

In the hydrogen-bond network of ice, orientation of water molecules, i.e. configuration of protons, is strongly correlated and geometrically frustrated under the Bernal-Fowler-Pauling ice rules: each pair of oxygen atoms holds one proton and each oxygen atom has two protons in its nearest neighbors. In general, materials with a strongly correlated and highly frustrated degree of freedom have potential for exhibiting dramatic and unusual responses to external stimuli. Nevertheless, little has been understood about cooperative dielectric and thermodynamic responses of ice to external perturbations at low temperature because the strongly correlated rotational motion of water molecules in ice has an extremely long relaxation time and loses ergodicity at low temperature; the orientational disorder in high temperature is inevitably frozen as an orientational glass upon cooling, resulting in finite residual entropy at low temperature. Therefore, unveiling hidden proton ordered states in ice has been a longstanding challenge of physical chemistry of condensed matters. Traditional ways of ordering proton configuration in ice are to chemically dope acidic or basic substances that catalyze proton rearrangement in ice at low temperature. Nowadays, ice XI is known to be the only phase with ferroelectric ordering among more than fifteen phases of bulk crystalline ice.

To open up a new route to unveil hidden exotic ferroelectric properties of protons with many-body interactions in ice beyond the current phase diagram, we have investigated a possibility of interface-induced ferroelectric proton ordering by focusing on heteroepitaxially grown crystalline-ice films on metal substrates as model systems [ref.2,5,6,8]. We have used recently developed phase-resolved sum-frequency generation (SFG) spectroscopy with heterodyne detection in an ultrahigh vacuum chamber [ref.9]. Although the SFG spectra obtained with the conventional homodyne detection show positive sign regardless of the orientation of water molecules, $\text{Im}\chi^{(2)}$ SFG spectra ($\chi^{(2)}$: the second-order nonlinear susceptibility) obtained by the heterodyne detection exhibits positive or negative sign for net orientation of OH with hydrogen pointing away (H-up) or toward substrate (H-down), respectively. Thus, heterodyne-detected SFG has a great advantage to directly observing local configuration of protons that cannot be investigated through other traditional experimental methods.

Recently, we have succeeded in directly demonstrating for the first time that the adsorbed first-layer water molecules prefer an H-down configuration on model platinum substrate: Pt(111) [ref.8]. The coverage dependence of the $\text{Im}\chi^{(2)}$ SFG spectra in the hydrogen-bonded OH stretching regions clearly reveals that the H-down proton ordering in the first layer is significantly pinned by the Pt(111) substrate and is subsequently propagated to the overlayer during the film growth. Temperature dependence of the SFG spectra revealed that such an exotic proton ordering is thermodynamically stable and has an extremely high critical temperature of ~ 175 K [ref.8], which is more than twice as large as that of ferroelectric bulk ice XI ($T_c \sim 72$ K). It was clarified that anisotropy and protolysis driven by the electrostatics at the heterointerface are key factors in stimulating the novel exotic ordering in the many-body correlated proton system [ref.2,8].

Furthermore, our results have a crucial consequence in the ubiquity of ferroelectric ice in nature. In space and polar stratosphere, ice is the most abundant solid substance condensed on dust particles. The concept of heterointerface-induced increase in T_c for the proton ordering suggests the existence of ferroelectric ice over a much vaster region in space and polar stratosphere than ever expected on the basis of $T_c \sim 72$ K for ferroelectric bulk ice XI.