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Austen in Amsterdam: Isotope effect in a liquid-liquid transition in supercooled aqueous solution

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Abstract

We investigate the H/D isotope effect in a liquid-liquid transition in crystallization-resistant supercooled aqueous solution. Using steady-state infrared spectroscopy and measuring thermal conductivities, we observe a ≈5 K shift in the onset temperature of the liquid-liquid transition, a value that is similar to the H/D isotope shifts of the HDA-LDA transition and of the Widom line of pure supercooled water (Kim et al., Science 358, 1589 (2017)), and that highlights the importance of isotope effects in water’s supercooled regime. By employing multivariate data analysis we find isosbestic point related to the phase transformation in both isotopic systems, indicating phase coexistence during the transition. This article is dedicated to the memory of Austen Angell, and we begin with some personal memories of his two stays at the University of Amsterdam.

1. Personal introduction: Austen in Amsterdam

Austen Angell and the University of Amsterdam have a long history, ranging from his sabbatical year in Amsterdam in 1971 to our joint research in the period 2015–2021 some 50 years later, and of which this article may be regarded as a coda. In this introductory section, we would like to give a short history of Austen’s stays in Amsterdam, based on personal and fond memories of the people involved.

1.1. 1971: The glassy behavior of salts

In the beginning of the 1970s, molten salts were a hot topic: not only because of their application in fuel cells, but also as potential cooling fluids in nuclear-energy plants: much more efficient than water because they would operate at a higher temperature (a nuclear plant being a Carnot engine!). The University of Amsterdam had appointed an associate professor, Jan van der Elsken, who set up a successful research group on this topic. Already at that time Austen was a scientist of worldwide renown, and his idea of fragile and strong glasses was hotly debated in the Van der Elsken group. They decided to invite Austen for a sabbatical stay. The plan was to investigate if salts consisting of non-spherical ions would exhibit fragile behavior. The Van der Elsken group was specialized in far-infrared spectroscopy, and the far-infrared spectrum of a liquid or glassy salt with multi-atomic, anisotropic ions could provide information on the rotational motion of the ions.

Austen did the experiments together with PhD students Gerard Wegdam and Rob Bonn, the father of one of the authors of this paper. Austen prepared the glassy salt himself. For this he used a specially designed heatable pipette with which he dropped molten salt droplets onto a cold metal plate. Austen standing in the lab with his hot pipette, accompanied by the loud hissing of the liquid salt droplets hitting the cold plate were a familiar sight and sound in the Van der Elsken lab. As Gerard, now an emeritus professor of the University of Amsterdam, recalls: “Austen was melting all kinds of stuff—he wanted to make a glass out of everything!”

It was Gerard who measured the far-infrared spectra of the glasses that Austen prepared. The sample cells for these far-IR experiments required a special type of material: diamond. These were provided by Rob, who had connections in an Amsterdam-based diamond company. Whenever a diamond was not suitable for selling, it was donated to the good purpose of physical chemistry. Rob would go there once a week to have a chat over coffee, and would return with the diamonds jingling in

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the pockets of his trousers. Wegdam: “Mind you, these diamonds were
whoppers, we had to keep them in a safe”. The critical moment came
when windows (size 1×1.5 cm) had to be cut from the whopper di-
amonds, often with fatal results. In addition there was the problem of
contamination by traces of water (ZnCl₂ being very hygroscopic, and
water a strong far-IR absorber). As Austen writes in the article about
these experiments, with characteristic carelessness and modesty: “we
believe the spectra seen in Fig. 1 are of almost as good quality as one can
hope to obtain for this difficult substance with present instrumentation”
[1]. While in Amsterdam, Austen also developed what he called the
“little squeezer”: an elegant high-pressure spectroscopy cell consisting of
two small diamond windows separated by a ring-shaped spacer and
mounted in thick stainless steel plates that were connected by a hinge.
Simply squeezing the plates together could generate extremely high
pressures—yet another example of what an excellent experimentalist
Austen was.

The far-IR measurements took many hours, and results were typi-
cally discussed in the evening, after which the group usually went to a
pub in Amsterdam (in these days the chemistry faculty was still located
in the Amsterdam city center). There were also regular sailing trips on
Jan’s boat. Photos taken during Wegdam’s PhD defence ceremony in
which Austen was one of the committee members show a perfectly
attuned quartet of researchers (Fig. 1, with Jan and Austen looking quite
a bit like Jack Lemmon and Tony Curtis).

1.2. 2015–2021: A liquid-liquid transition in supercooled aqueous
solution

Fastforward about 50 years: Gerard Wegdam, Rob Bonn and Jan van
der Elsken had retired, but Daniel Bonn, son of Rob Bonn, was now a
professor in Soft Matter physics at the University of Amsterdam. He had
met Austen at a conference, and they agreed Austen would visit the UvA,
to discuss a potential cooperation, but also as a sentimental journey. In
July 2015, Austen visited the UvA for a day, and had lunch with Daniel
and infrared-spectroscopist Sander Woutersen. During lunch on a sunny
terrace, the subject of liquid-liquid transitions in water came up: the idea
proposed by Poole, Sciortino, Essman and Stanley [2] that the anom-
alous properties of liquid water might be due to a second critical point
located at low temperature and high pressure, with the implied possi-
bility of a first-order transition between two liquid states of deeply
supercooled water. The problem was that these spectacular phenomena
were predicted to occur in a region of the phase diagram where water
inevitably crystallizes (the so-called “No man’s land”). One way to avoid
crystallization is adding solutes, and at the UvA we previously had tried
to use infrared spectroscopy to investigate potential liquid-liquid tran-
sitions in aqueous glycerol solutions, but with results that were difficult
to interpret.

The problem is that added solutes may prevent crystallization at low
temperatures (so “No man’s land” becomes accessible), but generally
also destroy the anomalous properties of water. Austen told us that he
had recently discovered how to solve this problem: by using a special
solute (hydrazinium trifluoroacetate) that mimics the hydrogen-bond
structure of water so well that the anomalies of water are preserved
while crystallization is still avoided. The compatibility of the hydrogen-
bond networks of solvent and solute was macroscopically observable as
ideal freezing-point depression behavior. Austen and his postdoc Zu-
feng Zhao had carefully investigated these solutions, and had discovered
that they exhibit a first-order like phase transition at very low temper-
ature. They had just published these results in Angewandte Chemie [3],
and Austen proposed to use infrared spectroscopy to investigate the
transition in more detail. This was the beginning of a wonderful coop-
eration. Austen visited Amsterdam again in 2017, and it was always
amazing how young at heart he was when Austen and Jenny arrived in
Amsterdam very late in the evening, we were concerned about their
dinner; but we received a enthusiastic message from Austen that they
had already gone to a Brazilian restaurant in the city center that was
open until 4 AM (“with live music!”).

The infrared measurements and complementary ab initio molecular
dynamics simulations [4] confirmed Austen’s earlier interpretation that
the transition in these aqueous solution was the analog of the liquid-
liquid transition in pure water proposed by Poole et al. [2], which to
that time had not been observed experimentally. Recently, the group of
Anders Nilsson has been able to observe the liquid-liquid transition in
pure water, in a series of spectacular experiments [5,6]. In this present
article, we report a follow-up study on the liquid-liquid transition in
hydrazinium trifluoroacetate solution, which in our lab has become
known affectionately as “Angell-mix”. Austen was dear to all of us, and
we dedicate this article to his memory.

2. Scientific introduction

The physical properties of liquid water exhibit many anomalies. In
particular, its thermodynamic susceptibilities, such as heat capacity,
isothermal compressibility and thermal expansion coefficient rapidly
increase upon cooling [7–13]. Among the theories that have been
developed to explain these thermodynamic anomalies, [2,14–20] the
liquid-liquid critical point (LLCP) hypothesis [2] is currently very prominent. In this theory, deeply supercooled water can occur in a high-density liquid (HDL) and low-density liquid (LDL) state, and these two liquid phases are separated by a phase-coexistence line in the p − T diagram, which ends in a liquid-liquid critical point located at a temperature well below the homogeneous nucleation temperature \( T_h \approx 240 \) K. The proposed LDL/HDL phase-coexistence line penetrates into the glassy region of water, where Mishima et al. famously observed a first-order phase transition between high- and low-density amorphous ices (HDA and LDA, respectively) [21]. The LLCP scenario provides a universal explanation of the anomalous susceptibilities, which can be explained from the increasing fluctuations as this critical point is approached [22–26].

Experimentally, observing the LLCP is difficult, given its location in the temperature range below \( T_h \), and above the temperature where amorphous water converts to ice (“No man’s land”) [27]. Kim et al. succeeded in crossing \( T_h \) using evaporative cooling of water in vacuum down to 227.7 K. Their femtosecond X-ray scattering experiments on supercooled micrometer-sized water droplets suggested the presence of maxima in the isothermal compressibility and correlation length, and interpreted this result by implying the existence of a LLCP [5]. However, alternative interpretations of these experiments have also been proposed [28,29]. More recently, Kim et al. have shown definitive and convincing evidence for the LLCP in supercooled water using femtosecond X-ray scattering on high-pressure supercooled water prepared by nanosecond isochoric heating: a discontinuous change in water structure was observed during decompression and prior to crystallization [6].

In an alternative approach to study deeply supercooled water, the addition of second components, such as ionic solutes, is used to prevent crystallization [30]. The problem with most added solutes is that they not only prevent crystallization, but also modify the structure of liquid water to such an extent that the thermodynamic anomalies disappear. Angell and Zhao solved this problem by using \( \text{N}_2\text{H}_4\text{H}_2\text{TFA} \), a solute that has little influence on the hydrogen-bond structure of water (as evidenced by ideal-mixing behavior) and effectively prevents crystallization. In fact, later MD and ab initio simulations showed that these solutions have a hydrogen-bond structure that closely resembles that of neat water at elevated pressure [4]. The calorimetric study by Angell and Zhao indicated a liquid-liquid transition (LLT) [29] in supercooled aqueous \( \text{N}_2\text{H}_4\text{H}_2\text{TFA} \) solution [3], and a subsequent infrared study showed that the two phases have vibrational spectra similar to those of high- and low-density amorphous water [4].

Here we report additional experiments to further characterize this LLT. Using infrared spectroscopy, thermal conductivity measurements and multivariate curve resolution techniques, we investigate the isotope effect in the transition temperature, and we characterize the coexistence of two phases during the transition. Both experimental techniques indicate an isotope effect that elevates the onset of the LLT by \( \approx 5 \) K for the deuterated system, a value similar to that observed for the HDA-LDA transition [31] and for the Widom line in pure water [5]. In the final section we discuss a recent report [32] that proposes that the phase transition observed in [3,4] might involve a nanoscopic phase separation.

3. Experimental

We investigate isotope effects related to a LLT in supercooled aqueous solutions and its deuterated counterpart by measuring their infrared absorption spectra and thermal conductivities whilst cooling down and reheating in a cryostat. To achieve a high degree of supercooling, we prepared samples of the anti-freezing agents \( \text{N}_2\text{H}_4\text{H}_2\text{TFA} \) and \( \text{N}_2\text{D}_2\text{TFA} \) in ultrapure \( \text{H}_2\text{O} \) (Milli-Q) and \( \text{D}_2\text{O} \) (Sigma, 99.9% D), respectively. For both systems we chose a molar fraction of \( x_{\text{OD}} = 0.84 \), to prevent both the loss of water’s anomalies, and the occurrence of a glass transition [4]. We used steady-state vibrational spectroscopy to probe the OH stretching mode at \( \approx 3400 \text{ cm}^{-1} \) and the OD stretching mode at \( \approx 2500 \text{ cm}^{-1} \). The frequency of these modes is very sensitive to the OH/D...O-bond length, and hence they are ideal indicators for structural changes in hydrogen-bonded systems [33,34]. Decoupling between OH and OD stretching modes is achieved by measuring isotopic mixtures with a H/D or D/H ratio of \( \approx 0.03 \) [35], e.g. looking at the OH stretching mode in the \( \text{N}_2\text{D}_5\text{TFA} \) in \( \text{D}_2\text{O} \) system and at the OD stretching mode in the \( \text{N}_2\text{H}_5\text{TFA} \) in \( \text{H}_2\text{O} \) system. We squeezed small volumes of the samples (\( \approx 0.6 \mu\text{L} \)) between two CaF\(_2\) windows and gradually supercooled them, followed by reheating, via liquid N\(_2\) in the brass holder of a cryostat. Prior to each measurement, we purged the sample chamber with He to prevent IR absorption by \( \text{H}_2\text{O} \) in the air. We then tracked changes in the hydrogen-bond structure of the samples by recording 4 infrared spectra per minute. Initially, cooling rates were set at 5 K/min until reaching slightly below the homogeneous nucleation temperature \( T_h \). Then, we changed the cooling rates to 1 K/min to probe the region between 180 K and 220 K (where the first-order transition is suspected) more precisely. Upon reaching \( \approx 180 \) K we reheated all samples back to room temperature, using the same heating rates as cooling rates before.

The temperatures were read off thermocouples, attached to the brass holder of the cryostat. To check for possible offsets in the temperature readout between the samples and the thermostats, we carried out a calibration measurement using a separate thermocouple at the position of the sample (see Supplementary Information, Fig. S1).

Thermal conductivities \( \kappa \) of aqueous \( \text{N}_2\text{H}_4\text{H}_2\text{TFA} \) and \( \text{N}_2\text{D}_5\text{TFA} \) solutions were measured via the 3Ω method, using an experimental setup described before [36]. The sample volume used for these measurements was \( \approx 1 \mu\text{L} \). The setup was introduced into a continuous-flow cryostat for the temperature-dependent experiments. To facilitate comparison with the IR data, the exact same cooling and heating rates were used in the thermal conductivity measurements.

4. Results and discussion

4.1. Infrared spectroscopy

All spectra shown in this section were baseline corrected by subtracting spectral offsets from the entire curves. No other post-processing techniques were used. The decoupled OH and OD stretching bands at \( \approx 3400 \text{ cm}^{-1} \) and \( \approx 2500 \text{ cm}^{-1} \) were used as probes for hydrogen-bond strength distribution for the 3% OH in OD and the 3% OD in OH systems, respectively. The temperature-dependent evolution of the infrared spectra for both OH and OD-rich systems is shown in Fig. 2. A decrease in temperature leads to a gradual redshift of the OH stretching mode in the OD-rich system (Fig. 2a), indicating strengthening (shortening) of hydrogen bonds, similar to what happens in neat supercooled water [37]. At the same time, we observe an increase in absorbance, which is also due to the increase in average hydrogen-bond strength [38]. At \( \approx 197 \) K, a transition to a new peak at \( \approx 3300 \text{ cm}^{-1} \) occurs, indicating a first-order like phase transition. Upon reheating, the phase transition reverses (Fig. 2b), until crystallization interrupts the supercooled state (Fig. 2c). We observed crystallization only during reheating, when the nuclei growth rate exceeds the rate of nucleation [39]. Plotting the absorbance at the OH stretching frequency of \( 3300 \text{ cm}^{-1} \) as a function of temperature, shows the sharpness of the transition and reveals a small hysteresis of \( \approx 4 \) K (Fig. 2d). These results are consistent with the ones reported in [4]. To study isotope effects in supercooled aqueous solution, a complementary system consisting of 3% OD in OH was analyzed. Fig. 2e–h shows the experiment repeated for this OH-rich system, in which the OD stretching mode at \( \approx 2500 \text{ cm}^{-1} \) was probed. Within the cooling-reheating cycle this system behaved analogously to the D2O counterpart: we observed a LLT when a new peak at \( \approx 2440 \text{ cm}^{-1} \) appears. We measured this new peak at 192 K instead of 197 K for the OD-rich system. This 5 K temperature shift indicates the presence of an isotope effect related to a LLT in the deeply supercooled regime of water. In addition to the OD- and OH stretching modes, we also analyzed the carboxylic CO stretching mode in the \( \text{D}_2\text{O} \) system as a reference...
Fig. 2. Temperature-dependent infrared spectra of isotopic mixtures of aqueous N$_2$H$_5$.TFA and N$_2$D$_5$.TFA solutions. (a–d) Cooling down and reheating of the 3% OH in OD system. As a probe for changes in hydrogen-bond structure we used the OH stretching mode. Arrows show the direction of the evolution of the spectra. During cooling (a) the spectra gradually red shift and become narrower. For better visibility we show every fourth measured spectrum. At $\approx$197 K, the sample undergoes a liquid-liquid transition, indicated by a sudden jump (visible by the larger spacing between consecutive spectra around the transition temperature) to a new broad peak at $\approx$3300 cm$^{-1}$ (dashed circle). Upon reheating (b), the phase transition reverses until crystallization arrests the liquid phases, suggested by the appearance of a distinct narrow peak at 3295 cm$^{-1}$ (c). d Plot of the absorbance at the peak maximum of the low temperature liquid phase as a function of temperature. The shift in peak location in absorbance at the phase transition region is again emphasised by a dashed circle. Reheating reveals a small hysteresis. (e–h) Cooling down and reheating of aqueous 3% OD in OH solutions. Temperature-dependent spectral changes of the OD stretching mode occur analogously to what we observed for the OH stretching mode in the OD-rich system. However, the onset of the phase transition is shifted by $\approx$ 5 K to lower temperatures, indicating the presence of an isotope effect in the supercooled regime of water. (i–l) Evolution of the CO stretching mode of the trifluoroacetate compound in the OD-rich system. Cooling, reheating and crystallization behave similarly to the OH/D stretching modes, albeit without the increase in absorbance. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The presence of an isosbestic point in the spectra is indicative of coexistence of two phases during the transition [40,41]. An isosbestic point is defined as the frequency at which the total absorbance of a system remains constant during spectral variation, thus providing evidence of a transition of one component to another. We used the multivariate curve resolution-alternating least squares (MCR-ALS) technique [42–44] to obtain the species spectra from our data. MCR-ALS demixes multi-component systems, calculates their pure spectra and the respective concentrations of each of their chemical constituents (see Supplementary Information for details). Applying the MCR-ALS algorithm to our IR data yields the pure component spectra for both OD- and OH-rich systems, as shown in Fig. 3a and b, respectively. In each isotopic system we find 2 components, representing high- and low-temperature phases separated by the phase transition. Fig. 3c shows a plot of the relative concentrations of each component as a function of temperature. The crossover point for both OD- and OH-rich systems (which are again shifted by $\approx$ 5 K) in the concentration profiles reveal the temperatures at which the two phases coexist in a 1:1 ratio.

4.2. Thermal conductivity

In addition to the IR experiments presented above we further characterize the LLT and its related isotope effect using thermal conductivity measurements. The temperature dependence of the thermal conductivity is shown in Fig. 4. For the data analysis we considered the temperature range below 260 K, as experimental limitations rendered the S/N ratio unsatisfying for higher temperatures. Here we observed that the addition of N$_2$H$_5$.TFA to water and N$_2$D$_5$.TFA to deuterated water leads to a significant decrease of the thermal conductivity, $\kappa$, that is from 0.6 Wm$^{-1}$ K$^{-1}$ in neat water to 0.37 Wm$^{-1}$ K$^{-1}$ and 0.38 Wm$^{-1}$ K$^{-1}$ in aqueous OD- and OD-rich hydrazinium trifluoroacetate solution, respectively. This behavior is also observed in other salt solutions [45]. Upon deuteration, $\kappa(T)$ decreases by $\approx$ 4%, reminiscent of what happens in neat water [46]. Cooling down causes $\kappa$ to increase roughly linearly in both isotopic systems. At $\approx$ 195 K for the D$_2$O sample (Fig. 4a) and 190 K...
Fig. 3. Pure component spectra of isotopic mixtures of aqueous $\text{N}_2\text{H}_5\cdot\text{TFA}$ and $\text{N}_2\text{D}_5\cdot\text{TFA}$ solutions, calculated by MCR-ALS. Both OD- (a) and OH-rich (b) systems show high- and low-temperature phases, separated by a LLT. The spectra cross at isosbestic points (black circles), which remain unchanged during the first-order like phase transition. Isosbestic points are located at 3365 cm$^{-1}$ and 2490 cm$^{-1}$ for the OD- and OH-rich systems, respectively. (c) MCR-ALS calculated concentration profiles for both high- and low-temperature phases presented in a (solid lines) and b (dashed lines). The concentration curves of both isotopic systems are shifted by $\approx 5$ K.

Fig. 4. Temperature dependence of the thermal conductivity $\kappa$ of aqueous $\text{N}_2\text{D}_5\cdot\text{TFA}$ (a) and $\text{N}_2\text{H}_5\cdot\text{TFA}$ (b) solutions. Both systems undergo reversible LLTs, characterized by peaks in the $\kappa$-$T$ curves. The temperatures of the onset of the LLTs match well with the results obtained from the IR measurements (Figs. 2 and 3). Overall, the thermal conductivity is $\approx 4\%$ smaller in the OD-rich sample. As observed in the spectroscopy measurements, crystallization interrupts the liquid phases upon reheating. Arrows highlight the direction of the cooling and reheating processes. c Comparison of the cooling ramps for both $\text{D}_2\text{O}$ (solid lines) and $\text{H}_2\text{O}$ (dashed lines) samples. An isotope effect induces a $\approx 5$ K shift between the onset temperatures in the peaks assigned to the LLTs.
for the H₂O sample (Fig. 4b), we observed pronounced peaks, which indicate the presence of a phase transition. Such peaks in κ(T) have been observed before, and assigned to abrupt and large enthalpy changes [47]. The lowering of κ(T) after the phase transition by ≈ 5% (which then stays temperature-independent) excludes the possibility of a glass transition, as the thermal conductivity of the LDA amorphous solid drastically exceeds that of liquid water [48]. Additionally, deuteration in amorphous solids increases κ [46], which does not happen in our measurements. Thus, the peaks indicate the presence of the same LLT that we observed in our IR experiments. The phase transition is completely reversible upon reheating (with a small thermal hysteresis, similar to what we saw in the IR experiments), until crystallization interrupts the supercooled state, accompanied by a dramatic increase in κ. As in the IR experiments, crystallization only occurred during reheating. The phase transition temperatures for both H₂O and D₂O obtained from the κ(T) measurements are in good agreement with the IR results. Additionally, and concordant with our IR findings, thermal conductivity measurements exhibit an isotopic temperature shift of ≈5 K.

4.3. Isotope effect in the transition temperature

Isotope effects in water have been studied extensively [5,31,49–57]. H/D substitution in water causes its vibrational spectrum to red-shift [33,58], and also influences phase-transition temperatures. Deuteration causes both melting point and boiling point to elevate, and a shift in the glass transition temperature [55]. By comparing heavy and light water melting curves in the pressure-temperature plane, Mishima found that the D₂O melting curves are shifted by about ≈ 3 K to the high temperature side with respect to the H₂O curves, indicating the influence of isotope effects on different phases of ice [53]. Recently, Kim et al. directly observed that an isotope effect shifts maxima in the isothermal compressibility and correlation length (the Widom line) of supercooled water-droplets by around 4 to 5 K [5]. These isotope effects can be attributed to nuclear quantum effects that result in delocalized protons affecting water’s librational and OH stretching vibrational motion [49,50,52,56,59]. Nuclear quantum effects were found to be temperature-independent: the structure factor of H₂O and D₂O between 275 K and 240 K is essentially the same, if a constant temperature shift of 5 K is taken into account [54]. Another temperature shift of ≈ 5 K between isotopically pure H₂O and D₂O samples was measured for the HDA-LDA transition [31]. This observation is especially important for the interpretation of our findings, since the IR spectral change during the LLT in aqueous N₂H₅.TFA solution resembles that in the first-order phase transition between HDA and LDA amorphous ices [4,60]. The similarity between the isotopic temperature shift that we find for the LLT in N₂H₅.TFA solution and the one found previously for both the HDA-LDA transition [31] and the Widom line [5] is in agreement with the idea (already suggested by the similarity of the IR spectra) that the observed transition is the liquid-liquid analog of the HDA-LDA transition between the two amorphous phases of water [21].

4.4. Liquid-liquid transition or reversible nanophase-separation?

Recently, Bachler et al. suggested that the phase-transition occurring in aqueous N₂H₅.TFA solutions might be related to a nano-phase separation rather than to a LLT [32]. This is similar to what was observed in other aqueous solutions, such as LiCl solutions, although in these cases no first-order phase transition occurs [61]. This idea is based on the results of high-pressure dilometry and X-ray diffraction experiments, which for aqueous N₂H₅.TFA solutions, show a behavior at odds with what is observed for water at atmospheric pressure. Specifically, (i) the X-ray diffraction patterns, measured from rapidly quenched N₂H₅.TFA solutions, did not show any sign of structural changes on reheating across the phase transition temperature, and (ii) no densification upon compression occurs. We hope that the experimental results and the scenario proposed in [32] will inspire further theoretical and experimental investigation into the microscopic origin of the observed transition. Here, we would like to discuss potential alternative interpretations of the findings of Bachler et al., also in the light of other experimental evidence.

Irrespective of the microscopic events during the phase-transition reported in [4], it seems puzzling that Bachler et al. observe no change in the diffraction patterns on crossing the transition temperature [32]. The OH stretching band is very sensitive to local changes in the H-bond network [33], and the marked changes in the IR absorption spectra should be reflected in the X-ray diffraction pattern as well. Specifically, it is very well established that there is an approximately linear relation between the OH stretching frequency of a hydrogen-bonded OH group and the O...O hydrogen-bond length. In a classic paper, Novak compared the OH stretching frequency and the O...O distance (measured using x-ray diffraction) in some hundred different compounds, and, by plotting these two quantities against each other, found a clear functional relation that forms the basis of all infrared spectroscopy on hydrogen-bonded liquids. Hence, a change in the OH stretching frequency should be accompanied by a measurable change in the X-ray diffraction. As a recent example, in the case of water-sorbitol mixtures, where water gets nano-segregated in the sorbitol amorphous matrix, structural changes observed in the IR absorption spectrum [62] are directly reflected in both X-ray and neutron scattering [63]. Furthermore, in the measurements of Bachler et al., crystallization peaks are already visible in the X-ray diffraction patterns at temperatures well below the phase transition temperature [32], whereas the IR measurements show no evidence for the presence of crystalline water at these temperatures. A possible explanation for the discrepancy might be the higher cooling rates (between 100 K/min and 1000 K/min [32]) necessary to produce the samples for the X-ray scattering measurements, compared to the much lower rates (1 K/min and 5 K/min) used in the DSC, IR absorption and thermal conductivity experiments. Since the phase-transition in N₂H₅.TFA solutions (x_water = 0.84) occurs at a temperature well below the liquidus melting point (≈60 K, see the phase diagram in [3]), a too high cooling rate might drive the supercooled liquid out of equilibrium at a temperature above the phase transition temperature, and so prevent it from completely transforming. Fast differential scanning calorimetry could shed further light on this issue.

The lack of the characteristic density jump upon compression at low temperature could instead be due to the effective pressure of water in the system of study, ≈150 MPa: at these high pressures, water in solution loses its density maximum [64], and its specific volume is already reduced prior to the application of pressure. It is also important to point out that, according to thermodynamic theories of the glass-transition [65,66], the low temperature phase is expected to lie well below the glass transition temperature. This is due to the sudden loss of entropy: any phase-transition from this out-of-equilibrium state would be then smeared out. In addition, recent simulations suggest that nanoscale unmixing-mixing between water and ions actually accompanies the transformation of water into a low-density phase [67]. Another interesting aspect to be considered is the role of the pH, which, as pointed out in [32], is acidic for N₂H₅.TFA solutions at x_water = 0.84. To rule out an eventual dependence of the phase transition on the pH of the solution, we have performed IR absorption measurements on a sample with neutral pH (see Supplementary Information, Fig. S2). As clearly evidenced by Fig. S2, the phase transition takes place analogously to the one under more acidic conditions, thus ruling out any pH dependence of the LLPT.

5. Conclusion

A FTIR-spectroscopy study, combined with multivariate curve resolution data analysis techniques and thermal conductivity measurements was carried out to study isotope effects and phase coexistence in supercooled aqueous solutions. A first-order like phase transition occurs for isotopic mixtures of D₂O and H₂O, with an isotope effect that shifts
the LLT temperature by ≈5 K. MCR-ALS analysis confirms the presence of isosbestic points that indicate coexistence between two distinct phases during the transition, with IR spectra (and hence hydrogen-bond strength distributions) resembling those of HDA and LDA. This particular resemblance and the isotope effect are also observed during the transition, with IR spectra (and hence hydrogen-bonding) of ice at the LLT temperature by

A. Nilsson, L.G.M. Pettersson, The structural origin of anomalous properties of water.


