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X-ray Raman scattering study of hydrothermal fluids: The case of aqueous sodium chloride solutions

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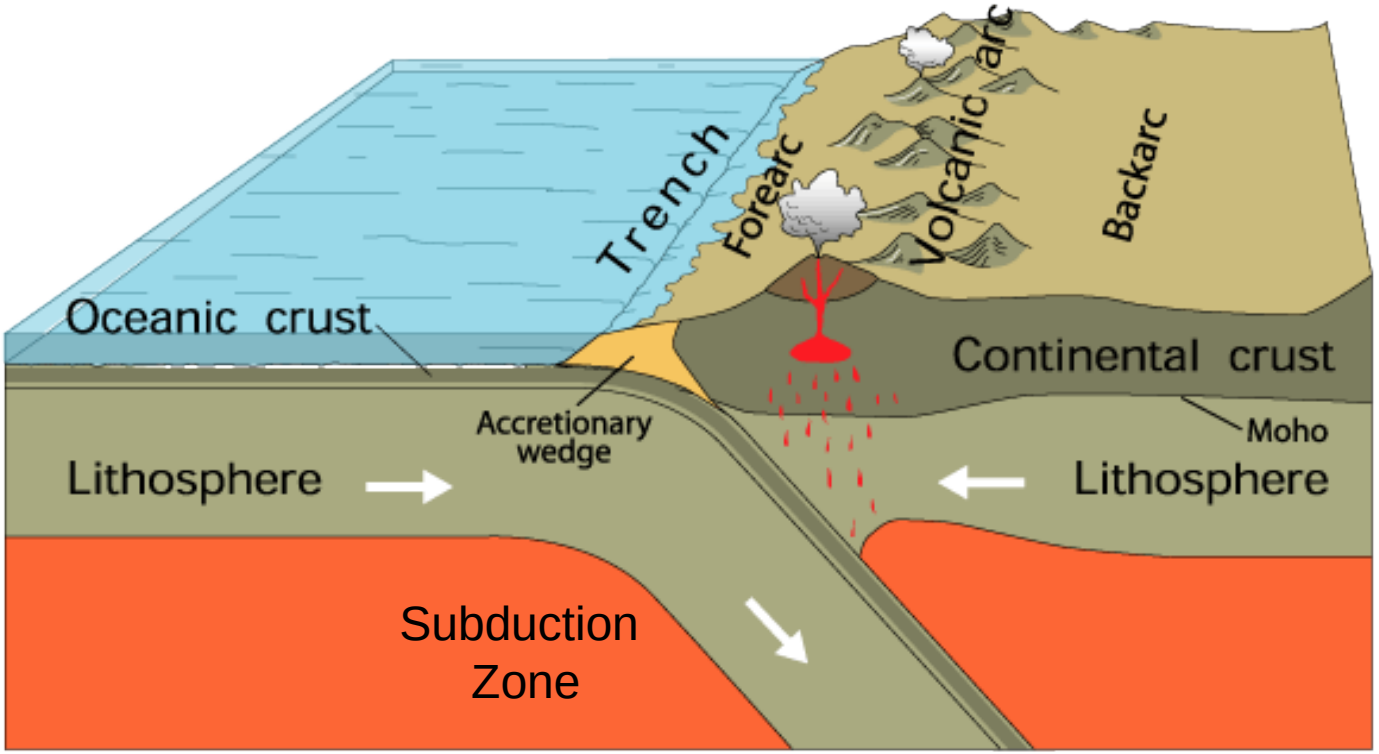
Motivation - hydrothermal fluids in geology



USGS

- An important factor in the formation of magma and volcanic arcs

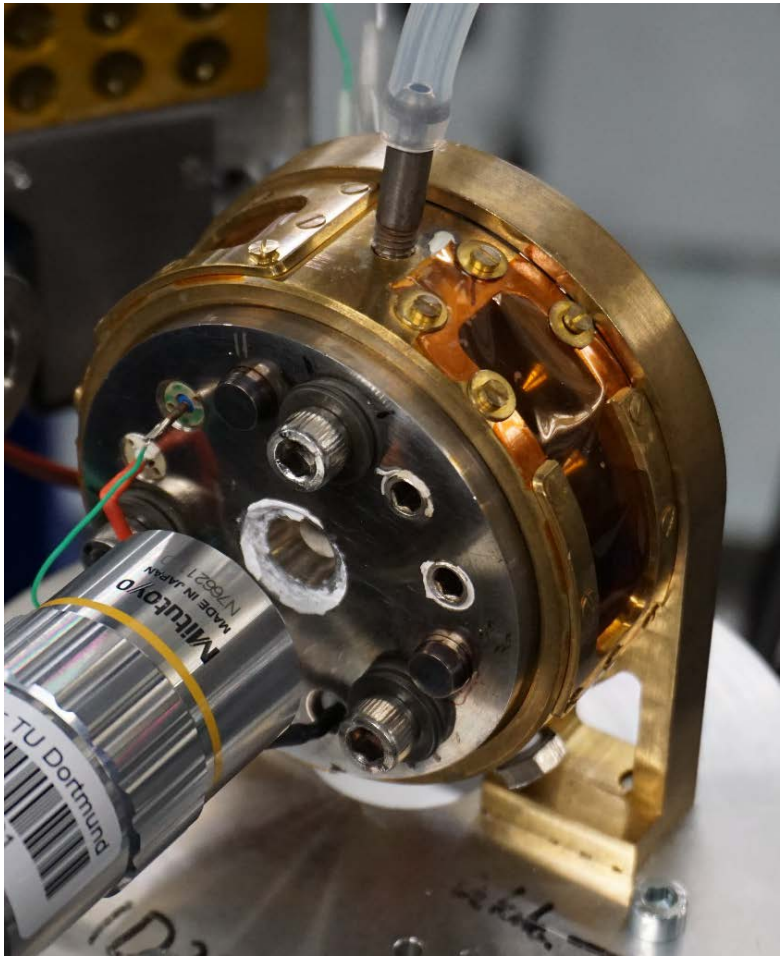
Motivation - hydrothermal fluids in geology

geologyin.com

ETH Zurich

- An important factor in the formation of magma and volcanic arcs
- Transport agent of energy and mass in the earth's mantle
  - Formation of ore deposits

Hydrothermal diamond anvil cell (HDAC)



C. Schmidt, K. Rickers, Am. Min. 2003

- Using a Bassett-type HDAC
- Temperature range from -190 to 800°C and pressures up to 4 kbar
- Using melting points of: azobenzene, sodium nitrate for temperature calibration with a precision of 1.5°C
- Flushing the cell with Ar+H_2 mixture to prevent oxidation of the metallic parts
- Utilizing microscope camera for live-view of sample during measurements

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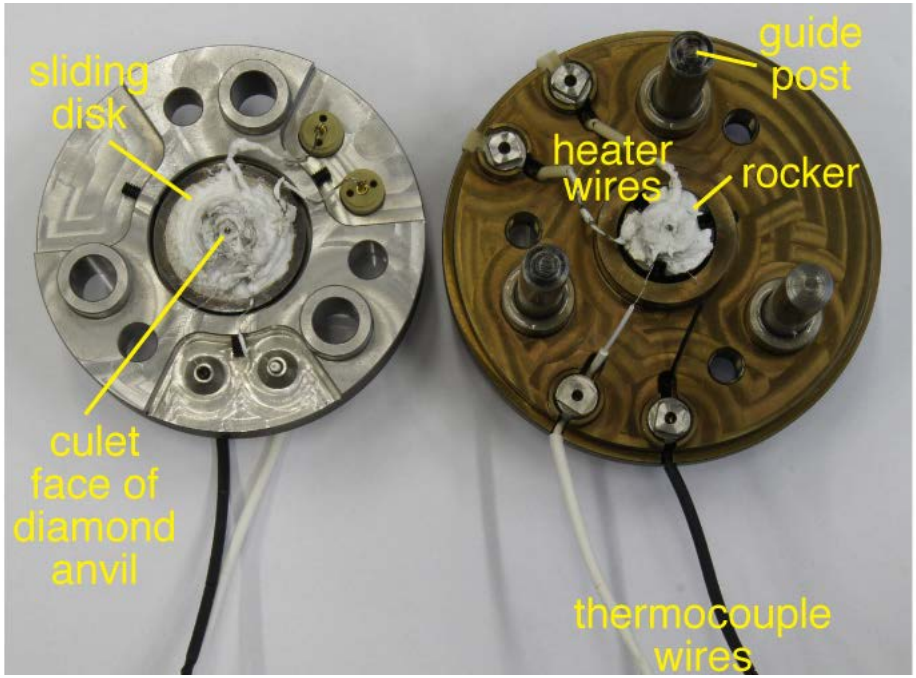
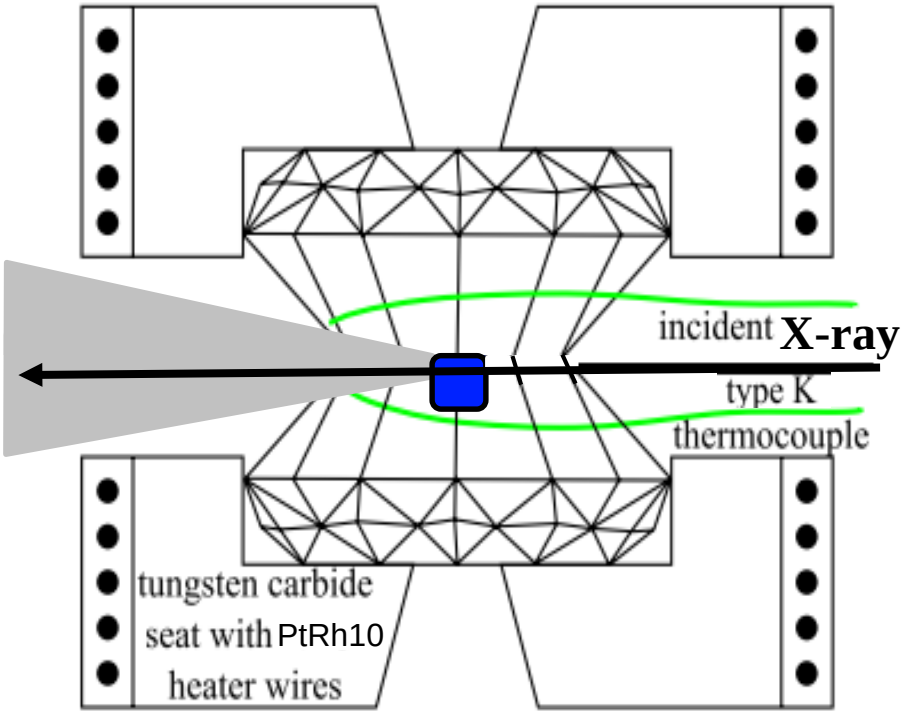
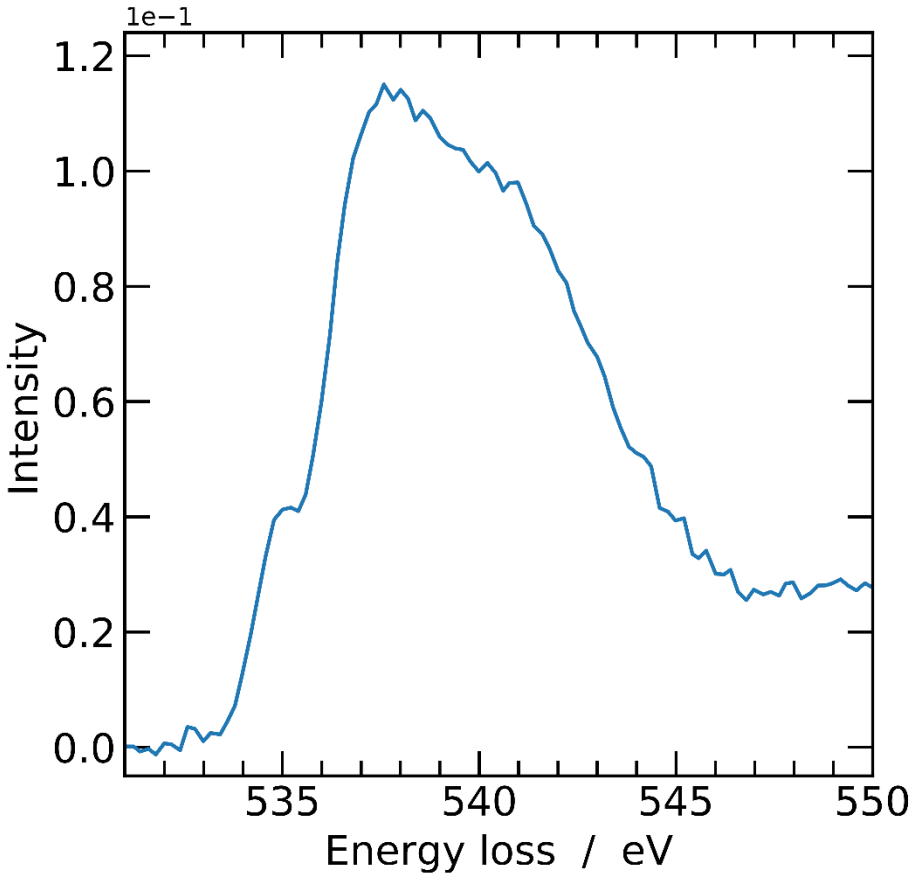


C. Schmidt, I. Chou



- Alignment of diamonds with one sliding and one rotational disk
- Using a laser drilled recess in one of the diamonds as sample chamber
  - No gasket needed!

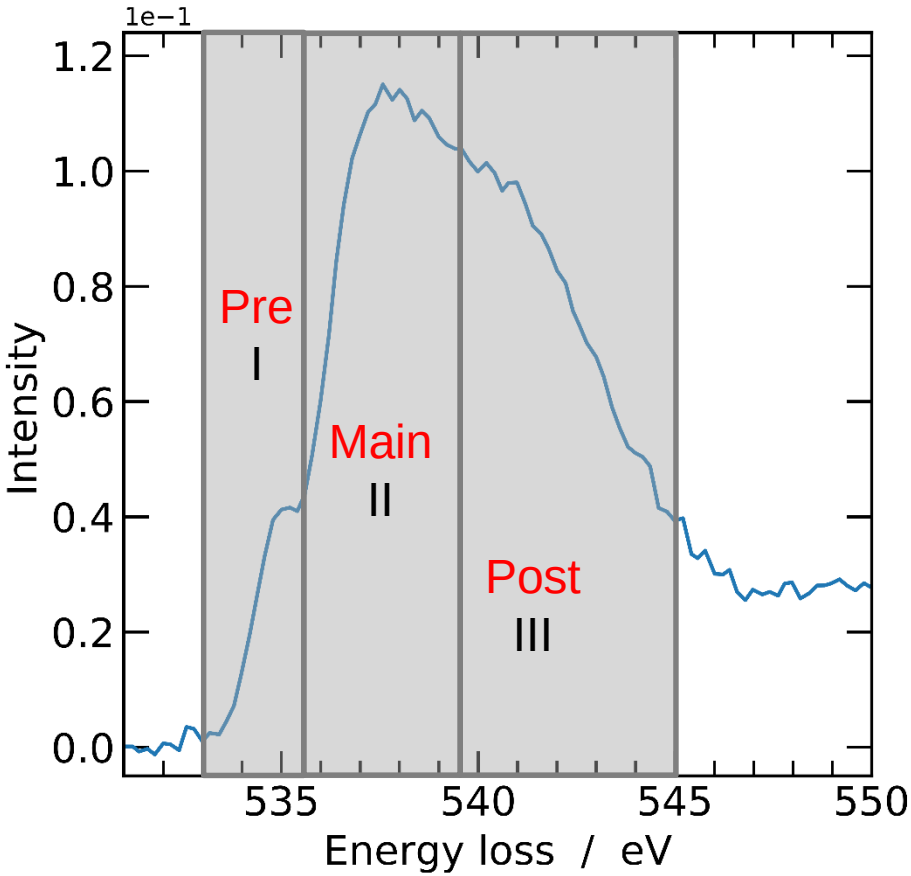
XRS at the oxygen K-edge

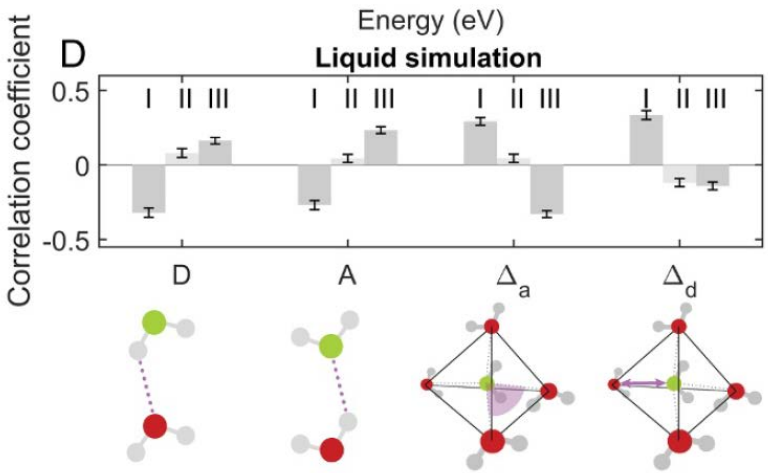


Ch. J. Sahle et al, PNAS, 2013

XRS at the oxygen K-edge

J. Niskanen et al,
Phys. Rev 2017; PNAS, 2019





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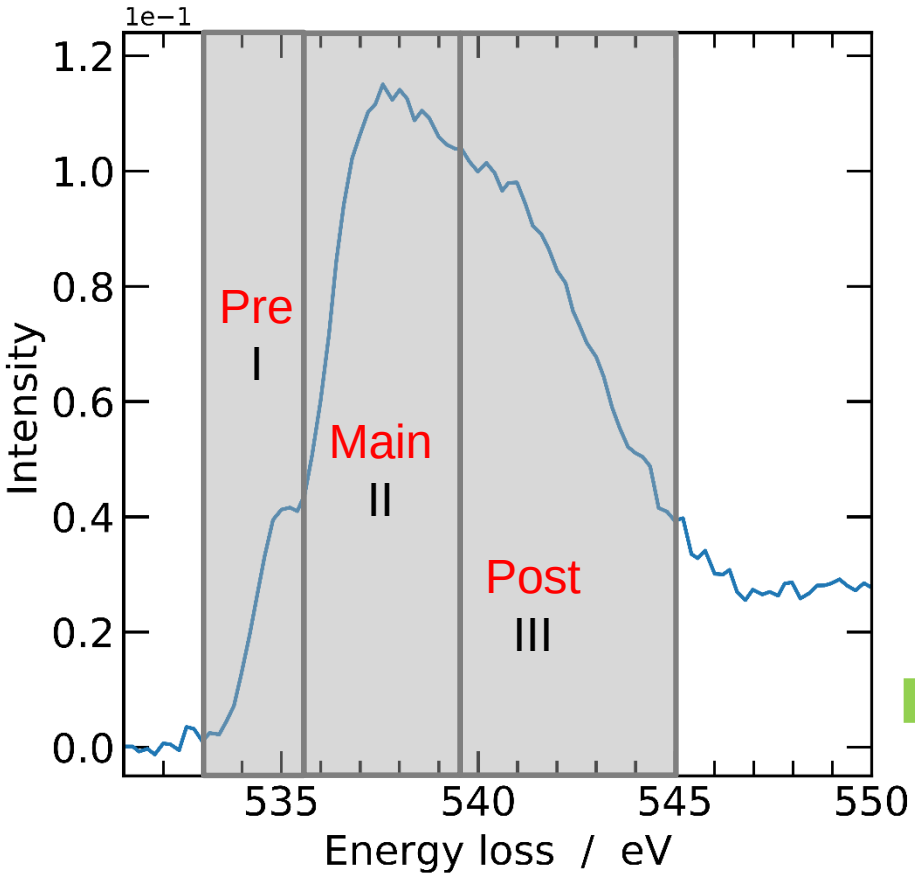

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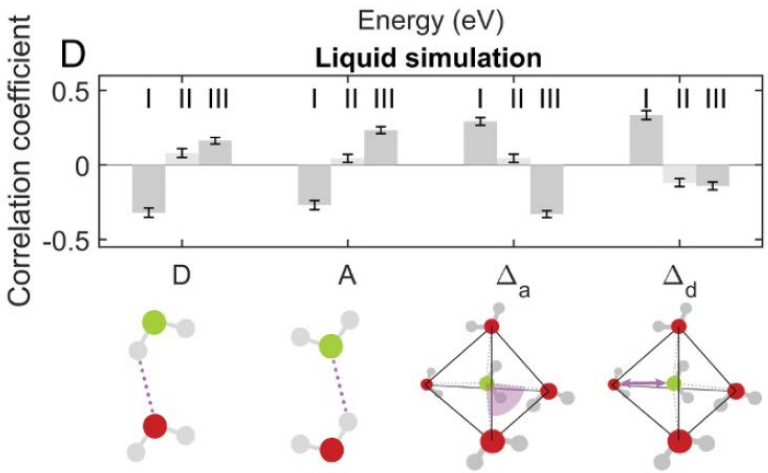
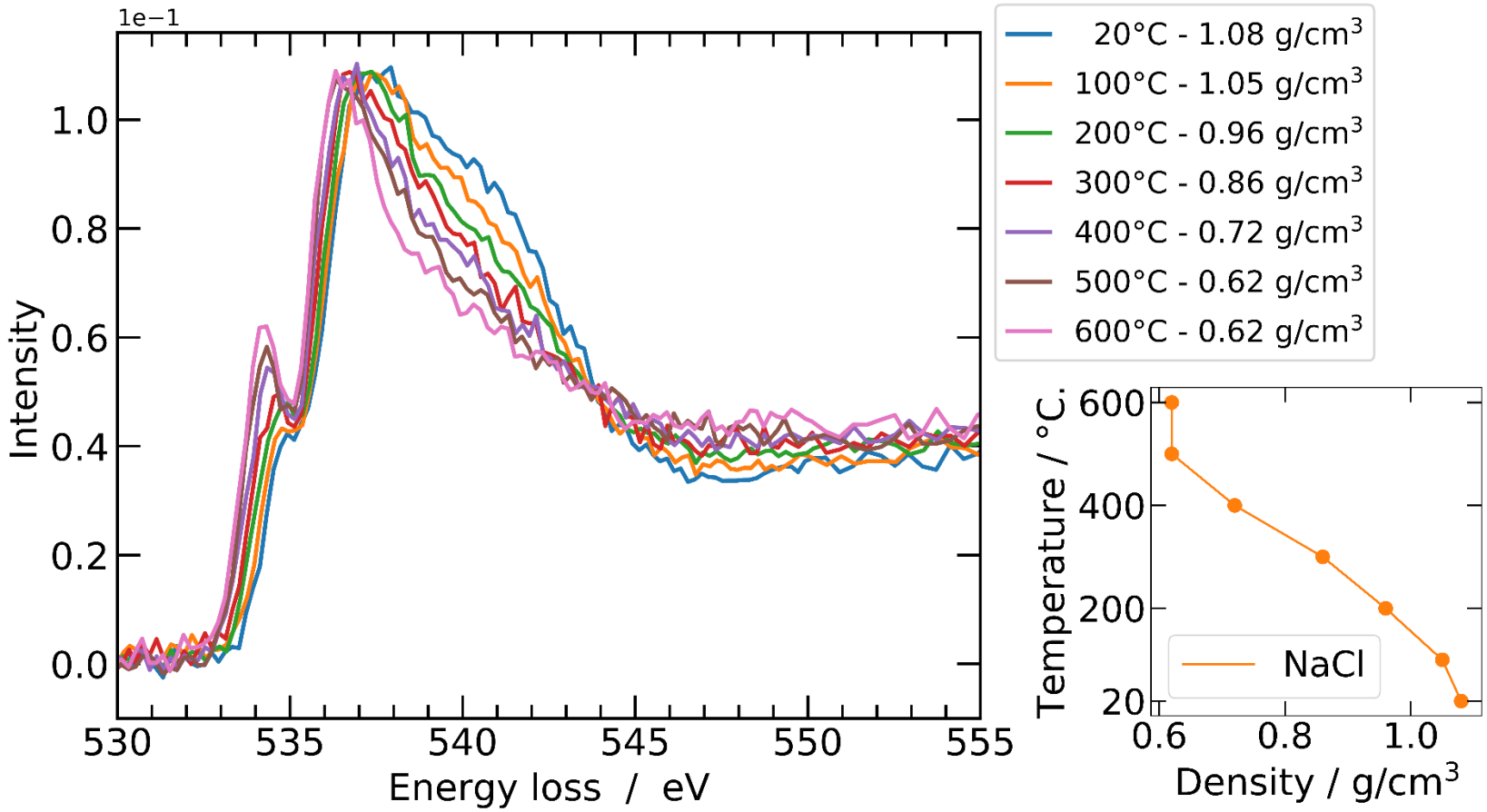


Spectral features are correlated to the local structural environment of the probed oxygen atom

XRS spectra of sodium chloride



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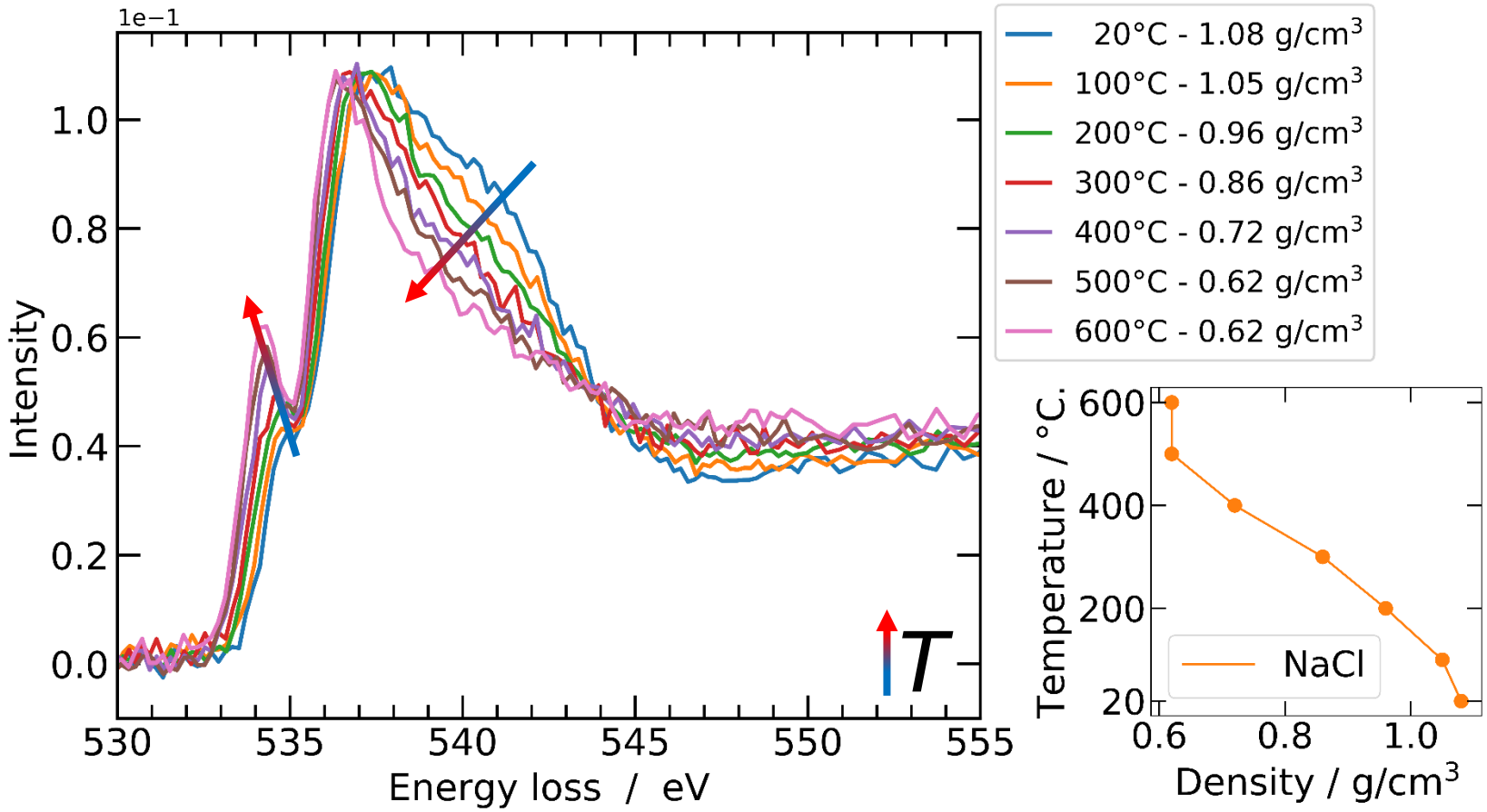

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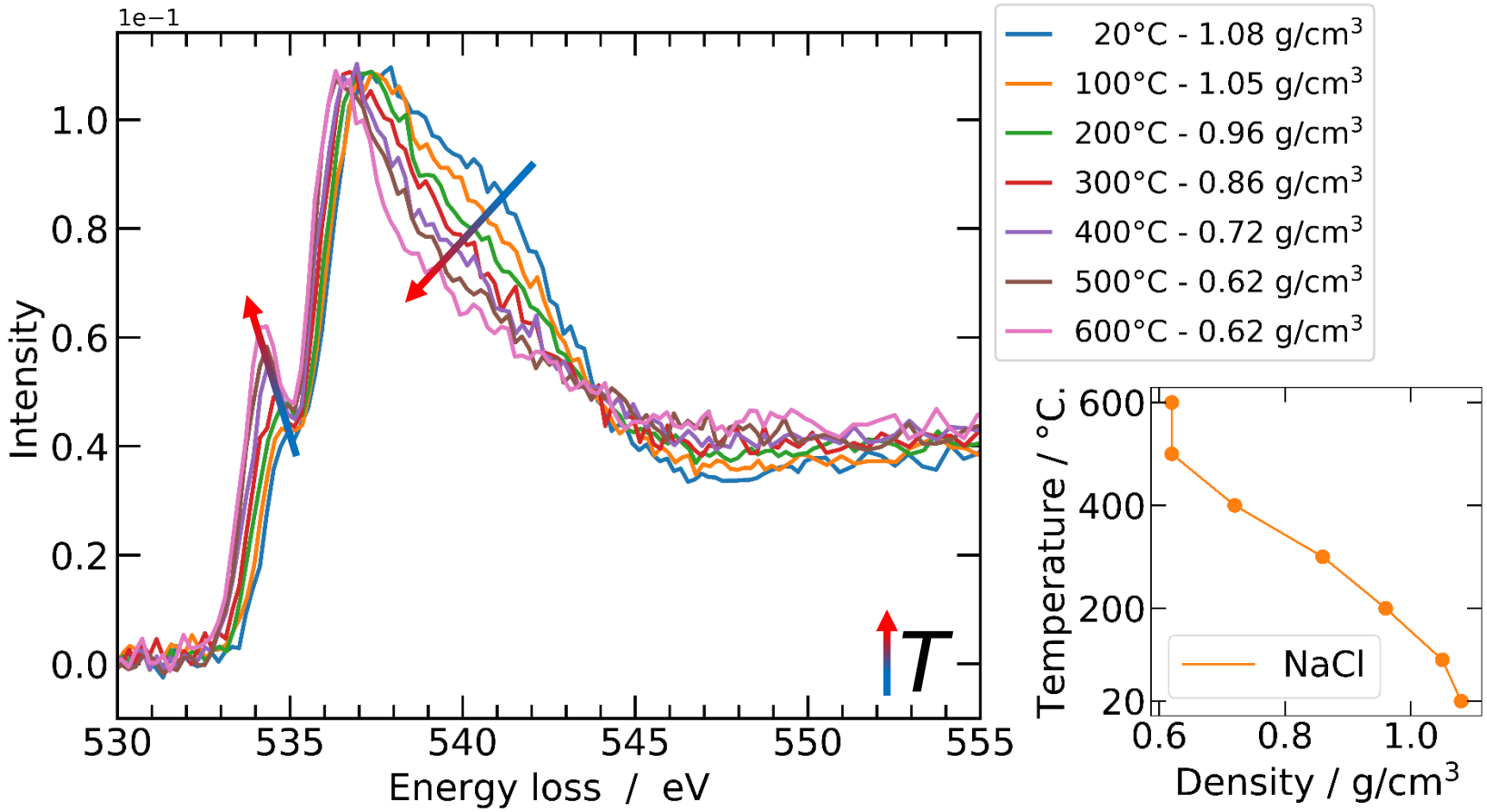
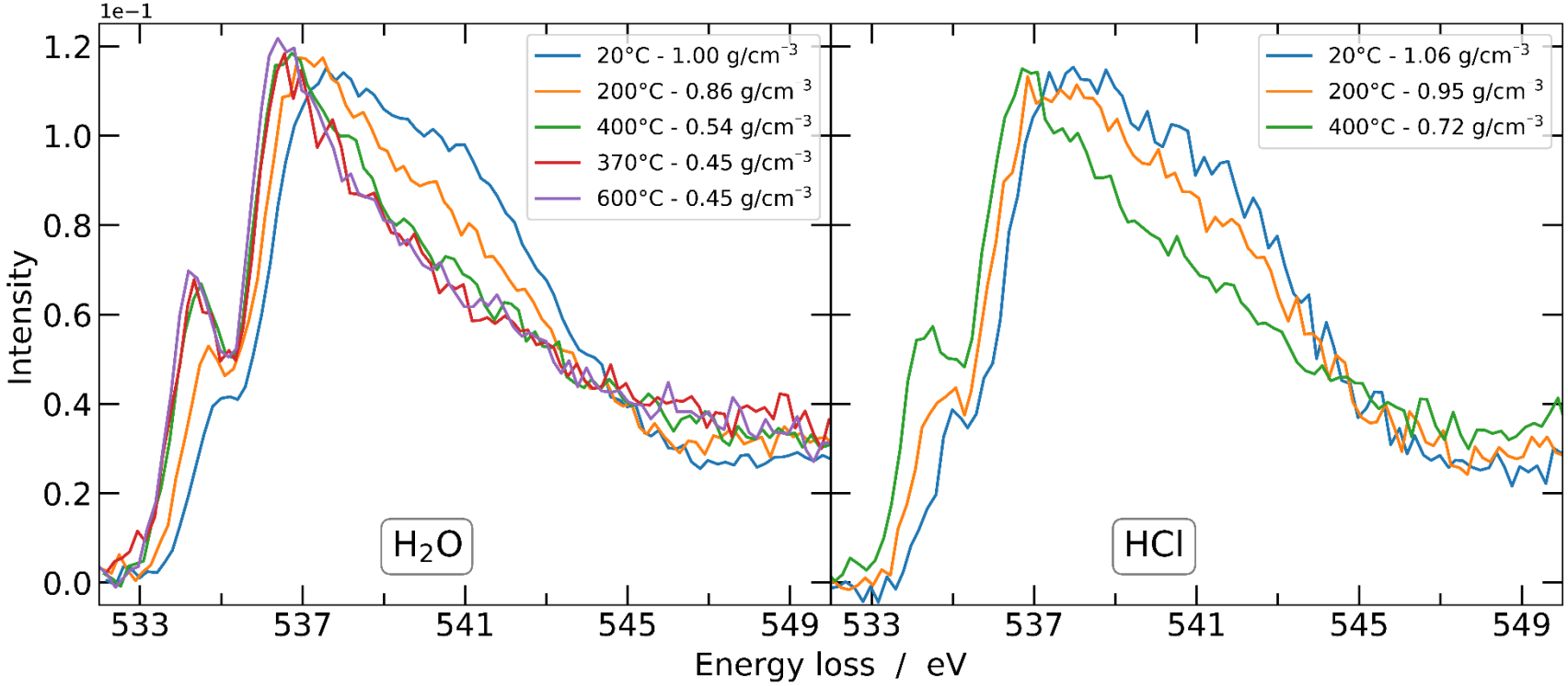
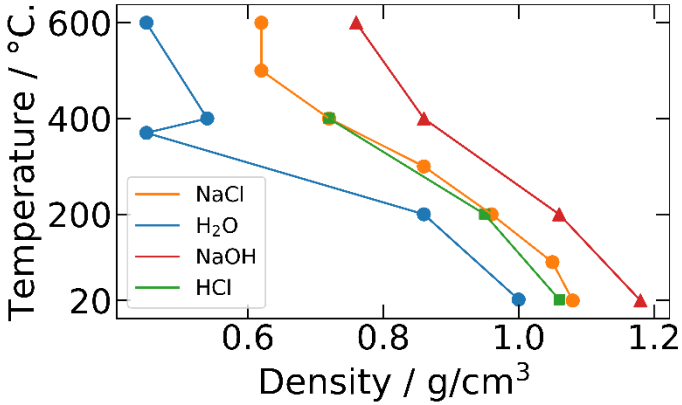


- Reduction in the total number of hydrogen bonded molecules
- General loss of tetrahedrality with increasing temperature

Hydrothermal H_2O, NaOH and HCl solutions

Ch. J. Sahle et al, J. Phys. Chem. B, 2017





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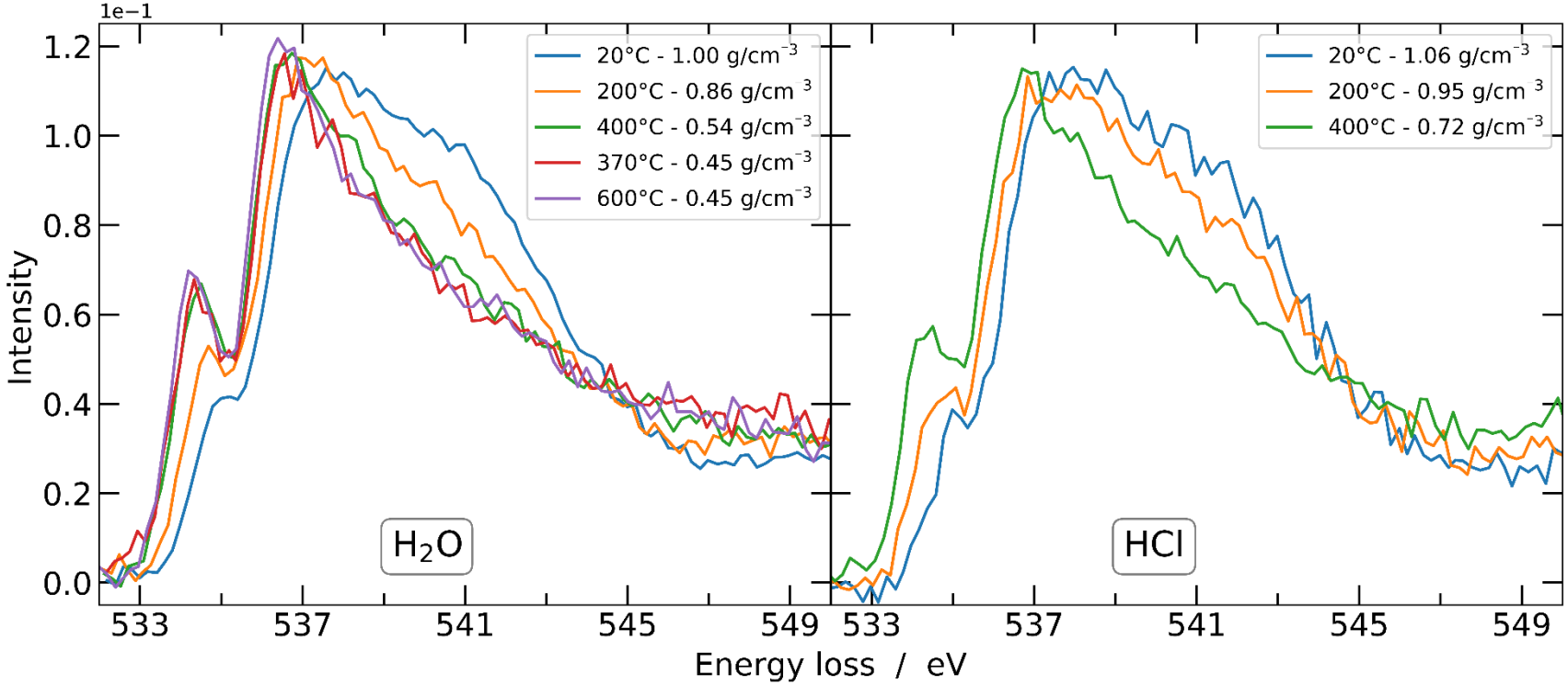
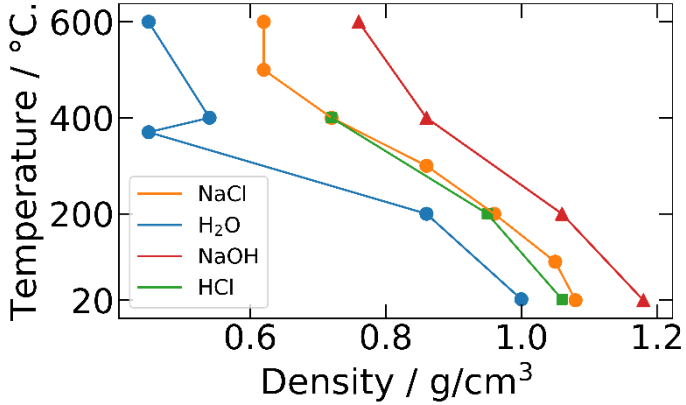
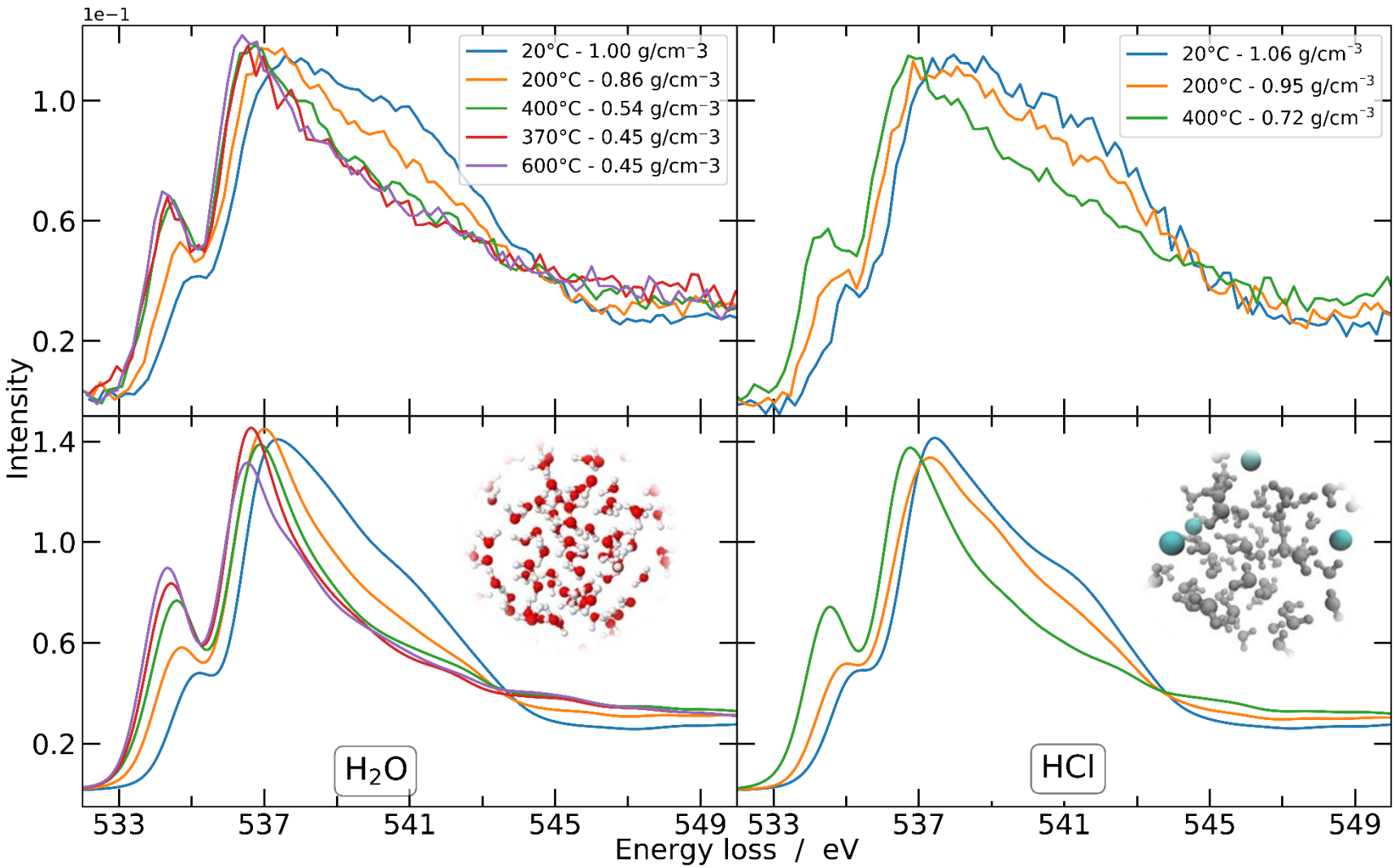




Overall spectral changes are similar to NaCl solution

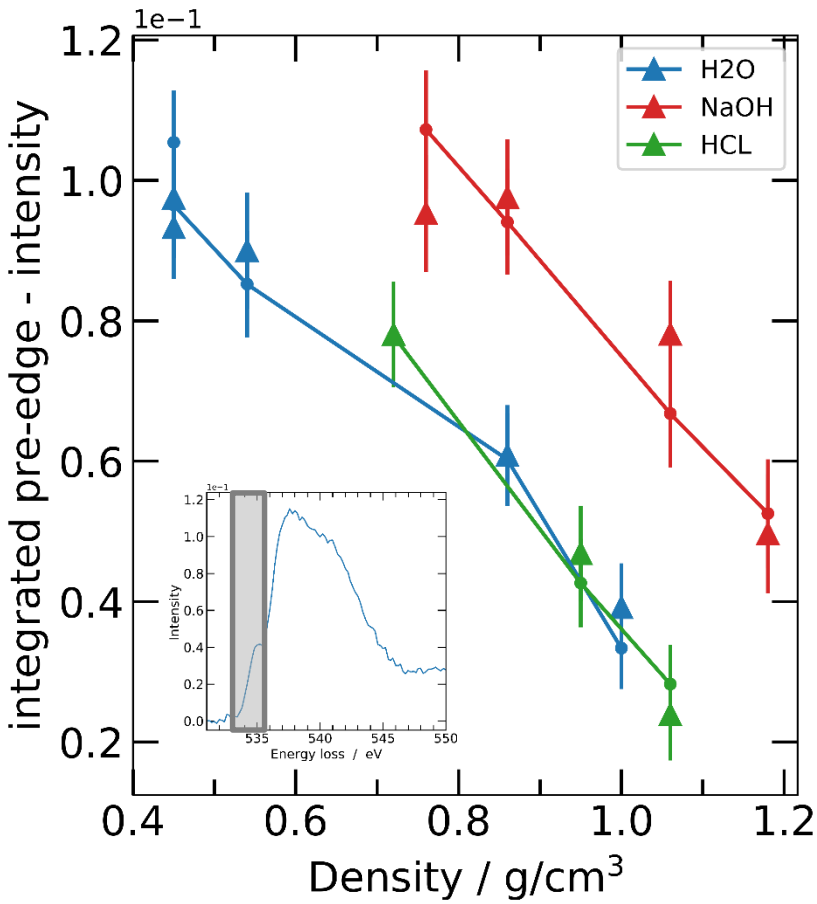
Comparison experiment – calculation

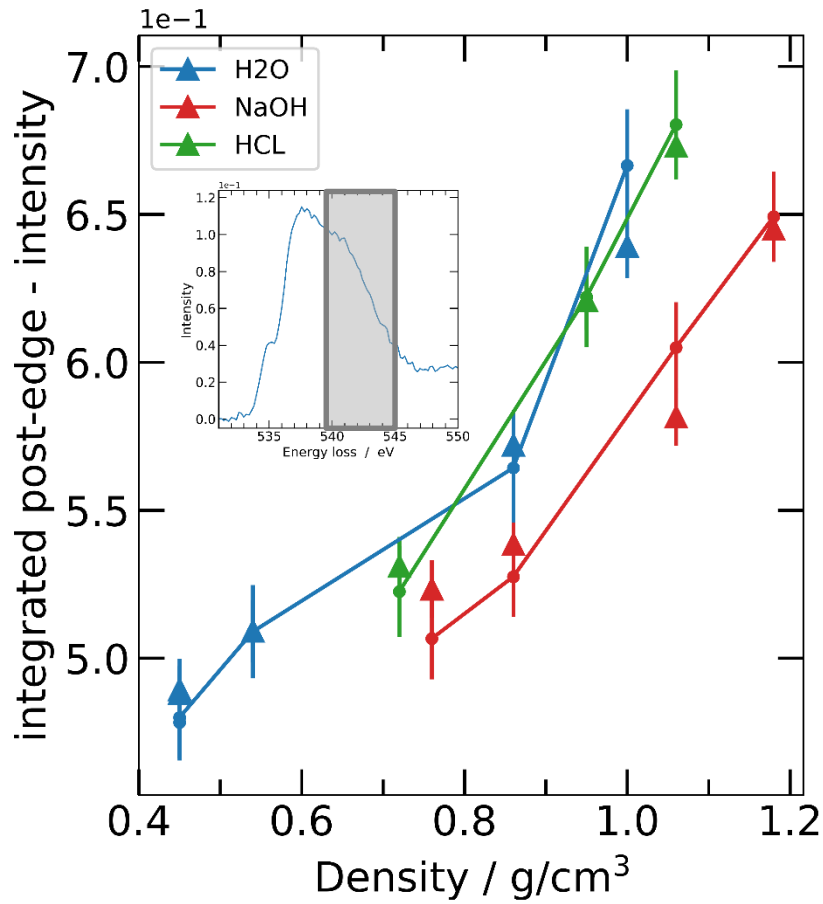


Ch. J. Sahle et al, J. Phys. Chem. B, 2017

K. Gilmore, Comput. Phys. Commun. 2015; ***OCEAN***

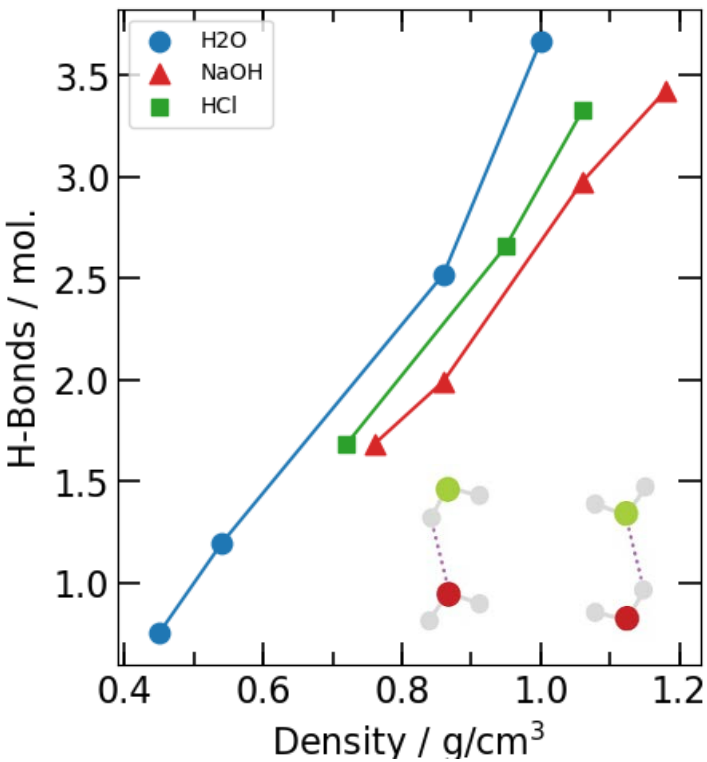
Quantitative comparison: experiment – calculation

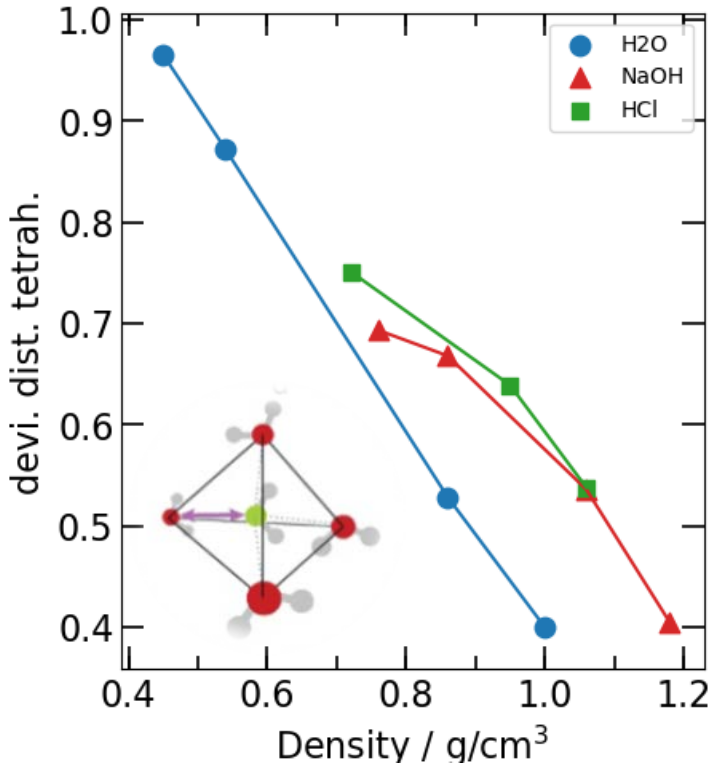




Experimental trends are almost completely reproduced

Extracted structural information





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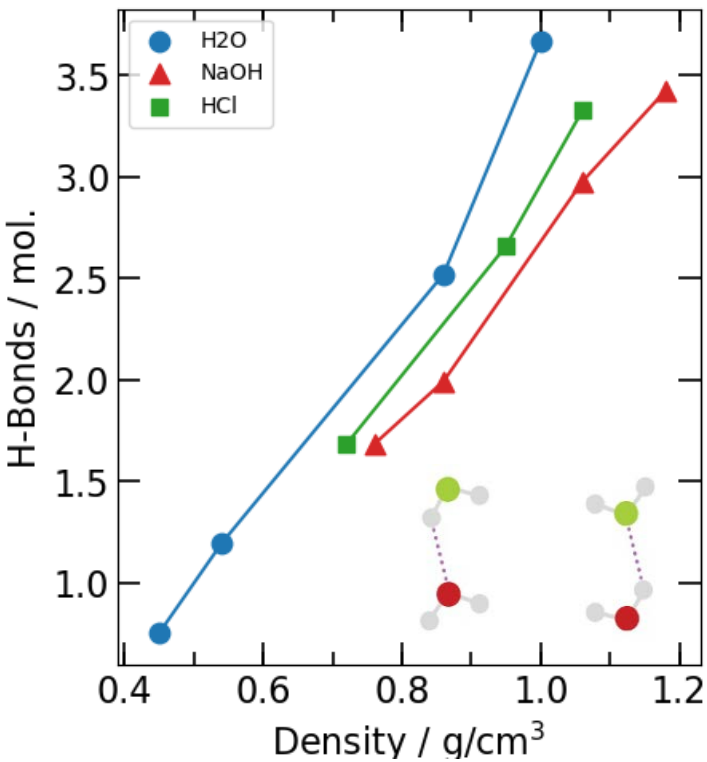
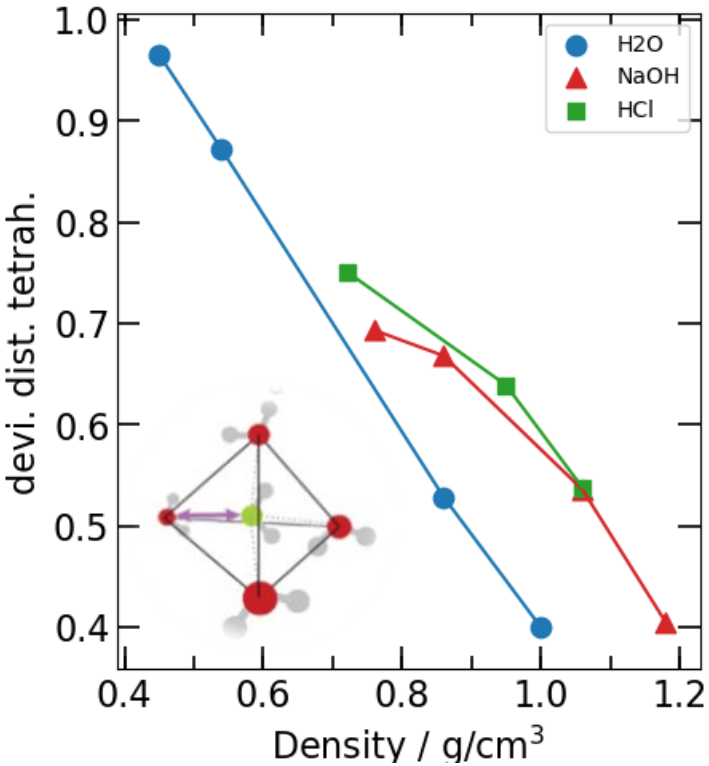
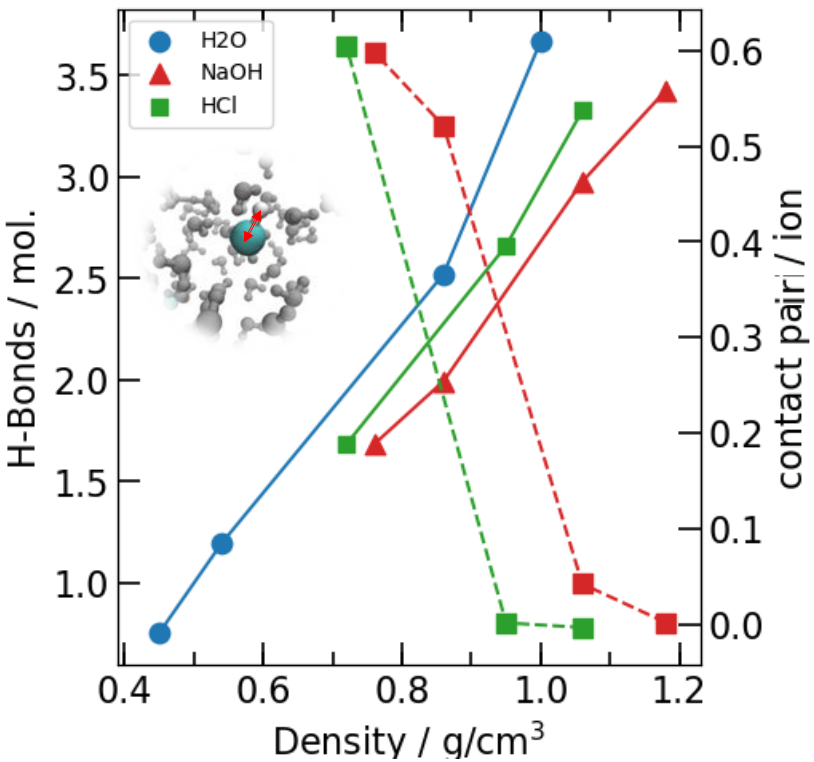
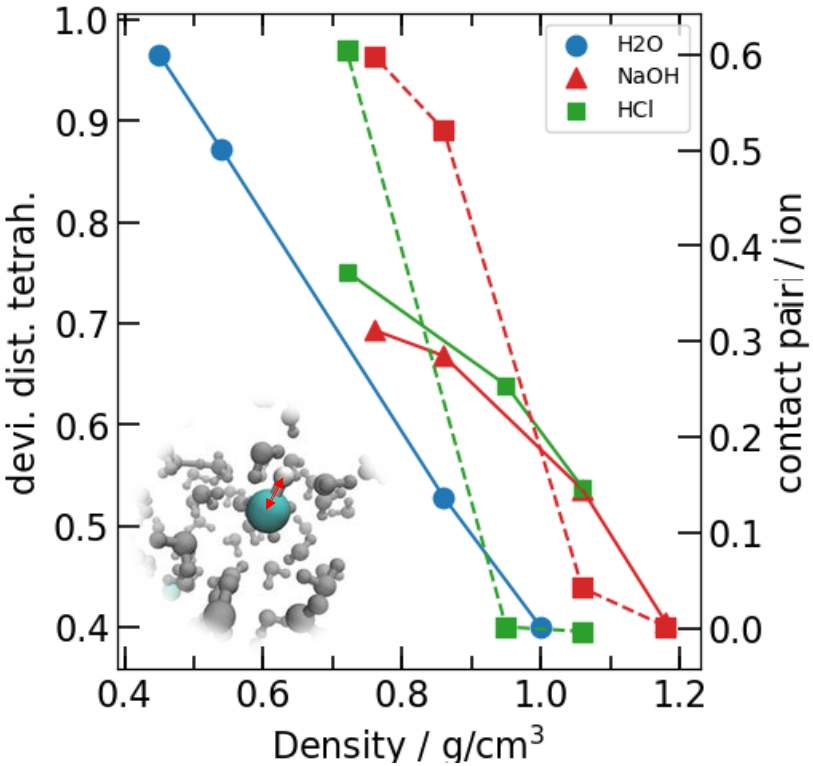




- Destabilizing effect of the dissolved salt ions on the water structure

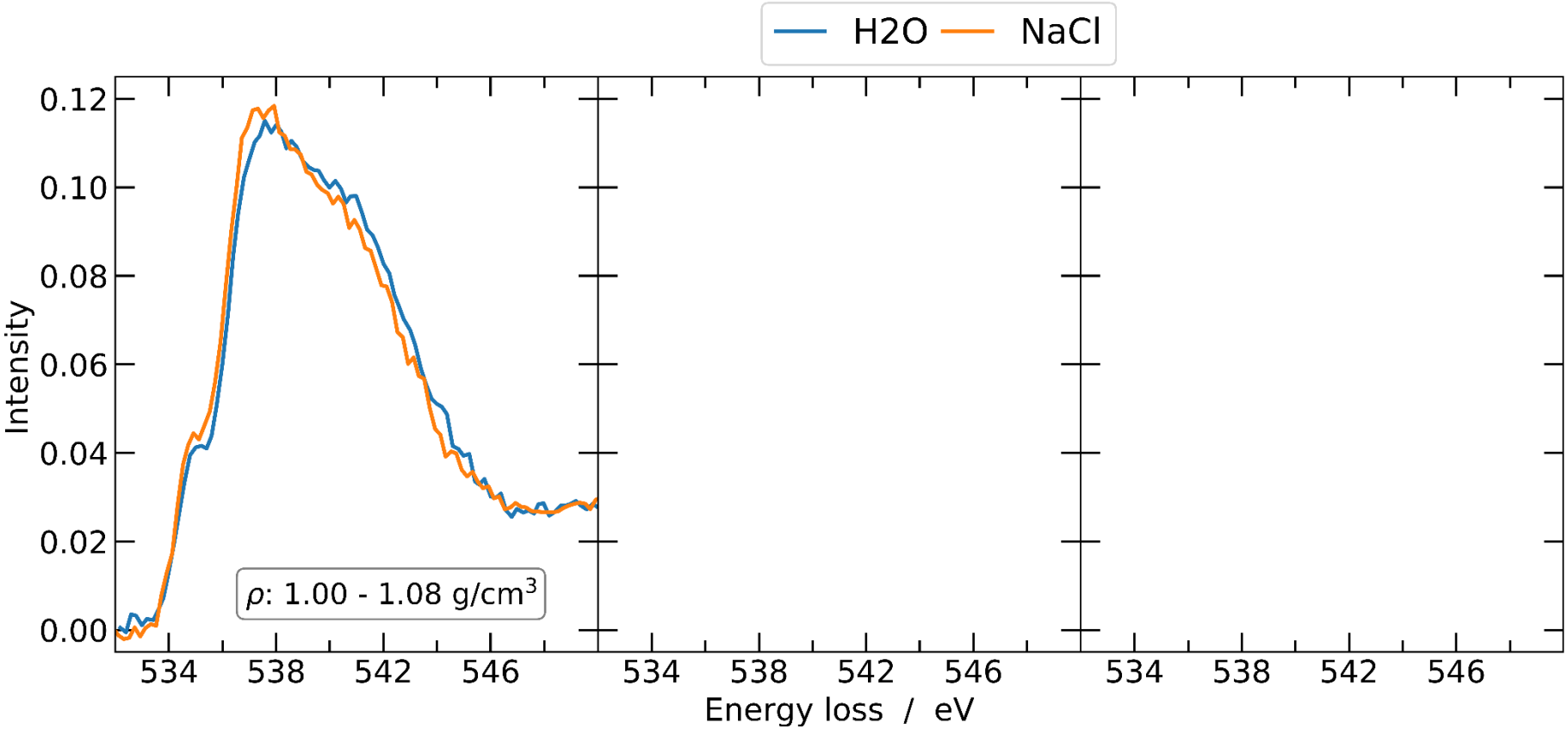
Contact ion-pairs

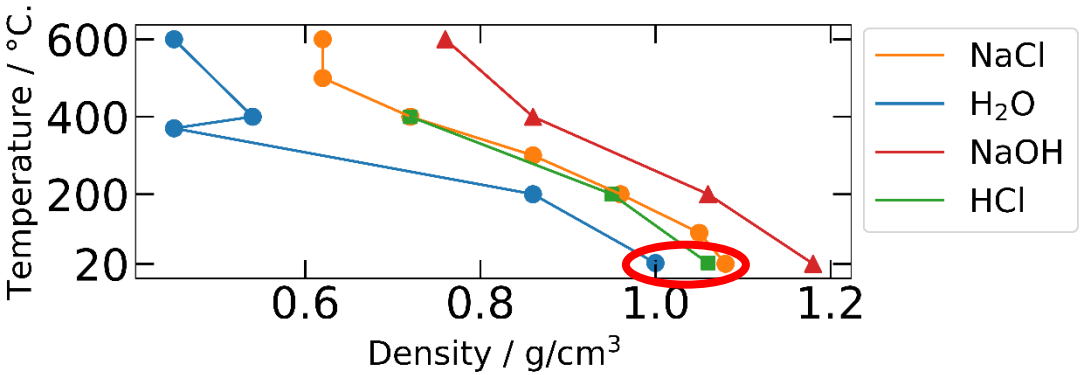




- Destabilizing effect of the dissolved salt ions on the water structure
- Formation of contact pair ions reduce the destabilizing effect
  - Structural similarity to pure water increases

Comparison of NaCl and H_2O





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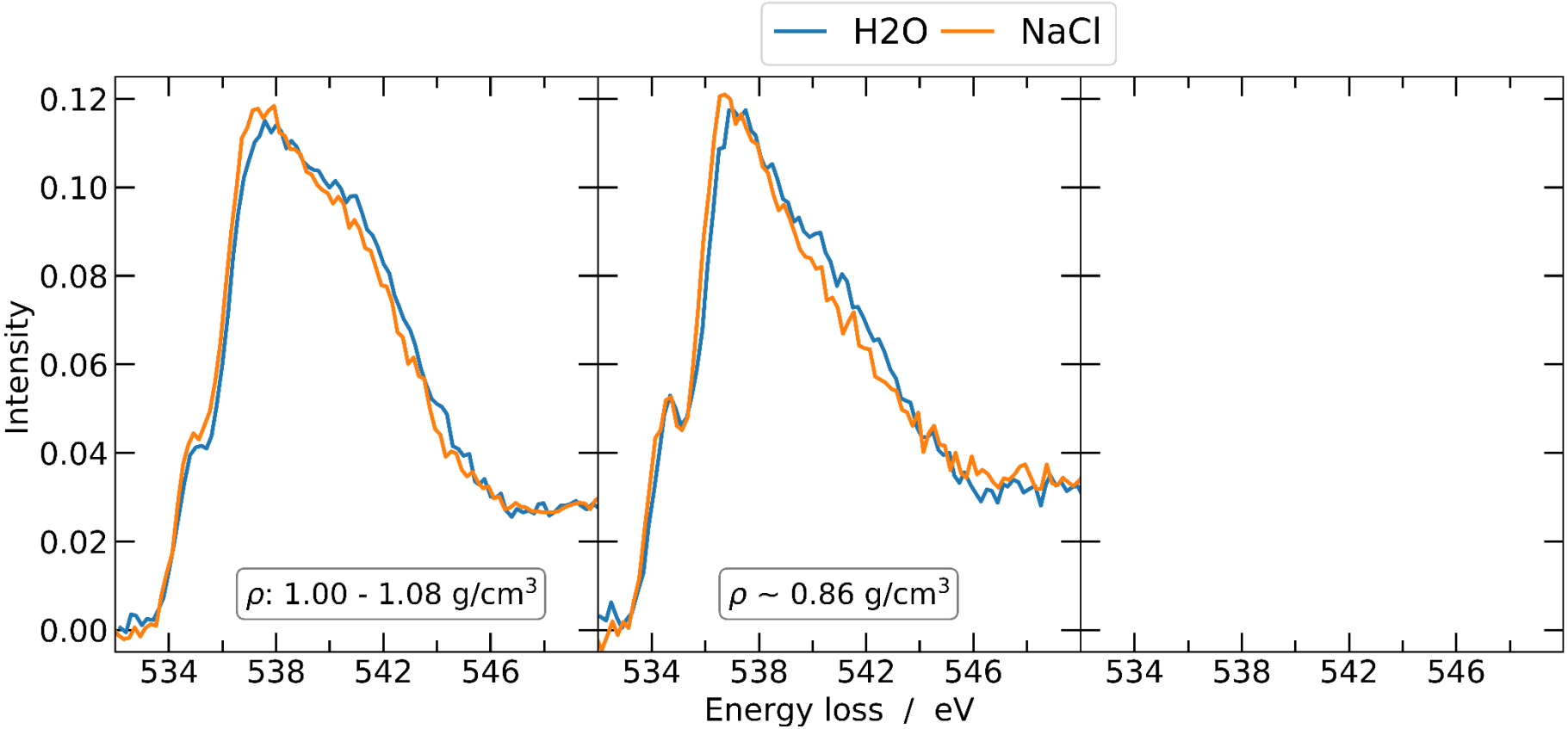

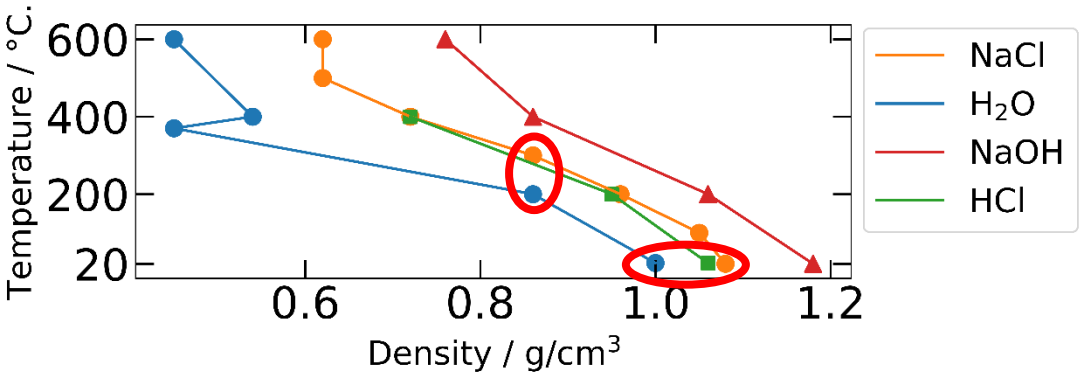

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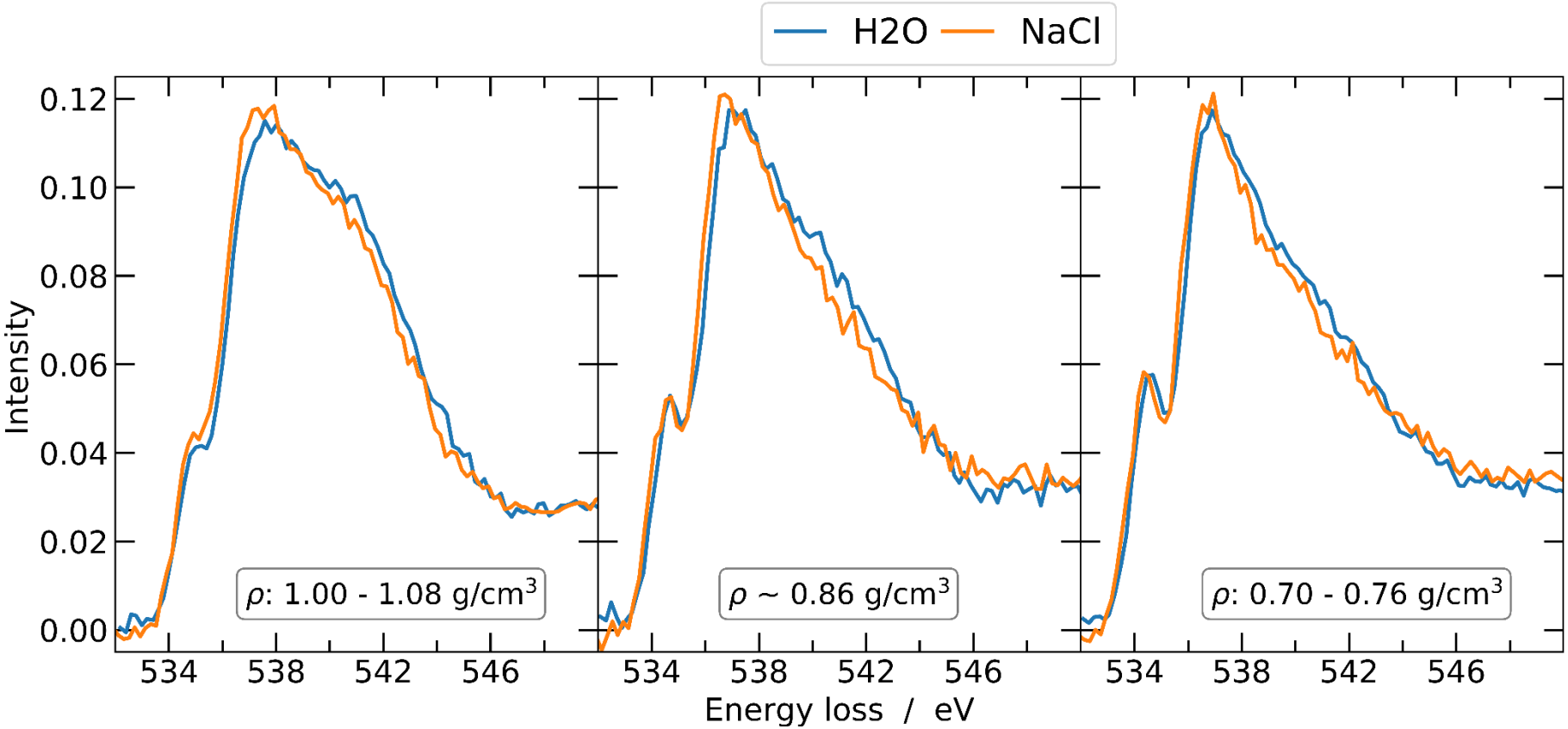

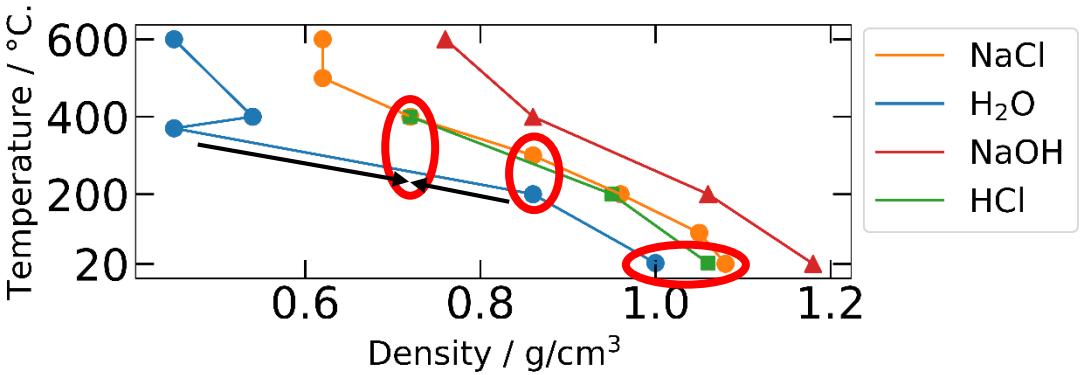

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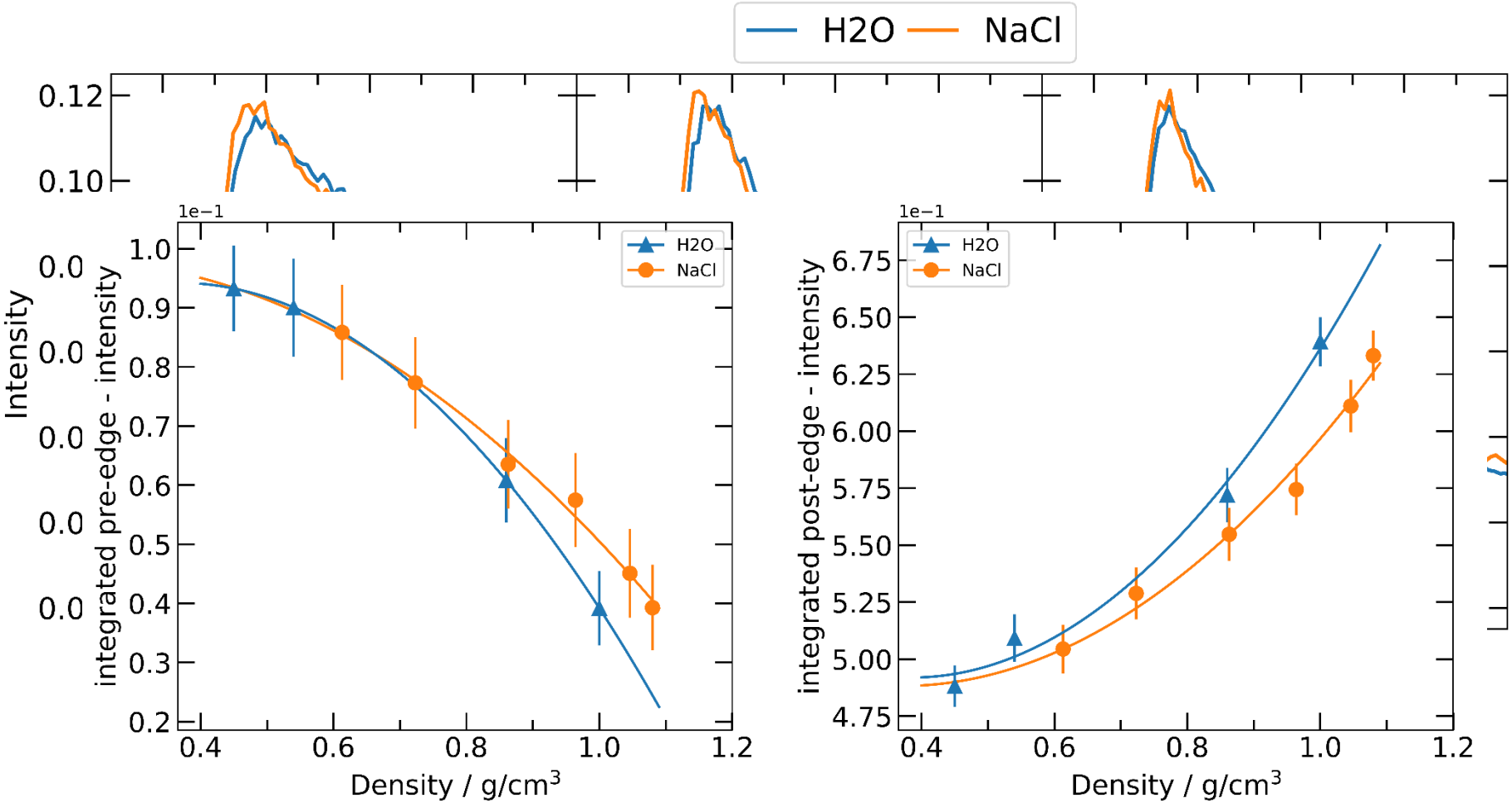

Acknowledgments

Christian Schmidt

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Sandro Jahn

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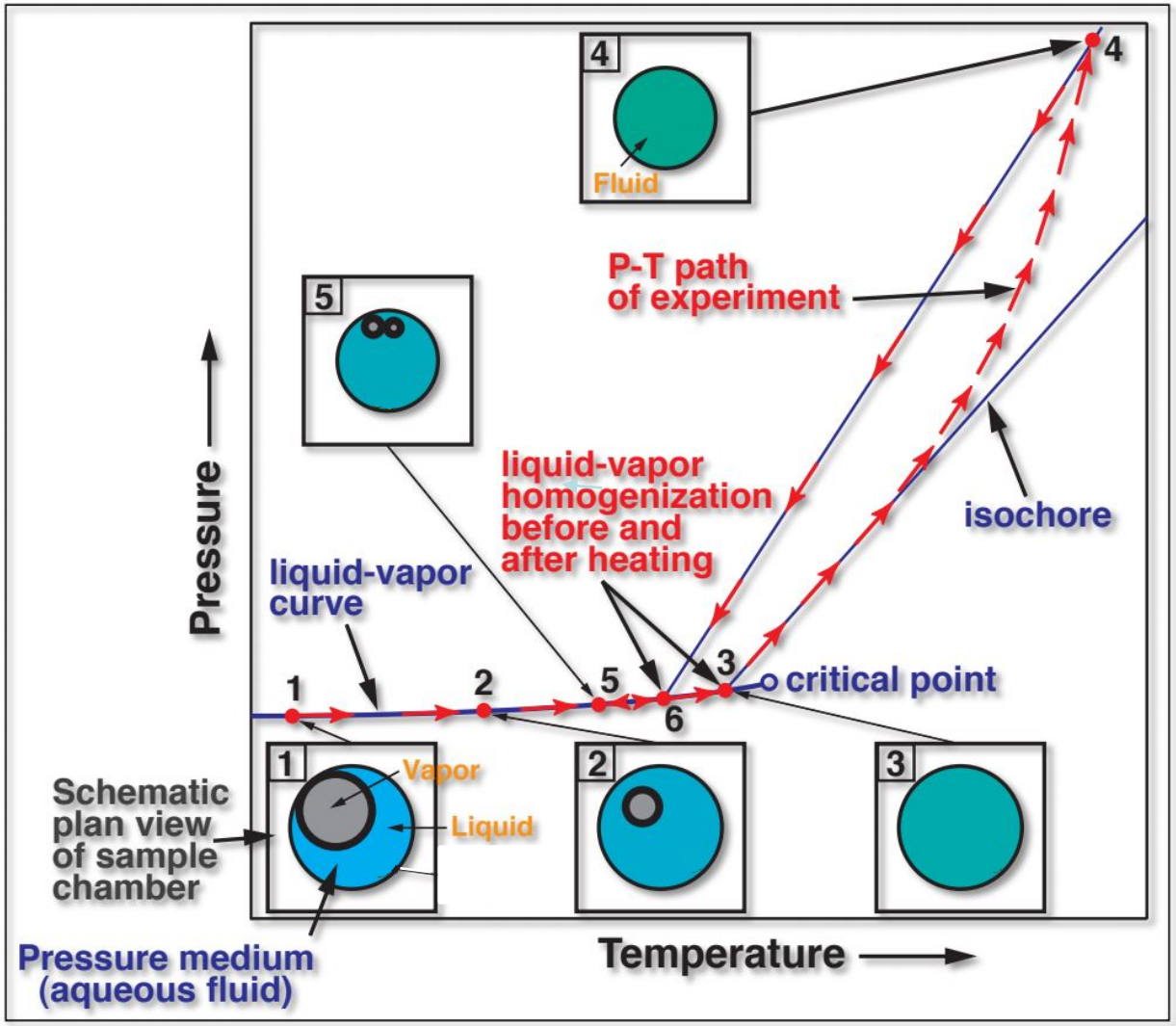
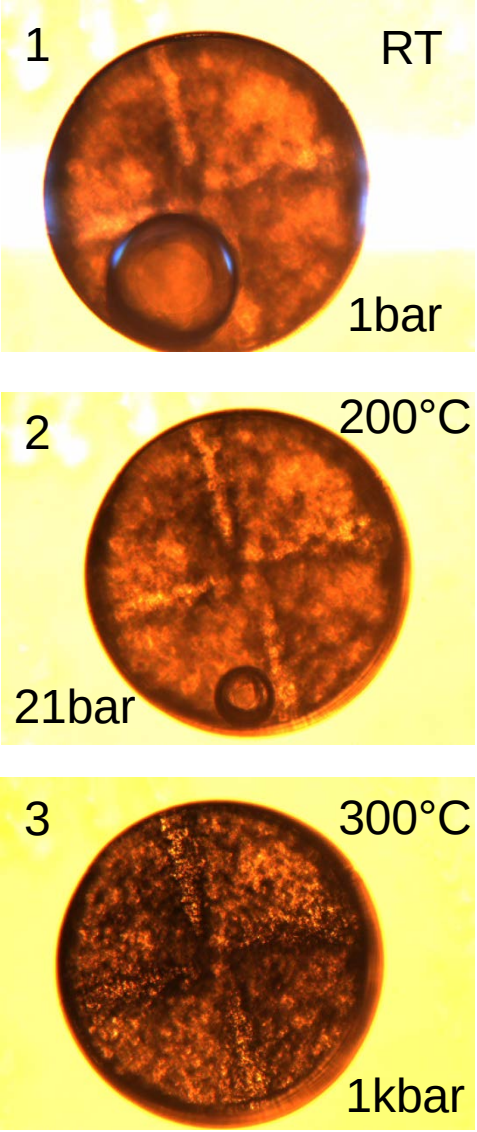
Thank you for your attention!

Determination of thermodynamic conditions



Modified from C. Schmidt, I. Chou