Emergent ferroelectric proton ordering in crystalline ice grown on surface-modified Pt(111) substrates

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Crystalline ice is a ubiquitous solid substance in nature and has more than fifteen polymorphs depending on temperature and pressure [1]. The thermodynamically stable phase under ambient pressure and temperature is hexagonal ice: ice Ih. Ice Ih is paraelectric and has disordered configuration of protons (orientation of water molecules) under the Bernal-Fowler-Pauling ice rules [Figure 1(a)]. It was suggested that the proton ordered ferroelectric phase of ice Ih, i.e. ice XI [Figure 1(b)], can stably exist below T_c~72 K [2]; this implies that ferroelectric ice exists on cold interstellar space and planets such as Uranus and Neptune [3], and would play important roles in chemical and physical processes [4].

Recently, using sum-frequency generation (SFG) spectroscopy, we have demonstrated that hexagonal crystalline ice grown on Pt(111) has extremely high-T_c (T_c~170 K) ferroelectric proton ordering [Figure 2] [5,6]. It was also shown that configurational anisotropy and protolysis driven by the electrostatistics at the heterointerface are key factors in stimulating novel exotic ferroelectric proton ordering [5]. Because ice in space typically exists in direct contact with mineral surfaces, our concept of heterointerface-induced increase in T_c for the ferroelectric proton ordering suggests the existence of ferroelectric ice over a much vaster region in space than ever expected from T_c~72 K for ferroelectric bulk ice XI [3].

To give more insight into the emergent ferroelectricity in ice, we have conducted SFG spectroscopy of crystalline ice grown on CO- and O-precovered Pt(111) substrates [7]. New unique features were observed in the growth process of ferroelectric ice and its thermodynamic stability, which will be discussed in details in our presentation.

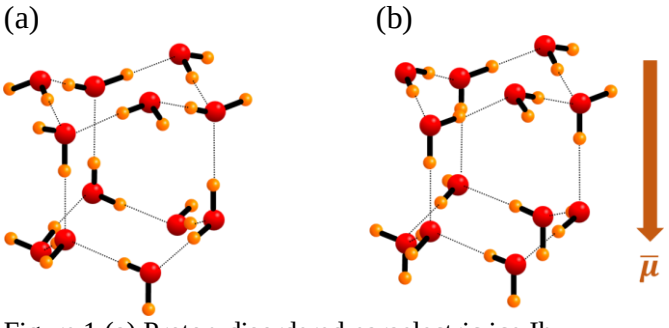

Figure 1 (a) Proton-disordered paraelectric ice Ih. (b) Proton-ordered ferroelectric ice XI.

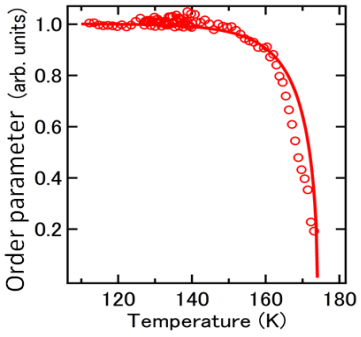

Figure 2 Temperature dependence of ferroelectric order parameter of ice/Pt(111).

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