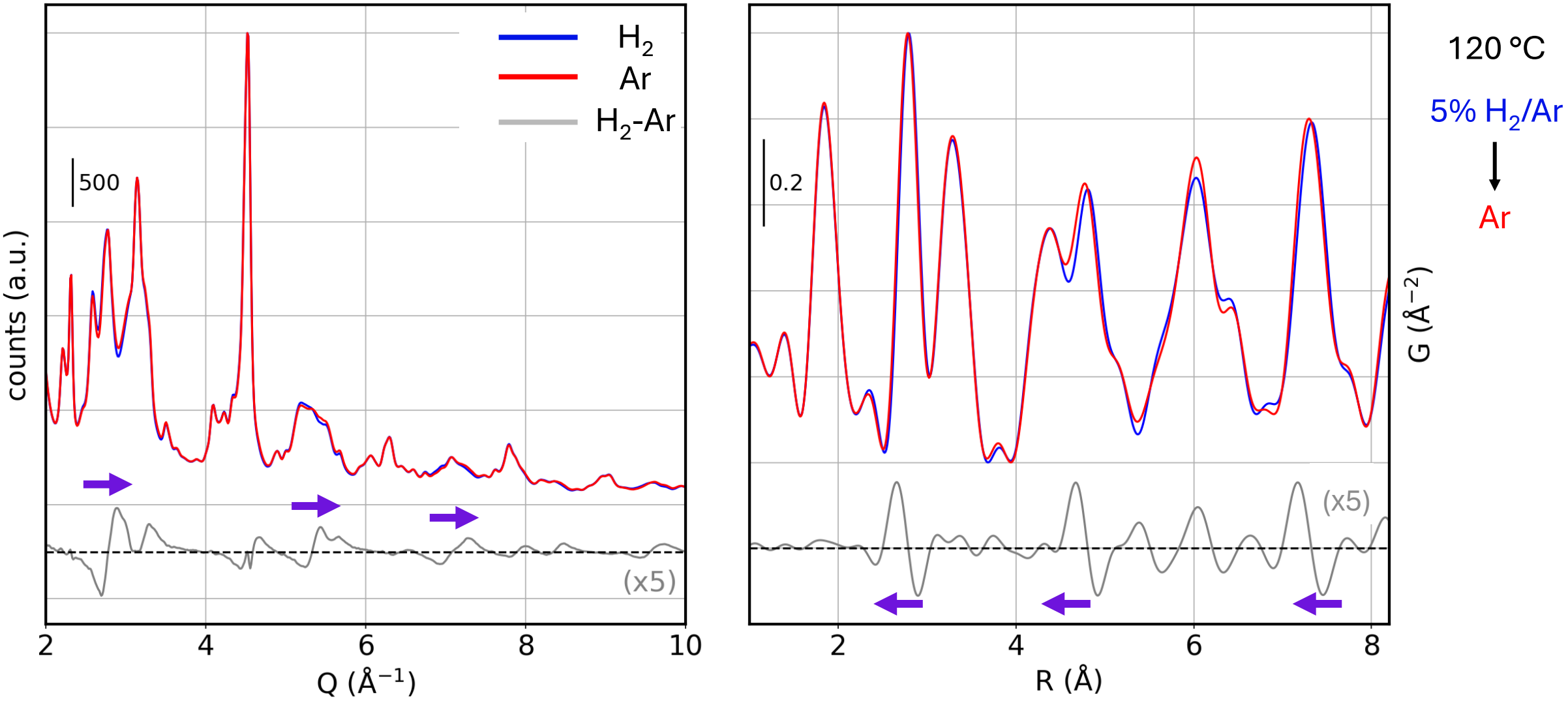


120 °C

5% H_2/Ar

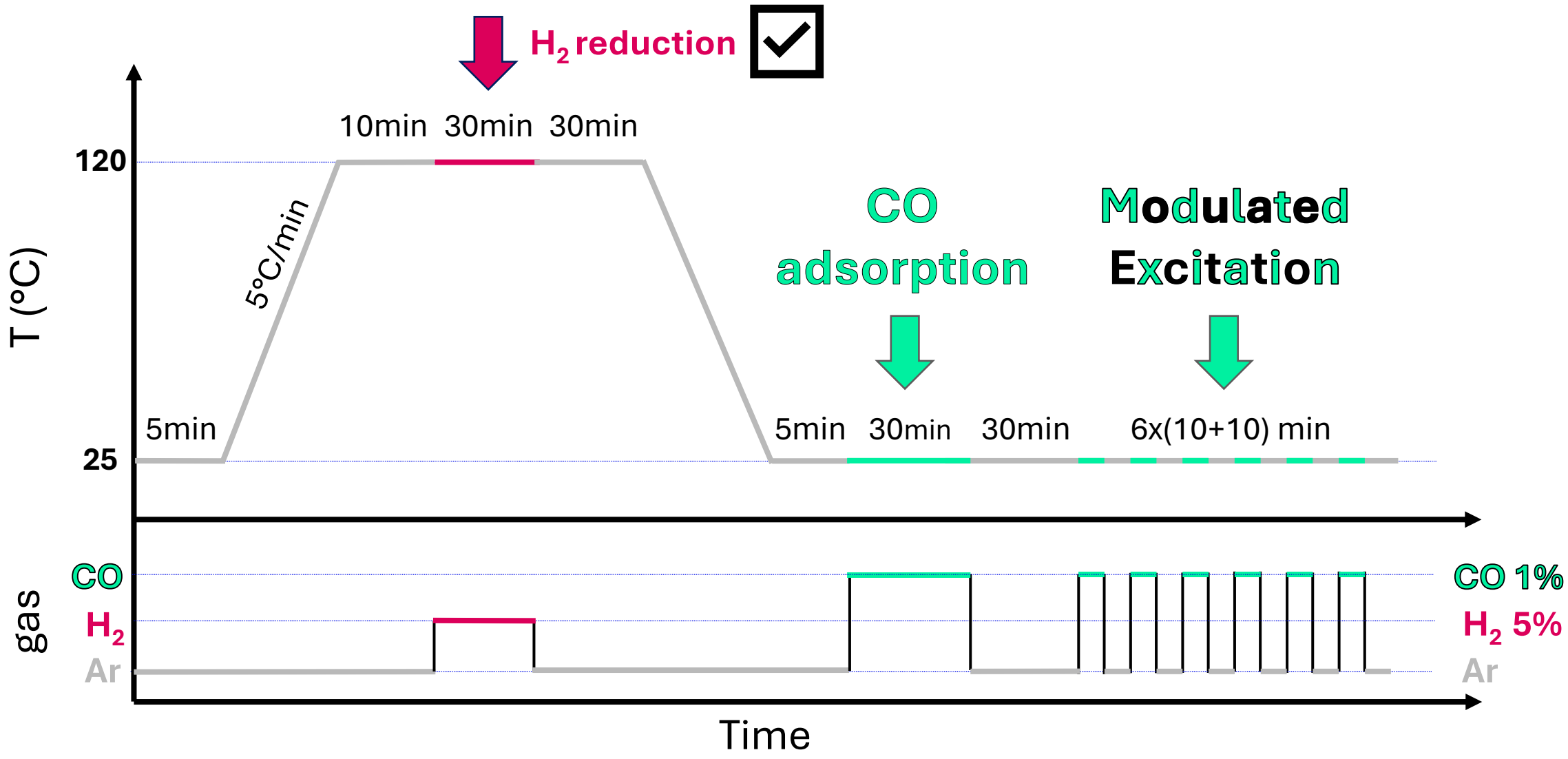
Very fast reduction → formation of metallic Pd and superficial hydrides…

Operando reduction

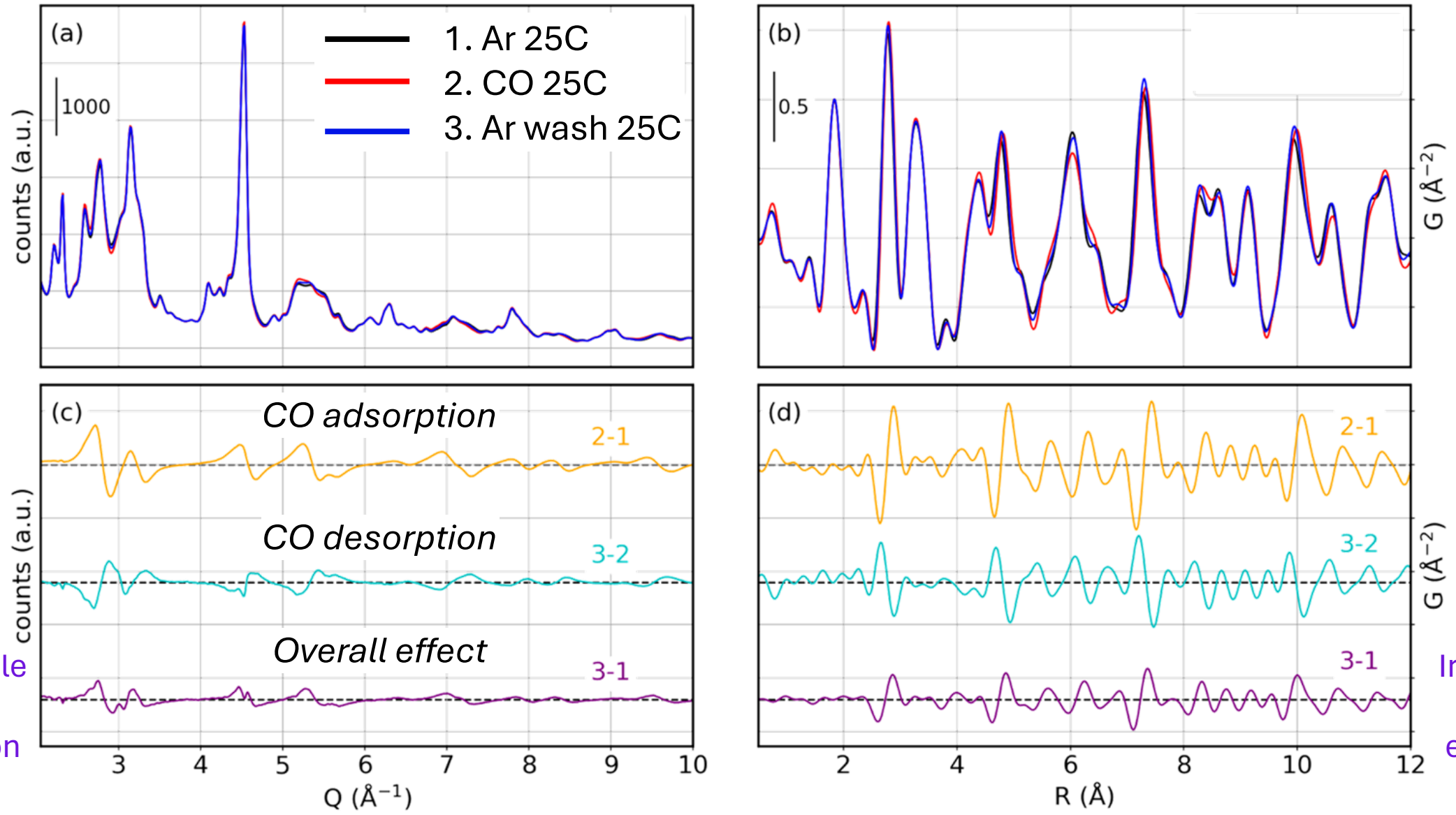


... that are removed during the wash in Ar

Experimental protocol



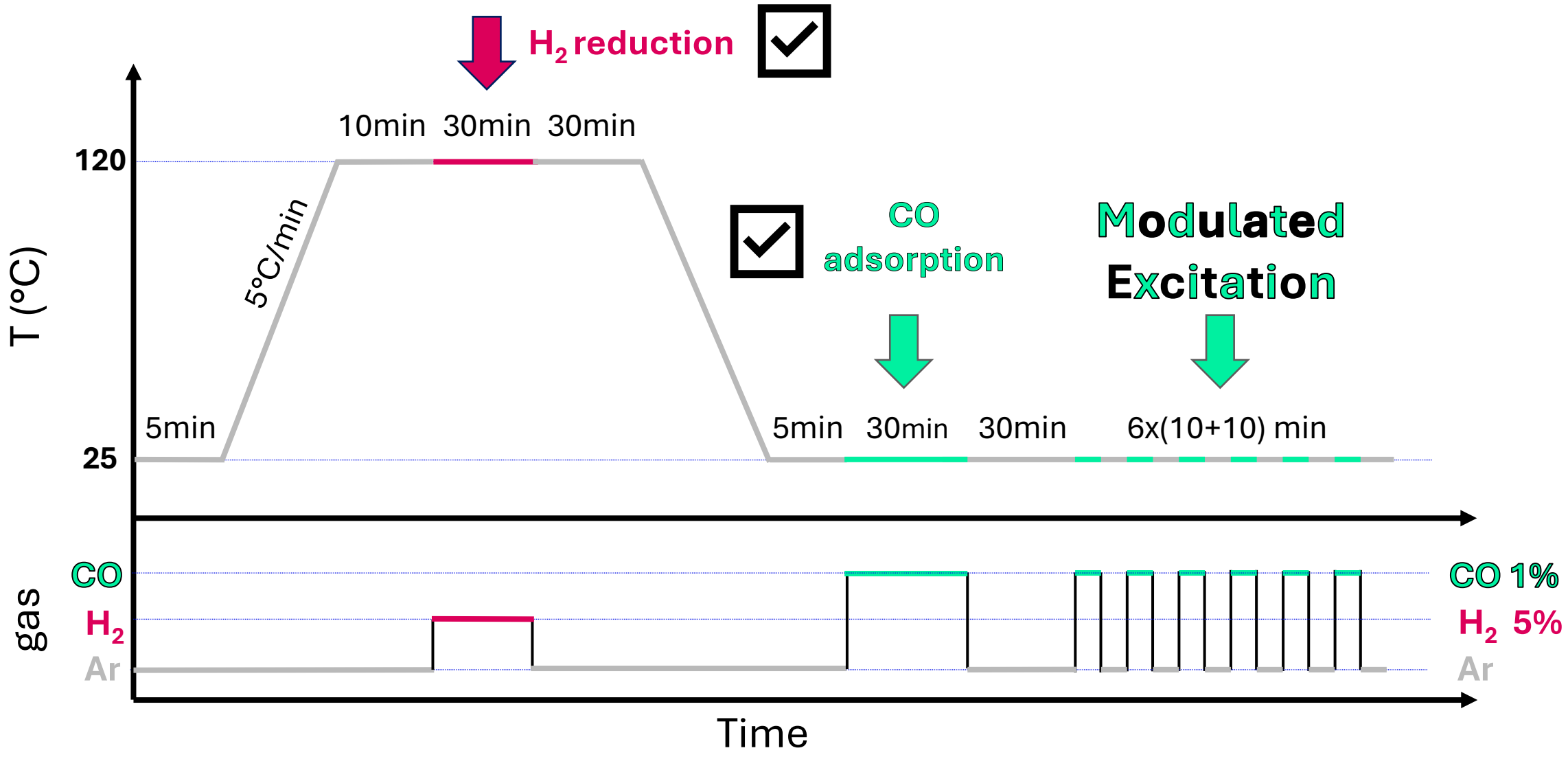
CO adsorption



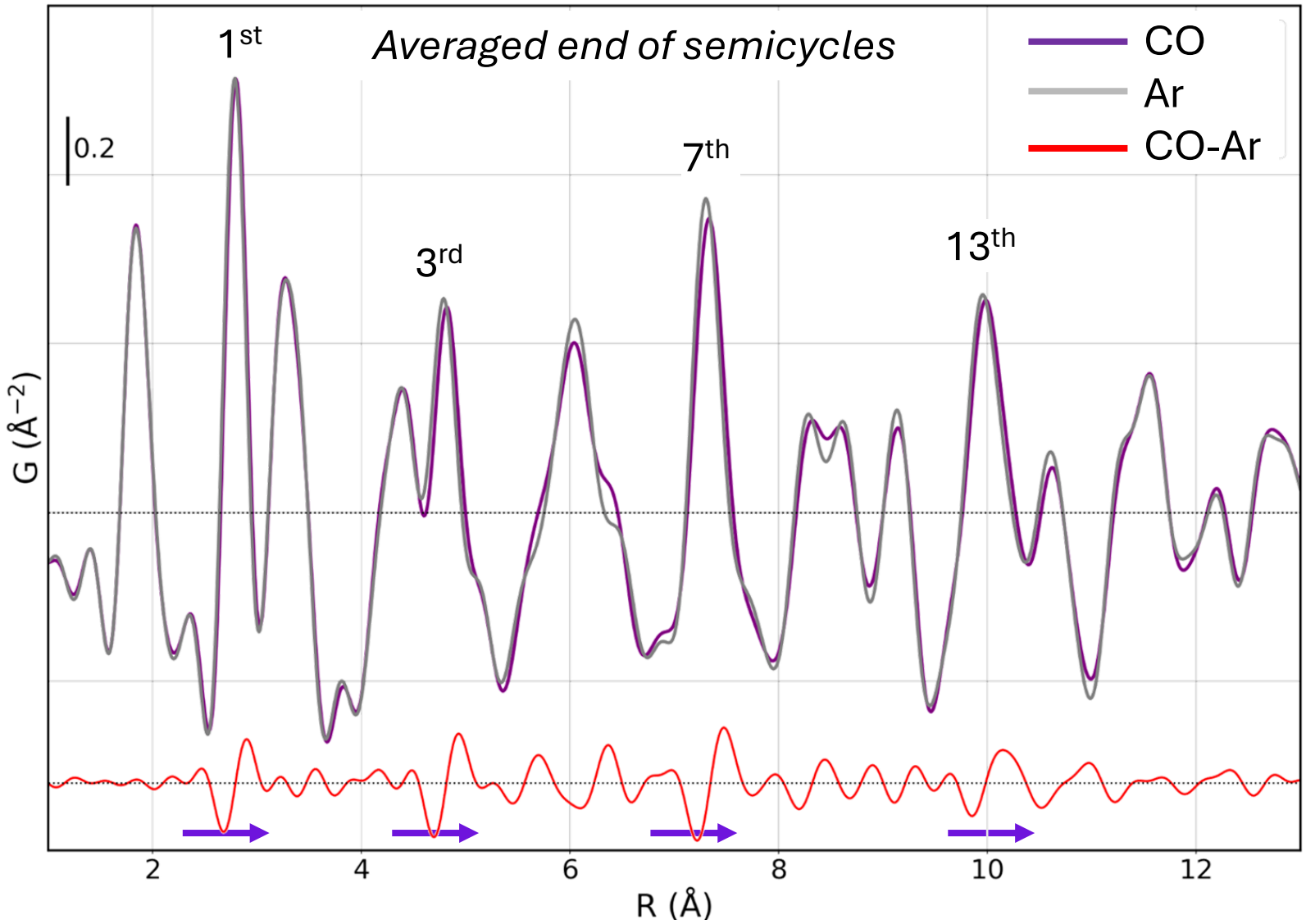
Irreversible net expansion

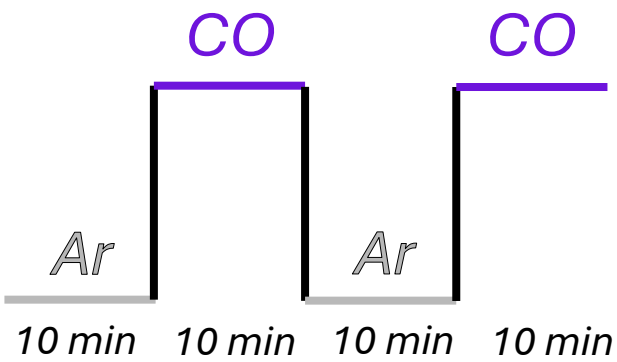
Irreversible net expansion

Experimental protocol



CO adsorption – Modulated Excitation

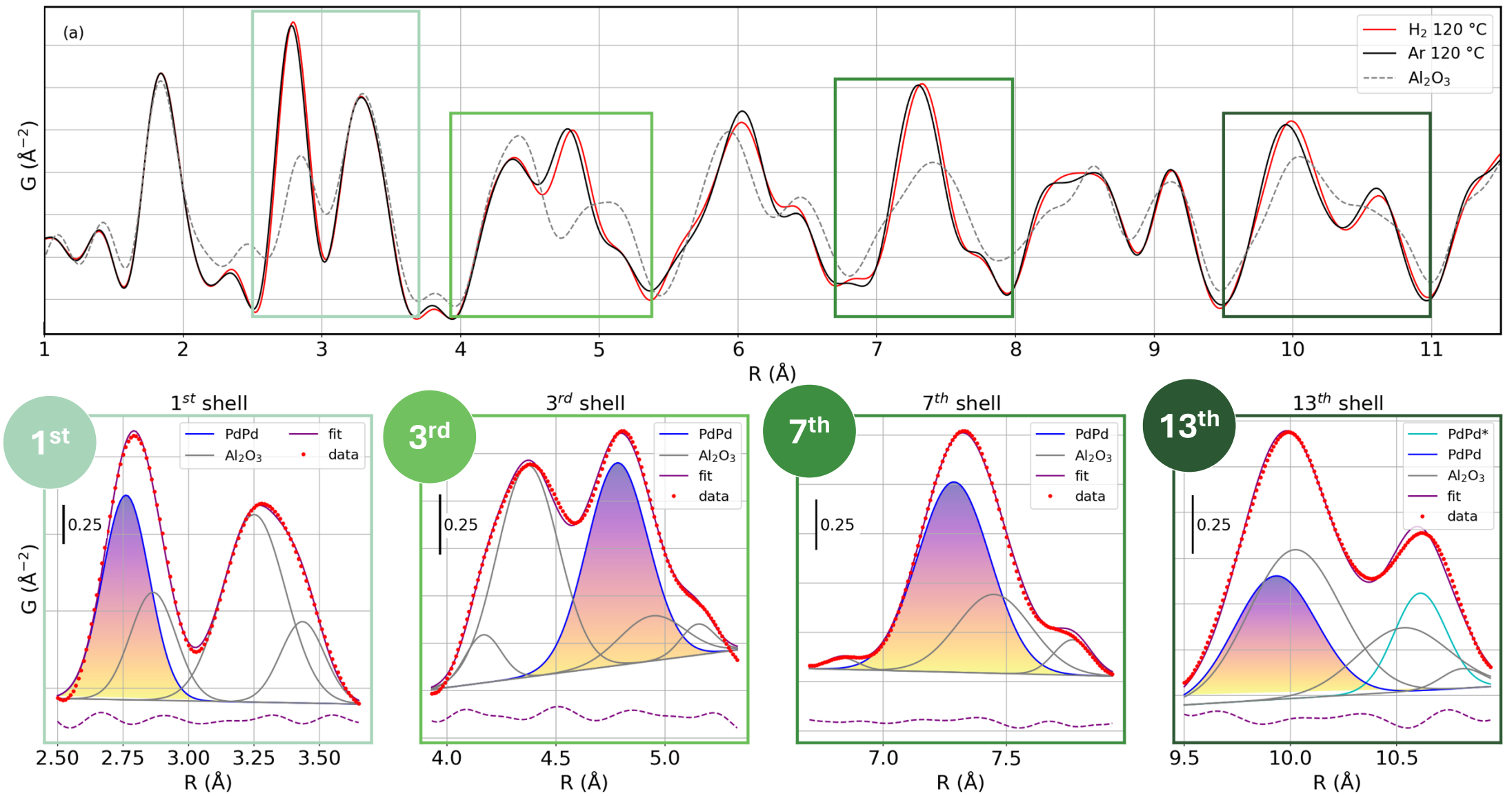




6 full cycles

Repeated CO adsorption induces a reversible an expansion

Model-free fitting



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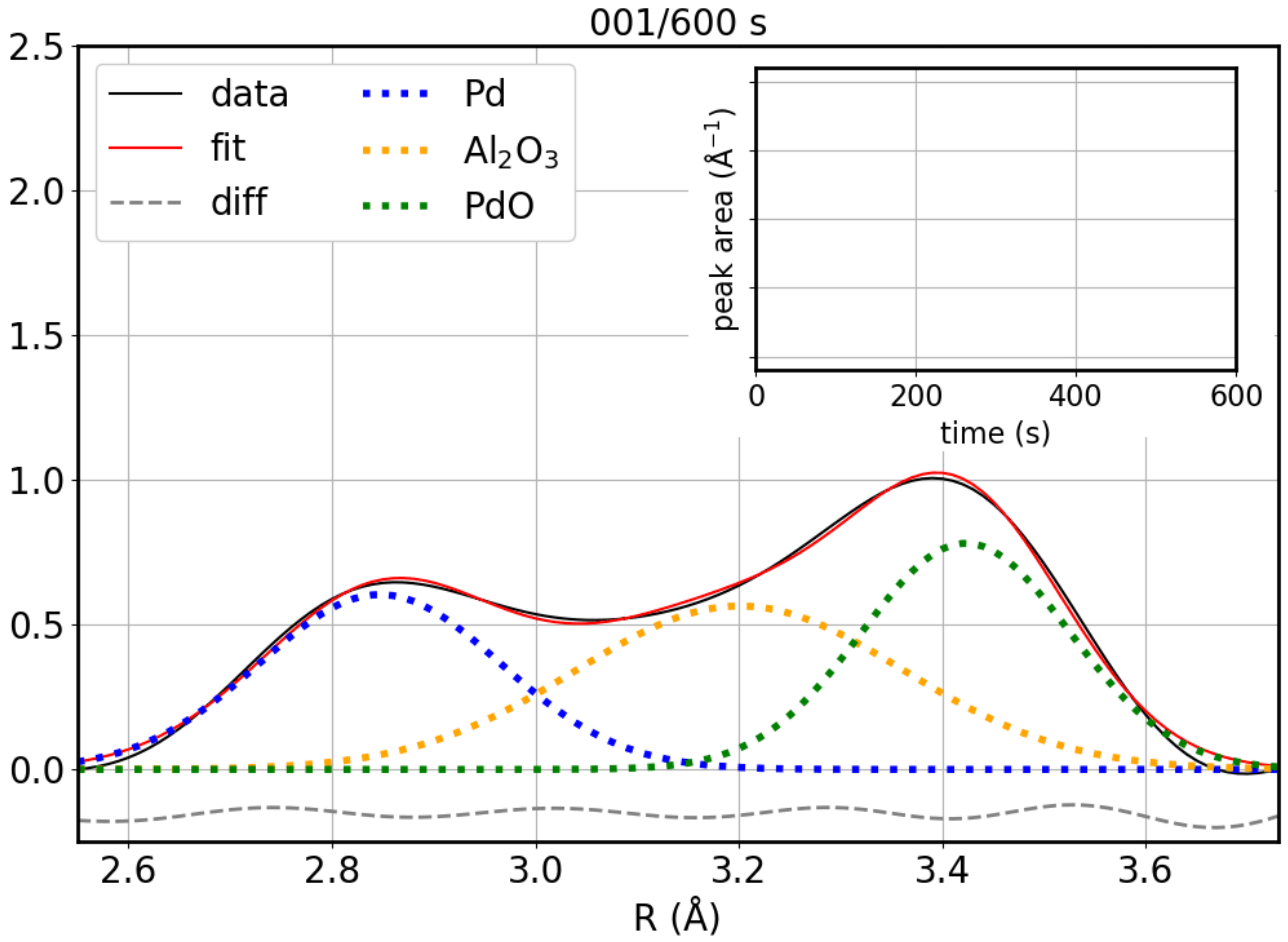
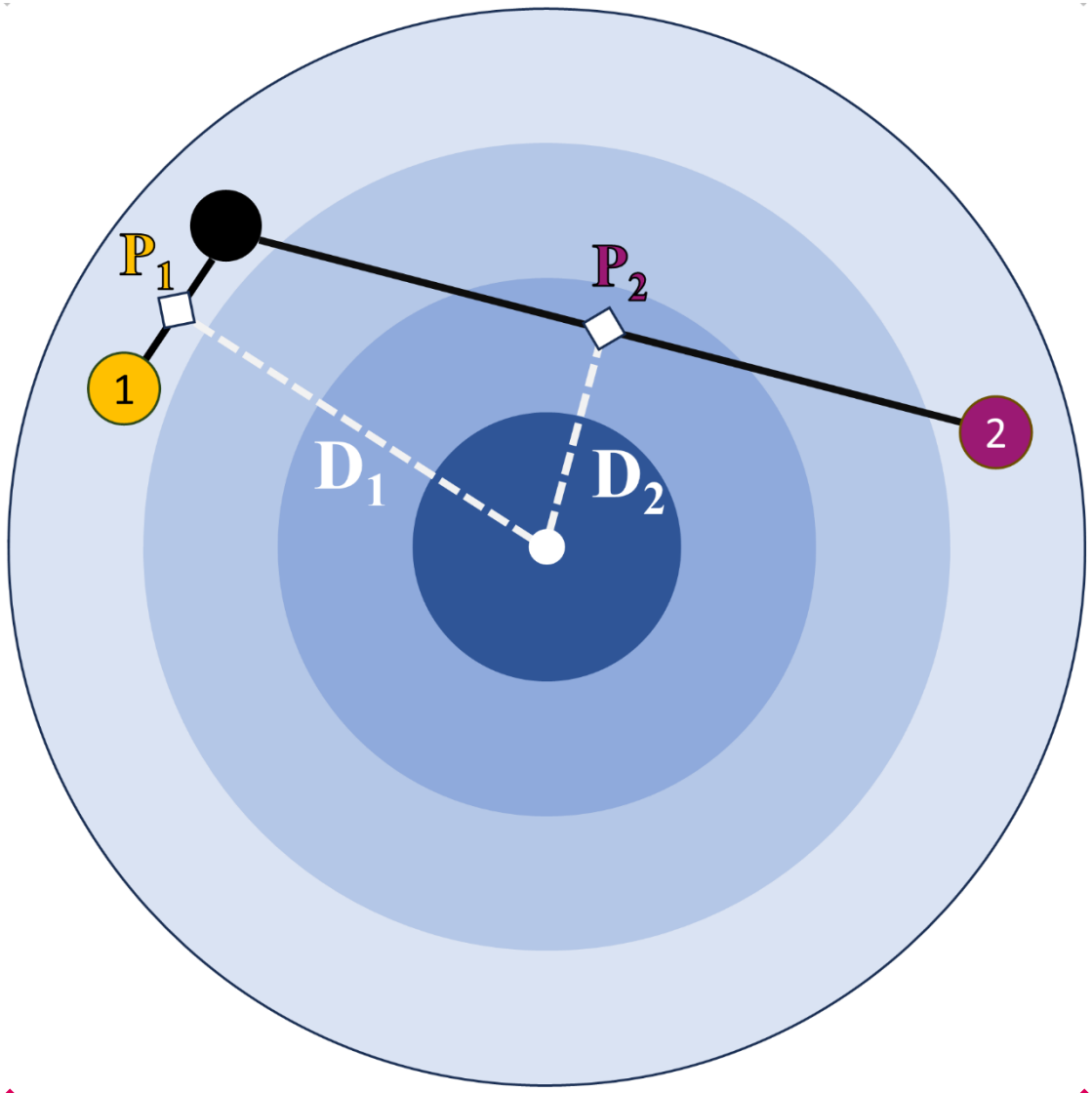


Peak position → expansion

Peak area → coherence/order

Example from liquid phase reduction of the same sample 65 °C, 10mM HCOONa in H_2O

Geometrical interpretation



- Descriptor -

D is the distance between the midpoint of the atomic pair and the particle center

Intuitively, if there is a change in the **core**...

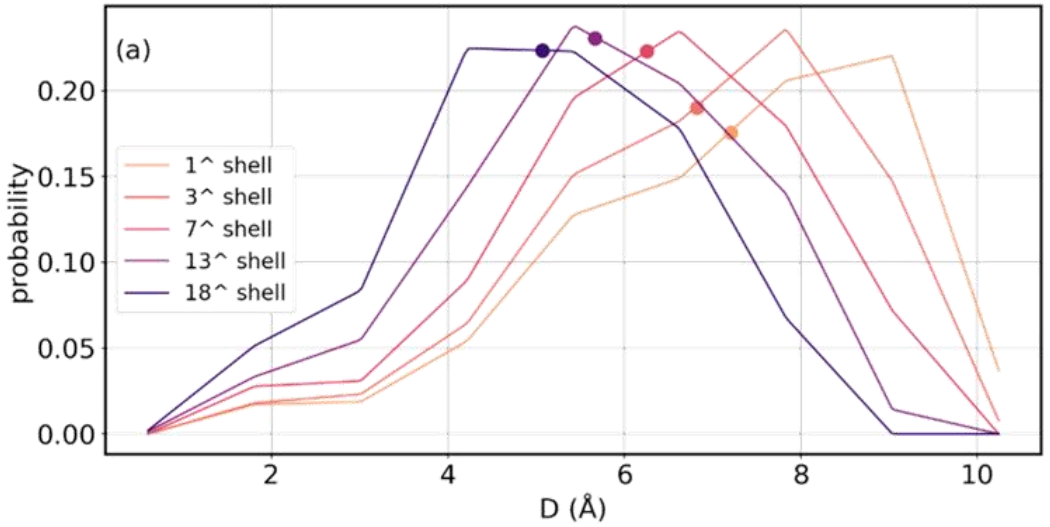
13th shell pair

is more affected than

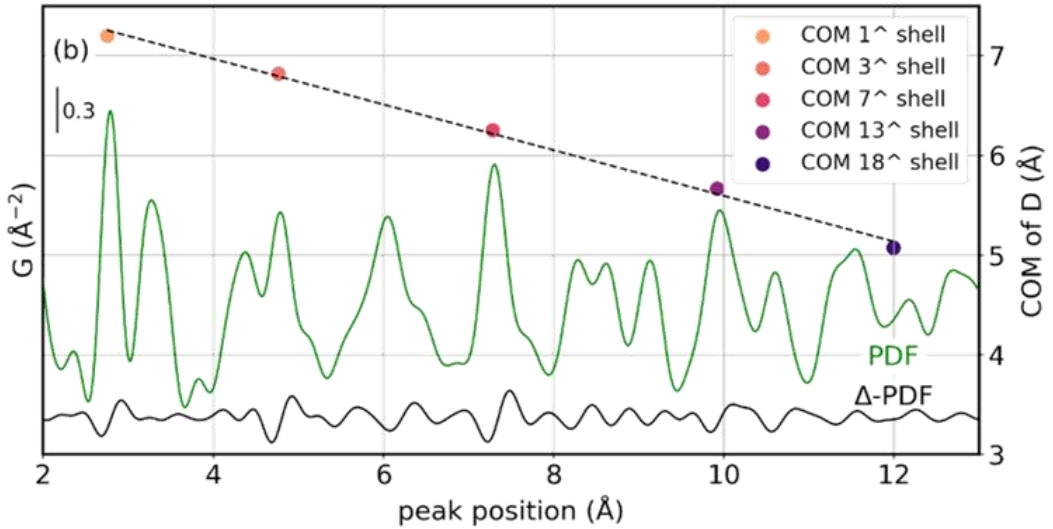
1st shell pair

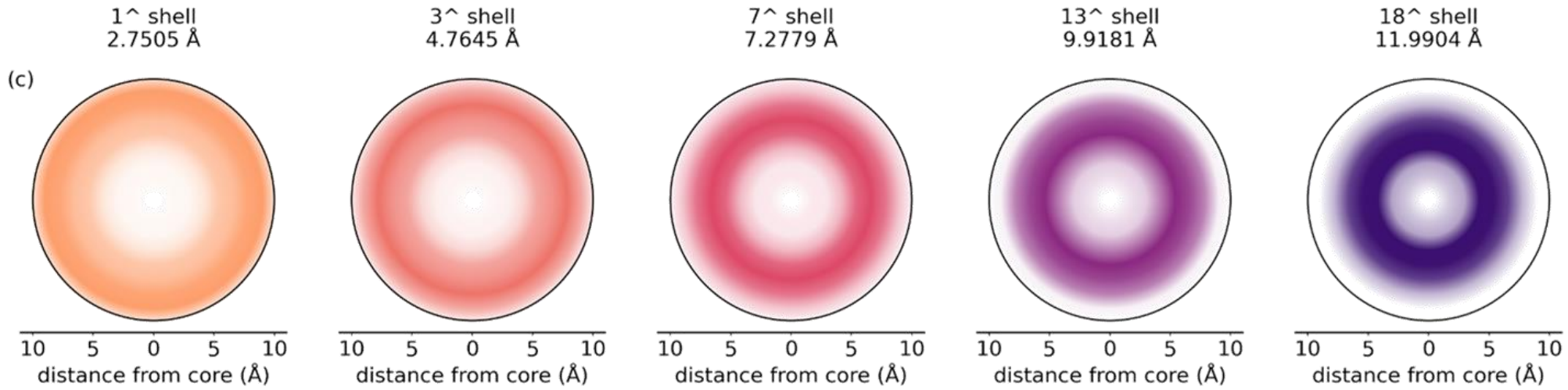
Geometrical interpretation

Probability distribution of D per each shell



Center of mass of each distribution





Geometrical interpretation

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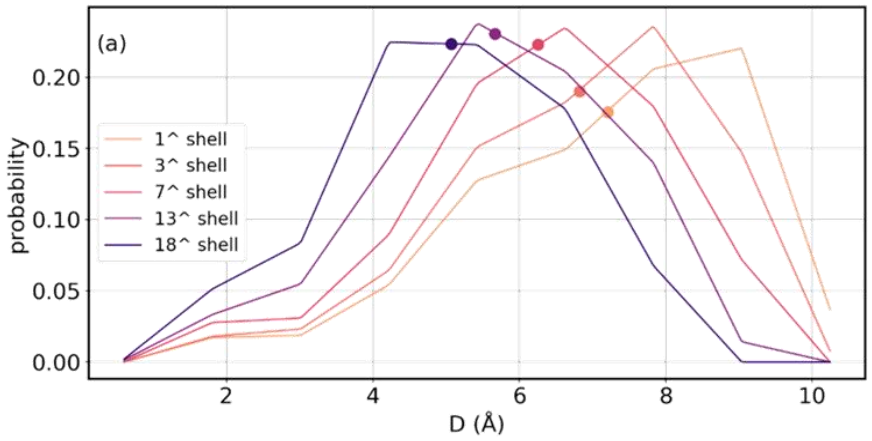
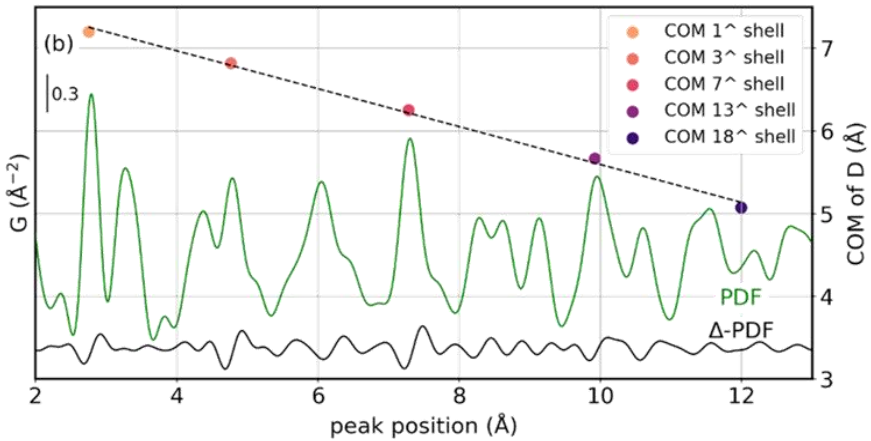
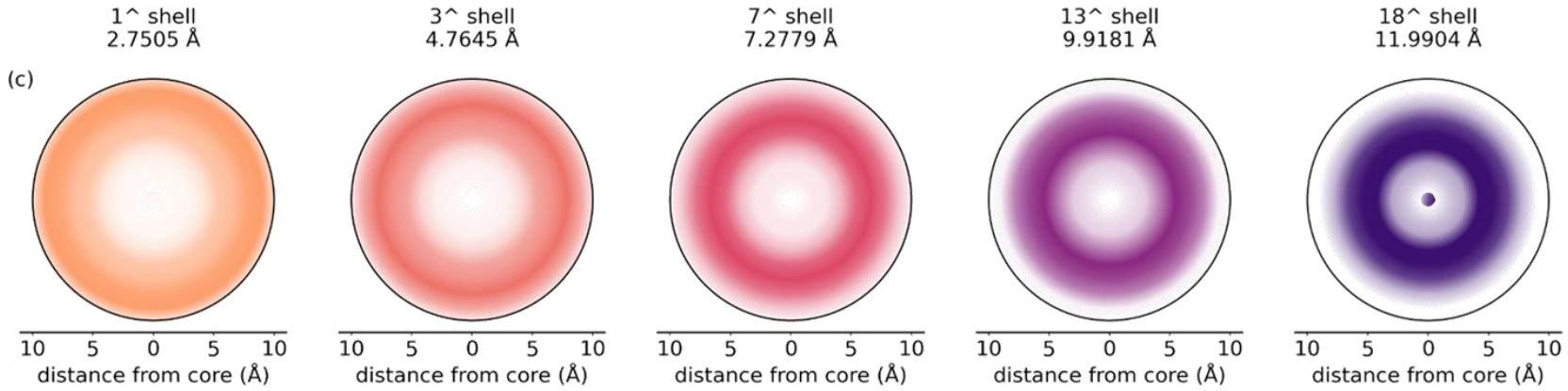


Center of mass of each distribution





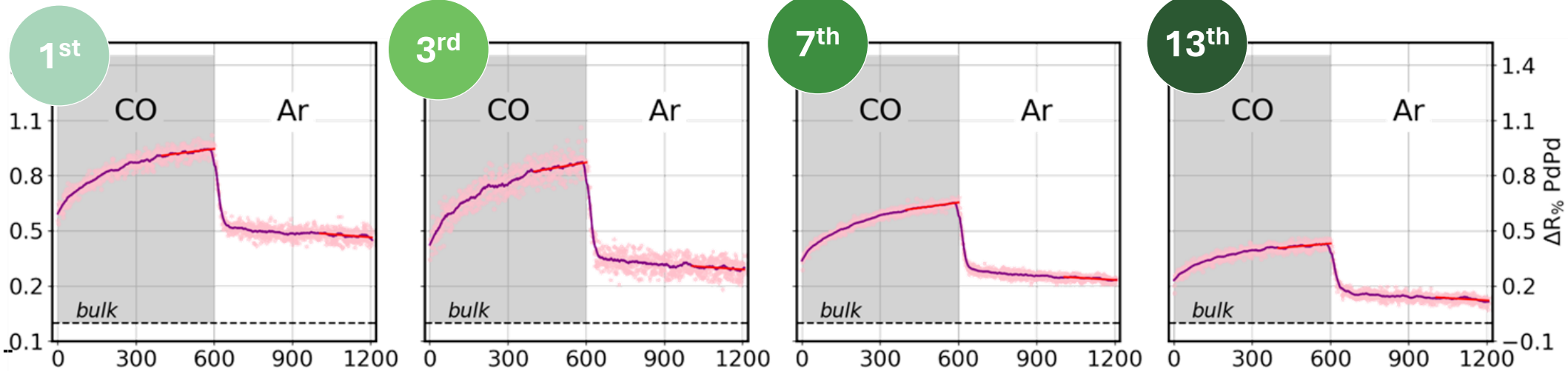
Shells of lower order are more representative of the surface

Shells of higher order are more representative of the bulk

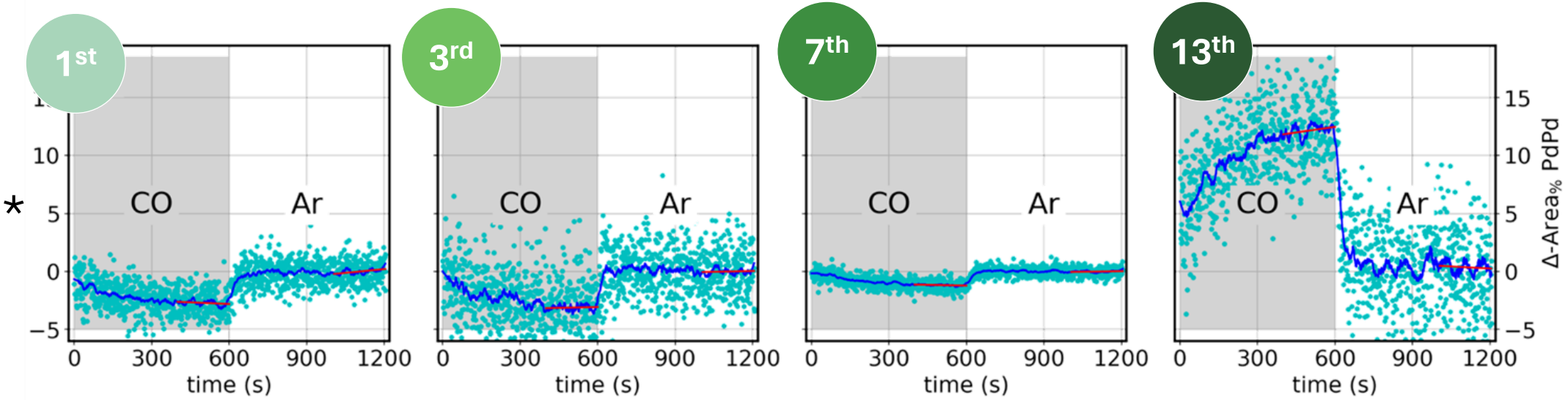
CO adsorption analysis results

PSI

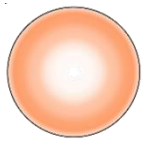
$\frac{\Delta R}{R}\%$



$\Delta A\%^*$



* Normalized to the value in Ar



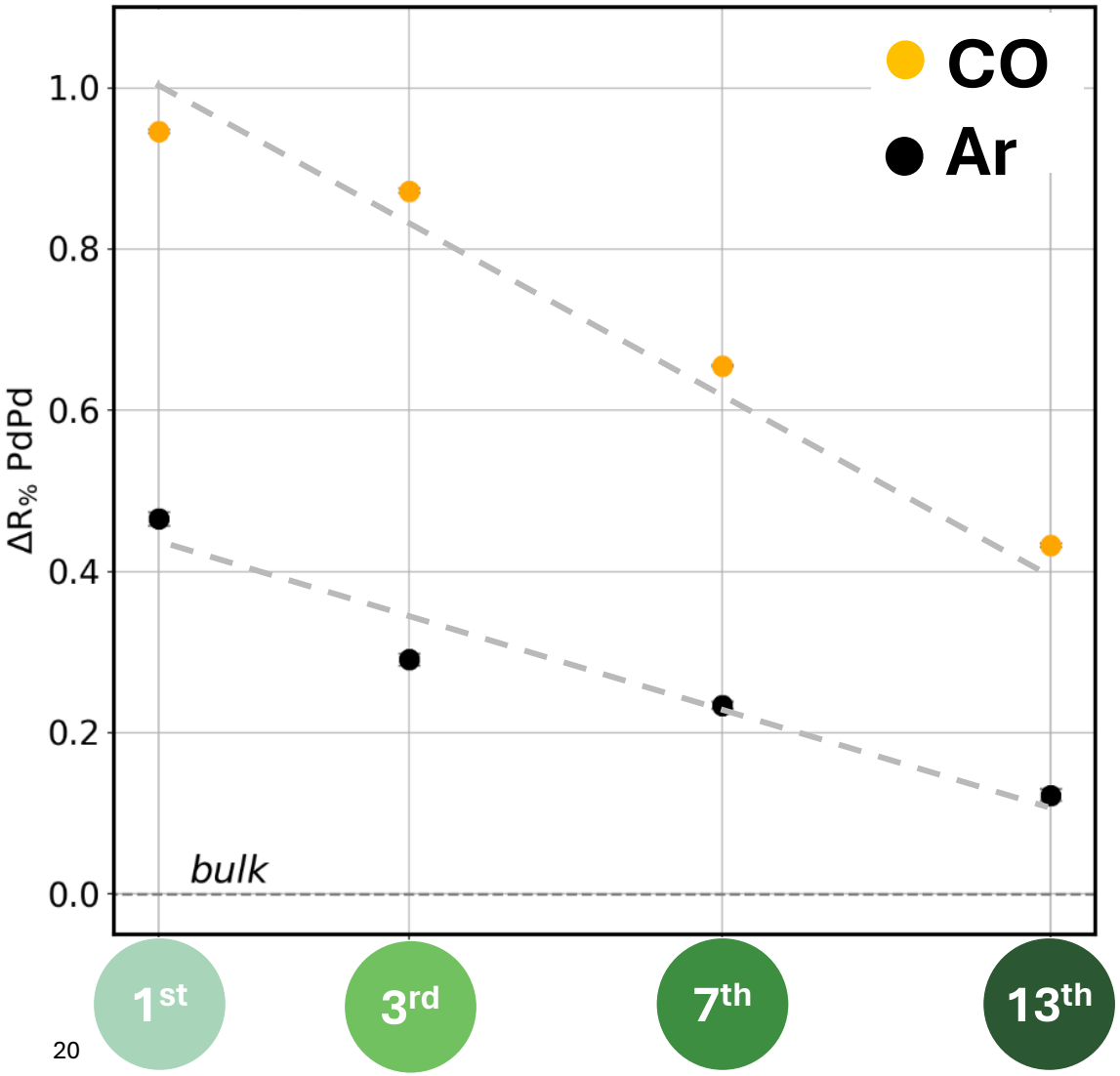
Short pairs
- Surface -

Long pairs
- Bulk -

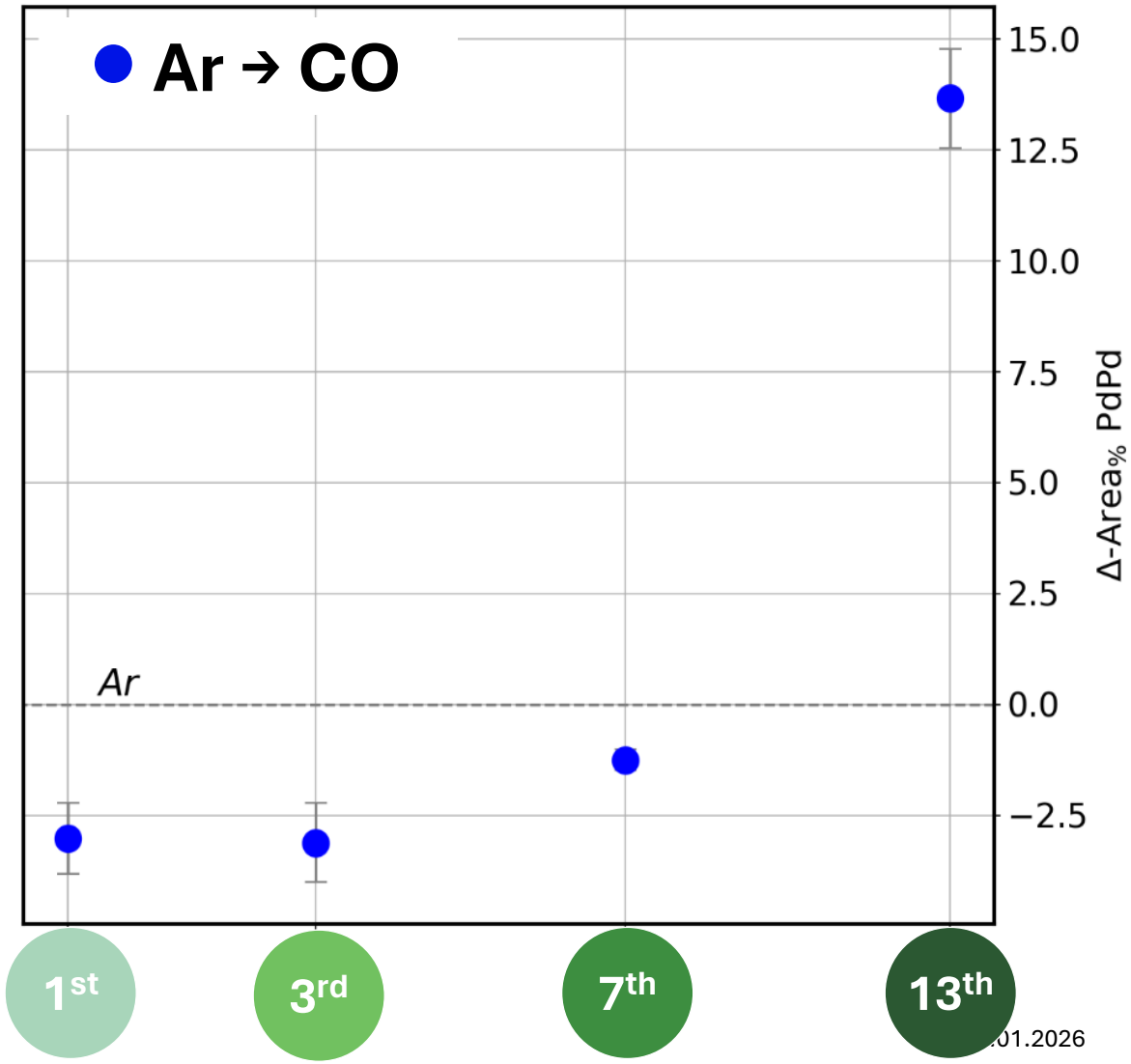
CO adsorption analysis results

PSI

Pd-Pd relative % ΔR



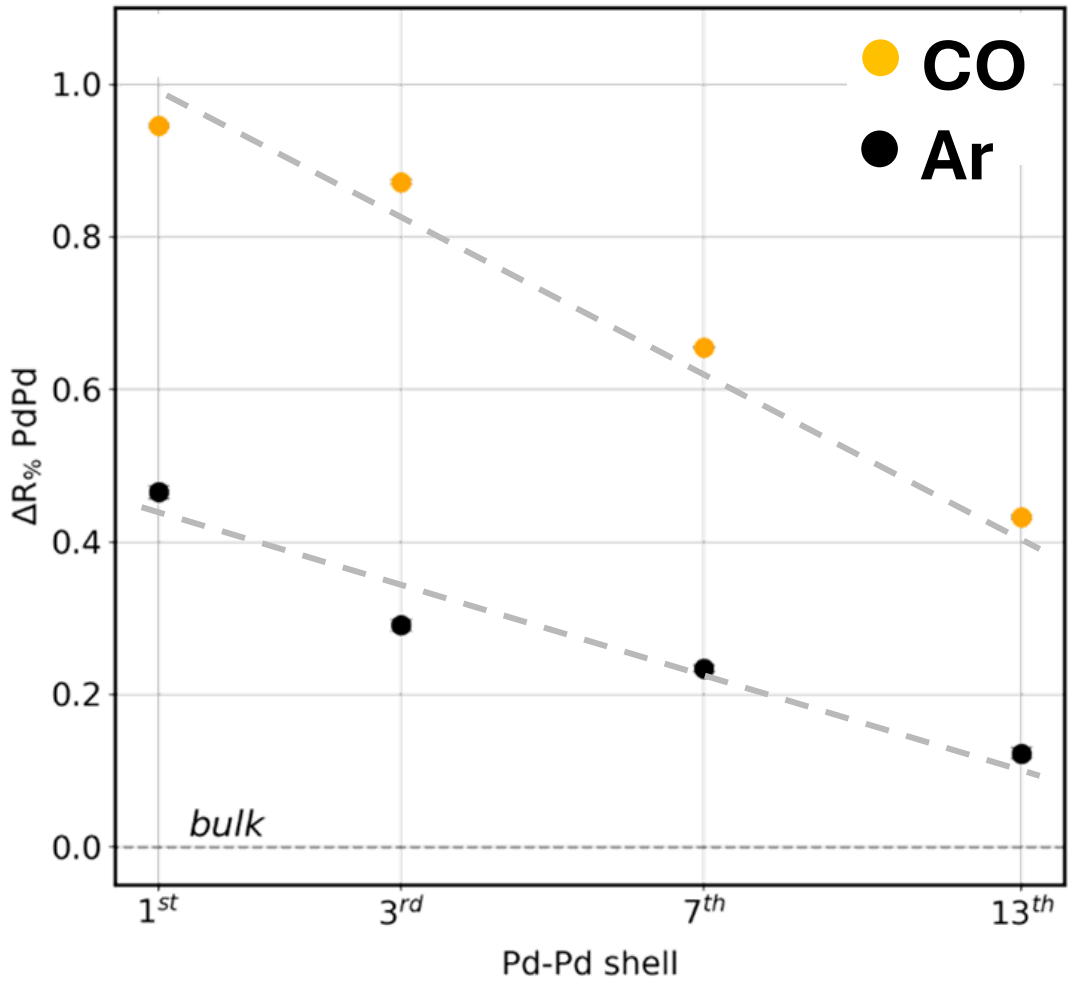
Pd-Pd relative % Δ-Area



CO adsorption analysis results

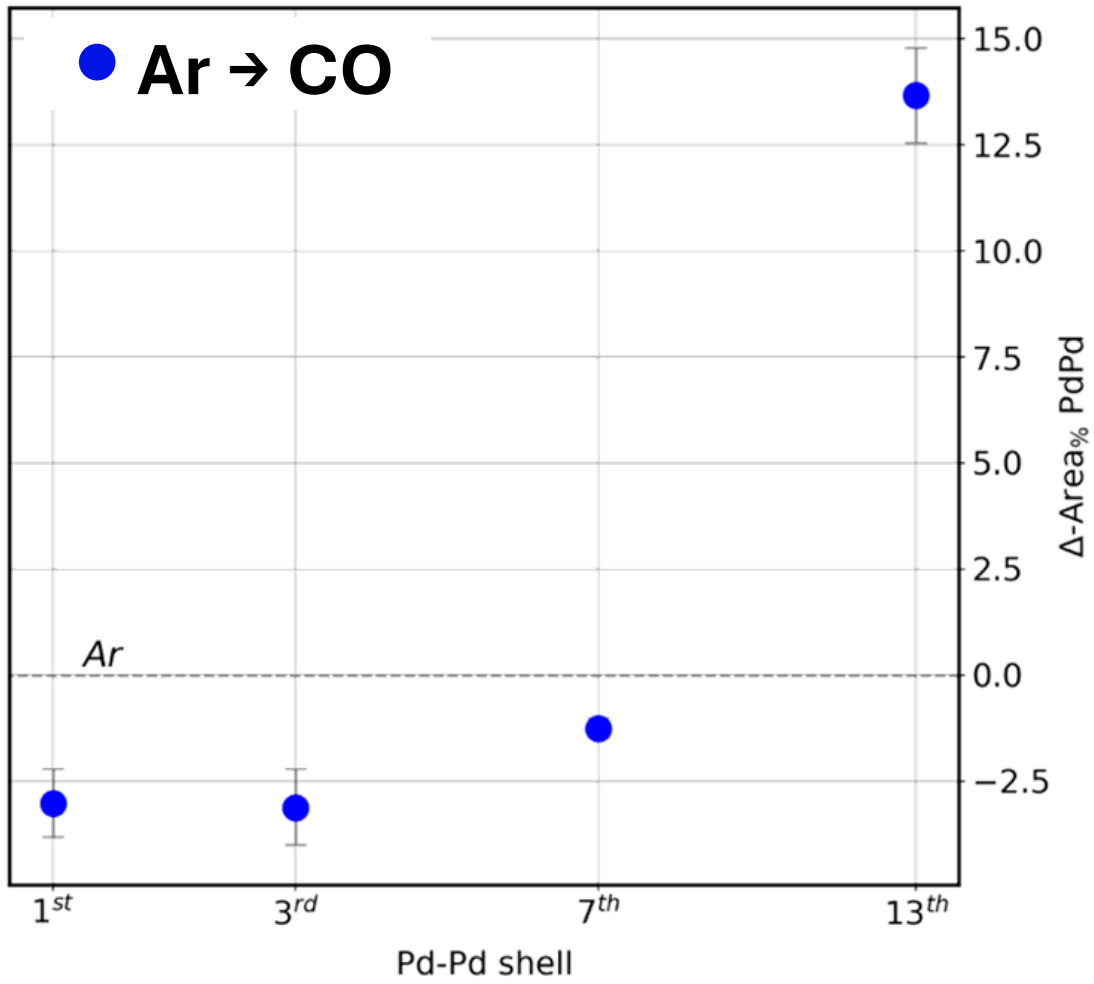
PSI

Pd-Pd relative % ΔR



widespread expansion
more prominent at the surface

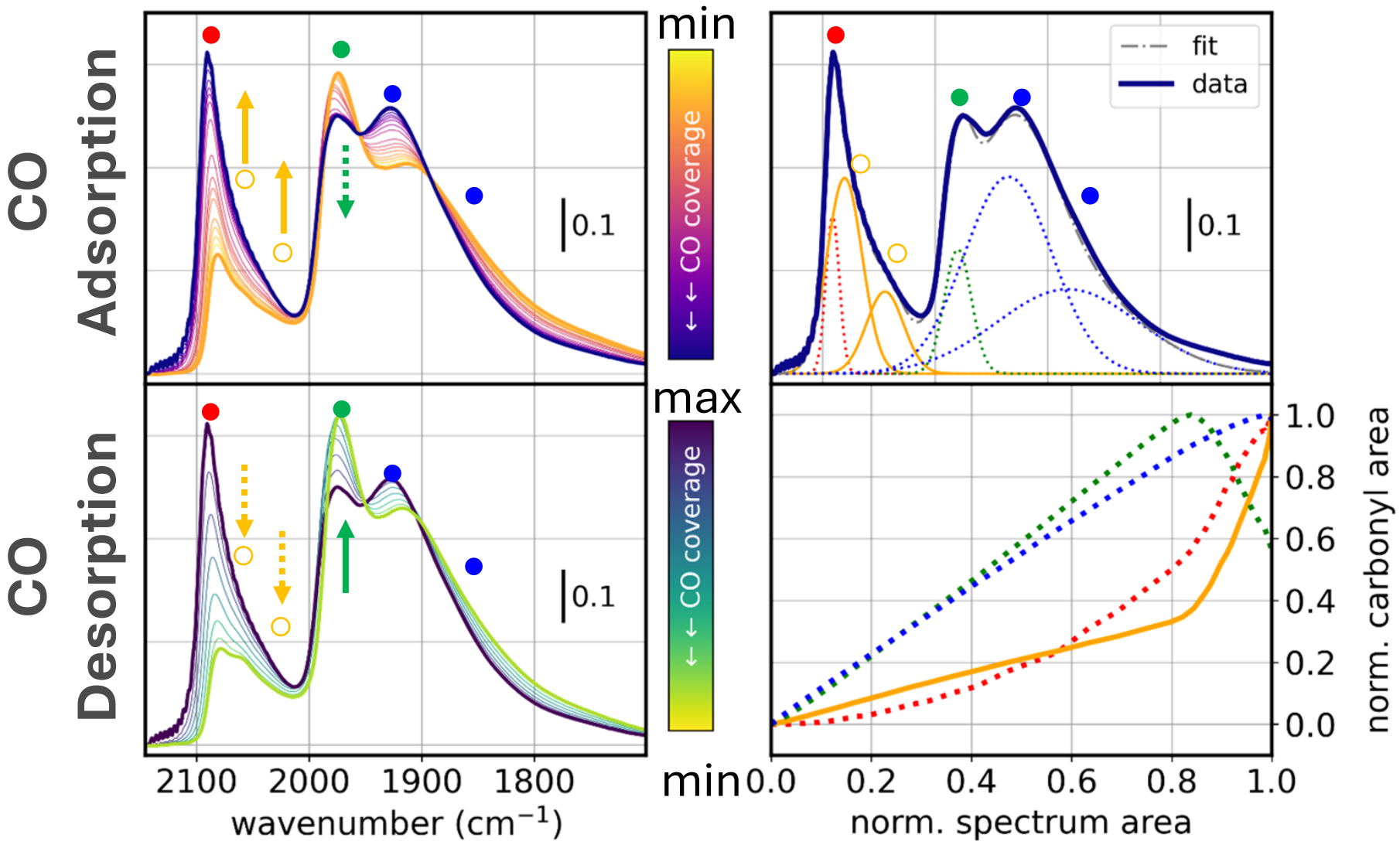
Pd-Pd relative % Δ-Area

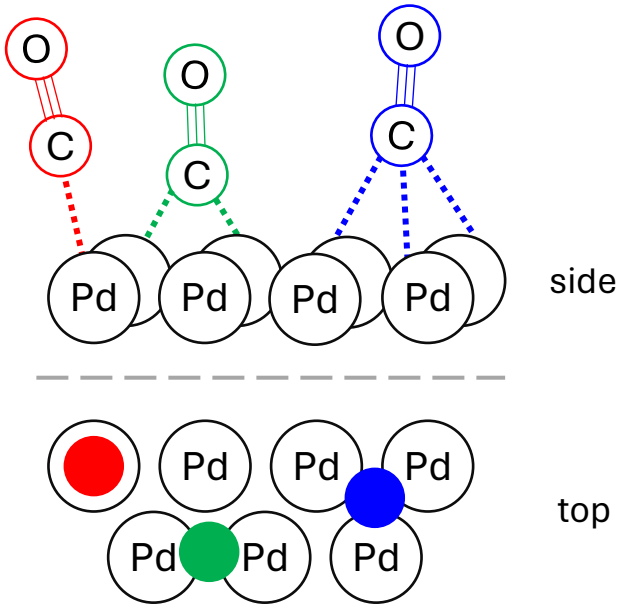


The surface loses coherence,
the bulk gains coherence

The perspective of Infrared Spectroscopy

or "why we looked into this in the first place"



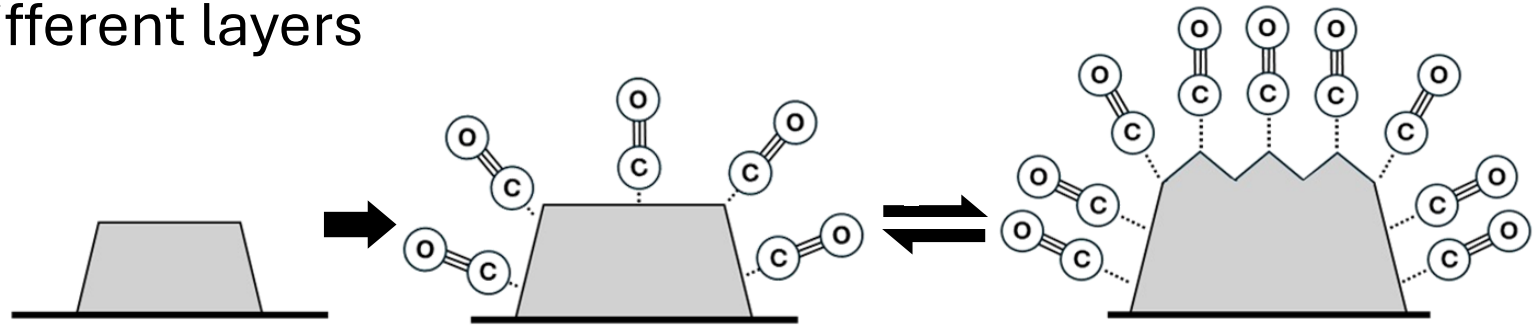


- linear
- **defective** linear
- bridged
- hollow

*Ricchebuono, **Bonavia** et al, ACS Catal 2024*

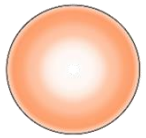
Conclusions and outlook

- The adsorption of CO greatly influences the Pd NPs structure in a complex way on different layers



adapted from Ricchebuono et al., ACS Catal 2024

- Geometrical considerations provide additional insights…
  - confirming the surface insights from IR spectroscopy
  - going deeper to reveal the full extent of the phenomenon



Short pairs
- Surface -

Long pairs
- Bulk -

⇨ Molecular dynamics simulations are in progress to validate these findings

Acknowledgements

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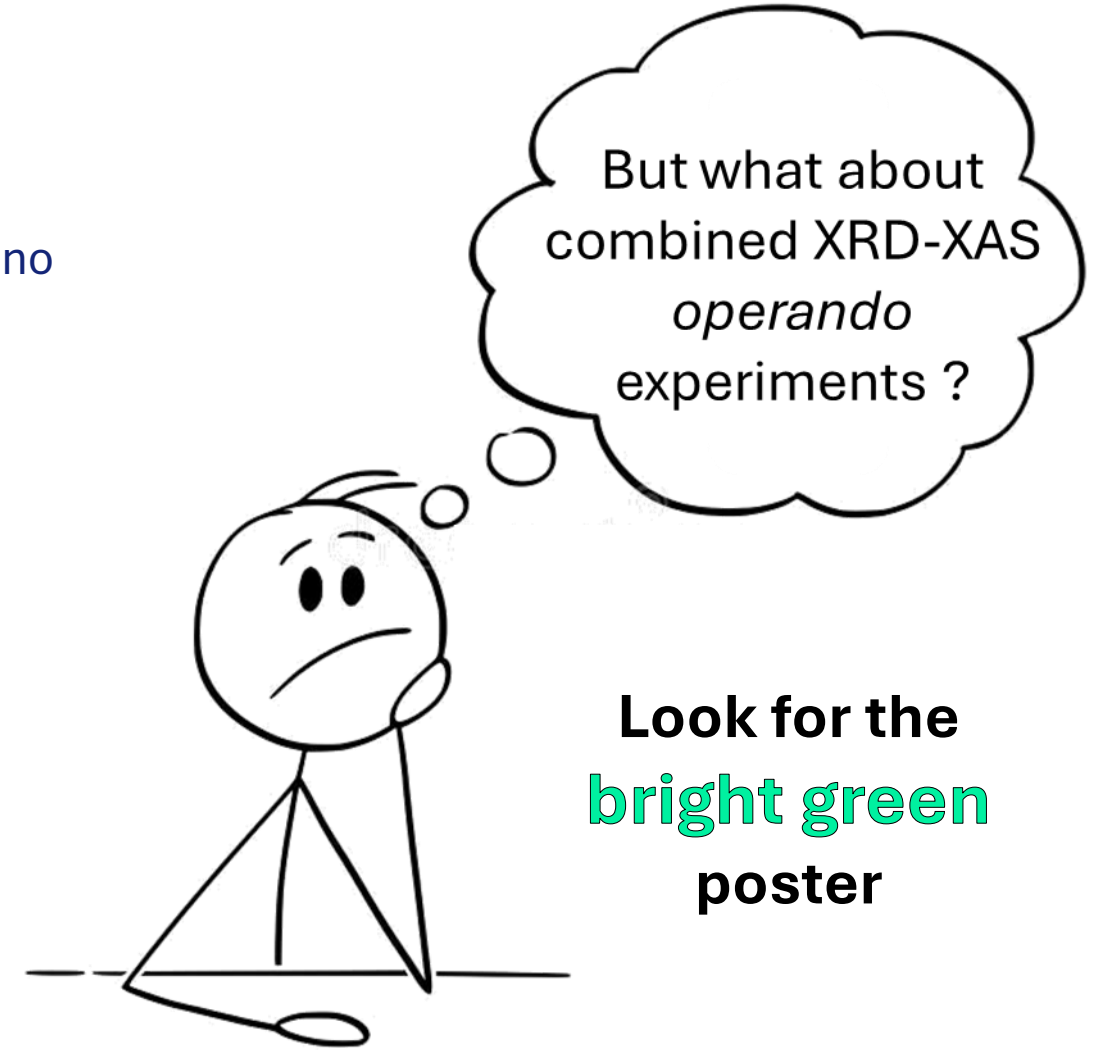

Look for the bright green poster

DEBYE beamline at the Swiss Light Source