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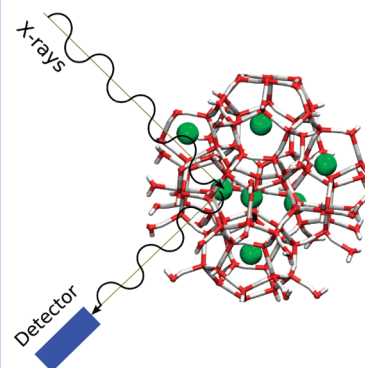
# Anomalous Energetics in Tetrahydrofuran Clathrate Hydrate Revealed by X-ray Compton Scattering

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**ABSTRACT** Changes in the ground-state electron momentum density of tetrahydrofuran clathrate hydrate are studied in a temperature range between 93 and 275 K by means of X-ray Compton scattering. At temperatures above 253 K, large rather unexpected differences from the Compton profiles of ice are observed. Configurational enthalpies are extracted and exhibit a rapid rise above 253 K, whereas a constant configurational heat capacity of  $0.23 \pm 0.07 \text{ J g}^{-1} \text{ K}^{-1}$  is found below 253 K. Density functional theory calculations suggest that this anomalous behavior originates from the structural change of the hydrate, however, no indication was found for the formation of hydrogen bonds between tetrahydrofuran and water molecules.

**SECTION** Statistical Mechanics, Thermodynamics, Medium Effects



Clathrate hydrates are inclusion compounds where guest molecules are enclosed in a hydrogen-bonded water cage network.<sup>1,2</sup> Tetrahydrofuran (THF) hydrate, in particular, has become a promising material for CO<sub>2</sub> recovery from flue gas<sup>3</sup> as well as for hydrogen storage,<sup>4,5</sup> although the storage capacity has recently been discussed controversially.<sup>6</sup> Below  $T = 277.6 \text{ K}$  and at ambient pressure, THF and water form hydrate structure sII consisting of two cage types.<sup>7</sup> Here only the large cages are occupied by THF molecules resulting in a stoichiometry of 17:1 (water/THF). Because THF hydrate can easily be synthesized, it has been part of many studies, where it was used as a prototype for all hydrates to investigate, for example, the hydrates' mechanical and thermal properties.<sup>2</sup> However, in contrast with other hydrates, calorimetric measurements of THF hydrate exhibit anomalies of the heat capacity for  $T \geq 260 \text{ K}$ , which have not been fully understood so far.<sup>8–10</sup> Besides, hydrates with oxygen-containing guests such as THF often show anomalies near the melting point, including, for example, thermal expansivity<sup>11,12</sup> and shear wave velocity.<sup>13</sup> Furthermore, recent molecular dynamics (MD) simulations proposed a strong guest–host interaction in hydrates with polar guests, resulting in the formation of hydrogen bonds between the two species;<sup>14–16</sup> in particular, this was observed in THF hydrate at temperatures near 250 K.<sup>17</sup> These processes may disturb the cage network and lead to a structural rearrangement.

Such a structural change was discussed in a recent publication where X-ray Raman scattering results suggested an increasing order in the local structure of THF hydrate at lower temperatures.<sup>18</sup> The Compton scattering results presented in this work strongly support these findings and will provide new

detailed information on the changes in the hydrate's local atomic scale structure and coordination.

To achieve this, we utilize X-ray Compton scattering spectroscopy, which is a powerful probe of local atomic scale structure.<sup>19</sup> Previous works have demonstrated how the difference Compton spectra (profiles) can be interpreted directly in terms of the intra- and intermolecular changes in the material, such as bond stretching, bending, and formation, and have shown that the Compton profile is highly sensitive to such structural effects.<sup>20,21</sup> These systematic studies enable us to connect the changes in the experimental spectra to the structural changes in the material. Density functional calculations are finally used to analyze the spectra in a quantitative manner. Any structural rearrangement in the material inevitably leads to different thermodynamic properties; therefore, any changes in the temperature-dependent difference Compton profiles also suggest changes in thermodynamic properties (and vice versa). This connection was recently demonstrated for hexagonal ice, where experimental Compton profiles were used to extract the configurational enthalpies.<sup>22</sup> Therefore, Compton spectroscopy reveals the obvious connection of thermodynamic and structural properties of the materials in a straightforward way. This approach is also in contrast with the calorimetry measurements of the thermal properties of materials where the configurational and vibrational contributions to the heat capacity cannot be easily separated.

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In this Letter, we report a Compton scattering study of THF hydrate for various temperatures between 93 and 275 K. Changes of the hydrate's local structure manifest in modifications of the Compton profiles (CPs). The shapes and amplitudes of the CP differences are discussed with respect to influences of thermal expansivity on the bond geometry and structural rearrangements due to the guest–host interaction of THF and water molecules. For temperatures below 253 K, the changes in the CP are weak, leading to a configurational enthalpy that changes linearly with respect to temperature. Therefore, only weak structural changes are suggested, that is, originated from the thermal expansion. In contrast, above 253 K, the CPs exhibit large differences. The configurational enthalpy rapidly increases, implying strong structural rearrangements of the THF hydrate's structure.

Compton scattering is inelastic X-ray scattering at high energy and momentum transfers.<sup>19</sup> It probes the ground-state electron momentum density  $\rho(\mathbf{p})$  and is thus highly sensitive to changes in the ground-state wave functions. During the past years, it has been demonstrated that Compton scattering provides unique information on, for example, the local structure and bonding in water and ice,<sup>20–25</sup> hydrogen bonding in ammonium fluoride<sup>26</sup> and alcohols,<sup>27</sup> and guest–host interactions studied in methane hydrate<sup>28</sup> and the isostructural silicon clathrates.<sup>29</sup> The measured quantity in Compton scattering experiments is the double differential scattering cross section, which is within the impulse approximation<sup>30</sup> directly proportional to the isotropic CP

$$J(p_q) = \frac{1}{2} \int d\Omega \int_{|p_q|}^{\infty} p \rho(\mathbf{p}) dp \quad (1)$$

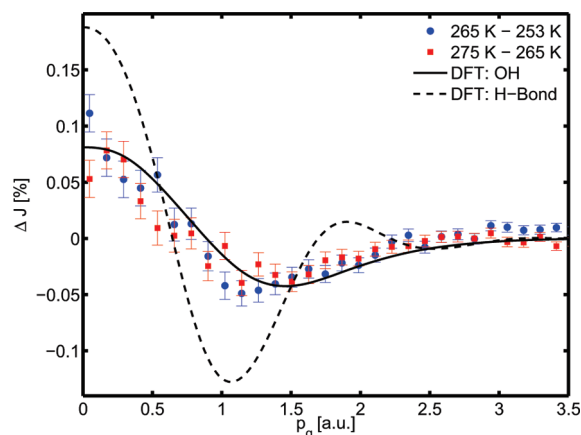
where  $p_q$  denotes a scalar electron momentum variable.

Because the isotropic CP  $J(p_q)$  yields information on the radial electron momentum distribution, expectation values of the momentum operator can be calculated.<sup>31</sup> In particular, the expectation value of the electron kinetic energy  $\langle T_e \rangle$  reads

$$\langle T_e \rangle = \frac{3}{m} \int_0^{\infty} p_q^2 J(p_q) dp_q \quad (2)$$

The total energy of the system is given by the virial theorem as  $E = -\langle T_{\text{tot}} \rangle$ , with the expectation value of the total kinetic energy  $\langle T_{\text{tot}} \rangle = \langle T_e \rangle + \langle T_n \rangle$  (within the Born–Oppenheimer approximation). The term  $\langle T_n \rangle$  denotes the kinetic energy due to the vibrational, translational, and rotational motion of the nuclei. In the case of Compton scattering, the contributions from the nuclei are minor,<sup>22</sup> and because the experiments were performed under isobaric conditions, the adequate measure of energy is the enthalpy,  $H$ . Therefore, the configurational enthalpy can be connected to the expectation value of the kinetic energy of the electrons via  $H^{\text{config}} = -\langle T_e \rangle$ .<sup>22</sup> By differentiation of  $H^{\text{config}}$  with respect to the temperature,  $T$ , the configurational heat capacity,  $c_p^{\text{config}} = (dH^{\text{config}})/(dT)_p$  can be obtained. Then, the total heat capacity is the sum of the configurational and vibrational contribution  $c_p = c_p^{\text{config}} + c_p^{\text{vib}}$ .

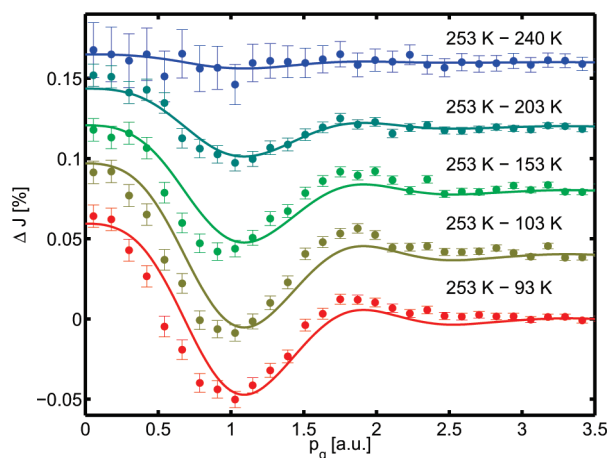
The experimental CP differences for  $T \geq 253$  K are shown in Figure 1. Most surprisingly, the shape of the differences deviates significantly from differences obtained for water and ice,<sup>20,22,24</sup> where typical oscillations were demonstrated to be



**Figure 1.** CP difference of THF hydrate at high temperatures. The solid line represents the difference of computed Compton spectra assuming a change of 0.5% of the OH bond length of the water molecules for  $\Delta T \approx 10$  K, whereas the dashed line represents the difference of computed CP of a hydrate cage with and without guest–host bonding. Because of different stoichiometries (water/THF) used for calculation of the dashed and solid lines, the amplitudes of both differences are not fully comparable.

a fingerprint of the hydrogen bonds. Furthermore, the amplitudes at  $p_q = 0$  atomic units (a.u.) of  $\sim 0.08\%$  for a difference with  $\Delta T \approx 10$  K are much larger than those measured in water or ice. By comparison with previous systematic studies about the intra- and intermolecular effects of  $\text{H}_2\text{O}$  molecules on the difference profiles, it is evident that the formation of a broad minimum at  $p_q \approx 1.4$  a.u. can be interpreted only as a change of the water's OH bond length.<sup>20</sup> Our DFT calculations suggest an unexpected contraction of the OH bond length by 0.5% of the water molecules at the lower temperature; see Figure 1. Up to now, such a change of bond length has not been observed by diffraction experiments,<sup>32</sup> but the high-temperature region has not been studied intensively so far. The observed change of the OH bond length is very large and could possibly originate in strong distortion of water cages. However, because Compton scattering is very sensitive to changes in the short-range structure, the change of the OH bond lengths dominates the difference spectra, suppressing influences of longer range distortions. The calculations demonstrate that the formation of hydrogen bonds between THF and water molecules is not expected because the shape of the difference profile due to the formation of the H-bond is very different from the experimentally observed spectrum; see Figure 1. The shape of the calculated difference indicates the break-up of one H-bond in the water network.<sup>20</sup> This finding agrees with recent single-crystal diffraction experiments where also no indication for guest–host hydrogen bonding in THF hydrate was found.<sup>16</sup> Nevertheless, the disturbance of the hydrate structure expressed by a change of the OH bond length is in line with our previous findings of an increased order at lower temperatures.<sup>18</sup>

The measurements for  $T \leq 253$  K show that the structural rearrangement of the hydrate stops at  $\sim 253$  K and that the dominating effect below this temperature is thermal broadening. The observed CP differences in this region change significantly slower than those in the higher temperature region;

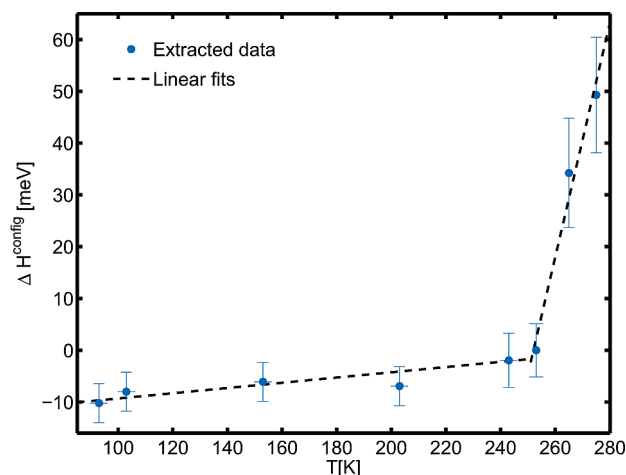


**Figure 2.** CP differences of THF hydrate at low temperatures. The measurement at 253 K is used as reference; the solid lines represent DFT calculations assuming different lattice constants. Curves are shifted by 0.04 % each for clarity.

also, the shape is very different; see Figure 2. The experimental data are compared with calculations where the thermal broadening was simulated by varying the OO distances of the water molecules according to the temperature-dependent lattice constant. A good agreement between experimental and computed CP differences is achieved, which strongly supports this conclusion. Therefore, a distortion of the hydrate cage above 170 K, as found by Jones et al.<sup>32</sup> by neutron diffraction measurements on deuterated THF hydrate, cannot be observed. Furthermore, the result is in line with results for ice at a wide temperature range.<sup>22</sup>

To obtain detailed information on the proposed structural change, configurational enthalpies of THF hydrate were calculated using eq 2. Because for  $p_q > 3.5$  a.u. no deviation from 0 occurs in the CP differences, the integration range was limited to  $0 \text{ a.u.} \leq p_q \leq 3.5 \text{ a.u.}$  To avoid contributions of systematic errors, for example, scattering from windows or air, only differences  $\Delta H^{\text{config}}$  are discussed in the following. The observed values of  $\Delta H^{\text{config}}$  are shown in Figure 3. For  $93 \text{ K} \leq T \leq 253 \text{ K}$ , the configurational enthalpy increases linearly with temperature, suggesting a constant configurational heat capacity of  $c_p^{\text{config,hyd.}} = (0.23 \pm 0.07) \text{ J g}^{-1} \text{ K}^{-1}$ . This value is approximately half of the value observed for ice  $c_p^{\text{config,ice}} = (0.44 \pm 0.11) \text{ J g}^{-1} \text{ K}^{-1}$ ,<sup>22</sup> although the total  $c_p$  of THF hydrate deviates only slightly from ice.<sup>10</sup> In contrast, for  $T \geq 253 \text{ K}$ , the configurational enthalpy increases rapidly. Although a linear relation of  $\Delta H^{\text{config}}$  and temperature cannot be postulated without doubt, a linear fit to the data results in a large configurational heat capacity of  $c_p^{\text{config}} = (4 \pm 2) \text{ J g}^{-1} \text{ K}^{-1}$ . However, as shown by Waite et al.,<sup>9</sup> who measured a similar anomaly in this temperature region, the total heat capacity is not constant for these temperatures. In their work, for  $T \approx 276 \text{ K}$ , a value of  $c_p = 6.2 \text{ J g}^{-1} \text{ K}^{-1}$  for the total heat capacity was found. This is in line with the extracted values of  $c_p^{\text{config}}$  for  $T \geq 253 \text{ K}$ , leading to the result that primarily a change of the configurational enthalpy is suggested at these higher temperatures.

Because configurational enthalpies can generally be estimated by MD simulations, a comparison of the measured



**Figure 3.** Differences of configurational enthalpies  $\Delta H^{\text{config}}$  of THF hydrate at various temperatures. The reference is  $T = 253 \text{ K}$  measured in both runs. The slopes of the linear fits provide the configurational heat capacities.

configurational heat capacities with MD simulations allows the evaluation of the accuracy of the simulations. For instance, in a previous MD study of THF hydrate, a value of  $c_p^{\text{config}} = 1.56 \text{ J g}^{-1} \text{ K}^{-1}$  was obtained for temperatures between 100 and 273 K.<sup>35</sup> However, this is approximately the value of the total heat capacity of THF hydrate and thus well above the measured configurational heat capacity.

In conclusion, we report a Compton scattering study of THF hydrate at temperatures between 93 and 275 K. For temperatures below 253 K, the CPs vary only weakly, which is in agreement with previous experiments on ice and can be interpreted in terms of thermal broadening. In contrast, above 253 K, large changes were observed. These are related to structural rearrangements of the hydrate at high temperatures, which result in a scaling of the water's OH bond length, evidenced by DFT calculations. The structural change is connected to a significant change in the experimental configurational heat capacity, which is constant below 253 K but rises by a factor of 20 above 253 K.

## COMPUTATIONAL AND EXPERIMENTAL DETAILS

We carried out density functional theory calculations using StoBe-deMon code,<sup>34</sup> employing triple- $\zeta$  plus valence-polarization level basis sets and generalized gradient approximation<sup>35,36</sup> for the exchange-correlation potential. For the analysis, the CP of the THF hydrate can be decomposed into various contributions as

$$J_{\text{hydr}}(p_q) = J_{\text{thf}}(p_q) + 17 \times J_{\text{cages}}(p_q) + J_{\text{thf-cage-int}}(p_q) + J_{\text{cage-cage-int}}(p_q) \quad (3)$$

where  $J_{\text{thf}}(p_q)$  and  $J_{\text{cages}}(p_q)$  are the contributions of an isolated THF molecule and the empty water cages, normalized to the number of electrons in a single THF molecule and in a single  $\text{H}_2\text{O}$  molecule, respectively.  $J_{\text{thf-cage-int}}(p_q)$  is the influence of guest–host interaction (per one THF molecule); correspondingly,  $J_{\text{cage-cage-int}}(p_q)$  is the contribution of the



cage–cage-interaction (per 17 water molecules). To calculate each of these profiles, we used an experimentally determined<sup>32</sup> structure for the cages, and for THF, we used the same structure as that used in ref 18. Compton profiles were calculated for whole water cages including 28 and 20 water molecules for the large and small cage, respectively. The interaction term  $J_{\text{thf-cage-int}}(p_q)$  was obtained by comparing the profile of a cage with THF inside with the profile of an empty cage plus isolated THF. Similarly,  $J_{\text{cage-cage-int}}(p_q)$  was calculated from the profiles of two isolated cages and two adjoining cages. Different orientations of THF inside the cages yielded only very weak differences, which can be neglected. For the calculations of the effect of the formation of hydrogen bonds between THF and water molecules, the structures presented in ref 17 were used.

CPs of THF hydrate at various temperatures ranging from 93 to 275 K were measured at beamline ID15B of the European Synchrotron Radiation Facility (ESRF).<sup>37</sup> The energy of the incident X-rays was 86.95 keV. The scattered intensity was measured by a 13-element Ge solid-state detector at a scattering angle of 165° with a momentum resolution of  $\Delta p_q \approx 0.6$  a.u. at the Compton peak ( $p_q = 0$  au). To guarantee the required extreme detection stability, we realized a constant incident photon flux at the sample by using a special absorber feedback system. The statistical accuracy was better than 0.03% units at  $p_q = 0$  a.u. for the measurements at temperatures 253–275 K (run 1) and better than 0.01% units for the measurement at temperatures 93–253 K (run 2), both within a 0.03 a.u. momentum bin. In run 1, the sample cell described in ref 38 was used to achieve a high temperature stability. The sample thickness was 5.4 mm. A stoichiometric 17:1 liquid mixture of water/THF was added to the cell and cooled to the supercooled temperature of 275 K. Then, hydrate formation was initiated by stirring of the mixture by a rotating magnet placed in the cell, guaranteeing hydrate formation without occurrence of ice. However, because temperatures below 250 K cannot be reached with this setup, an adapted cell for a cryostat was used for temperatures below 253 K. This cell has the same thickness as the other one, and the preparation of THF hydrate was performed in the same way. The formation of hydrate was verified by X-ray diffraction. To check the data for consistency, spectra were saved every 10 min and checked for deviations larger than the statistical accuracy. The raw data were corrected for absorption and the dead times of the detector<sup>39</sup> before converting to momentum scale by using the relativistic cross section correction.<sup>40</sup> Afterward, we carefully performed a correction for multiple scattering by taking into account the geometry of the scattering region in the sample. This was essential because of the wide temperature range used in this work. Finally, the positive and negative momentum sides of the CPs were averaged.

## AUTHOR INFORMATION

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