Configurational Energetics in Ice I*h* Probed by Compton Scattering

The ubiquitous water and ice exhibit various unusual macroscopic properties, which can be attributed to the local intra- and intermolecular interactions (i.e., both covalent and hydrogen bonding, cf. Fig. 1). Consequently, the ensuing configurational energies are of fundamental importance. Whereas calorimetric data - including both vibrational and configurational contributions - is readily available, experimental information on configurational energies is not easily obtainable. In fact, such information has hitherto been obtained only indirectly by somewhat simplistic modeling of spectroscopic data (see, e.g., Ref. [1]).

Compton scattering, which is inelastic X-ray scattering at large energy and momentum transfers, provides information on the ground-state electron momentum density. The technique has recently been shown to provide fundamental information on both intra- and intermolecular bonding (see, e.g., Refs. [2,3]). Interestingly, a formal connection between the Compton scattering data (the so-called Compton profile) and the total electronic energy has been known to exists for more than 30 years [4]. However, experimental limitations have so far hindered the experimental utilization of this unique property.

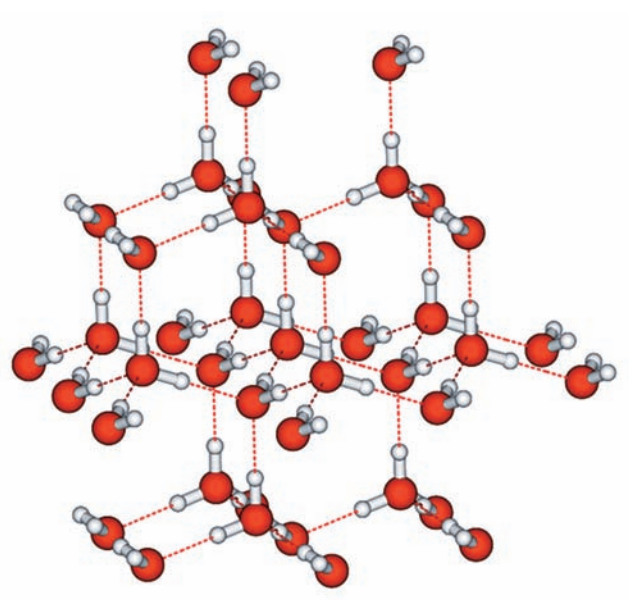

Fig. 1. Structure of ice I*h*.

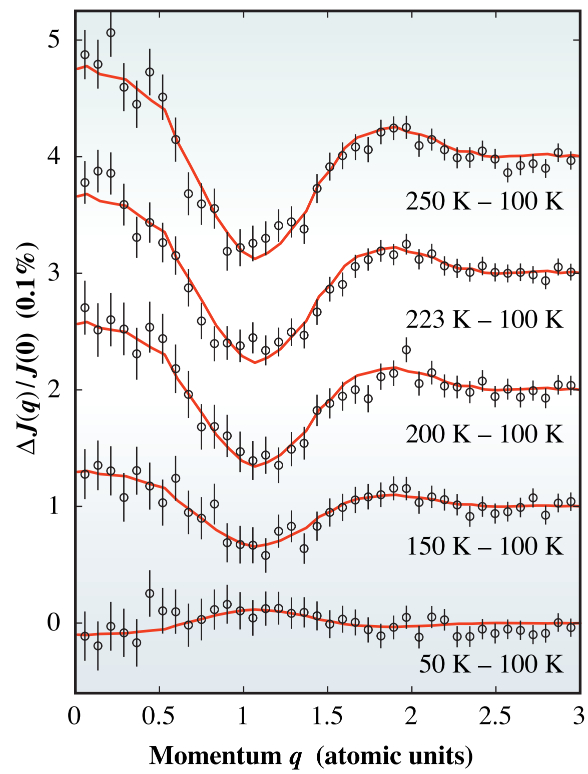

Fig. 2. Temperature-induced changes in the Compton profiles of polycrystalline ice I*h*. The reference Compton profile is acquired at T = 100 K.

We have studied the temperature-induced changes in the ground-state electron momentum density of polycrystalline ice I*h* by Compton scattering at beamline **BL08W** [5]. The experimental data is shown in Fig. 2. Due to the unprecedented accuracy and consistency currently obtainable, the experimental data can be directly interpreted in terms of configurational enthalpies (see Fig. 3). The configurational enthalpy is found to evolve linearly with respect to temperature above T = 100 K, leading to a constant configurational heat capacity c_p = 0.44±0.11 $Jg^{-1}K^{-1}$ in this temperature regime. Obtaining these fundamental quantities experimentally is important e.g. for assessing the accuracy of molecular-dynamics simulations schemes.

It should be noted that the present experimental approach is, in principle, limited by neither the specific binding (e.g., ionic, covalent, or hydrogen bonding) nor the thermodynamic state of the system (Compton scattering being applicable to solids, liquids, and gases, alike). Combined with the current experimental accuracy, as demonstrated in the present study, energetic studies on a variety of different systems should be feasible by means of Compton scattering.

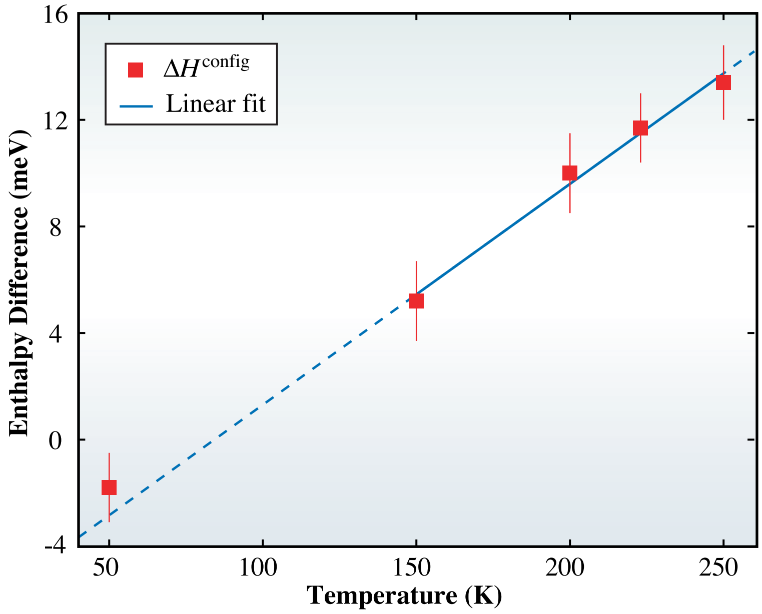

Fig. 3. Temperature-induced changes in the configurational enthalpy (per molecule) as determined from Fig. 2.

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