



Calorimetric Observation of the Melting of Free Water Nanoparticles at Cryogenic Temperatures

C. Hock,¹ M. Schmidt,² R. Kuhnen,¹ C. Bartels,¹ L. Ma,^{1,3} H. Haberland,¹ and B. v. Issendorff¹

¹*Fakultät für Physik, Universität Freiburg, Hermann-Herder-Straße 3, 79104 Freiburg, Germany*

²*Laboratoire Aimé Cotton, CNRS, Bâtiment 505, Université Paris Sud, 91405 Orsay Cedex, France*

³*The Department of Physics, Nanjing University, 210093 Nanjing, China*

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We present an experimental study of the thermodynamics of free, size-selected water cluster anions consisting of 48 and 118 molecules. The measured caloric curves of the clusters are bulklike at low temperatures but show a well-defined, particle-size specific transition at 93 ± 3 K for $(\text{H}_2\text{O})_{48}^-$ and 118 ± 3 K for $(\text{H}_2\text{O})_{118}^-$. At the transition temperature the heat capacity strongly increases, which marks the onset of melting.

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Melting of water is the archetypical example of a phase transition. Little is known, however, about this process on a nanoscopic scale. Although nanometer sized water particles play an important role in Earth's atmosphere [1,2] and interstellar space [2–4], even their melting points are unknown. Detailed experimental results exist only for water confined in nanoscopic pores [5,6]; here, however, the interaction with the surrounding surface has a strong and not very well defined influence. For free particles, evidence for melting or freezing transitions has been obtained but without full temperature control or in nonequilibrium situations. Electron diffraction on supercooled water droplets, e.g., showed that droplets with about 5000 molecules freeze when they reach a temperature of approximately 200 K [7], but this is certainly a transition far from equilibrium. Infrared spectroscopy on neutral water nonamers gave some evidence for a melting transition; the transition temperature, however, could only be estimated to lie between 65 and 186 K [8]. Similar infrared spectroscopy experiments on size-selected and temperature controlled water cluster anions have been performed recently [9] but did not address the question of phase transitions. Theory can provide only limited assistance. Water has resisted a full theoretical description so far, even though dozens of approaches are in use, ranging from simple point charge models for the water molecules to full *ab initio* calculations [10]. Most of the common models are unable to correctly reproduce the melting point of bulk ice [11]. It is therefore unlikely that they can provide a reliable description of the thermodynamics of small water clusters. This is especially true for low temperatures. Most simulations treat the motion of the water molecules classically. Water, however, is definitely a quantum system at low temperatures. At 100 K, bulk ice has a heat capacity of about $2k_B$ per molecule [12], which means that only two of the six intermolecular vibrational degrees of freedom (three translational and three librational modes) are thermally populated; the remaining four are frozen out. A classical calculation will therefore strongly overestimate the energy in the system, and it is

questionable whether in this case phase transitions can be described correctly. There are first attempts to simulate water clusters treating the atomic motion quantum mechanically [13,14], but unfortunately the numerical effort is enormous, so that currently only very small systems can be handled.

In spite of these problems, many calculations targeting the caloric curves of water clusters have been performed within the past decades [15–20]. The results differ quantitatively due to the different types of models used but qualitatively agree in one aspect: They describe a phase transition at temperatures between 100 and 210 K (depending on model and cluster size), which does not exhibit a latent heat but manifests itself in a clear increase of the heat capacity. Since at the transition temperature bond length fluctuations strongly increase and a concomitant diffusion of molecules sets in, the transition has been interpreted as melting of the clusters.

In this Letter, we present the experimental caloric curves of two mass-selected water clusters $(\text{H}_2\text{O})_{118}^-$ and $(\text{H}_2\text{O})_{48}^-$, which not only confirm this behavior but also characterize the transition in detail.

In the experiment negatively charged water clusters $(\text{H}_2\text{O})_n^-$ are thermalized in a temperature controlled radio frequency multipole trap by collisions with helium buffer gas at a pressure of about 10^{-3} mbar [21], transferred into high vacuum, mass-selected, and photofragmented by a laser pulse (1064 nm, 5 mJ/cm²). The recorded fragment mass spectra are sensitive to the inner energy of the thermalized clusters, which allows us to link temperature and energy and deduce caloric curves, as described earlier [22,23]. We use negatively charged clusters because they have a strong absorption in the near IR, which is due to an excitation of the “hydrated” electron [24]. Since the clusters are relatively large, we do not expect an important influence of their charge state on the caloric curve. The excited state of the attached electron has been shown to decay in less than 200 fs by coupling to vibrational modes of the cluster [25]. This complete energy transfer from

electronic to vibrational degrees of freedom is crucial for the experiment, since the photofragmentation process is assumed to take place in thermal equilibrium. We performed several tests to verify the validity of this assumption. We repeated the measurements on $(\text{H}_2\text{O})_{118}^-$ at a different photon energy (1.6 eV), obtaining identical results. We furthermore checked that the number of evaporated molecules per energy absorbed [2.17 ± 0.15 molecules/eV for $(\text{H}_2\text{O})_{118}^-$ and 2.23 ± 0.15 molecules/eV for $(\text{H}_2\text{O})_{48}^-$, which is close to earlier results for smaller sizes [26]] depends neither on the initial cluster temperature nor on the number of absorbed photons. Based on these tests, we estimate the systematic error of the measured energy values to be less than 10%.

Figure 1 shows the results for the two cluster sizes investigated. In the upper graph (a), the average energy per molecule of the clusters is plotted as a function of the heat bath temperature. Both curves exhibit three character-

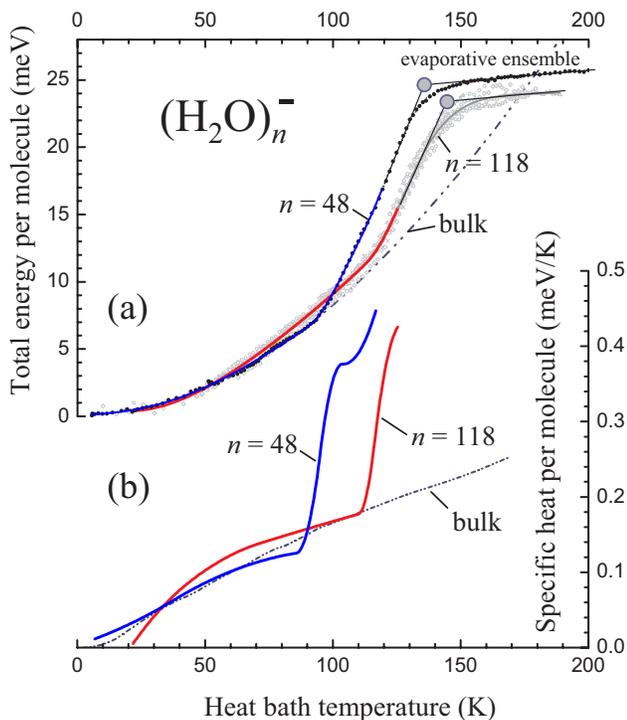


FIG. 1 (color online). Experimental results for water cluster anions consisting of 48 and 118 water molecules. (a) The mean inner energy per molecule of an ensemble of $(\text{H}_2\text{O})_n^-$ clusters as a function of the heat bath temperature. Black, full dots: $n = 48$; gray, open dots: $n = 118$. At lower temperatures, the experimental points represent the caloric curve of the mass-selected clusters. The solid, thick lines are cubic spline fits to the caloric curves; the dashed-dotted line is the caloric curve of bulk ice [12]. The large gray dots indicate the evaporative ensemble energies and temperatures that result from the extrapolations of the caloric curves up to the evaporative ensemble (thin black solid lines). (b) The specific heat per molecule of the clusters calculated by the differentiation of the spline in (a). The sudden increase marks the onset of the melting transition.

istic temperature regions. At the lowest temperatures ($T < 100$ K), the internal energy grows with a slowly increasing slope. In the second region, between about 100 and 140 K, the energy increases with a strongly enhanced slope; in the highest temperature region ($T > 140$ K), it then levels off. We will start the discussion with this last region.

At high heat bath temperatures, the clusters evaporate water molecules during thermalization, which lowers their temperature. As soon as this evaporative cooling perceptibly compensates the thermalization, the cluster ensemble temperature falls below the one of the heat bath, which leads to the flattening of the curve in Fig. 1(a). The curve saturates at an inner energy E_{evap} of the cluster for which the evaporative cooling is in equilibrium with the heating by the heat bath. The flattening therefore indicates the transition between a canonical ensemble and an evaporative ensemble [27,28]. The position of the bend between the canonical and the evaporative part of the curve gives both the energy E_{evap} and the corresponding temperature T_{evap} of the evaporative ensemble, as described in Ref. [28]. We found $T_{\text{evap}} = 144 \pm 6$ K and $E_{\text{evap}} = 23.5 \pm 1$ meV/molecule for $(\text{H}_2\text{O})_{118}^-$ and $T_{\text{evap}} = 136 \pm 6$ K and $E_{\text{evap}} = 24.8 \pm 1$ meV for $(\text{H}_2\text{O})_{48}^-$. We have shown earlier that the thermal evaporation rate of an evaporative cluster ensemble can be treated as an effective equilibrium vapor pressure [28]. At the maximum temperature that the water clusters can reach under the current experimental conditions, their effective vapor pressure is many orders of magnitude below the pressure of the triple point of water (612 Pa). At a pressure below its triple point pressure, a bulk material normally cannot melt; it can only undergo a solid to gas phase transition, that is, sublimate upon heating. Bulk water therefore can melt only at a pressure higher than 612 Pa; we will see below that water clusters behave differently in this respect.

Because of its Arrhenius character, evaporative cooling can be neglected at more than 20 K below T_{evap} . Thus here the measured curves represent the caloric curves of the clusters, which are indicated in Fig. 1 by thick lines.

As mentioned above, at the lowest temperatures the slopes of the caloric curves of both clusters approach zero due to the freezing out of the vibrational degrees of freedom. For comparison, in Fig. 1(a) the caloric curve of bulk ice [12] is shown as well. The measured cluster curves are close to identical to this curve. Bulklike caloric curves have already been observed for other cluster systems such as sodium [22], gallium [29], and aluminum [30]; however, this was usually in temperature ranges around or above the Debye temperatures of the systems. In our case this observation is even valid at temperatures far below the Debye temperature, where more and more of the vibrational modes are frozen out. The fact that in this region the water clusters exhibit a practically bulklike curve therefore shows that they must have a vibrational density of states similar to that of bulk ice.

Above the transition temperatures of $T_{\text{tr}} = 93 \pm 3$ K for $(\text{H}_2\text{O})_{48}^-$ and $T_{\text{tr}} = 118 \pm 3$ K for $(\text{H}_2\text{O})_{118}^-$, the caloric curves bend upwards and significantly deviate from that of the bulk. The rather abrupt nature of the transitions can be clearly seen in Fig. 1(b), where the heat capacity of the clusters is shown, as obtained by the numerical differentiation of spline fits to the caloric curves. At the transition temperature, one observes a strong increase of the specific heat.

Does this transition indicate melting of the clusters? Melting of bulklike systems is characterized by a latent heat, which leads to a peak in the heat capacity curve. We do not observe such peaks for the water clusters. This could be due to the onset of evaporation, which does not allow us to measure the caloric curve beyond T_{evap} . It is possible that the heat capacity becomes smaller again at higher temperatures, which would mean that we observe just the rising part of a heat capacity peak. But even if there is no such peak and the heat capacity keeps rising monotonically (which is well possible as the maximum value measured is still about a factor of 2 below that of liquid water at room temperature), this is not in contradiction with a melting transition. Melting transitions with a vanishing latent heat, exhibiting just a change of the heat capacity, are in fact quite common for clusters. Experimentally, such a behavior has been observed for many metal clusters [30,31]. For water clusters, transitions of this kind were seen in several classical molecular dynamics simulations [15–20], where the melting has been additionally identified based on the calculated trajectories of the molecules.

The temperature at which the transition occurs is only one-third of the bulk melting temperature, but it is within the range of the simulation results, especially if one takes into account that quantum effects can lower the transition temperature [14]. The fact that the transition of the smaller cluster size occurs at a lower temperature is also in agreement with a melting transition, as smaller particles in general tend to have lower melting points. All of this gives strong evidence that the observed transition is related to melting.

It should be noted, however, that melting does not mean that the water clusters immediately become fully liquid. The highest heat capacity observed in the region above the transition temperature (0.45 meV/K molecule = $5.2k_B$ /molecule) is still significantly smaller than the classical value of $6k_B$ /molecule that would be obtained if all translational and librational modes were populated, and this does not even take into account that the heat capacity of a liquid is usually much higher than that of a solid due to anharmonic contributions (room temperature liquid water, e.g., has a heat capacity of 1 cal/gK = $9.1k_B$ /molecule). This means that also above the transition temperature some of the intermolecular degrees of freedom are still frozen out. Further evidence that the cluster has not entirely given up its solid structure even at the evaporative ensemble

temperature comes from the observation of magic numbers in mass spectra of “hot” water cluster anions and cations [32,33]. The difference between the solid and the “liquid” state of the cluster will therefore be rather subtle and far from the distinct change occurring in the case of the familiar melting of bulk ice.

In this respect, there seems to be some similarity with the glass transition of low-density amorphous ice, which under heating changes into a supercooled liquid at about 136 K (the liquid then crystallizes at about 150 K) [6]. Apart from the comparable temperature range there are also structural similarities: Most calculations predict rather low symmetry structures for water clusters with sizes as studied here [34]; the local arrangement of the water molecules could therefore be rather similar in the clusters and in the amorphous ice or supercooled liquid. There is, however, an important difference: While amorphous ice and supercooled water are metastable phases of water, the water clusters studied here are most probably in their lowest free energy state, i.e., in thermodynamic equilibrium. Although it is possible to produce metastable structures of water cluster anions under special conditions [35], this seems rather improbable in our experiment where the clusters are heated close to their evaporation ensemble temperature before they are slowly cooled down to the selected temperature. Furthermore, neither the calorimetric measurements nor accompanying photoelectron spectroscopy characterization of the cluster anions [36] gave evidence for a significant contribution of such metastable structures. The observed transitions can therefore be assumed to be true equilibrium transitions.

In summary, we have measured caloric curves of free, size-selected water cluster anions $(\text{H}_2\text{O})_{48}^-$ and $(\text{H}_2\text{O})_{118}^-$. The curves are bulklike at low temperatures, demonstrating that the vibrational density of states of the clusters is similar to that of bulk ice. At particle-size specific temperatures, a sudden increase of the heat capacity occurs, which marks the onset of a gradual melting transition. This observation represents a first step towards a size-dependent phase diagram of water.

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