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Water

Water, water, everywhere

Water is the molecule of life, without which metabolism or reproduction is impossible. To the chemist water is the most widely used solvent, which may even be turned from a polar to an apolar solvent in its supercritical state [1]. Water is found almost everywhere, either as a gas in the atmosphere, as a liquid in the hydrosphere or as one of its many solid forms in the cryosphere. While two thirds of Earth's surface is covered by oceans, water in Earth's interior exists in the form of two solid high-pressure ices, called ice VI and ice VII. Bizarrely, these phases are stable at temperatures up to 600°C - without melting – and need pressures of at least 10 kbar to form. Via tectonic processes such ices emerge to Earth's surface as diamond inclusions and may hence be termed minerals [2]. In space, water is even more ubiquitous, where most of the water in our universe is found as an amorphous solid in molecular interstellar dust clouds. Silicaceous or carbonaceous particles are covered in a non-crystalline, highly porous form of ice termed amorphous solid water (ASW) [3]. These dust clouds, such as the Horsehead Nebula (cf. Figure, right) are the starting point for the evolution of both molecules themselves and solar systems. An understanding of the chemical reactions taking place for molecules trapped in the micropores of ASW under the influence of heavy radiation (UV-irradiation, X-ray, electron bombardment) is still lacking largely, in spite of its importance. For example, the answer to the question as to why we find naturally L-, but not D-amino acids might reside in the micropores of ASW. Very recently the James Webb Space Telescope (JWST, cf. Figure, middle) has reached its final position and has started to rewrite astrochemistry based on pictures that make use of near
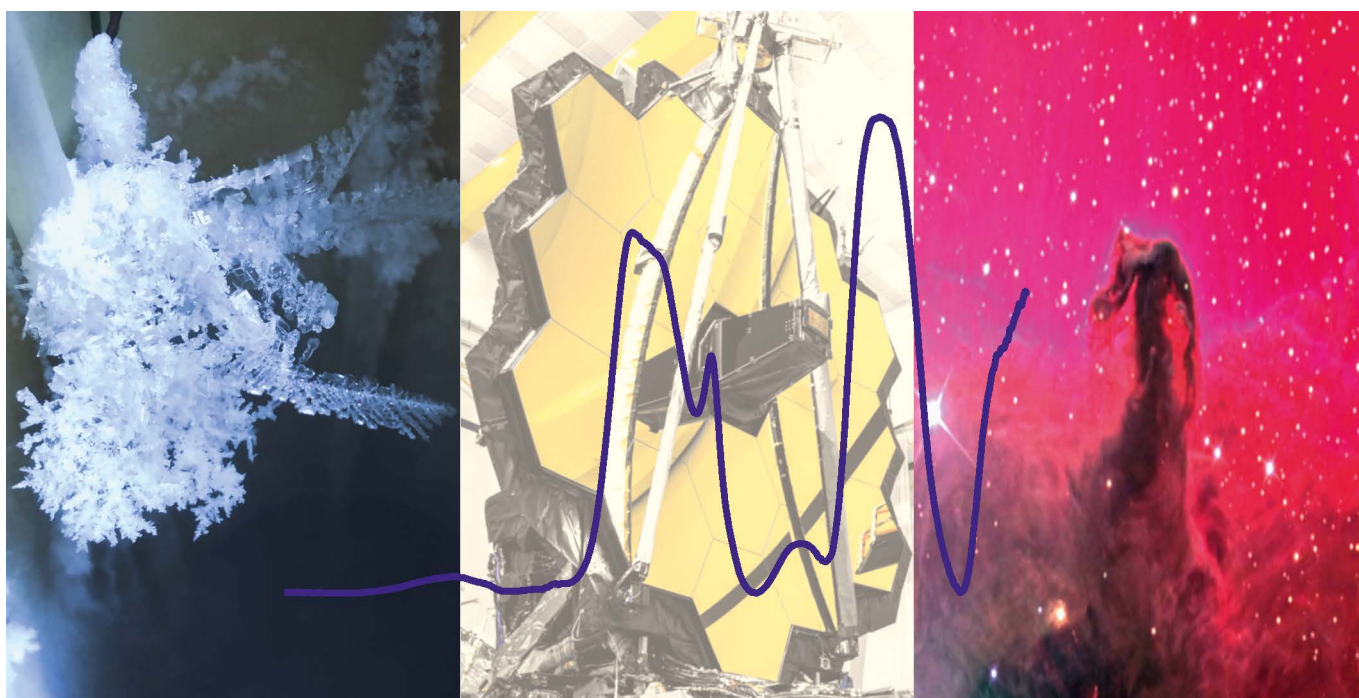

Figure: Left: Ice crystals grown in our laboratory experiments on near-infrared spectra of crystalline and amorphous H_2O ices. Middle: The James Webb Space Telescope overlaid with the near infrared spectrum of ice IX (blue line) from our work in ref. [4]. Right: The Horsehead Nebula (Orion constellation) as an example for an interstellar dust cloud, where water exists as porous amorphous solid water (ASW). Picture credits: Left: Christina M. Tonauer. Middle: NASA/Chris Gunn (CC.BY.2.0). Right: Ken Crawford (CC.BY.3.0). Pictures (Middle, Right) were cropped and the contrast was altered.

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infrared (NIR) light. Part of its mission will also be to explore icy bodies in space. In our lab we have made 20 different types of crystalline and amorphous ices and collected their NIR spectra to support this mission and to allow for ice phase identification [4, 5]. The Figure shows as an example the NIR spectrum of ice IX, which might be present in icy moons of Jupiter.

Ice polymorphism

H_2O seems like a simple molecule. One might think that all secrets of a substance of such importance have been revealed through research. Yet, spectacular properties of water keep being discovered. In the last 25 years we have witnessed the era of ice polymorphism, in which ices XII - XX have been discovered [6]. For instance ice XVIII was reported in 2019, which is a form of ice that shows superionic properties [7]. In metals the high electric conductivity is caused by an electron gas, i.e., electrons that are delocalized in the lattice of metal cations. In superionic ice the hydrogen atoms are delocalized and float around freely in the lattice of oxygen atoms. That is, the molecular nature of water breaks down, only the stoichiometry of H_2O is retained. This is only possible at extremes of temperature and pressure, where typically several thousand °C and Mbar of pressure are required to reach the superionic state. At milder temperatures, but still in the Mbar regime, the hydrogen atoms stop floating around and are localized exactly at the midpoint between two oxygen atoms. This form of ice is known as ice X and can be called an atomic ice crystal, which might be present in the interior of the ice giants Uranus and Neptune [8]. In the very rich kbar pressure regime ice forms a large range of polymorphs, all of which are molecular in nature. That is, they form a hydrogen bond network, where each water molecule is tetrahedrally surrounded by four water molecules – a motif known as the Walrafen pentamer. Different ice phases differ in terms of their oxygen atom network, where not only six-membered rings (such as in common hexagonal ice, cf. Figure, left), but also smaller and larger rings of sizes 4 to 12 are known [8]. In some cases even ring threading, similar to the situation in the Olympic rings is known [8]. Currently, 13 such ice polymorphs are known in this regime, where the first ones, ices II and III, were discovered by Gustav Tammann in Göttingen and Percy Bridgman in Harvard about 120 years ago. Ice XIX was only discovered in 2018 in our own research group [9], and its crystal structure was reported simultaneously by a research group in Tokyo [10] and again by our research group in 2021 [11]. In terms of its oxygen atom network ice XIX is almost exactly identical to ice VI and ice XV. The difference between these ices relates to the subnetwork of hydrogen atoms, which is fully disordered in ice VI and partly ordered in ices XV and XIX, such that the latter two carry anti-ferroelectric properties. In a recent computational study about 50 different ice polymorphs have been suggested [12], i.e., we are experimentally less than halfway.

Anomalous liquid water: a tale of two liquids

In the liquid state, particularly in the supercooled liquid state, water is even more fascinating, and probably even less well understood than ice polymorphs. More than 70 anomalies, distinguishing water from almost every other substance, have been collected. They can be grouped into phase anomalies (see paragraph above), thermodynamic anomalies, dynamic anomalies and density anomalies, where the density maximum at 4°C is probably the most appreciated anomaly of water. Interestingly, thermodynamic response functions such as the isobaric heat capacity seem to diverge near a temperature of -50°C upon cooling. One possibility to explain this is a two-liquid model of water, an idea that was first brought up by Wilhelm C. Röntgen in the late 19th century. In this model the single component substance H_2O can spontaneously decompose into two distinct liquids, both of composition H_2O. These liquids are then distinguished by means of their mass density, where a low- and a high-density liquid of densities 0.92 g/ml and 1.15 g/ml exist [13]. Ambient temperature water is then regarded as a mixture composed of two thirds of the low- and one third of the high-density liquid. At room temperature these two liquids experience density fluctuations that are so fast that H_2O is not separable. It is called "supercritical" by some researchers then, where this refers to a second critical point that is hard to verify experimentally. Some experiments have provided hints for this second critical point to be located at -50°C and at slightly elevated pressures [14]. Only below -50°C the fluctuations mixing the two liquids are slow enough so that a spontaneous phase separation into two liquids, with a clear phase boundary between the two is possible. This resembles the process of separating oil and water in the separatory funnel in an organic chemistry lab. The only difference is that H_2O is a one-component system that separates into two liquids, whereas oil/water is a two-component system that separates into two liquids. In our research group we have devoted a few years of experiments to find experimental ways how to prepare and how to characterize these two liquids. Our best way is to produce two distinct types of amorphous ice first and then heat them beyond their glass transition temperatures located at -137°C for the low-density liquid and at -157°C for the high-density liquid [15]. Above this temperature the amorphous solid turns into a liquid that is even more viscous than honey and called "ultraviscous" and "deeply supercooled". The observation of (pure) liquid water in its bulk state at -157°C in fact represents a world record for the observation of water in its liquid form [15]. Previously, it was thought that supercooling of water, without crystallization occuring, is only possible down to temperatures of -38°C at ambient pressure and -90°C at elevated pressures, where the homogeneous nucleation temperature limits its existence. This homogeneous nucleation limit is bypassed in our experiments either by hyperquenching [16] or by pressure-amorphization of ice [17]. Both techniques lead to non-crystalline (solid) ice at liquid nitrogen temperature, which upon heating slowly get less viscous. Both the low- and the high-density liquid ultimately do crystallize upon continued heating at the cold-crystallization temperature. Yet, we have identified a window of about 20°C broadness, in which the ultraviscous low- and high-density liquids can be kept stable for hours or even weeks [15]. Generations of chemists have studied water as a solvent at room temperature, filling textbooks with chemical reactions in aqueous solution. It is now of great interest how chemical reactions differ in these two types of liquid water – a research field called "cryo-chemistry", which is mostly unexplored territory. Most definitely, water will also reveal more of its surprising properties in future and will keep exciting us.

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Christina Maria Tonauer (*1993) ist Doktorandin in der Gruppe von Thomas Loerting, Universität Innsbruck. In ihrem von der Österr. Akademie der Wissenschaften (ÖAW) finanzierten DOC-Projekt beschäftigt sie sich u. a. mit Nahinfrarot-Spektroskopie verschiedener amorpher und kristalliner Eisformen. In einem Projekt im Rahmen des Centers for Molecular Water Sciences (CMWS) arbeitet sie in Zusammenarbeit mit der Arbeitsgruppe von Melanie Schnell am DESY in Hamburg an einem Verständnis der photochemischen Prozesse in amorphen Eisformen. 2022 wurde sie mit dem Agnes-Pockels Dissertationspreis der Bunsen-Gesellschaft ausgezeichnet.

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Thomas Loerting (*1973) studierte und promovierte an der Universität Innsbruck und ist ebendort seit 2008 Professor für Physikalische Chemie. Hauptforschungsgebiete sind Wasser und Eis sowie wässrige Lösungen und Clathrat-Hydrate unter extremen Bedingungen. Er absolvierte Auslandsaufenthalte im Labor des Nobelpreisträgers Mario J. Molina am M.I.T. (2001-2003) sowie von Roland Böhmer an der TU Dortmund (2014). Seine Forschungen wurden unter anderem mit dem Bessel-Preis der Alexander von Humboldt Stiftung, dem Nernst Haber Bodensteinpreis der Bunsen-Gesellschaft sowie dem Starting Grant des Europäischen Forschungsrats ERC ausgezeichnet.