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Compton scattering study of water versus ice I*h*: Intra- and intermolecular structure

K. Nygård,[1,*] M. Hakala,[1] S. Manninen,[1] A. Andrejczuk,[2] M. Itou,[2] Y. Sakurai,[2] L. G. M. Pettersson,[3] and K. Hämäläinen[1]
[1]*Division of X-ray Physics, Department of Physical Sciences, P.O. Box 64, FI-00014 University of Helsinki, Finland*
[2]*JASRI, SPring-8, 1-1-1, Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan*
[3]*Department of Physics, AlbaNova, Stockholm University, S-10691 Stockholm, Sweden*

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The hydrogen-bond geometries in water and polycrystalline ice I*h* are studied using synchrotron radiation-based Compton scattering data of unprecedented statistical accuracy and consistency. By combining the experimental data with model calculations utilizing density functional theory, we show that the technique provides unique and complementary information on hydrogen bonding in water. The comparison of water and ice indicates the necessity of including a local intra-intermolecular geometric correlation for water, relating the intramolecular O-H bond length to the corresponding hydrogen-bond geometry. By using the hydrogen-bond geometries obeying this correlation, we demonstrate a further constraint on the angular distortions of the hydrogen bonds in water.

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Understanding the complex interactions between water molecules in the condensed phases has been a longstanding goal in chemical physics. However, despite extensive studies, the detailed local structure of water is still open to research [1–8]. Recent studies have focused on the local coordination; the traditional picture [3] of water molecules participating in almost four intact hydrogen bonds (H-bonds) on an average was recently questioned [5]. A closely related question is structural correlations in water (e.g., intra- versus intermolecular bond length and H-bond length versus angle), the experimental information of which has to our knowledge hitherto been restricted to crystal hydrates [9–11]. Considering the vast importance of understanding the microscopic structure of water, complementary information on these issues is essential.

In this work we have applied x-ray Compton scattering (CS) using synchrotron radiation combined with density functional theory (DFT) analysis to study the H-bond geometries in water as compared to polycrystalline ice I*h*. The technique has foremost been applied to studies on the electronic structure of solid-state systems, focusing on, e.g., fermiology [12], electron correlation effects [13], and novel materials [14]. However, recent computational studies have predicted that CS also provides fundamental information on the coordination and H-bond geometry in water [15,16], hence the technique is emerging as a unique, complementary tool for structural studies of molecular liquids [17,18]. In the present work we have analyzed the CS data from water by comparison to the corresponding data from ice I*h*, utilizing H-bond length and angle distribution functions (DFs) based on a nuclear magnetic resonance (NMR) study [19]; this approach has also been applied to the CS data from water in the 0.5°–90 °C temperature range [18]. We show that CS provides both intra- and intermolecular structural information on water, the major findings being summarized as follows. A good agreement between experiment and our computational model can be found only by taking into account a local intra-intermolecular geometric correlation: the average intramolecular O-H bond length (r_{OH}) in water depends strongly on the corresponding H-bond length (R_{HO}) and angle (β) (see Fig. 1 for geometric definitions). An elongation of the H-bond in water leads to a systematic shortening of the O-H bond, in good agreement with both *ab initio* Car-Parrinello molecular dynamics (CPMD) simulations [20,21] and observations for crystal hydrates at short R_{HO} lengths [9]. Secondly, the agreement can be further improved by including an intermolecular correlation between the H-bond length and its possible angular distortions. This correlation is in agreement with our earlier finding [18], delineating an excluded region in the (R_{HO}, β) values for the H bonds similarly as reported for crystal hydrates [11].

X-ray CS uniquely probes the electronic ground state [22,23]. The experimental data is interpreted in terms of the Compton profile (CP), which for isotropic systems (e.g., wa-

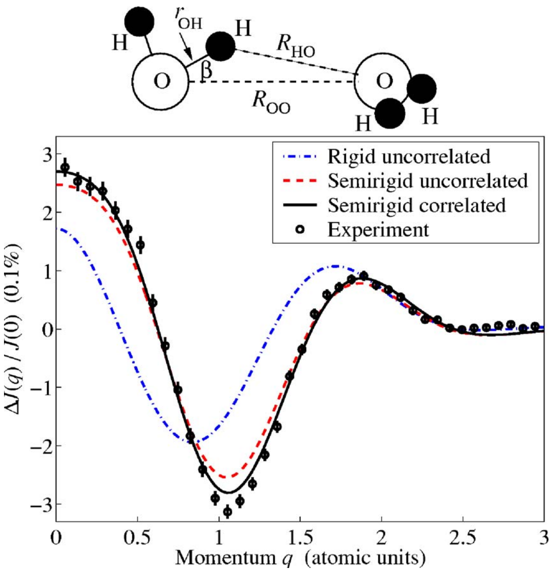

FIG. 1. (Color online) Top: The geometric definitions. Bottom: The difference between the CPs acquired from water (25 °C) and polycrystalline ice I*h* (−50 °C).

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[*]Electronic address: kim.nygard@helsinki.fi

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ter and polycrystalline ice Ih) is given by [23]

$$J(q) = \frac{1}{2}\int_0^{4\pi} d\Omega \int_{|q|}^{\infty} N(\mathbf{p}) p dp. \tag{1}$$

Here $N(\mathbf{p})$ is the ground-state electron momentum density and q a scalar momentum variable. Structural studies of water using CS are based on the observation that distortions in the H-bond geometry induce a characteristic oscillatory feature in the CP [15,16,24–28]. This feature has been attributed predominantly to the nearest-neighbor exchange interaction of the water molecules [15,25–27], including smaller contributions from charge transfer and polarization [15,28], as well as many-body (i.e., cooperative and anticooperative) effects [16,27]. It should be noted that we use this feature only as an effective fingerprint of the H bonds [15,16], realizing that the interpretation in terms of covalency [24] is widely considered ambiguous [25–27].

The method to calculate the CPs of water and ice Ih is based on pairwise nearest-neighbor interactions [16], an approach that has also been successfully applied to CS from water at different temperatures [18]. The H bonds are treated as mutually independent, including the exchange, charge transfer, and polarization contributions within a dimer approximation, while neglecting the many-body contributions. Thus the CP for a given water system can be written as [16]

$$J(q) \approx J_{\text{mon}}^{\text{ref}}(q) + \sum_{\alpha} f^{\alpha} \frac{1}{2}[J_{\text{dim}}^{\alpha}(q) - 2J_{\text{mon}}^{\text{ref}}(q)]. \tag{2}$$

Here α indexes the different H-bond geometries: $\{f^{\alpha}\}$ is a DF, $\{J_{\text{dim}}^{\alpha}(q)\}$ the CPs of a set of model dimers, and $J_{\text{mon}}^{\text{ref}}(q)$ the CP of a reference monomer. The possible dependence of the intramolecular bond length r_{OH} on the corresponding H-bond geometry (i.e., both H-bond length R_{HO} and angle β) can be included by modifying the geometry of the model dimers.

We use a fixed H-bond geometry for ice Ih, i.e., in our model of Eq. (2) we need only one model dimer $J_{\text{dim}}^{\text{ice}}(q)$ (for the geometric parameters, see below). The proper normalization in this model requires $\Sigma_{\alpha} f^{\alpha}=4$ (i.e., each molecule has four nearest neighbors). For water we adopt the same normalization, albeit the H bonds can be largely deformed (i.e., shortened/elongated and/or bent). Thus the CP difference of water and ice Ih, $\Delta J(q)=J^{\text{water}}(q)-J^{\text{ice}}(q)$, is given by

$$\Delta J(q) \approx \sum_{\alpha} f^{\alpha} \frac{1}{2}[J_{\text{dim}}^{\alpha}(q) - J_{\text{dim}}^{\text{ice}}(q)], \tag{3}$$

the sum being over the H-bond geometries in water. The H-bond length $f_{\text{HO}}(R_{\text{HO}})$ and angle $f_{\beta}(\beta)$ DFs used for $\{f^{\alpha}\}$ are based on NMR measurements and DFT simulations of the proton magnetic shielding tensor [19,29], where structures from CPMD simulations were utilized [30].

We calculate the momentum density $N(\mathbf{p})$ within Kohn-Sham (KS) DFT [31,32], utilizing the STOBE-DEMON code [33] and gradient-corrected exchange-correlation functionals [34,35]. For oxygen we use a triple-ζ valence plus polarization-type basis set and for hydrogen a primitive set [36] augmented by one p function in a $[3s,1p]$ contraction. The use of KS orbitals as the single-particle wave functions in CS simulations on water has been shown to be in good agreement with similar calculations using Hartree-Fock (HF) and Møller–Plesset perturbation theory methods [15,25]. In particular, upon studying CP differences of water dimers as in the present work, HF and DFT results very closely coincide [37].

The experimental work was carried out at the SPring-8 (Hyogo, Japan) and the ESRF (Grenoble, France) synchrotron radiation facilities. The data shown in Fig. 1 was collected at the beamline BL08W (SPring-8) [38] utilizing 115 keV primary radiation with a beam size of 2(H) $\times$2(V) mm^2. The scattered radiation was measured using a ten-element Ge solid-state detector at 178° scattering angle, leading to a resolution of 0.63 atomic units (a.u.) of momentum. The extremely small experimental inaccuracy of the CP difference was 0.016% of $J(0)$ at the Compton peak ($q=0$ a.u.) within a 0.08 a.u. momentum bin. As the CP differences are small, the consistency of the data was monitored carefully throughout the experiments. The data was corrected for background, absorption, and multiple scattering before converting to momentum scale using the relativistic cross-section correction [39]. Water (25 °C) and polycrystalline ice Ih (−50 °C) were confined in a 1.5 mm thick cell with kapton windows. The quality of the ice Ih samples was verified by x-ray diffraction, utilizing different freezing procedures.

The experimental data is presented in Fig. 1 as a difference curve between the CPs acquired from water and ice Ih. Based on previous studies [15,16,18] we can predominantly attribute the CP difference to longer H bonds in water (on average) compared to ice Ih. A noteworthy detail, however, is the feature (peak) at $q\sim 1.9$ a.u., which is not present in the experimental temperature-dependent water data [18]. Below we show that this feature is connected to the different intramolecular geometries between water and ice Ih [40,41].

For the ice Ih CP computations, we use the fixed experimental bond lengths of $r_{\text{OH}}^{\text{ice}}=0.98$ Å [41] and $R_{\text{OO}}^{\text{ice}}=2.763$ Å [42] with linear H bonds [43]. For water, we use three different models for the intra- and intermolecular geometries:

(i) *Rigid uncorrelated:* A rigid intramolecular geometry, with $r_{\text{OH}}=0.97$ Å for all water molecules (i.e., the average experimental value from Ref. [40]), is used. The H-bond geometry is described using the mutually uncorrelated [29] bond length and angle DFs of Ref. [19] [i.e., $f^{\alpha}=f_{\text{HO}}(R_{\text{HO}})f_{\beta}(\beta)$]. This corresponds to the "Uncorrelated" model of Ref. [18].

(ii) *Semirigid uncorrelated:* As above, except an intra-intermolecular correlation [$r_{\text{OH}}=r_{\text{OH}}(R_{\text{HO}},\beta)$] is taken into account.

(iii) *Semirigid correlated:* As the "Semirigid uncorrelated" model, including also a correlation between the length and possible angular distortions of the H bond.

In order to computationally reproduce the amplitude of the experimental CP difference of Fig. 1, the H-bond length DF $f_{\text{HO}}(R_{\text{HO}})$ of Ref. [19] was set to peak at $R_{\text{HO}}^{\text{peak}}=1.89$ Å. The effect in the CP difference of including intramolecular oscillations (O-H stretch and H-O-H bend vibrations) and proton zero-point motion, as compared to using their average

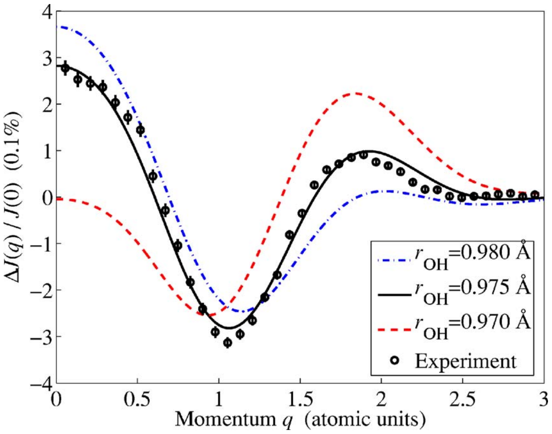

FIG. 2. (Color online) The impact of intramolecular O-H bond length r_{OH} on the individual dimer CP difference [right-hand side of Eq. (3)]. The geometrical parameters of the model dimer $J_{\mathrm{dim}}^{\alpha}(q)$ (corresponding to water) are $R_{\mathrm{HO}}=1.90$ Å and $\beta=0$ °C, while the reference dimer $J_{\mathrm{dim}}^{\mathrm{ice}}(q)$ (corresponding to ice Ih) is defined by $r_{\mathrm{OH}}^{\mathrm{ice}}=0.98$ Å, $R_{\mathrm{HO}}^{\mathrm{ice}}=1.783$ Å and $\beta^{\mathrm{ice}}=0$ °C. The absolute area of the CP difference is normalized to the experimental data.

values, is negligible within the present experimental accuracy and has been neglected in this work. Moreover, for water the intermolecular low-frequency vibrational modes (librations, vibrations in the R_{HO} distances and β angles) are implicitly included in the models for the H-bond geometries [19]. Since a variance in the internal H-O-H angle of the water molecule affects the CP very modestly [16], the ideal tetrahedral H-O-H angle is used for both water and ice Ih [44].

From Fig. 1 we observe that the "Rigid uncorrelated" model is in apparent disagreement with our experimental CS data. We note that agreement is not improved by imposing, within the rigid-molecule model, an intermolecular correlation between the H-bond length and angle [45] (not shown in Fig. 1). Rather, agreement in spectral shape can be obtained only by adjusting the intramolecular O-H bond length with respect to the geometry (i.e., both length and angle) of the corresponding H bond. We determine this correlation, as a first approximation, by least-squares fitting of the individual dimer CP differences [right-hand side of Eq. (3)] to the experimental CP difference of Fig. 1. In practice, the intramolecular bond length r_{OH} of the αth model dimer involved in the H bond is the adjustable parameter, and the computational CP difference $[J_{\mathrm{dim}}^{\alpha}(q)-J_{\mathrm{dim}}^{\mathrm{ice}}(q)]$ is compared to the experimental one in terms of the spectral shape (see the example in Fig. 2). The "Semirigid uncorrelated" model as shown in Fig. 1 is finally obtained by performing the sum in Eq. (3) using just such an adjusted set of dimer CPs.

The resulting systematic $(r_{\mathrm{OH}},R_{\mathrm{HO}})$ correlation is shown in Fig. 3 for different β angles. It should be noted that the r_{OH} length in our model for water is obtained only relative to the chosen reference O-H bond length of ice Ih ($r_{\mathrm{OH}}^{\mathrm{ice}}=0.98$ Å); however, choosing another reference value would simply shift all the r_{OH} values by the corresponding amount, the nonlinear effects being an order of magnitude smaller. The O-H bond length converges to $r_{\mathrm{OH}}\sim0.967$ Å for large R_{HO} values (cf. $r_{\mathrm{OH}}=0.958$ Å for isolated water monomers [46]). Also shown is an averaged correlation derived from different crystal hydrates [9] (experimental data extending only up to $R_{\mathrm{HO}}\sim2.0$ Å). Our $(r_{\mathrm{OH}},R_{\mathrm{HO}})$ correlation for water is in reasonable agreement with the hydrate-based one; the deviation for $R_{\mathrm{HO}}\gtrsim1.75$ Å (coincidentally the region constituting the majority of H bonds in water [19]) is contained within the large scatter of the crystal-hydrate data [9]. We further note that the influence of the H-bond angle on the $(r_{\mathrm{OH}},R_{\mathrm{HO}})$ correlation could not be observed for the crystal hydrates due to the aforementioned scatter [9].

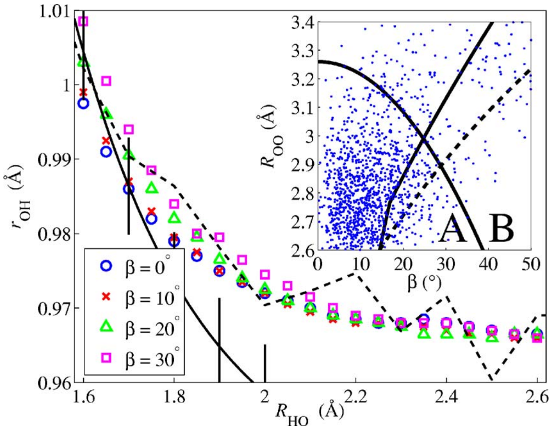

FIG. 3. (Color online) Correlation between the intramolecular bond length r_{OH} and the corresponding H-bond length R_{HO} in water for various H-bond angles β. The solid line is an averaged correlation derived from different crystal hydrates [9] (the errorbars denoting the root-mean-square deviation), while the dashed line is derived from *ab initio* CPMD simulations [20,21]. Inset: The excluded region (solid line) for nearest-neighbor H-bond geometries in water. The dashed line corresponds to a previously found excluded region [18], while the dots are H-bond geometries derived from *ab initio* CPMD simulations [20,21]. The zones A and B, defined by Wernet *et al.* for intact and broken H bonds [5], are also shown.

Also presented in Fig. 3 is the $(r_{\mathrm{OH}},R_{\mathrm{HO}})$ correlation averaged over the H-bond angles β (and shifted vertically by −0.037 Å) from *ab initio* CPMD simulations [20,21] for deuterated water (fictitious electron mass parameter 600 a.u., microcanonical *NVE* ensemble with temperature fluctuating around 27 °C, ∼1500 H-bonds analyzed). Despite the lack of nuclear quantum effects [47] in the CPMD simulation, the agreement with the CS result is striking, thus bringing further support for our model calculations.

The Semirigid uncorrelated model is in reasonable agreement with the CS data. However, discrepancies between experiment and the model are observed in the relative amplitudes of the extrema. These can partly be attributed to the presence of short and largely bent H bonds still included in the model. The angular distortions of the H bonds are known to influence the CP systematically: the induced change in the CP for a specific angular distortion is larger, the shorter the H bond [16]. Thus we introduce a further correlation between the H-bond length and its possible angular distortions. In practice, we impose a maximum bend angle $\beta_C(R_{\mathrm{HO}})$ on the Semirigid uncorrelated model by least-squares fitting to the experimental data, i.e., for each R_{HO}, H-bond geometries with angle β larger than $\beta_C(R_{\mathrm{HO}})$ are excluded. This kind of a constraint resembles the experimental finding in crystal hydrates [11]. In determining $\beta_C(R_{\mathrm{HO}})$ we require that, for each H-bond length R_{HO}, bending to $\beta_C(R_{\mathrm{HO}})$ induces changes in the CP of equal strength compared to the corresponding linear H bond. This gives the "Semirigid correlated" model in Fig. 1. A similar correlation was also obtained from our previous study of water at different temperatures [18]. The best fit thus obtained for $\beta_C(R_{\mathrm{HO}})$ determines an excluded region (solid line in the inset of Fig. 3) for nearest-neighbor H-bond geometries in water. This restriction, however, is not unique [18]; it rather provides a qualitative trend for the angular distortions. A comparison with CPMD simulations [20,21] again shows a good agreement.

The present CS data thus impose strong restrictions on both the intramolecular O-H bond lengths and the intermolecular H-bond geometries in water, providing a direct test for different geometric DFs beyond the NMR-based ones used here. Using the Semirigid correlated model we can furthermore relate our findings to the discussion initiated by Wernet *et al.* [5] concerning the average number of intact H bonds per molecule (n_{HB}) in water. n_{HB} can be determined by CS only indirectly by studying the DFs used in our models for water. Adopting the geometric H-bond criterion of Ref. [5] (see inset of Fig. 3), we find $n_{\mathrm{HB}} \sim 3.8$, in a reasonable agreement with the direct calculation from CPMD snapshot structures ($n_{\mathrm{HB}} \sim 3.6$) [5]. However, the impact of the H-bond angles should be noted. In principle the lowest limit obtained by varying the angular distortions, while keeping the NMR $f_{\mathrm{HO}}(R_{\mathrm{HO}})$ at room temperature unmodified, is $n_{\mathrm{HB}} \sim 3.1$. We further note that CPMD simulations might predict too sharp radial DFs (see, e.g., Refs. [30,48]); one approach to correct for this has been elevated temperatures (30–75 °C) in the simulations [3,48], thus leading to broader DFs. We model the sensitivity to this kind of possible broadening, as a first approximation, by using the NMR DFs at higher temperatures. For example, adopting the NMR DFs at $T=60$ °C [49] produces a good agreement with experiment yielding $n_{\mathrm{HB}} \sim 3.4$ (the lowest limit by varying the angles as above being ~ 2.7). We note that the obtained values for n_{HB} are larger than reported in Ref. [5]. However, CS does not contain information on whether the bonding is symmetric or asymmetric [18].

Finally, we discuss how the results are affected by certain underlying assumptions in our models. By adopting the NMR DFs for water and the experimental bond lengths in ice [41,42], the only adjustable parameter in our models for water (in addition to the introduced correlations) is the peak position $R_{\mathrm{HO}}^{\mathrm{peak}}$ of the $f_{\mathrm{HO}}(R_{\mathrm{HO}})$ DF. There is a small disparity in the value of $R_{\mathrm{HO}}^{\mathrm{peak}}$ compared to $R_{\mathrm{HO}}^{\mathrm{peak}}=1.85$ Å in Refs. [1,19], which could be either related to our approximations or to the NMR DFs. However, the value of $R_{\mathrm{HO}}^{\mathrm{peak}}$ and the NMR DFs do not affect the found correlation between the O-H bond length and the H-bond geometry and their effect on the (R_{HO},β) correlation is minor. The second assumption to be noted is the fourfold average coordination in water. This is a parameter which allows us to utilize effectively the model of Eq. (3) for the CP difference of water and ice I*h*. It has also been found to give a good agreement with the temperature-dependent water data [18]. Third, structural disorder [50] and thermal motion [50–52] in ice have been neglected, since their effect is minor, according to the analysis of polycrystalline ice I*h* CPs acquired at different temperatures [53].

In conclusion, we have applied Compton scattering combined with DFT analysis to compare the H bonding in water and polycrystalline ice I*h*. Utilizing model computations, we have shown that the technique provides unique and complementary information on the local H-bond geometries in water, confirming our recent theoretical predictions [16]. In particular, agreement between experiment and theory is found only by introducing a local intra-intermolecular geometric correlation, relating the intramolecular O-H bond length to the corresponding H-bond geometry. Second, a qualitative restriction on the H-bond angular distortions with respect to the H-bond length has been demonstrated. Third, an average number of intact H bonds per water molecule larger than reported in Ref. [5] is implied. These results are in reasonable agreement with the H-bond geometries present in CPMD simulations.

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[44] The slight disparities between internal H-O-H angles used and experimental averages do not affect our results.
[45] Using, e.g., the two "Correlated" models of Ref. [18].
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