Raman Spectroscopy of Phase Transitions in the H-Sublattice of H_2O-Ices

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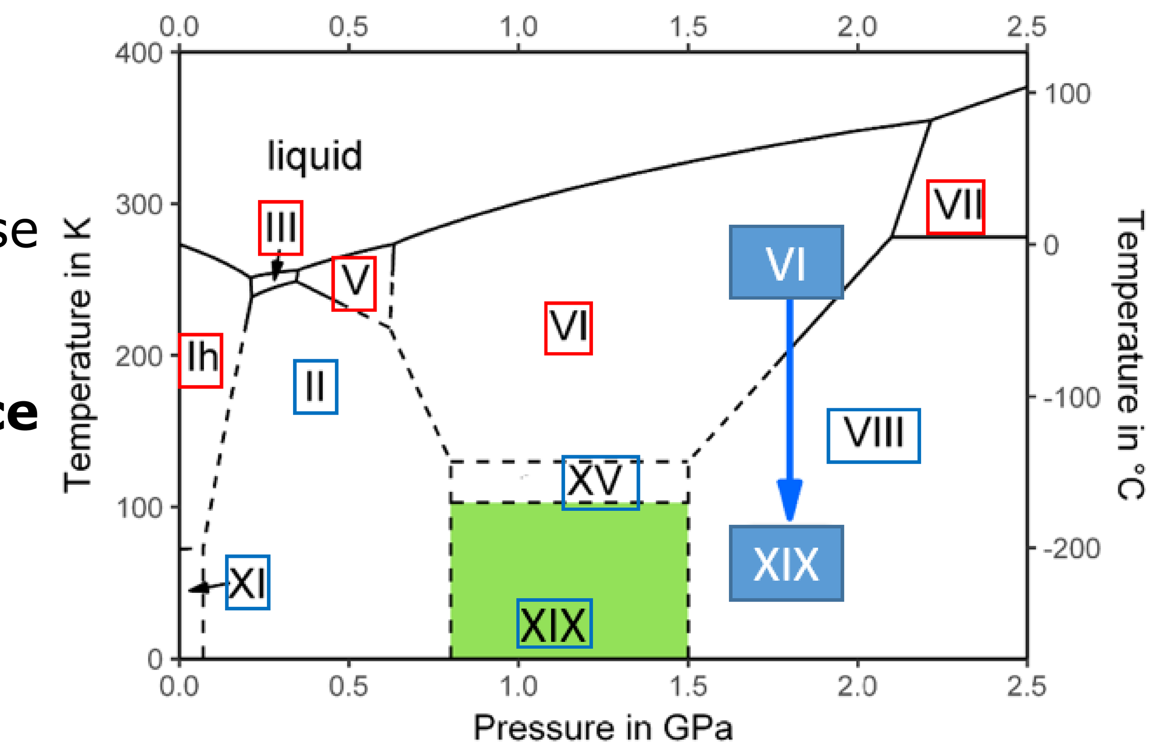
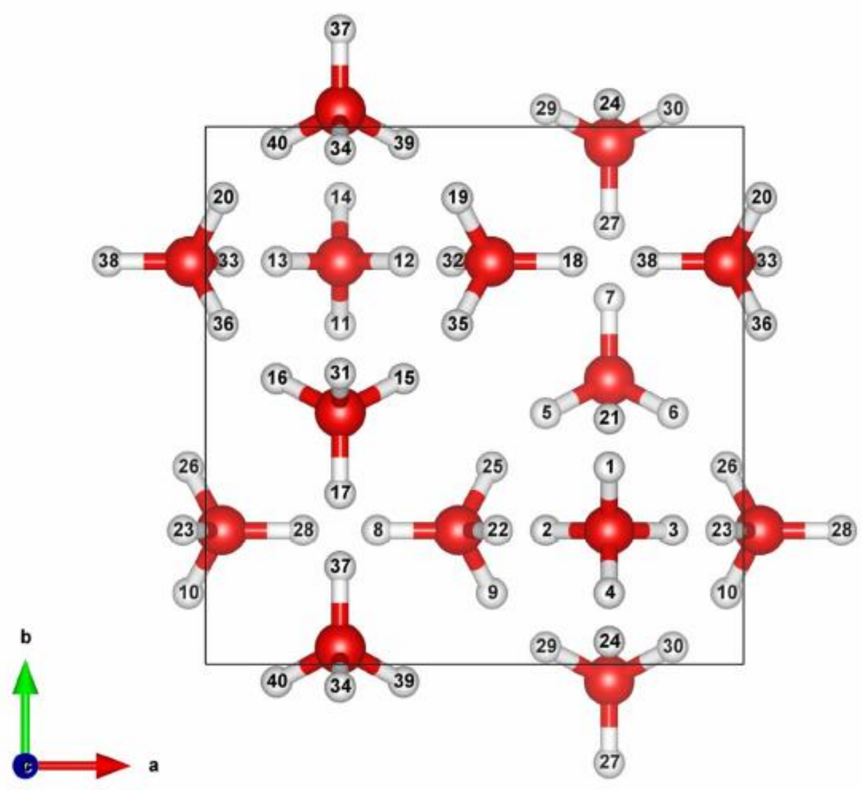
Introduction:

- In total, 20 different crystalline structures of water ice have been discovered [1,2,4].
- One reason for that diversity is the existence of both one H-disordered high-temperature phase and one H-ordered low-temperature phase for most oxygen lattice.
- In 2017, an alternatively H-ordered proxy of ice VI additionally to ice XV was discovered – **ice XIX** [1].
- Its structure was resolved in 2020 and the unit cell has twice the size of that of ice VI & XV.
- That is the first known example of alternative H-ordering.



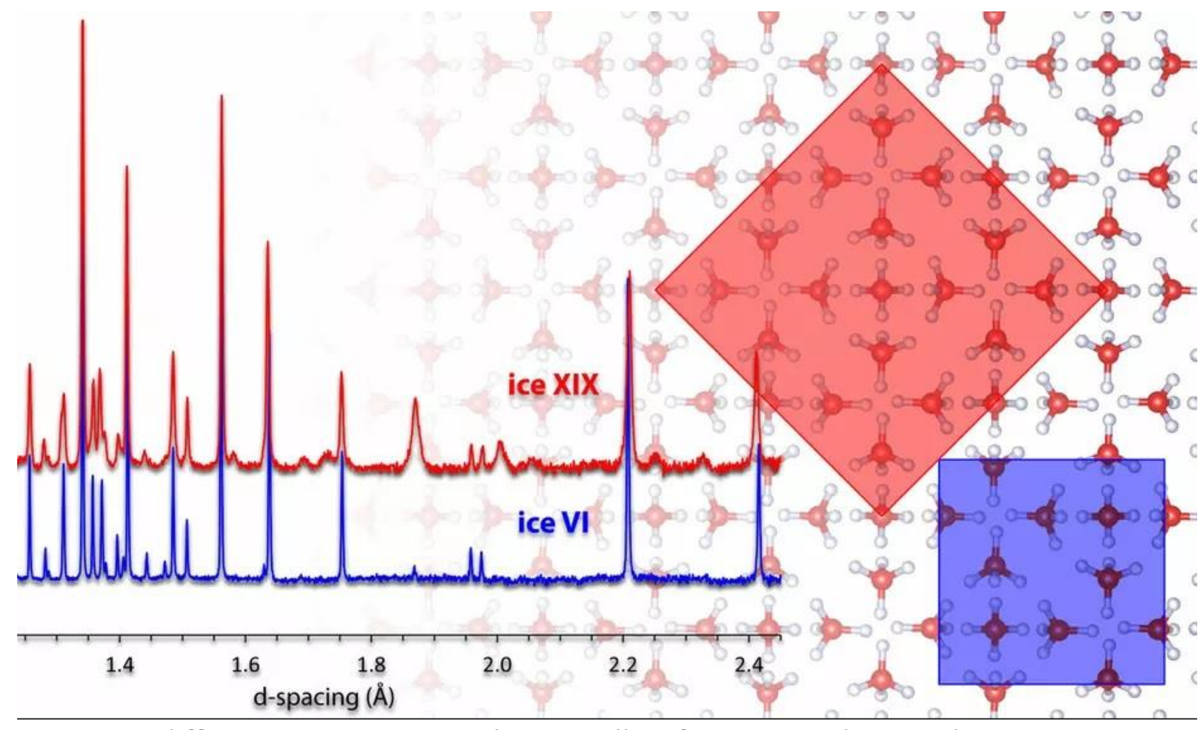
Phase Diagram of crystalline H_2O-ices in the pressure range of 0-2.5 GPa, adapted from [1]. H-ordered phases are depicted blue, H-disordered phases red. (Only stable phases are shown)



Unit cell of ice VI/XV; in H-disordered forms, all H-positions are occupied randomly and equally through the crystal, in H-ordered ones their positions within the unit cell are clearly determined. For the ice VI unit cell, 45 clearly defined different arrangements are theoretically possible. [5]

Goal:

- **Determination of mechanism and kinetics of the first known H-order-order transition in ice chemistry.**
- **Investigation of potential other examples for alternative H-ordering.**



Neutron diffraction patterns and unit cells of ice VI and XIX; the volume of the ice XIX-unit cell is approximately twice that of ice VI and ice XV [2].

Method:

- **Raman-Spectroscopy** is a method in order to detect inter- and intramolecular vibrations of a sample by a special scattering effect – Stokes scattering.
- After undergoing Stokes scattering the energy of the scattered light is reduced by the vibrational energy.
- These differences can only be measured if the inciting light is monochromatic. In these experiments a laser of 521 nm wavelength are used.
- As inter- and intramolecular vibrations get detected, Raman spectroscopy is especially sensitive for structural differences in the H-sublattice.

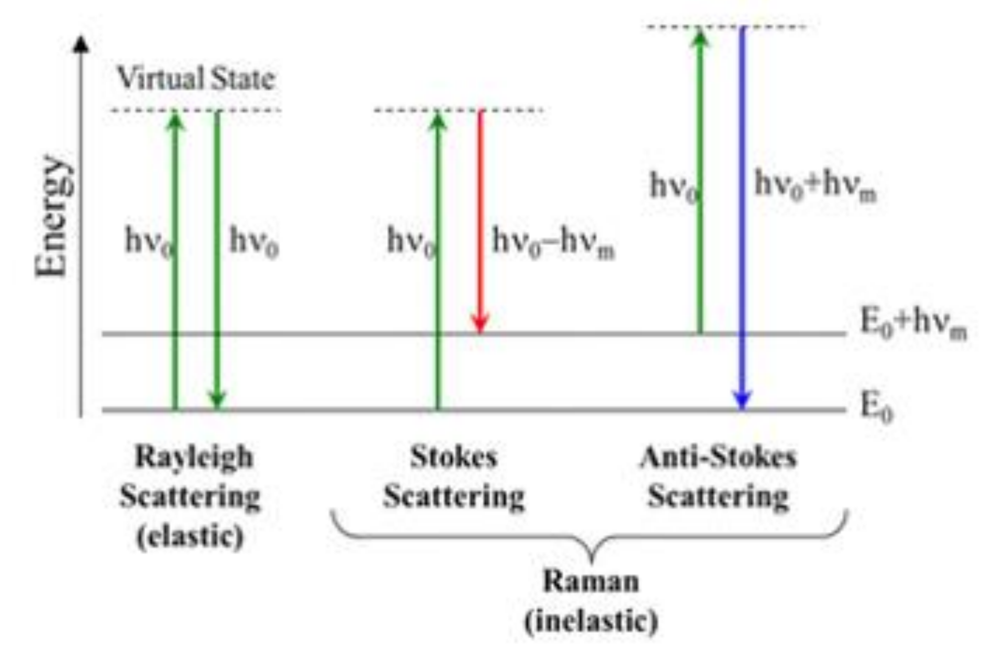
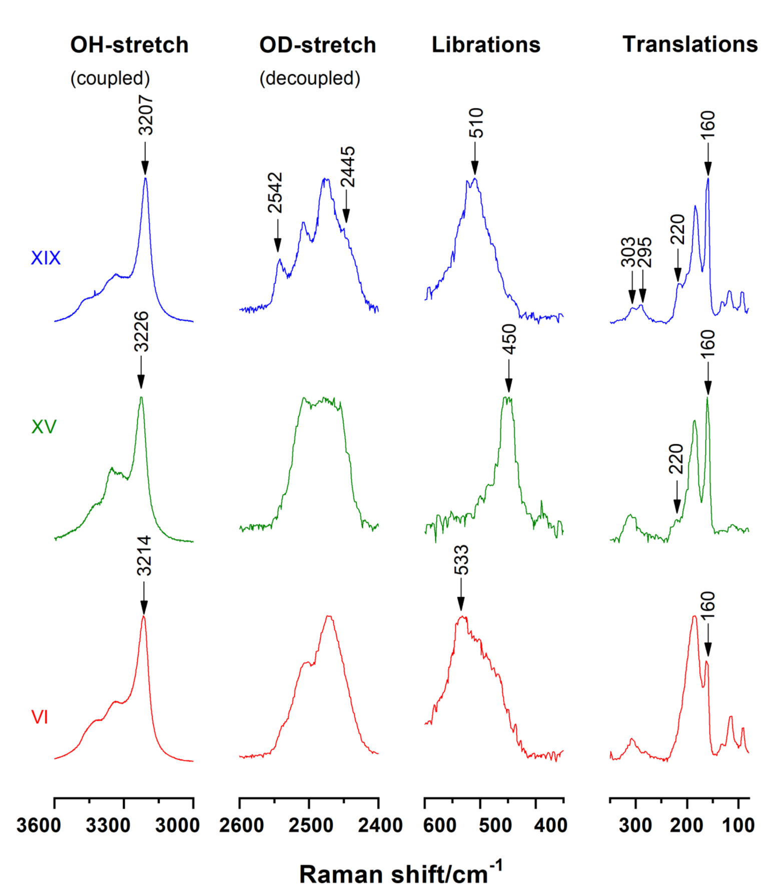


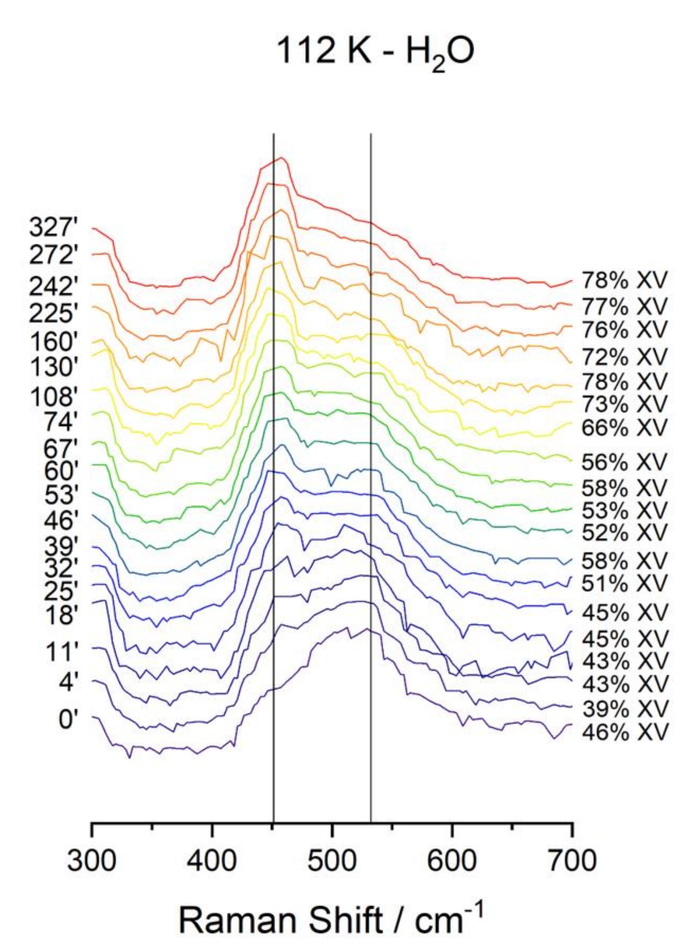
Illustration of the difference between elastic Rayleigh scattering – known e.g. from rainbows – and inelastic Stokes scattering regarding their energy balance [6].

Results:

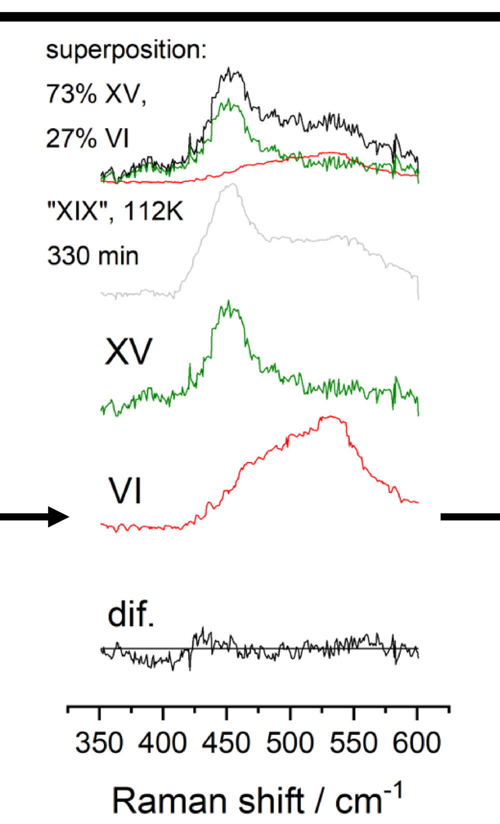
- Raman spectra of ice VI, XV and XIX are distinguishable from each other.
- The complete H-order-order transition can be traced through Raman spectroscopy.



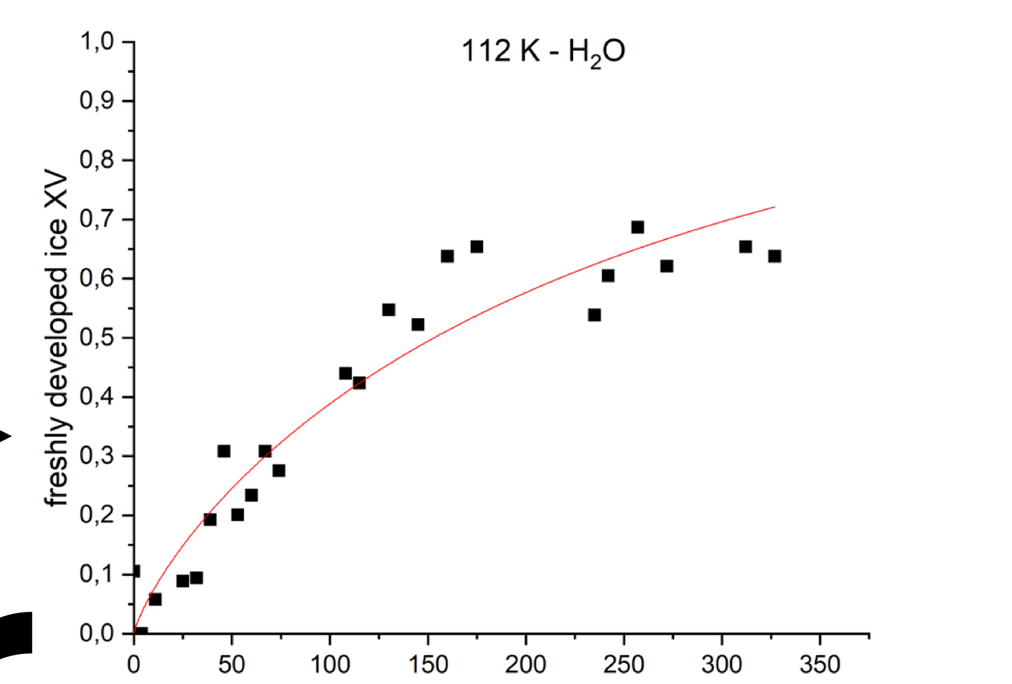
Comparison between the Raman spectra of ice VI, XV and XIX. The pattern of decoupled OD-stretching vibrations is especially characteristic for ice XIX, whereas that of librational vibrations is so for ice XV. [3]



Development of the ice XV-buildup at 112 K.

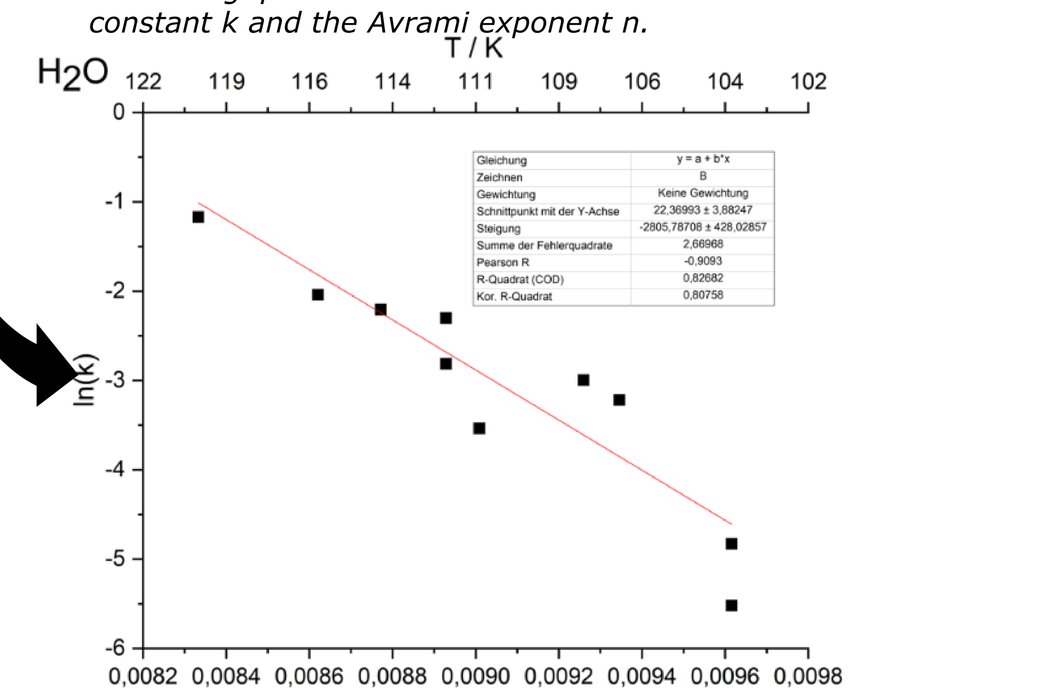


The ice XV-fraction can be determined for each spectrum through the superposition of reference spectra.



All ice XV-fractions of that measurement can than be plotted against time and fitted with the Avrami-equation in order to derive interesting parameters for that transformation such as the rate constant k and the Avrami exponent n.

- Ice XIX is heaten to different temperatures and Raman spectra are recorded there isothermally. *(top, right)*
- The ice XIX and ice XV-fraction are calculated by superpositions. *(top, middle)*
- These fractions can be plotted against their transformation time. Through Avrami fits parameters of interest such as the rate constant k – informing about the pace of the transition – and the Avrami exponent n – informing about its spatial expansion – can be derived. *(top, left)*



Rate constants k measured at different temperatures are fitted according to the Arrhenius equation in order to obtain the activation barrier of the ice XIX -> XV transformation.

Activation energy for ice XIX -> XV:

$E_A \approx 23$ kJ/mol

Sources:
[1] T. Gasser, et al., Chem. Sci. 9 (2018), 4224-4234
[2] T. Gasser, et al., Nat. Commun. 12 (2021), 1128
[3] A. Thoeny, et al., Phys. Chem. Chem. Phys. 21 (2019), 15452-15462
[4] H. Koenig, Zeitschrift für Kristallographie 105 (1943), 279-286
[5] K. Komatsu, et al., Scientific Reports 6 (2016), 28920
[6] bwtek.com/raman-theory-of-raman-scattering/Fig. R4