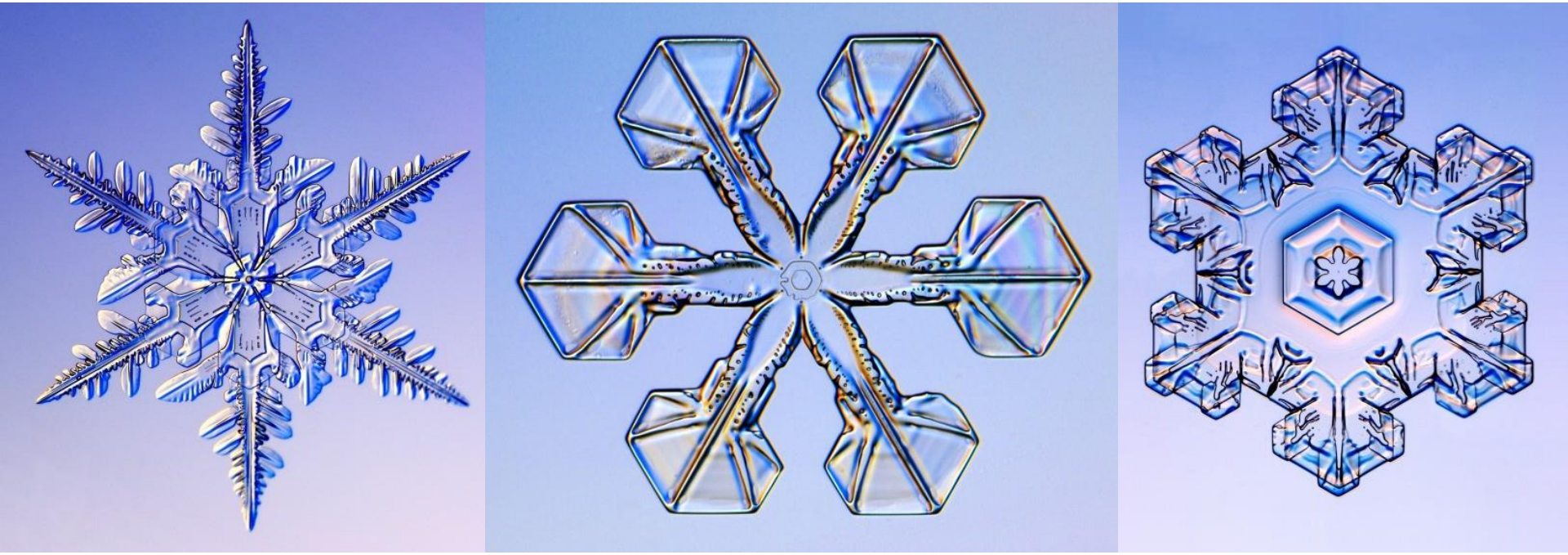
Ice – a miraculous material

Neutrons Matter, 7th International Workshop on Electron-volt Neutron Spectroscopy



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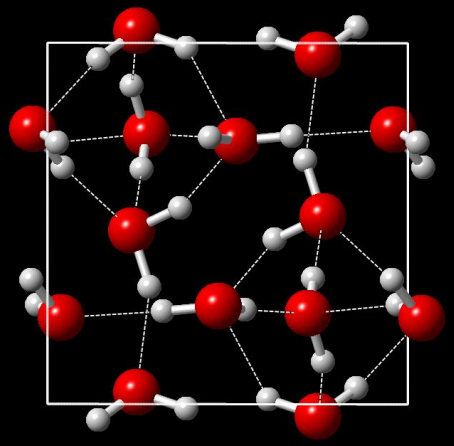
Importance of ice

pivotal role in cosmological & geological processes



scientific trailblazer

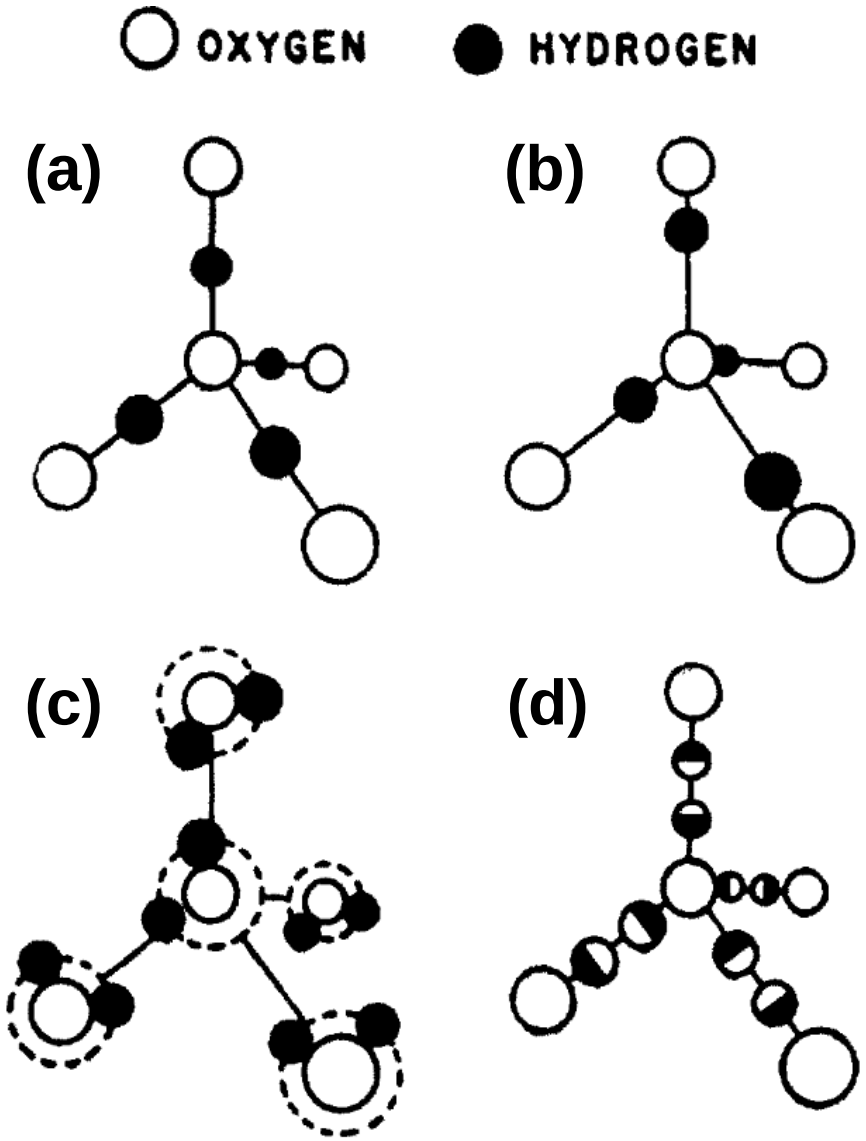
key to understanding liquid water

popular culture

energy storage in clathrate hydrates

influences & regulates our climate

Early structural models



(a) Barnes model: hydrogen atoms midway between oxygen atoms

(b) Bernal-Fowler model: H_2O molecules with defined orientations

(c) Hydrogen molecules rotating around oxygen atoms

(d) Pauling model: two half-occupied hydrogen sites along each hydrogen bond

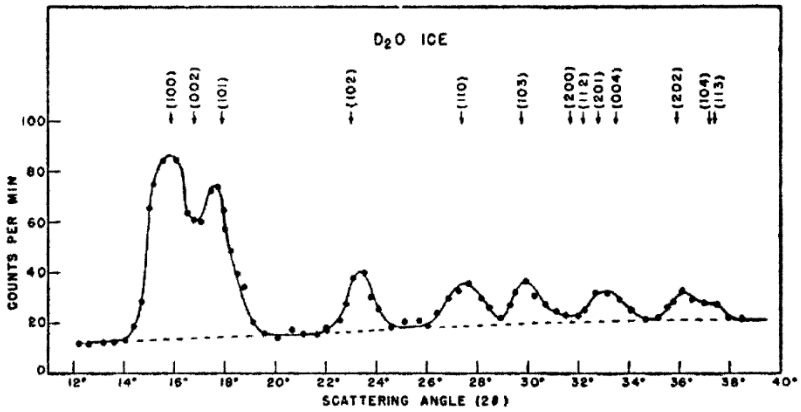
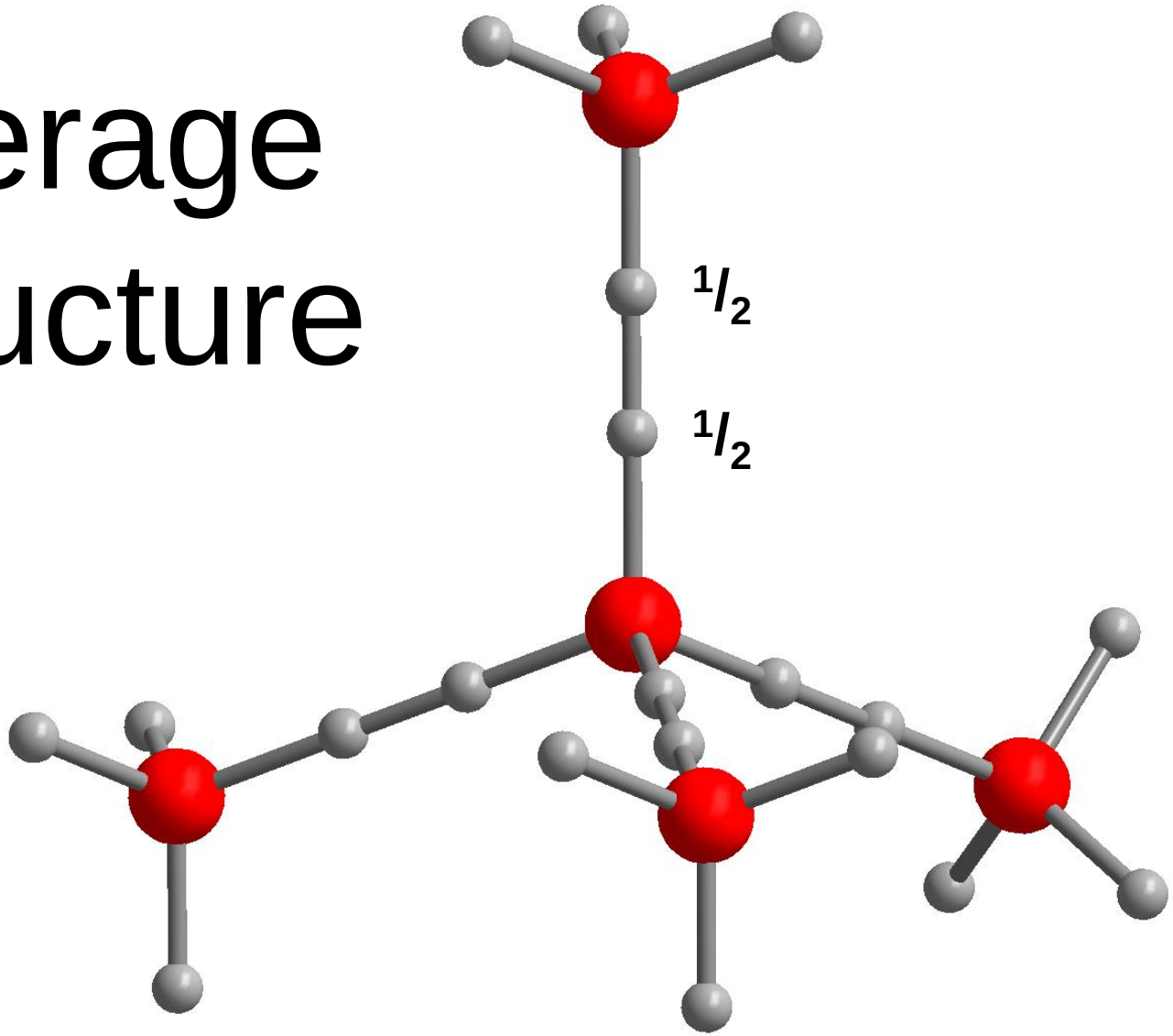


FIG. 1. Neutron diffraction powder pattern of heavy ice (D_2O) taken at −90°C with neutrons of wave-length 1.06A.

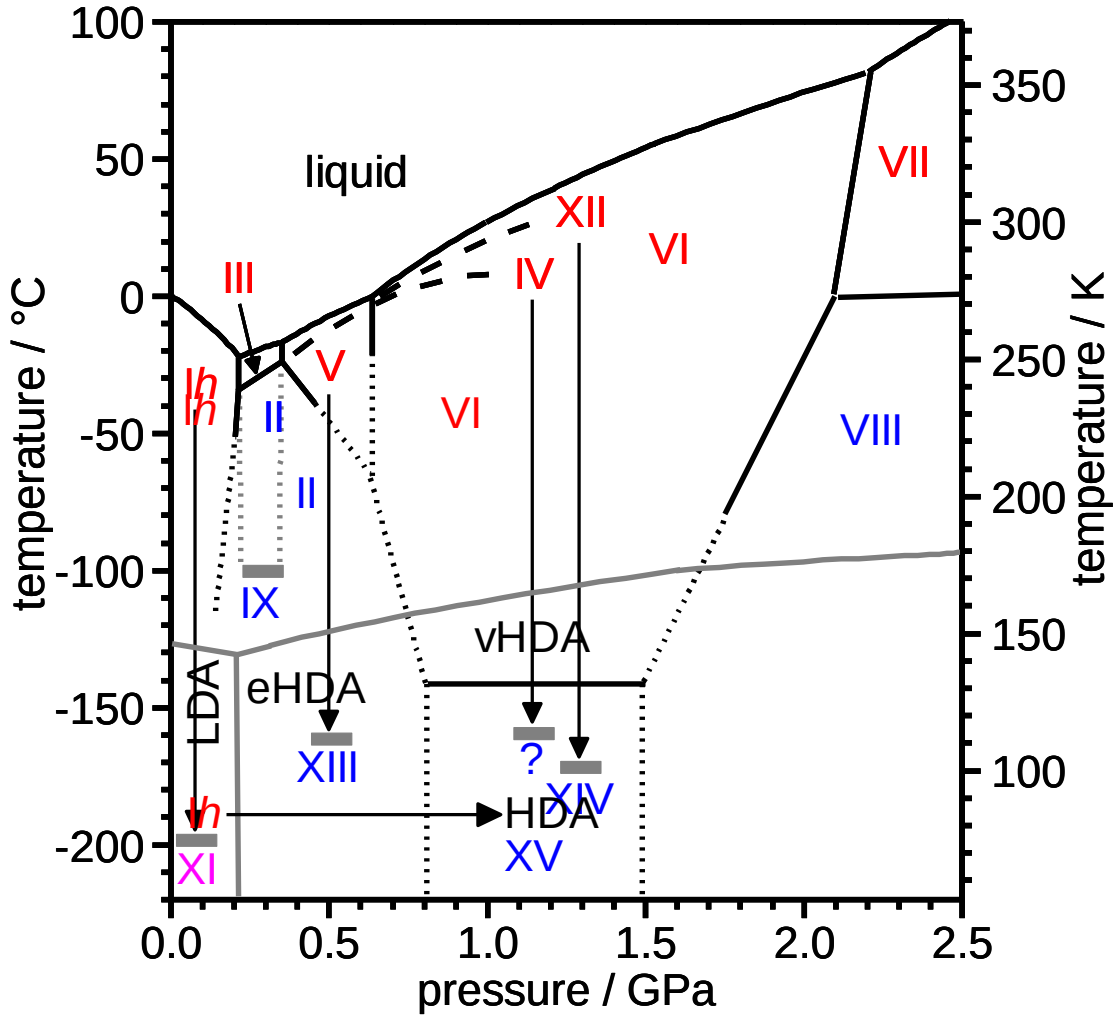
E. O. Wollan, W. L. Davidson, C. G. Shull, Phys. Rev., *75* (1949) 1348

Structure of ice

average structure



Phase diagram of ice



- hydrogen-disordered ice
- hydrogen-ordered ice (anti-ferroelectric)
- hydrogen-ordered ice (ferroelectric)
- amorphous ices

C. G. Salzmann, P. G. Radaelli, A. Hallbrucker, E. Mayer, J. L. Finney, Science, 311 (2006) 1758
C. G. Salzmann, P. G. Radaelli, E. Mayer, J. L. Finney, Phys. Rev. Lett., 103 (2009) 105701
O. Mishima, L. D. Calvert, E. Whalley, Nature 1984, 310, 393.
O. Mishima, L. D. Calvert, E. Whalley, Nature 1985, 314, 76.

Open questions and outline

(1) Structural nature of the amorphous ices?
Do they resemble glassy liquids at low temperature?
Or should they be seen as disordered crystals?

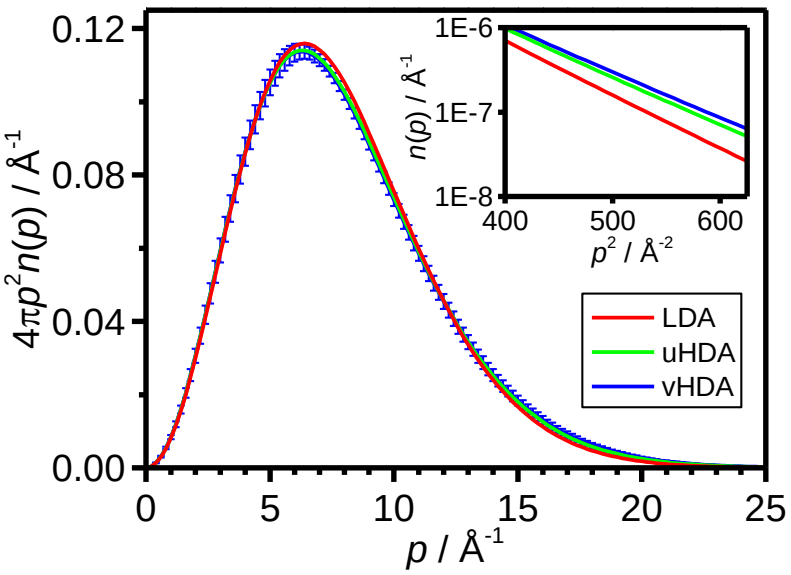
(2) How close to equilibrium are the amorphous ices?
Question of structural relaxation upon thermal annealing is key.

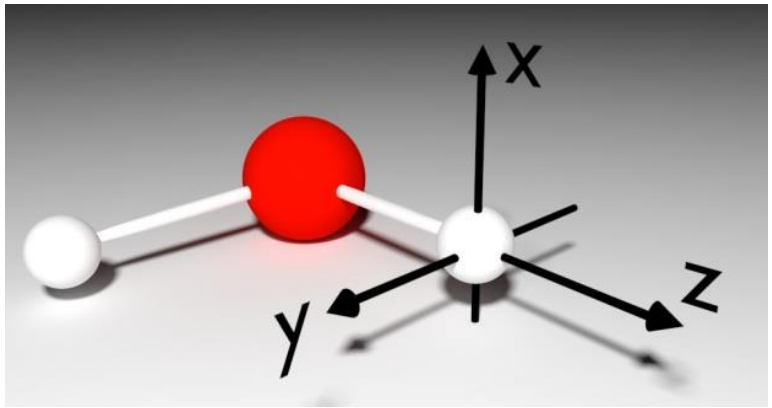
(3) Mechanisms of the glass transitions?
True glass transitions in the sense of glass to liquid transitions?

(4) Reason for the fragile to strong transitions?

(1) Deep-inelastic neutron spectroscopy of the amorphous ices
(2) Mechanism of the pressure-induced amorphisation
(3) Structural relaxation of LDA upon thermal annealing
(4) Mechanism of the glass transitions of the amorphous ices

DINS of the amorphous ices





Momentum distributions modelled as spherical averages of multivariate Gaussians:

$$4\pi p^2 n(p) = \int \frac{\delta(p - |p|)}{\sqrt{8\pi^3}\sigma_x\sigma_y\sigma_z} \exp\left[-\frac{p_x}{2\sigma_x^2} - \frac{p_y}{2\sigma_y^2} - \frac{p_z}{2\sigma_z^2}\right] \mathrm{d}^3p$$

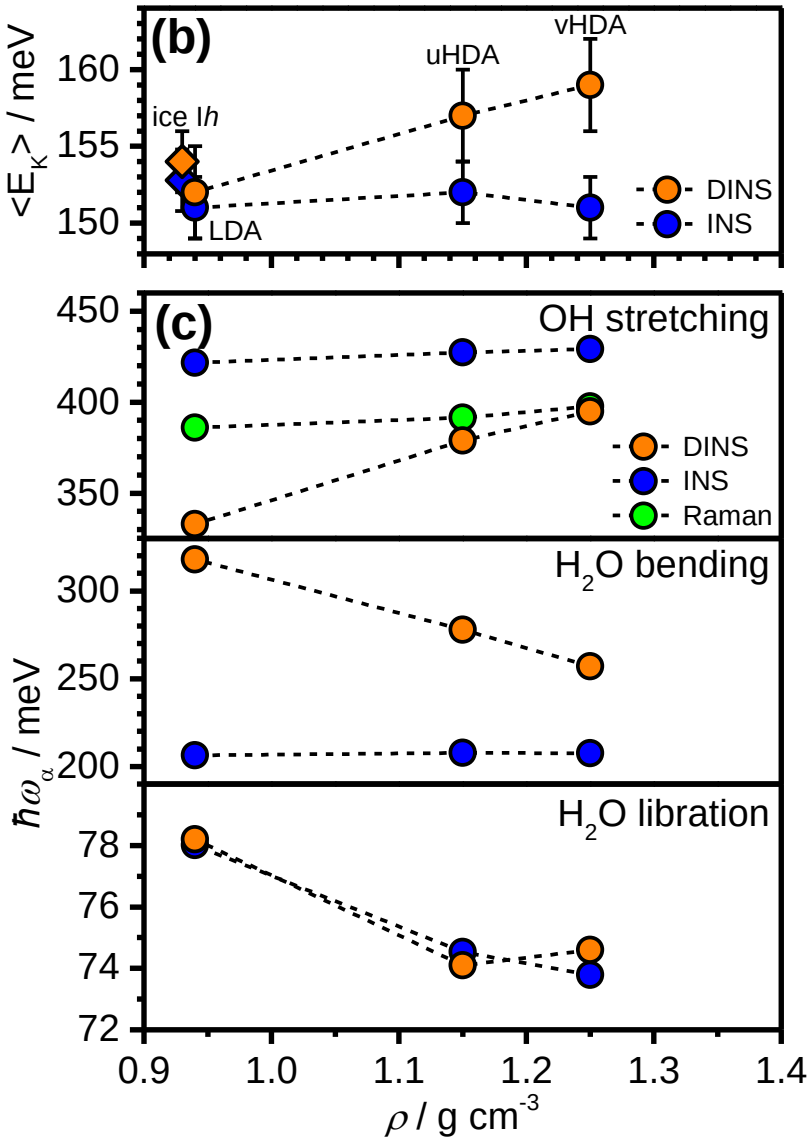
Directional mean kinetic energies $\langle E_k \rangle_x$, $\langle E_k \rangle_y$ and $\langle E_k \rangle_z$, total mean kinetic energy $\langle E_k \rangle$ as well as principle frequencies ω_x, ω_y and ω_z.

Motions in *z* direction contribute mainly to the high-momentum tail because H-atoms are most tightly bound in this direction.

Weaker hydrogen-bonding in the denser forms of ice (pressure-distance paradox).

A. Parmentier, J. J. Shephard, G. Romanelli, R. Senesi, C. G. Salzmann, Carla Andreani, J. Phys. Chem. Lett., 6 (2015) 2038-2042
A. Parmentier, C. Andreani, G. Romanelli, J. J. Shephard, C. G. Salzmann, R. Senesi, Front. Phys. 13 (2018) 136101

DINS of the amorphous ices



Increase in total mean kinetic energy with density is mainly caused by increases in $\langle E_k \rangle_z$.

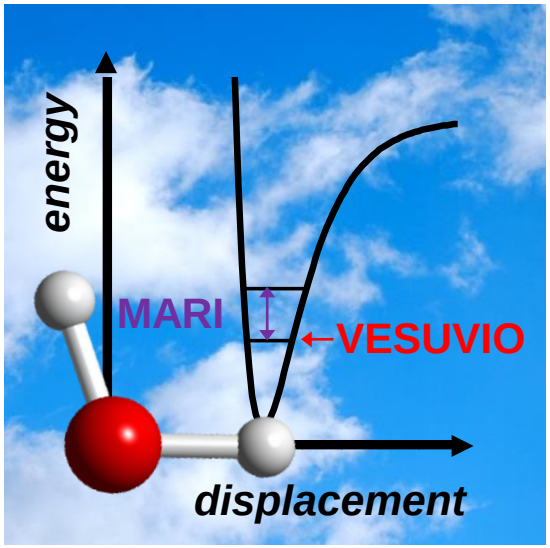
General trends are blueshifts in the O-H stretching and redshifts in the librations.

The trends from DINS, INS and Raman paint a consistent *qualitative* picture of hydrogen atoms being more constrained / localised in the lower density forms due the stronger hydrogen-bond network.

Quantitatively speaking, much greater changes are observed in the DINS data reflecting the fact that the binding of hydrogen atoms in the ground state is fully captured in DINS.

A. Parmentier, J. J. Shephard, G. Romanelli, R. Senesi, C. G. Salzmann, Carla Andreani, J. Phys. Chem. Lett., 6 (2015) 2038-2042
A. Parmentier, C. Andreani, G. Romanelli, J. J. Shephard, C. G. Salzmann, R. Senesi, Front. Phys. 13 (2018) 136101

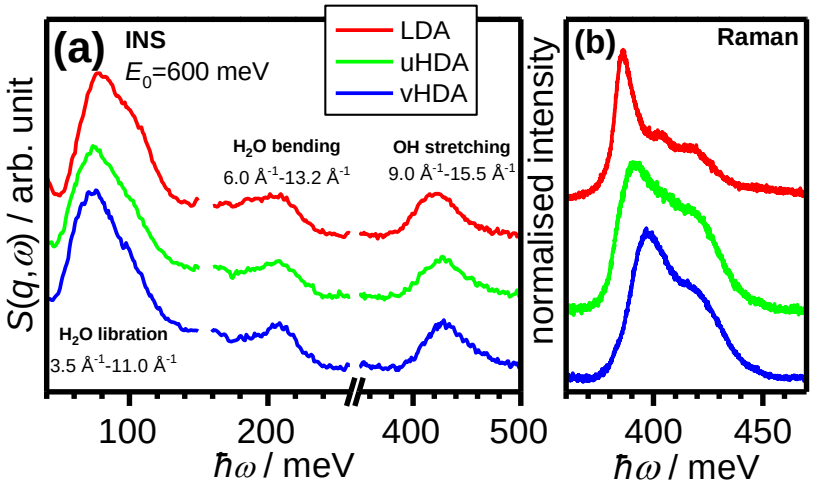
Anharmonicity constants from DINS & INS



Absolute energy of the first vibrationally excited state calculated as:

$$\frac{\hbar\omega_{\mathrm{str}}^{\mathrm{DINS}}}{2} + \hbar\omega_{\mathrm{str}}^{\mathrm{INS}} = \frac{3}{2}\hbar\omega_{\mathrm{str}}^{\mathrm{INS}}\left(1 - \frac{3}{2}\chi_{\mathrm{e}}\right)$$

The anharmonicity constant, X_e, is the only unknown.

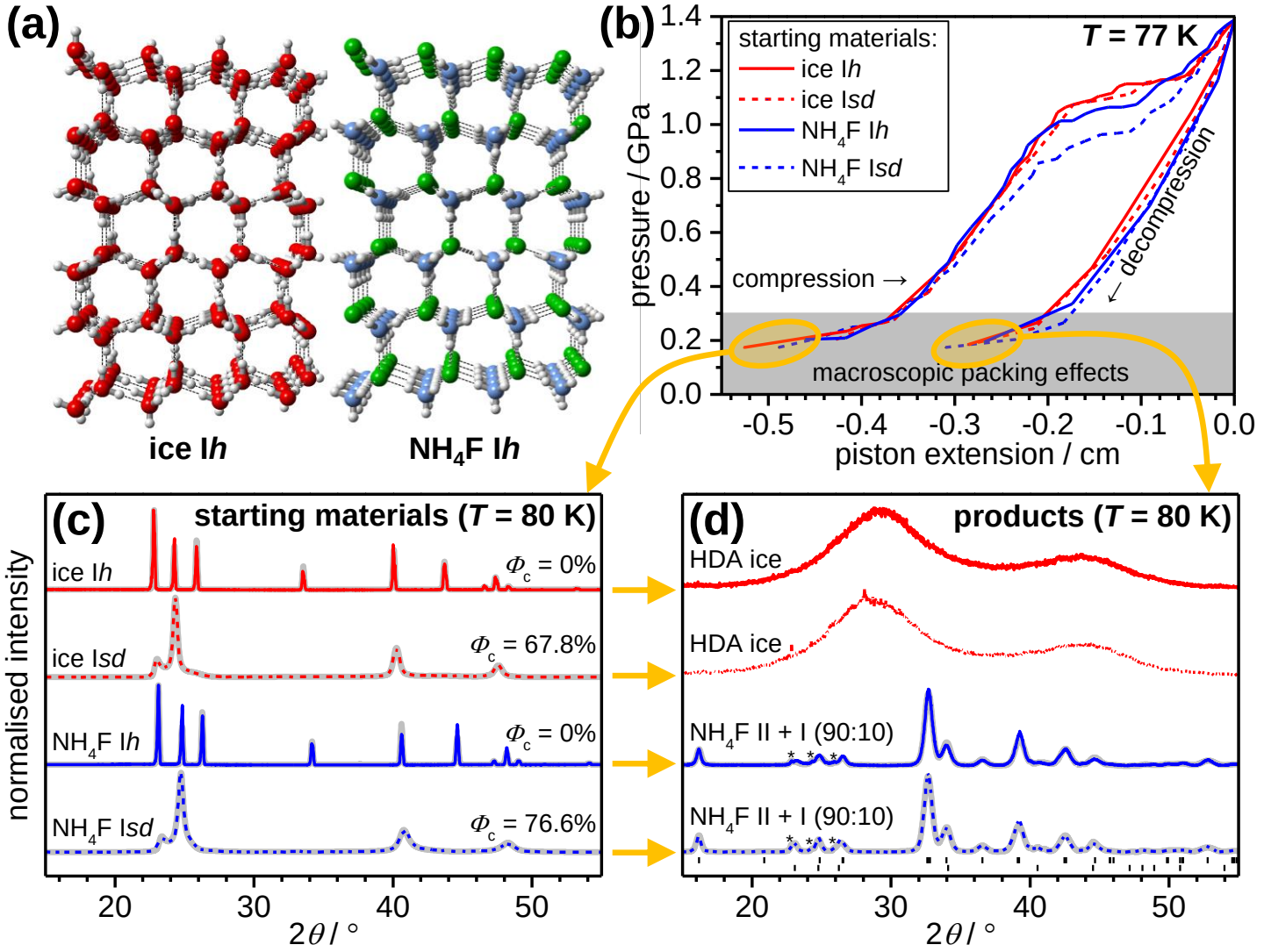


X_e(LDA) = 0.046
X_e(uHDA) = 0.025
X_e(vHDA = 0.018

Now have a quantitative measure for the much greater anharmonicity of O-H stretching in LDA.

A. Parmentier, J. J. Shephard, G. Romanelli, R. Senesi, C. G. Salzmann, Carla Andreani, J. Phys. Chem. Lett., 6 (2015) 2038-2042
A. Parmentier, C. Andreani, G. Romanelli, J. J. Shephard, C. G. Salzmann, R. Senesi, Front. Phys. 13 (2018) 136101

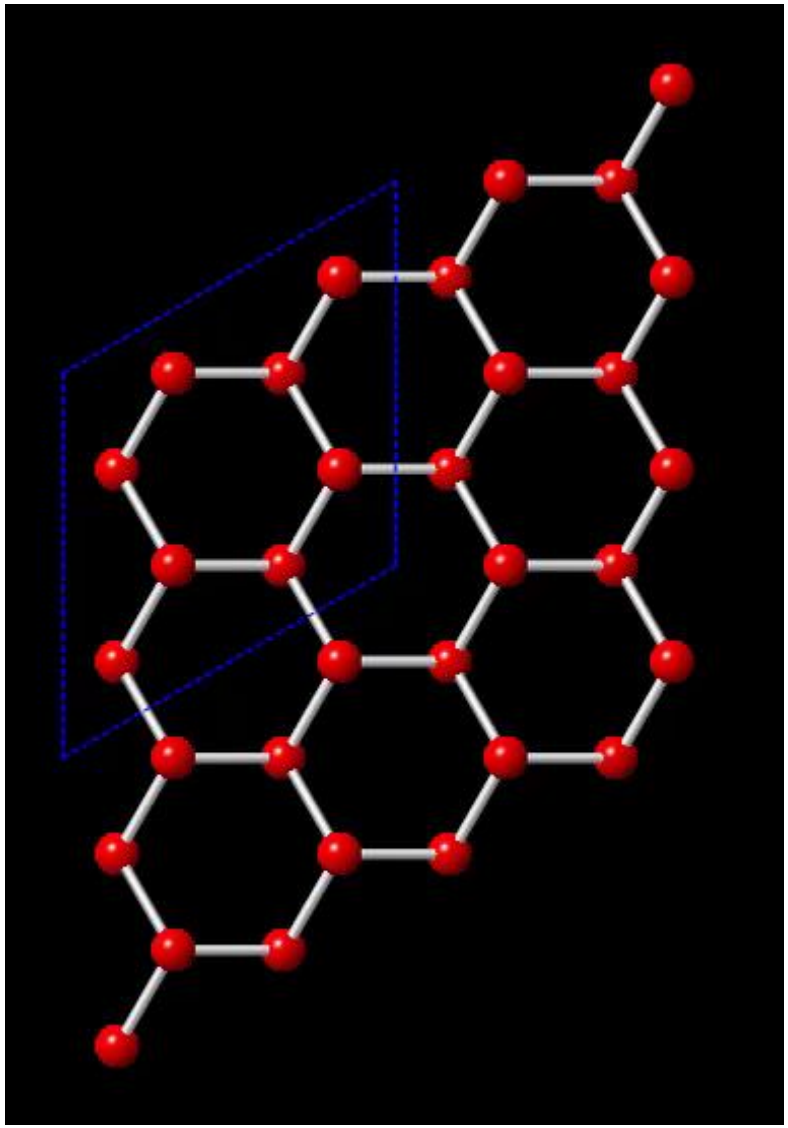
Pressure-amorphisation of ice I



Ice and ammonium fluoride show similar pressure-collapses.
Yet, the product materials are different. (NH_4F II ⇔ ice IV)

J. J. Shephard, S. Ling, G. C. Sosso, A. Michaelides, B. Slater, C. G. Salzmann, J. Phys. Chem. Lett., 8 (2017) 1645-1650

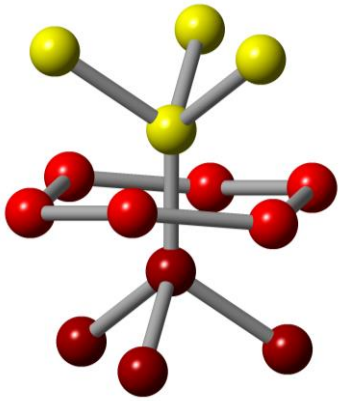
The ice I to ice IV pathway (EKC)



Engelhardt-Kamb collapse:
Achieves a 37% increase in density while only breaking the interlayer hydrogen bonds (25%).

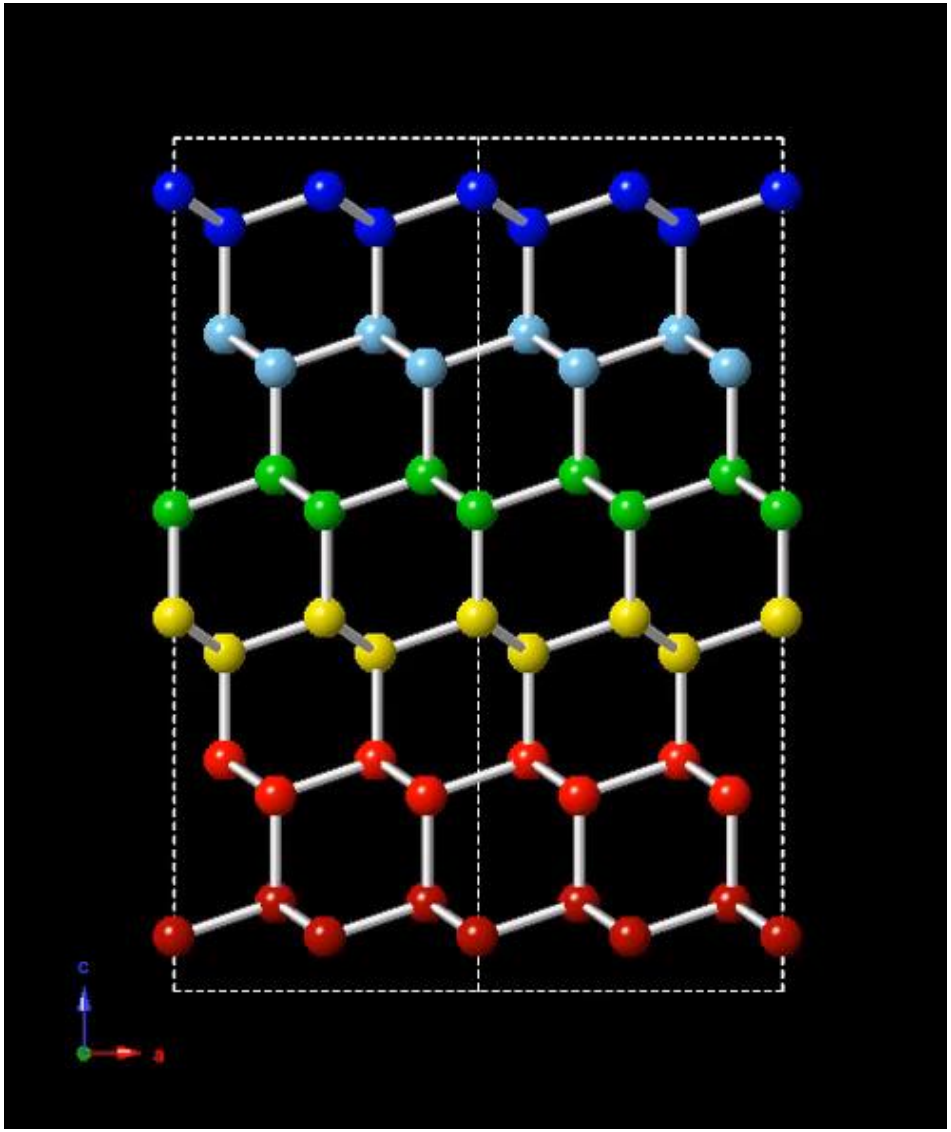
Collapse is highly anisotropic and takes place predominately along the [001] direction.

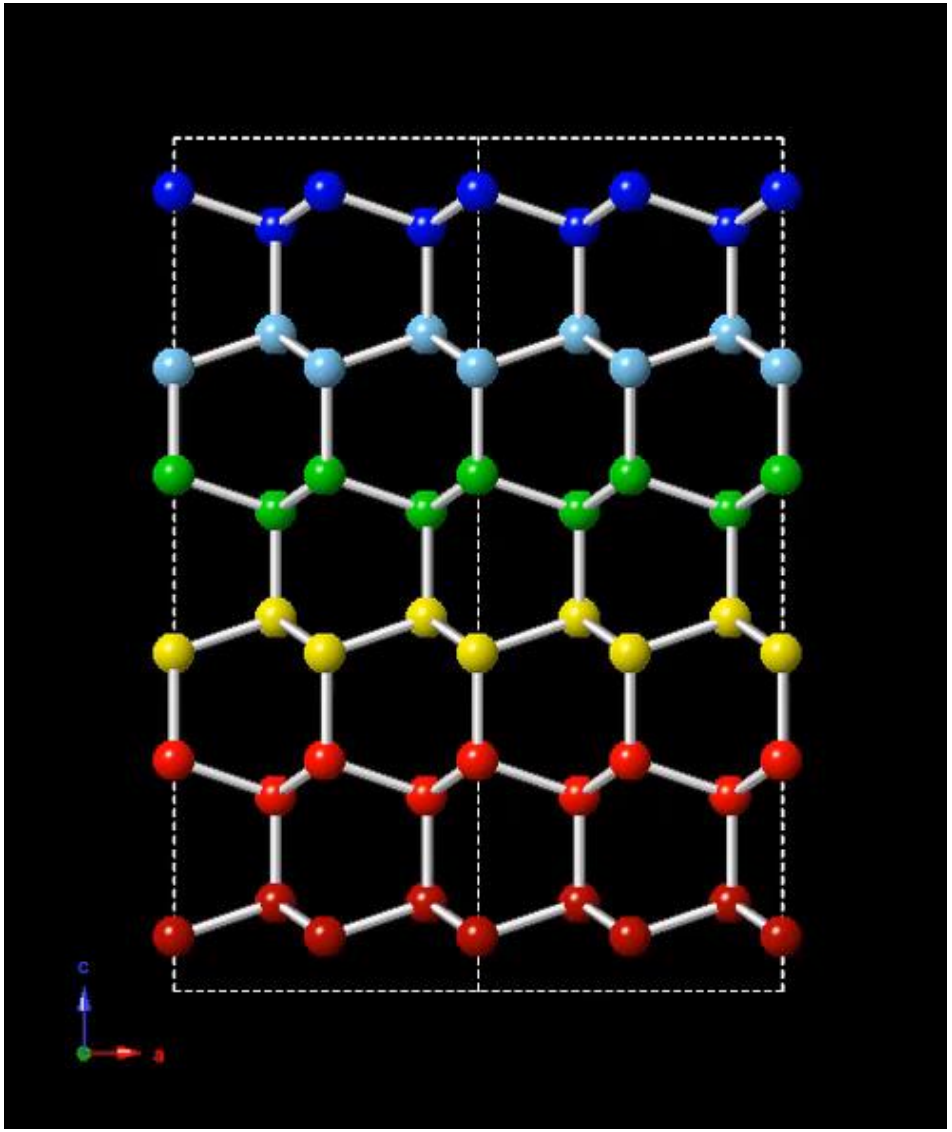
Important mechanism for densification under kinetically controlled conditions.



H. Engelhardt, B. Kamb, B, J. Chem. Phys., 75 (1981) 5887−5899
J. J. Shephard, S. Ling, G. C. Sosso, A. Michaelides, B. Slater, C. G. Salzmann, J. Phys. Chem. Lett., 8 (2017) 1645-1650

From cubic / hexagonal starting materials





“Rebuckling” of layers.

Shearing of layers is needed.

J. J. Shephard, S. Ling, G. C. Sosso, A. Michaelides, B. Slater, C. G. Salzmann, J. Phys. Chem. Lett., 8 (2017) 1645-1650

Mechanism of pressure amorphisation

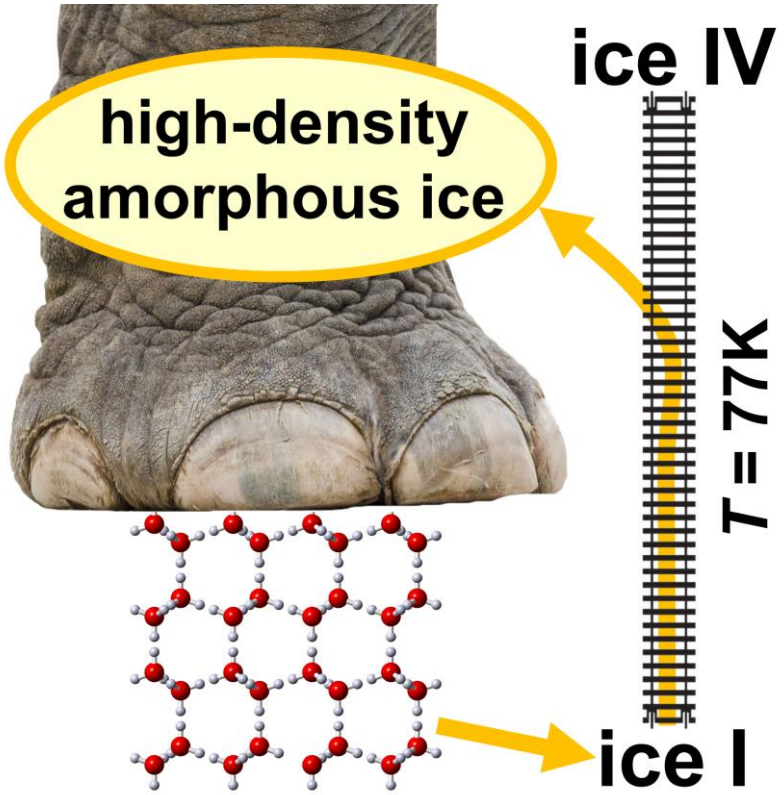
Similar onset pressures and volume collapses suggest that ice I and NH_4F I suffer from similar mechanical instabilities which mark the onsets of the EKC.

Both materials do not follow the EKC through completely.

Important to recall that the water molecules display orientational disorder in ice I.

Chances of breaking and successfully reconnecting a hydrogen bond are 50%.

HDA is a “derailed” state along the ice I to ice IV pathway (no structural connection with the liquid).



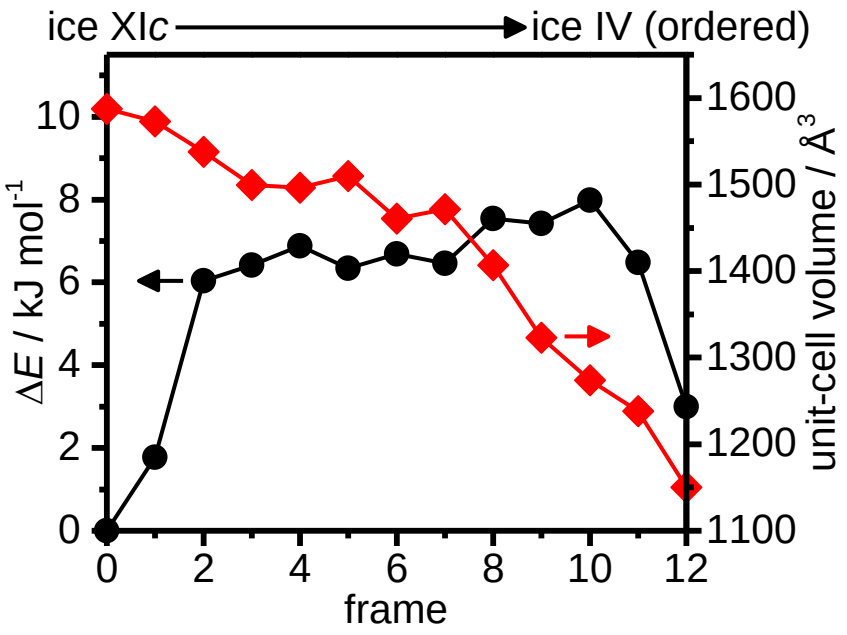
J. J. Shephard, S. Ling, G. C. Sosso, A. Michaelides, B. Slater, C. G. Salzmann, J. Phys. Chem. Lett., 8 (2017) 1645-1650

Mechanism of pressure amorphisation

Problem of hydrogen-bond mismatches could be resolved with molecular reorientations.

Upon heating HDA around its “natural” pressure of 1 GPa, the crystallisation to ice IV has the smallest activation energy.

First strong diffraction peak of pressure-annealed HDA coincides with strongest ice IV Bragg peaks.



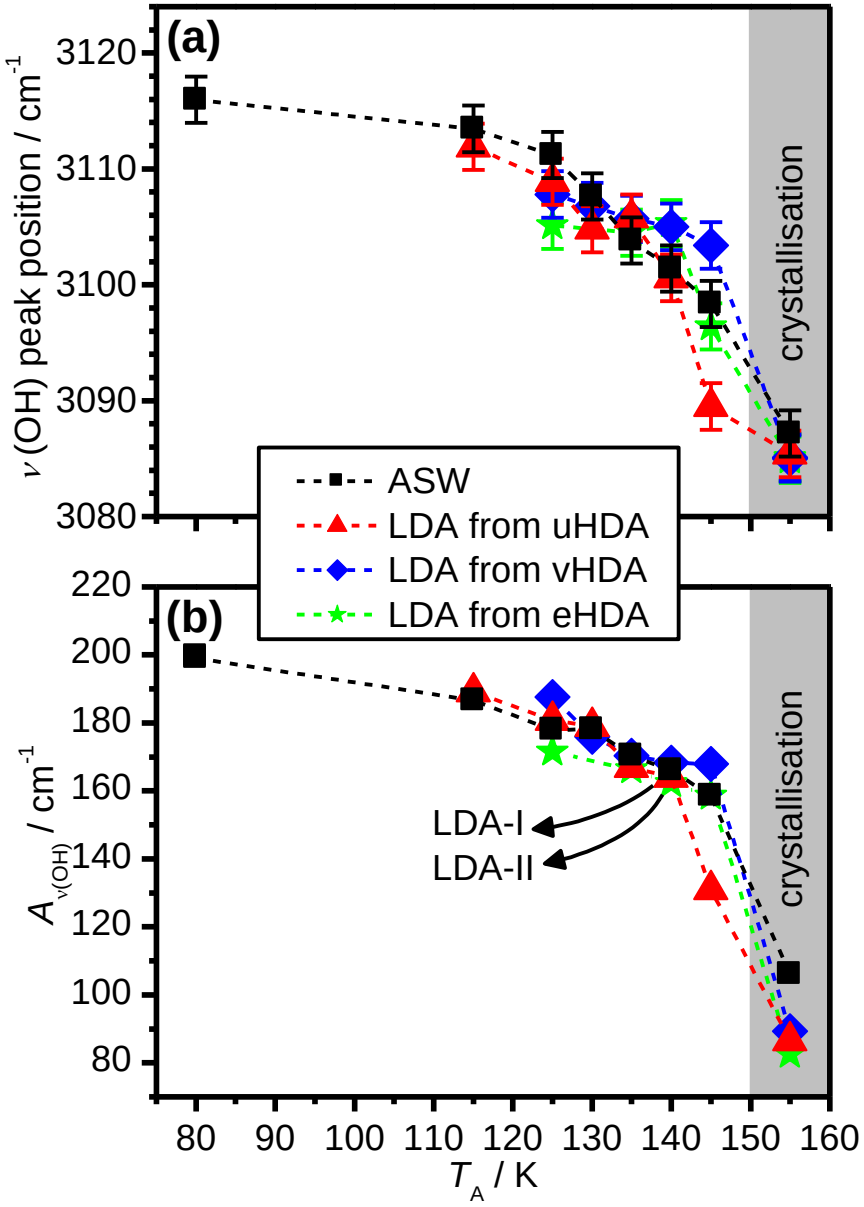
Strong spectroscopic similarities between pressure-annealed HDA and ice IV.

Previously discussed crystalline ice I remnants in HDA can now be explained.

Hydrogen-ordered ice XIc is likely to undergo EKC.

J. J. Shephard, S. Ling, G. C. Sosso, A. Michaelides, B. Slater, C. G. Salzmann, J. Phys. Chem. Lett., 8 (2017) 1645-1650

Structural relaxation of LDA upon annealing

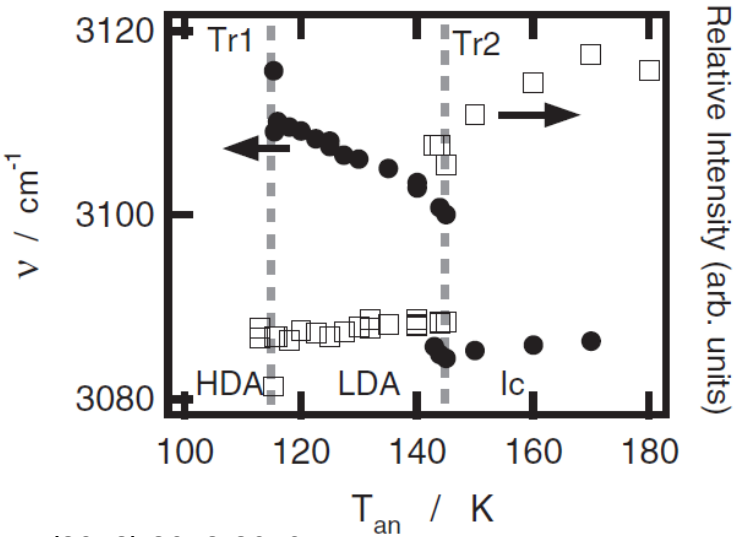


Similar structural relaxation process for LDAs from different HDAs.

A gradual structural relaxation process takes place upon heating LDA.

Process is separate from crystallisation and does not seem to reach completion before crystallisation.

Difficult to reconcile with a glass transition to the liquid.



J. J. Shephard, J. S. O. Evans, C. G. Salzmann, J. Phys. Chem. Lett., 4 (2013) 3672-3676.
Y. Suzuki, O. Mishima, J. Phys. Soc. Jpn. 72 (2003) 3128.

Extension of the glass-transition terminology

Kauzmann: The phenomenon of the glass transition is not restricted to liquids but is, in principle, possible for all noncrystalline materials.

W. Kauzmann, Chem. Rev. 43 (1948) 219.

glassy liquids:	translational disorder	rotational disorder
glassy crystal:	translation order	rotational disorder
glassy liquid crystals:	translation disorder	rotational order

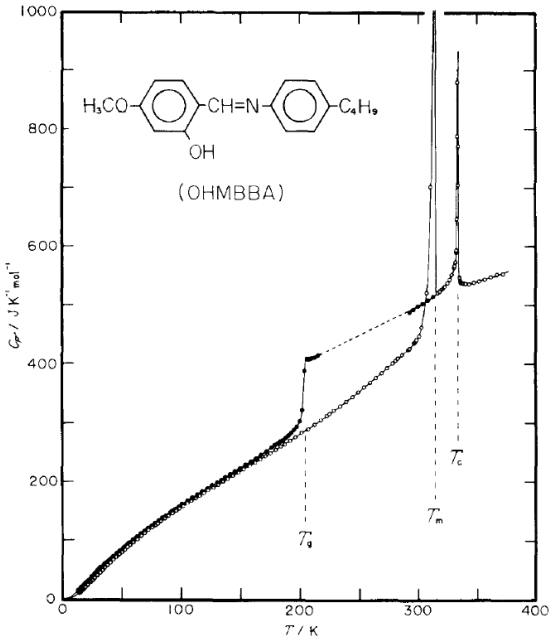
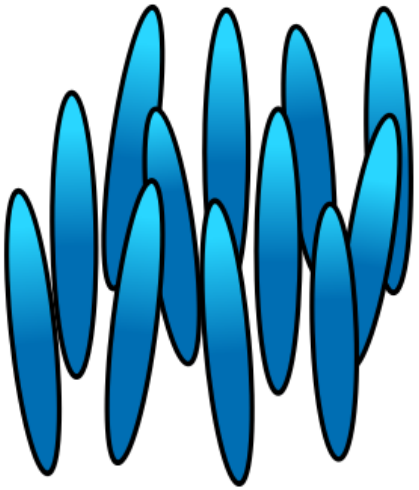
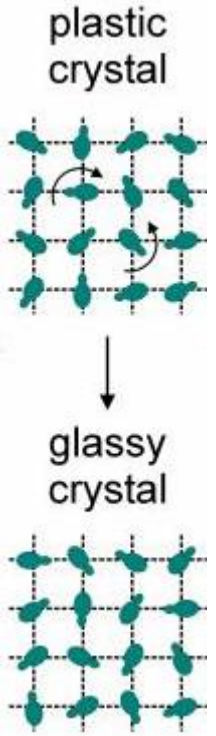


Fig. 12. Heat capacity *versus* temperature curve of OHMBBA.

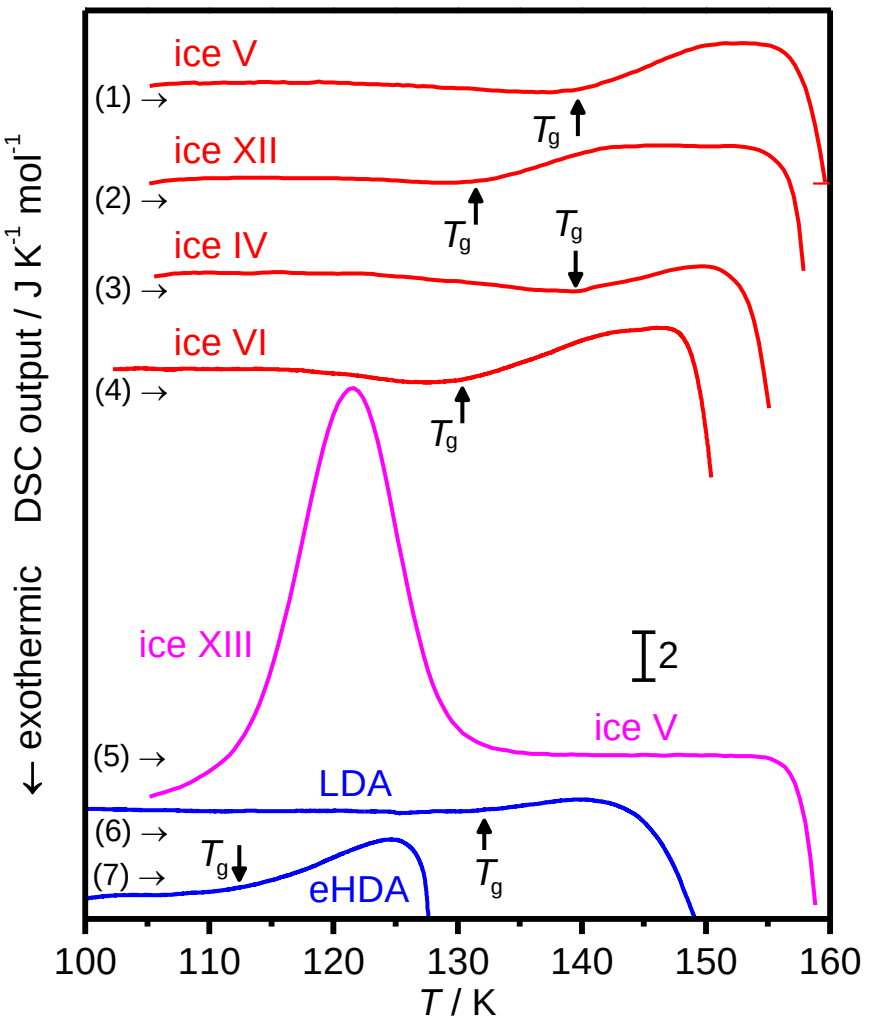


Liquid crystal



H. Suga, S. Seki, J. Non-Cryst. Solids 16 (1974) 171.

Glass transitions of hydrogen-disordered ice



The hydrogen-disordered crystalline ices show glass transitions.

Correspond to kinetic unfreezing of reorientation dynamics.

No ΔC_p feature for HCl-doped ice V.

Similar features are observed for the amorphous ices LDA and eHDA.

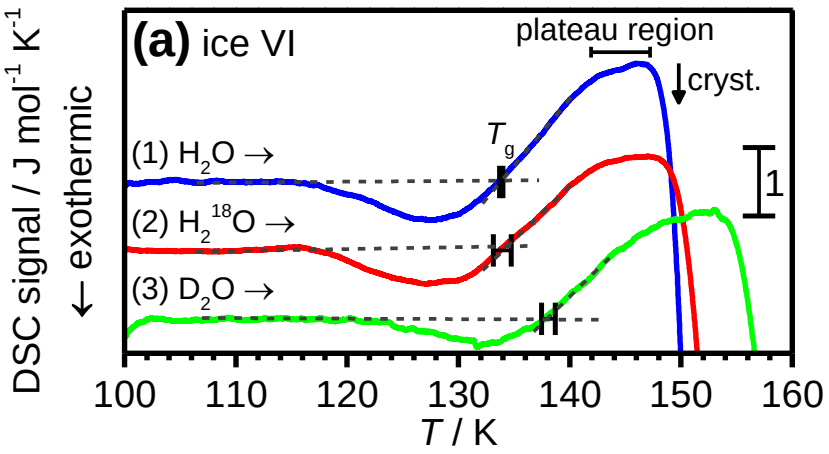
Have been assigned to the glass-to-liquid transitions.

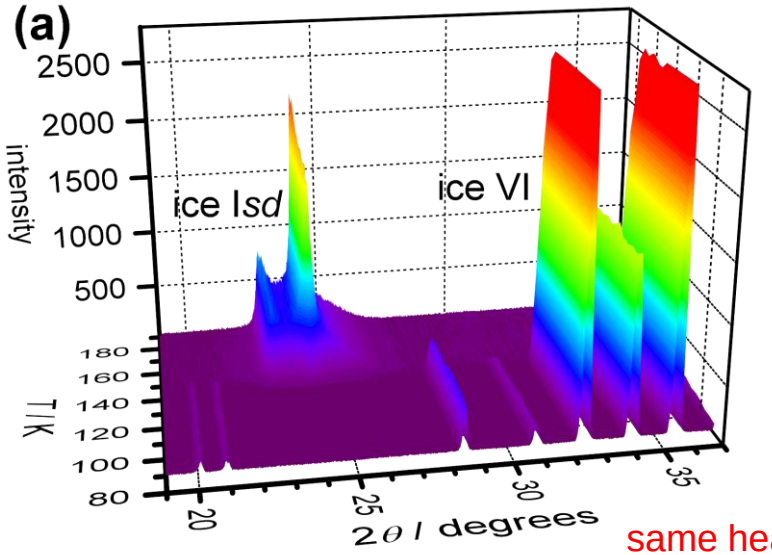
Glass transitions with similar ΔC_p values have also been observed for inorganic hydrates and clathrate hydrates.

Is the underlying mechanism the same for all these glass transitions?

C. G. Salzmann, P. G. Radaelli, A. Hallbrucker, E. Mayer, J. L. Finney, Science, 311 (2006) 1758-1761.
C. G. Salzmann, P. G. Radaelli, B. Slater, J. L. Finney, Phys. Chem. Chem. Phys., 13 (2011) 18468-18480.
J.J. Shephard, C.G. Salzmann, J. Phys. Chem. Lett. 7 (2016) 2281.

Molecular reorientation dynamics of ice VI





T_g of ice VI stays fixed upon going from H_2O to $H_2{}^{18}O$ but shifts towards higher temperature upon going from H_2O to D_2O.

Going from H_2O to $H_2{}^{18}O$ or D_2O increases the molecular weight from 18 to 20 g mol^{-1} in both cases.

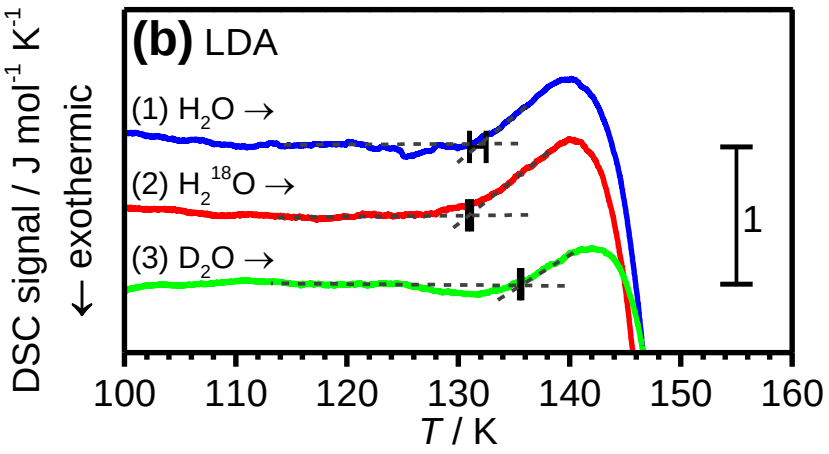
The observed isotopic shift pattern is consistent with a change in reorientation dynamics and no translational diffusion.

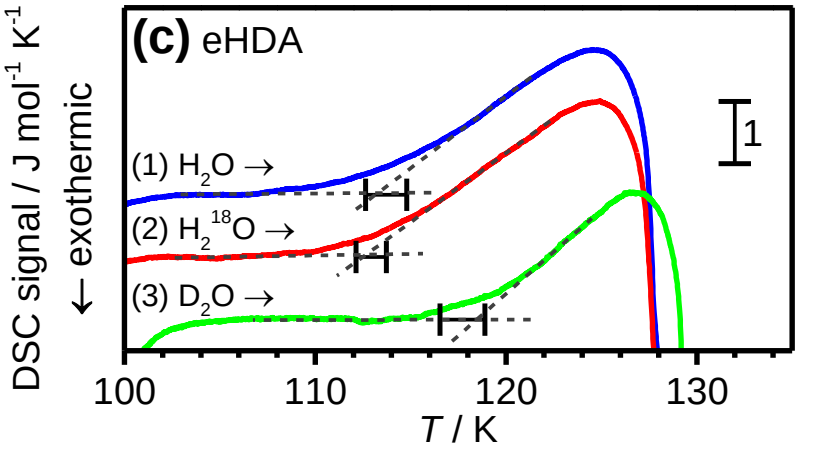
The absence of translational diffusion at and above T_g is also confirmed by XRD.

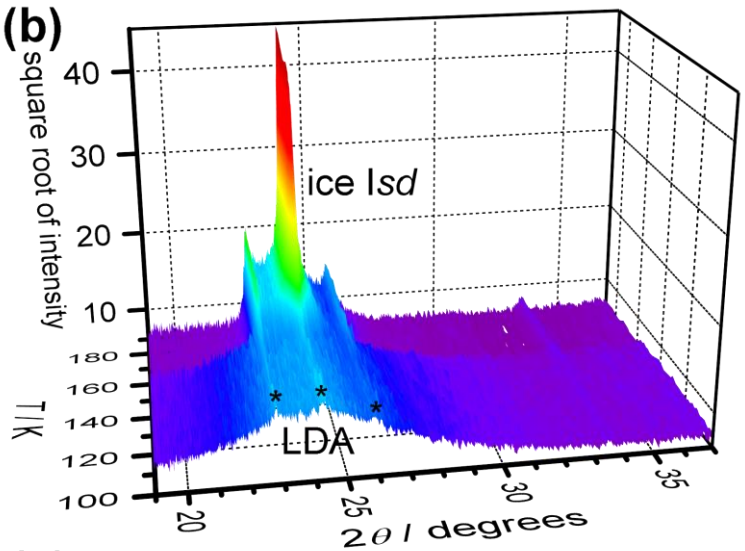
same heating rate as DSC

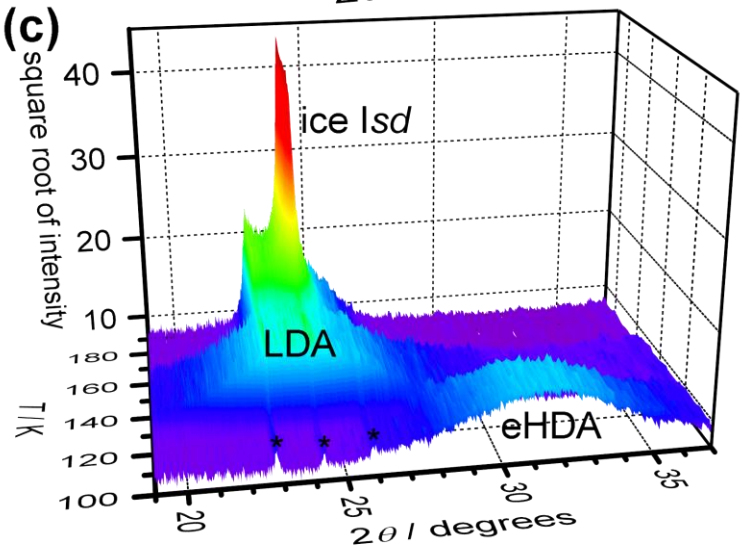
J.J. Shephard, C.G. Salzmann, J. Phys. Chem. Lett. 7 (2016) 2281.

Isotopic shift patterns of LDA and eHDA







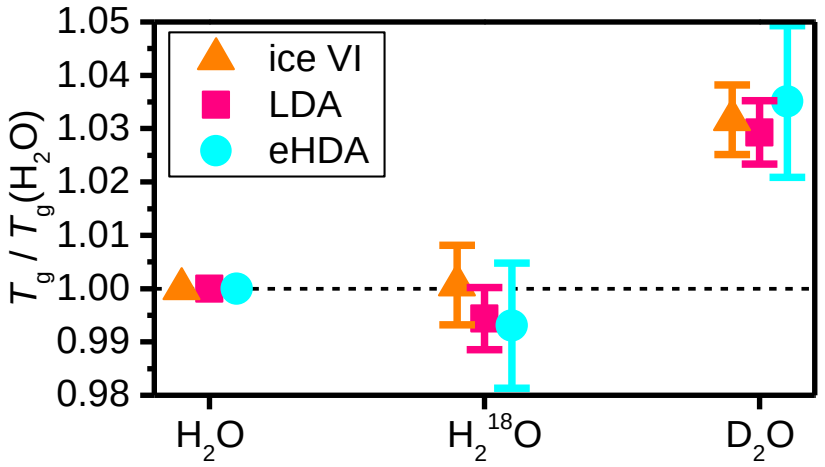


Amorphous samples are well-relaxed.
LDA and eHDA show the same isotopic shift pattern as ice VI.

same heating rate as DSC

J.J. Shephard, C.G. Salzmann, J. Phys. Chem. Lett. 7 (2016) 2281.

Nature of the glass transitions



The glass transitions of the amorphous ices are governed by molecular reorientation processes.

Mechanism of molecular reorientation in the ices is thought to be defect-mediated and therefore highly cooperative.

Diffusion processes in the amorphous ices and liquid water are very different which explains their *strong* and *fragile* properties.

Water is a *fragile* molecular liquid - the amorphous ices are *strong* network materials.

The "reorientation scenario" seems to resolve the previous controversies.

see also: M. Fisher, J.P. Devlin, J. Phys. Chem. 99 (1995) 11584.

Unfreezing of translation diffusion is the *strong* to *fragile* transition.

J.J. Shephard, C.G. Salzmann, J. Phys. Chem. Lett. 7 (2016) 2281.

Acknowledgement

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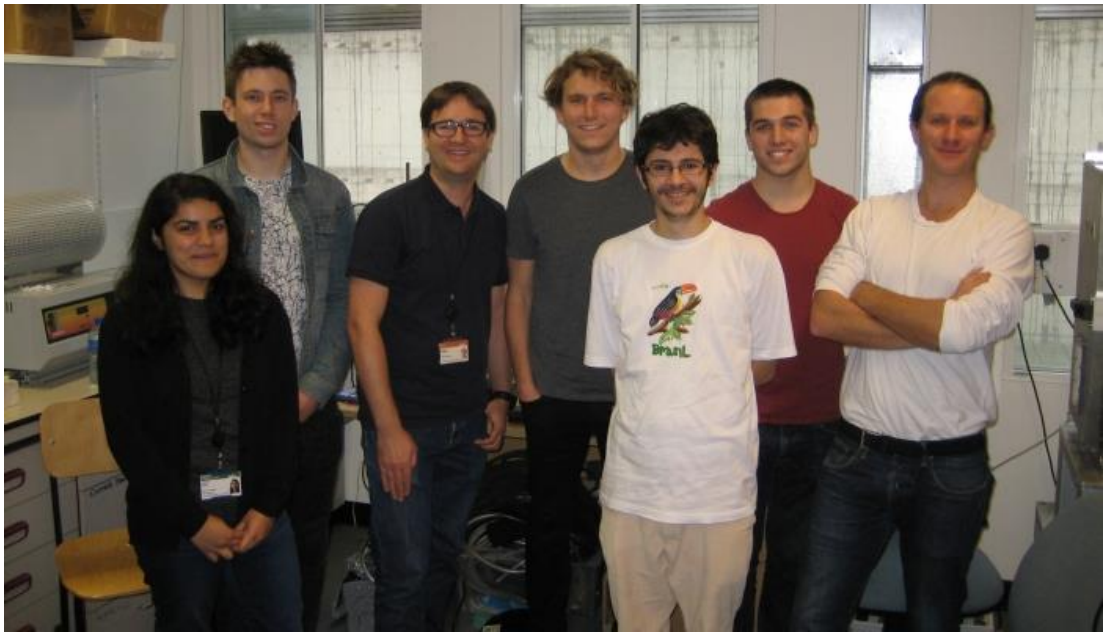

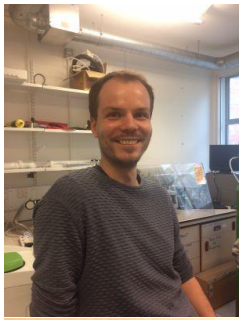

Ben Slater, Angelos Michaelides,
Sanliang Lin, Gabriele Sosso, John Finney
Rome: Carla Andreani, Roberto Senesi,
Giovanni Romanelli, Alexandra Parmentier
Paris: Stefan Klotz **Durham:** John Evans

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