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Existence of clathrate-like structures in supercooled water: X-ray diffraction evidence

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ABSTRACT

X-ray diffraction study of supercooled water has been performed using an imaging-plate X-ray detector down to −15 °C. The peak at ~10.8 Å, which grows with decreasing temperature, in the radial distribution function $\{D(r) - 4\pi r^2\rho_0\}$ indicates the existence of clathrate-like structures in supercooled water. It is suggested that anomalous properties of water, which become more pronounced at low temperatures, are closely linked to the development of clathrate-like structures in water at low temperatures.

1. Introduction

There have been a large number of X-ray and neutron diffraction studies of liquid water at various experimental conditions [1–7]. An accurate characterization of the structure of liquid water is of vital importance for clarifying thermodynamic properties and other properties of liquid water. In particular, anomalous properties of liquid water at low temperatures are considered to be closely linked to the structural changes associated with decreasing temperature [8–10].

In the early stage of the structural studies of liquid water, the study of Bernal and Fowler [11] had received most serious consideration. They suggested that liquid water retains in part a hydrogen-bonded structure similar to that of ice I_h. This picture was supported by the X-ray diffraction study by Narten and Levy [1,2] and has been regarded as the most adequate one in most X-ray and neutron diffraction studies although there have been several different views inferred from other spectroscopic and/or structural analysis [12–14].

In this report, we present X-ray diffraction evidence for the existence of clathrate-like structures in supercooled water, different from the widely accepted structural picture of liquid water at ordinary and supercooled temperature regions [1–7]. We believe that the development of clathrate-like structures in supercooled water can resolve most of the unresolved mysteries associated with so-called 'anomalous properties' of water at low temperatures [8–10].

2. Experimental

X-ray diffraction measurements have been carried out for purified water contained in a quartz capillary of 2-mm diameter at temperatures from −15 to 25 °C by using a Rigaku diffractometer with an X-ray generator of a rotating anode and an imaging-plate X-ray detector (IP) of 200 mm × 400 mm which is cylindrically putted on a circumference at a distance of 150 mm (camera length) from the center of the capillary. Water in the capillary was exposed to the X-ray (MoKα) beam of 1 mm-diameter for 30 min at a given temperature controlled by blowing thermostated nitrogen gas. Diffraction data after usual corrections were collected for $2\theta = 1.6$–$130°$ ($s = 4\pi\sin\theta/\lambda = 0.25$–$16.0$ Å^{-1}) with a 0.2° step and treated by the KURVLR program to obtain the radial distribution function, $D(r) - 4\pi r^2\rho_0$ (abbreviated as RDF), for the stoichiometric unit volume containing one water molecule as described in previous papers [15–17]. The pixel size of IP is 0.1 mm × 0.1 mm corresponding to the resolution of 0.02° for θ. It has been confirmed that the S/N ratios in the scattering intensities and RDF are comparable to those obtained by the measurements of (2.5–3.0) × 10^5 counts for each 2θ with a scintillation counter on the conventional θ–θ X-ray diffractometer.

3. Results and discussion

First we show the RDFs within the distance (r) of 15 Å at four different temperatures (Fig. 1). To test the reliability of our experimental data, we also show the RDFs obtained by our reanalysis of the experimental data of Narten and Levy [2]. In the original reports [1,2], they reported their results in the form of $D(r)$ below 10 Å so that the peaks above 10 Å are not explicitly given. The most significant feature of the RDFs shown in Fig. 1 is that the structuring of the longer distance above 10 Å is becoming more and more distinct with decreasing temperature: the RDF at −15 °C reveals one clear peak at ~10.8 Å. It must be emphasized here that the

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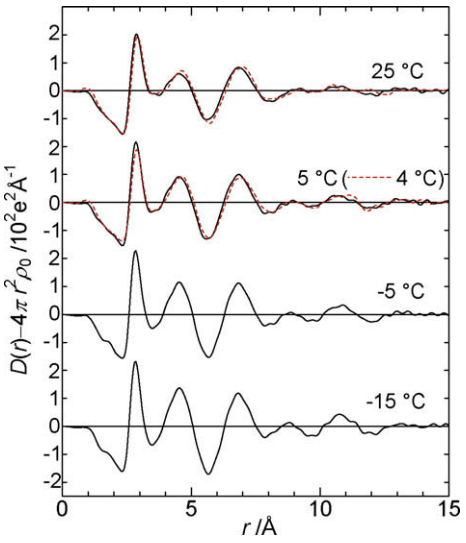

Fig. 1. Radial distribution functions (RDFs) of liquid water at several temperatures. Solid curves: RDFs obtained in this work, dotted curves: RDFs obtained by reanalyzing Narten-Levy's X-ray data at 4 °C and 25 °C [2].

RDFs below 10 Å agree quite well with the previously reported ones [7]. Therefore, we are confident that the peak at ~10.8 Å is real one and important for clarifying the structure of supercooled water. Even in the RDF at 4 °C of Narten and Levy shown in Fig. 1, we can observe the peak at ~11.1 Å though it is still very weak. The rapid growth of the peak with decreasing temperature implies its importance for clarifying the structure of supercooled water.

We must point out that the similar RDF for liquid water at 25 °C is already reported by Takamuku et al. [18], in which they studied the structural changes of the water-1,4-dioxane system with solution composition. They also used an imaging-plate X-ray detector, which is considered to give sensitive and reliable data. We can notice a clear peak above the noise level at around 10.6 Å in their RDF for pure liquid water at 25 °C (Fig. 2 in Ref. [18]) although it is very weak as compared with other peaks below 8 Å.

Currently the most widely accepted structural model for liquid water at atmospheric pressure and at ordinary temperature is the ice-I-like structural model initially proposed by Danford and Levy [19] and supported by many others [3–5]. This picture is essentially supported by the recent excellent review by Head-Gordon and Hura [7]. They examined the X-ray and neutron diffraction data published

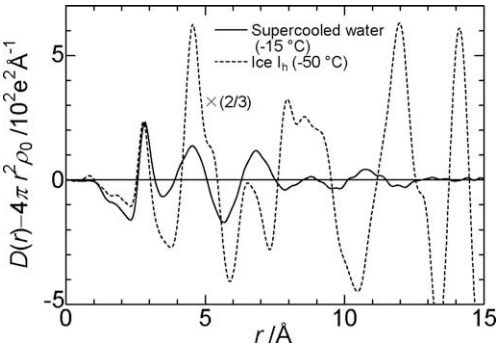

Fig. 2. Comparison of the RDF of supercooled water at −15 °C (solid curve) with that of emulsified ice (I_h) at −50 °C shown with a reduced scale of 2/3 (dotted curve). The composition of the emulsion used for obtaining the RDF for ice I_h consists of water (66.7 wt.%), methylcyclohexane (29.8 wt.%), and Span65 surfactant (3.5 wt.%). The emulsion was made by stirring the mixture for more than 10 min with a small blender of the rotating rate of 8000 rpm.

in last thirty years in detail and reported that the overall agreement of the published data is satisfactory. However, the reliable distance (r) of those data is shorter than 10 Å and no mention has been made about the peak at ~10.8 Å. Bellissent-Funel et al. [20] made a neutron diffraction study on supercooled D_2O water down to −31.5 °C and obtained the neutron RDFs up to 15 Å, reporting that the neutron RDFs of supercooled D_2O water at −10.5 and −31.5 °C appear to approach to that of low-density amorphous D_2O ice, which has the ice-I-like structure, with decreasing temperature.

So far as the radial distribution functions below 10 Å are concerned, the ice-I-like structural model is compatible to all their main features although different explanations might be possible. Therefore, the first step should be directed to check whether or not the peak at ~10.8 Å is compatible with the RDF expected from the ice-I-like structure in liquid water. Thus we used the RDF for emulsified ice (ice I_h) as a model of liquid water structure having ice-I-like structure. Fig. 2 shows the comparison between the RDF of supercooled water at −15 °C and that of emulsified ice I_h at −50 °C. Evidently, the 10.8 Å peak is unobservable in the latter RDF curve. Furthermore, the RDF of the ice I_h has very strong peak at ~12 Å while the RDF of supercooled water at −15 °C shows a minimum at ~12 Å. In accord with this observation, we reconfirm the conclusion by Bellissent-Funel et al. [21] that the structure of hyperquenched glassy water has the ice-I-like structure since we can see a peak at ~12 Å in the RDF (Fig. 2 in Ref. [21]) for hyperquenched glassy water. Thus, it is evident that the ice-I-like structure is incompatible with the RDFs of supercooled water. However, there is some difficulty in regarding the neutron diffraction results on supercooled D_2O liquid at −10.5 and −31.5 °C by Bellissent-Funel et al. [20] as favorable evidence for the existence of clathrate-like structures in supercooled water. Although there is a weak peak at ~11 Å in the neutron RDF of liquid D_2O at −31.5 °C, its peak position is very close to that of amorphous D_2O ice. Therefore, it is very difficult to discern the structural differences between supercooled D_2O liquid at −31.5 °C and amorphous D_2O ice. Probably the contribution from deuterium atoms obscures the structural differences in the neutron RDFs between liquid and amorphous D_2O.

We are aware that an interesting comparative argument was already made for amorphous solid water by Boutron and Alben [22]. They compared two models, the compact CRN model (CRN: continuous random network) which is regarded as the best structural model for LDA (low density amorphous ice), and the cage CRN model which has the cage-like structures known to exist in the clathrate hydrates. They pointed out that both have very similar X-ray RDFs (four peaks at ~2.75, ~4.5, ~6.7, and ~8.6 Å) up to 10 Å, differing first in the fifth peak at ~10.6 Å present in the cage model but absent in the compact CRN model. These peak distances including 10.6 Å for the cage-like structures reported in Ref. [22] are very close to those of 2.83, 4.54, 6.82, ~8.8, and ~10.8 Å, respectively, found in the X-ray RDF for supercooled water at −15 °C in this work. The small differences in the peak distances are attributable to the difference between solid and liquid states. Therefore, it can be concluded that the appearance of the peak at ~10.8 Å is the clear evidence for the existence of the clathrate-like local structures in supercooled water. Another point obtained from their results, which will be used in the discussion of the last part of this Letter, is that amorphous solid ice, which corresponds to glassy water and low density amorphous ice, has the ice I-like structure. In fact, we can see a clear peak at ~12 Å in the X-ray RDF for the CRN structure (Fig. 2 in Ref. [22]).

Before going on to the next section, another important point obtained from RDFs in Fig. 1 is that the peak at ~10.8 Å is getting weaker with increasing temperature and that the RDF above 10 Å becomes featureless. Accordingly the distinction between the clathrate-like structure and the ice-I-like structure seems meaningless at the higher temperatures (>~40 °C) [23].

Pauling was the first to propose a clathrate-like structural model for the structure of liquid water [12] and his model has been taken up as the starting point in every clathrate-like structural model. He adopted a gas hydrate structure of type I where 46 water molecules exist in a cubic unit cell and construct eight cages of two dodecahedra and six tetrakaidecahedra per unit cell. Instead of a guest molecule, he put one water molecule in the center of each cage in his model (Fig. 3A). On the other hand, Narten and Levy [1] rejected the clathrate-like model by the reason that when the original Pauling model is adopted the density of liquid water becomes very low and the average number of the near-neighbor water molecules becomes 3.41 significantly smaller than the experimental one (approximately 4.4 at 25 °C), which is not compatible with the X-ray diffraction results. To remedy these defects they added the second water molecules in each cage, but it produces the short distances between water molecules (2.6 Å in the dodecahedron, and 2.7 Å in the tetrakaidecahedron), incompatible with the experimental X-ray results. However, we can avoid the short distance absurdity and increase the liquid density by arranging the second water molecule at each center of the hexagonal faces of tetrakaidecahedra instead of placing them in the insides of dodecahedra and tetrakaidecahedra (Fig. 3B). By this modification the number of water molecules in a unit cell becomes sixty and the liquid density gets larger but still 5% lighter than the observed one at −15 °C. The average number of the near-neighbor water molecules now becomes 4.67 within 3.10 Å, where the nearest distance between water molecules is regarded as 2.82 Å based on the analysis of $D(r)$ at −15 °C. The peak at ~10.8 Å corresponds to the center-center distance between the two adjacent dodecahedra and there are many O-O combinations, which give rise to the distance in the range of 10.5–11.1 Å, in the two nearest dodecahedra.

Although we used the modified Pauling model (Fig. 3B) as the basic clathrate-like structure in supercooled water to calculate

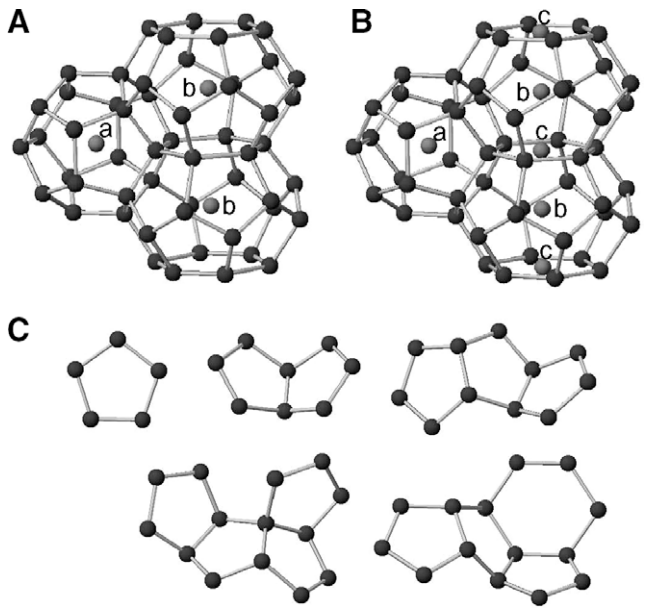

Fig. 3. (A) The structure of the Pauling's clathrate model for liquid water. It consists of the hydrogen-bonded network based on the gas-hydrate structure of type I (methane hydrate type) with extra water molecules by placing one molecule in the center of each cage of dodecahedra (denoted by a) and tetrakaidecahedra (denoted by b). (B) The structure of the modified Pauling model. The modification is made by placing one extra water molecule at each center of the hexagonal faces of tetrakaidecahedra (denoted by c). In this figure, the balls express the oxygen atoms, the hydrogen atoms are not expressed, and the lines show hydrogen bonds between oxygen atoms. (C) Examples of the fragmental configurations of the clathrate-like structures which are expected to exist in supercooled water.

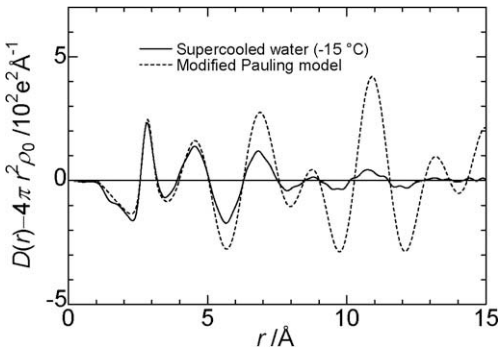

Fig. 4. Comparison of the RDF of supercooled water at −15 °C (solid curve) with the calculated RDF (dotted curve) based on the modified Pauling model. In the calculation of the RDF for the modified Pauling model, the root mean square deviations (σ's) are taken to be 0.11, 0.35, and 0.60 Å for the H_2O–H_2O pairs at $r = 2.82$, $r = 2.87$–3.10, and $r > 3.10$ Å, respectively, and the intramolecular and hydrogen-bonding pairs are also considered.

the RDF, it is plausible that such complete clathrate-like structure is not the only local structures in supercooled water. Rather, the various fragmental configurations of the clathrates (Fig. 3C) and the deformed ones are considered to be the main local structures in supercooled water, at least, at lower degree of supercooling. To strengthen our conclusion, we compare the observed RDF at −15 °C with the calculated RDF for the idealized clathrate-like structure (Fig. 4). The peak positions of the constructed RDF agree quite well with those of the observed one at −15 °C. Therefore, the modified Pauling model can reproduce the peak positions of the observed RDF of supercooled water very well although it is an idealized structure.

At this stage it would be appropriate to note that the RDF curve at 25 °C in this work shows satisfactory agreement with those of recent papers (Table 1) [24–26]. As described in the paper by Sorenson et al. [24], Narten and Levy's X-ray scattering studies [1,2], neutron scattering experiments by Soper and Phillips [25], and by Soper, Bruni, and Ricci [26] are generally cited as the reliable and definitive sources for the RDFs of liquid water at ambient conditions. From Table 1, we know that there are some scatters even in the peak positions of recent typical $g(r)$s ($g(r) = D(r)/4\pi r^2\rho_0$ or RDF $= 4\pi r^2\rho_0\{g(r) - 1\}$) [27] and that the RDF (or $g(r)$) presentation is limited in most cases below $r = 10$ Å.

From the X-ray RDF for glassy water at 77 K [21], we can read the peak distances as 2.75, 4.5, 6.8, 8.8 and 11.9 Å for the first to

Table 1
Typical $g_{OO}(r)$ values of liquid water at ordinary temperature

Source data	$g_{OO}(r)$ (Å)			Notes
	1st peak	2nd peak	3rd peak	
Narten and Levy[a]	2.85			
	2.84	4.50	6.86	[e]
	2.89	4.60	6.90	[f]
Soper and Phillips[b]	2.88	4.50	6.75	[e]
Soper et al.[c]	2.79	4.48	6.72	[e]
Hura et al.[d]	2.73	4.44	6.66	[e]
This work	2.85	4.48	6.82	

Here the peaks of $g(r)$ in X-ray diffraction are regarded as those of $g_{OO}(r)$ where $g(r) = D(r)/4\pi r^2\rho_0$ and RDF $= 4\pi r^2\rho_0\{g(r) - 1\}$.
[a] Refs. [1,2] (X-ray diffraction).
[b] Ref. [25] (Neutron diffraction).
[c] Ref. [26] (Neutron diffraction).
[d] Ref. [5] (X-ray diffraction).
[e] Cited from Ref. [24].
[f] Recalculated in this study.

the fifth peak, respectively. The amorphous low density ice also gives very similar values for the peak positions [21]. The closeness of these values of the first three peaks with those for liquid water at ordinary temperature indicates that the ~10.8 Å peak of supercooled water is different in origin from the ~12 Å peak of glassy water. Thus, we can confirm again that the structure of supercooled water is different from that of glassy water which has been assigned to have ice-I-like structure and that it is clathrate-like at least at deep supercooling temperature region (~−15 °C).

Now we have clear X-ray evidence that clathrate-like structures become dominant in supercooled water with decreasing temperature. On the other hand, there have been ample X-ray and neutron diffraction studies [3,7,21,28] to show firmly that glassy water and amorphous low density ice have the ice-I-like structure. Therefore, the fragile-to-strong transition, which has been asserted to take place at somewhere between the liquid water at ordinary temperature and the one at low temperatures just above T_g (~160 K) [29,30] and has been the main unresolved issue for the interpretation of anomalous properties of liquid water [10,31], may be nicely explained as the structural change from the 'clathrate-like' supercooled water to the 'ice-I-like' cold water just above T_g. Accordingly, the manner of the structural changes observed in supercooled water is very much similar to those of the structural changes observed in liquid sulfur and tellurium [30]. In the liquid sulfur, chain-like sulfur species abruptly become unstable at ~159 °C, giving rise to a λ-like C_p anomaly when we observe C_p from high temperature ($T >$ ~200 °C) to low temperature. Liquid tellurium shows many anomalies, which are caused by the gradual transition from metal to semiconductor with decreasing temperature from 450 to 350 °C, very similar to those of liquid water [8–10].

We are currently accumulating X-ray diffraction data on emulsified water sample down to −35 °C and will report the results in near future.

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