Angstrom-scale interface modification extensively tunes thermodynamic ordering of strongly correlated protons in ice

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Abstract:
The static and dynamic behaviour of strongly correlated many-body protons in nanoscale hydrogen-bond networks plays crucial roles in a wide range of physicochemical, biological and geological phenomena in nature. However, because of the difficulty of probing and manipulating the proton configuration in nanomaterials, controlling the cooperative behaviour of many-body protons remains challenging. By combining proton-order sensitive nonlinear optical spectroscopy and well-defined interface modification at molecular/atomic scale, we demonstrate the possibility of extensively tuning the emergent physical properties of strongly correlated protons beyond the
thermodynamic constraints of bulk hydrogen bonds. Focusing on heteroepitaxially
grown crystalline ice films as a model of a strongly correlated and frustrated proton
system, we show that the emergence and disappearance of a high-$T_c$ proton order on the
nano- to mesoscale can be readily switched by angstrom-scale interface engineering.
These results and concept are also applicable to other hydrogen-bonded materials, thus
paving the way to the design and control of emergent properties of correlated proton
systems.
An ultimate goal in material science is to fabricate materials with desired characteristics by intentionally controlling their physical properties. Heteroepitaxially grown thin films on different materials often exhibit electronic structures and properties (magnetism\textsuperscript{1–3} and conductivity\textsuperscript{4–6} etc.) distinct from those in the intrinsic bulk state, as has been demonstrated, for example, in inorganic materials composed of strongly correlated many-body electrons\textsuperscript{1–6}. In materials with strongly correlated degrees of freedom, the ground state tends to be macroscopically degenerate. Such systems can exhibit exotic macroscopic properties\textsuperscript{7} when this ground state degeneracy is eliminated by symmetry-breaking external perturbations imposed at heterointerfaces\textsuperscript{1–6}. Therefore, introducing inversion-symmetry breaking in strongly correlated degrees of freedom is a promising strategy for developing novel functional properties.

In addition to electrons, protons are among the fundamental elementary particles that make up matter. Many-body protons in hydrogen-bonded (H-bonded) materials such as ice (H\textsubscript{2}O)\textsuperscript{8–14}, protonic inorganic ferroelectrics KH\textsubscript{2}PO\textsubscript{4}\textsuperscript{15,16}, and organic molecular crystals\textsuperscript{17,18} typically exhibit a strongly correlated behaviour. A unique feature of these protonic systems is that the configurations of many-body protons in the H-bond network are macroscopically degenerate and geometrically frustrated under the ice rules\textsuperscript{9}, in which each molecule (unit) donates two protons to adjacent molecules and receives two protons from other adjacent molecules\textsuperscript{8–18}. The collective motion of the correlated protons plays key roles in stimulating exotic physical properties such as proton–electron coupled polarization, conductivity, and optical properties\textsuperscript{17,18}.

In analogy to strongly correlated electrons, heteroepitaxially grown nanosystems of strongly correlated protons have a potential to exhibit novel functional properties under the symmetry breaking field. To unveil the emergent properties of such protonic nanomaterials, an \textit{in-situ} observation technique to probe directly and noninvasively the proton configurations under the
material growth processes and operating conditions is highly desirable. However, the experimental techniques commonly used to evaluate proton configurations in materials, such as neutron diffraction, typically require a macroscopic amount of the sample with dimensions on the order of millimeters. Therefore, the detection sensitivity of neutron diffraction is still inadequate for application to interfacial systems with thicknesses on the angstrom to nanometre scale. Combining density-functional theory calculations, X-ray absorption spectroscopy (XAS) can be a powerful tool to investigate the proton configurations of the molecules in direct contact with substrate surfaces, whereas it is difficult to apply XAS to the measurement of proton configurations in the nanofilms grown on the upper layers of interfacial contact layers. Due to such experimental limitations, it remains challenging to unveil emergent properties of strongly correlated proton in H-bond nanosystems.

Sum-frequency generation (SFG) vibrational spectroscopy offers one promising approach to tackle this challenge. SFG is a type of second-order nonlinear optical process induced by infrared (IR) and visible light, and its vibrational spectrum is given by the vibrational response of the second-order nonlinear susceptibility $\chi^{(2)}$. Due to coherent nature of this process, SFG has high detection sensitivity down to submonolayer level and a unique selection rule that requires the inversion symmetry to be broken. In the case of materials composed of O-H⋯O type H bonds, the magnitude of the vibrationally resonant $\chi^{(2)}$ for the O-H stretching mode directly reflects the extent of net proton ordering. Notably, the vibrationally resonant $\chi^{(2)}$ of the O-H stretching mode has a phase shift of $\pi$ between two opposing vibrational dipoles perpendicular to the interface, which enables the ordered direction of protons in the H-bond network to be determined uniquely. Therefore, SFG vibrational spectroscopy has great advantages in sensitively probing the structure and ordering properties of many-body protons in H-bonded nanosystems.

In this study, by combining proton-configuration-sensitive SFG vibrational spectroscopy...
with interface modification techniques at the molecular/atomic scale (Fig. 1a), we demonstrate for the first time the possibility of drastically changing the ordering properties of many-body correlated protons in heteroepitaxially grown H-bonded materials. As the most basic platform for studying the nature of strongly correlated proton nanosystems, we choose an ice crystal with a well-defined local tetrahedral geometry of H bonds\(^{10}\). Referring the crystalline ice films heteroepitaxially grown on the pristine Pt(111) substrate\(^{21}\), we clearly demonstrate that interface modification with an angstrom-thick monolayer of molecules or atoms (Figs. 1b and 1c)\(^{30,31}\) drastically alters the thermodynamic properties of configurational order and disorder of many-body protons at the nano- to mesoscopic scales.

Specifically, SFG measurements (Fig. 1a) were conducted, using \(p, p, p\) polarizations for the SFG signal and visible (VIS; 800 nm, 4 ps duration) and infrared (IR; 3150–3450 cm\(^{-1}\), 150 fs duration) incident light, respectively, under ultrahigh vacuum conditions. In the case of nanofilms on metal substrates, \(ppp\)-SFG signals are dominated by the ZZZ component of \(\chi^{(2)}\)\(^{22,26,32}\), where the Z-axis of the lab frame is defined to be parallel to the surface normal (see Supplementary Section IV). In this setup, the OH oscillators parallel to the surface normal dominantly contribute to the SFG signal. To simplify the spectral shape of the OH stretching mode, we targeted epitaxially grown crystalline ice composed of HDO molecules isotopically diluted with D\(_2\)O molecules\(^{33}\). Saturated single layers of CO molecules with well-defined c(4×2) symmetry (Fig. 1b) and O atoms with p(2×2) symmetry (Fig. 1c) were pre-adsorbed by exposing the clean Pt(111) surface to the CO gas (~5×10\(^{-7}\) Pa) at 100 K\(^{34}\) and O\(_2\) gas (~1×10\(^{-5}\) Pa) at 150 K\(^{31}\), respectively. On these substrates, crystalline ice films were grown at 140 K\(^{35-37}\). Fig. 1d shows the SFG (\(|\chi^{(2)}|^2\)) vibrational spectra of ~100 bilayer (BL) thick crystalline HDO ice films deposited on pristine, CO-precovered, and O-precovered Pt(111) substrates at 140 K. As \(|\chi^{(2)}|^2\) is related to the magnitude of proton ordering of the OH groups parallel to the surface normal, the intense SFG peaks observed on the pristine and CO-precovered Pt(111) surfaces
(Fig. 1d) indicate the growth of crystalline ice films with net ferroelectric proton ordering along the surface normal. The results on the pristine Pt(111) surface agree well with those of previous studies. The smaller SFG peak of the ice films grown on the CO-precovered Pt(111) surface compared to that of those on pristine Pt(111) indicates that less proton ordered ice is grown on the CO layer. The peaks of the OH stretching band on both substrates are located at ~3275 cm\(^{-1}\).

Notably, the peak frequency of O-H stretching band for the isotope diluted water ice reflects the strength of H bonds and thus correlates well with the intermolecular O-O distance \(R_{\text{oo}}\). Therefore, based on the well-known correlation between the O-H stretching frequency and \(R_{\text{oo}}\) (Fig. S1), we can estimate the \(R_{\text{oo}}\) of the proton-ordered crystalline ice films on these substrates to be 2.76±0.02 Å, which is identical to the \(R_{\text{oo}}\) of common hexagonal bulk ices: ice-Ih (paraelectric phase) and ice XI (ferroelectric phase of ice-Ih). The most striking feature is observed for the ice films on the O-precovered Pt(111) surface, wherein the peak intensity is much smaller compared to those of the other two surfaces (Fig. 1d). Because \(\chi^{(2)}\) is zero for centrosymmetric systems, this result suggests that proton configuration is mostly isotropic and disordered in the films of ice on the O-precovered surface.

The emergence and disappearance of the net proton order become more evident from the thickness dependence of the SFG intensity (Fig. 1e). The extremely small increase for the O-precovered surface indicates that the proton configuration in this ice film is almost completely disordered; a paraelectric ice film is grown on the O-precovered Pt(111). In contrast, the SFG intensity continues to increase with the film thickness on both the CO-precovered and pristine Pt(111) surfaces. The smaller increase rate for the ice films on CO-precovered Pt(111) compared to that of the ice films on pristine Pt(111) (Fig. 1e) clearly indicates that the ice film with smaller degrees of proton ordering continues to grow on the CO-precovered Pt(111) substrate without saturation. Notably, these differences in SFG observation were found under the conditions where no appreciable differences in the ice films on the three substrates were
confirmed in the conventional infrared reflection absorption (IRAS) spectra (Fig. 2, see also Supplementary Section I for details); therefore, the water molecules adsorbed on these substrates form almost the same hexagonal ice films in terms of translational structure and H bonding distance of $R_{oo} \approx 2.76 \, \text{Å}$, but the degree of orientation order of the molecules, i.e., the configuration order of the protons, in their H-bond networks is completely different (Fig. 1), as observed by SFG.

To verify in which direction the O-H bonds orient, we also measured Im$\chi^{(2)}$-SFG spectra using the phase-resolved heterodyne-detection technique. The remarkable feature of the vibrationally resonant Im$\chi^{(2)}$ spectrum is that it exhibits positive and negative peaks for OH oscillators pointing upward and downward, respectively, due to the phase difference of $\chi^{(2)}$ by $\pi$ depending on the H-up/H-down configuration. The negative peak of the Im$\chi^{(2)}$ spectra for the ice films on CO-precovered Pt(111) (Fig. 3a) reveals that water molecules on this substrate prefer net-H-down proton configurations. We also confirmed that the ice films on Pt(111) show net H-down proton configurations (Fig. S2a, see Supplementary Section II), in good agreement with the results of a previous study. From the intensity difference of the Im$\chi^{(2)}$ spectra, the magnitude of the net-H-down proton order of first water layer on the CO-precovered Pt(111) substrate is estimated to be $\approx 50\%$ smaller compared to that on the pristine Pt(111) substrate (see Supplementary Section IV for details). The smaller proton ordering on CO-precovered Pt(111) is attributed to the difference in the direct interaction between the water molecules in the first layer and the substrate. Indeed, the peak frequency for the first-layer OH oscillators directly interacting with the pristine Pt(111) substrate ($\approx 3350 \, \text{cm}^{-1}$, Fig. S2a) is more redshifted from the peak frequency for the free OH oscillators ($\approx 3690 \, \text{cm}^{-1}$, Fig. S3a) than that for the OH oscillators interacting with CO molecules ($\approx 3620 \, \text{cm}^{-1}$, Fig. S3a). The more redshifted feature indicates that the protons in the first-layer water molecules on the pristine Pt(111) substrate interact more strongly with the substrate; thus, they are more significantly pinned in the
H-down configuration than those on the CO-precovered Pt(111) substrate. The more weakly pinned H-down proton configuration in the first water layer on CO-precovered Pt(111) propagates to the subsequent overlayers during the epitaxial growth, resulting in a less ordered proton configuration in the mesoscopic scale multilayer ice film on this substrate than that on pristine Pt(111) (Figs. 1d and 1e).

In contrast to these substrates, the Im$\chi^{(2)}$ spectrum derived from the weak SFG signal for the paraelectric ice films on the O-precovered Pt(111) surface exhibits a positive and negative bipolar band shape (Fig. 3b). The small bipolar peaks are derived from the H-bonded H-up and H-down O-H oscillators at the surface of hexagonal ice as reported in previous SFG studies on the surfaces of paraelectric crystalline ice-Ih$^{32,40}$. The growth of a proton-disordered ice multilayer suggests the absence of anisotropy along the surface normal in the first-layer water molecules on the O-precovered Pt(111) substrate, which is consistent with previous reports that the first-layer water molecules on the O-precovered Pt(111) prefer parallel orientation along the surface$^{41,42}$. Therefore, our results show on a solid basis that modulation of the proton configuration at the interface by an angstrom-thick monolayer of molecules and/or atoms has a critical impact on the ordering properties of the strongly correlated protons in the H-bond network at the nano- to mesoscopic scale.

In the case of the ferroelectric phase of bulk ice (ice XI), a disordering transition to the paraelectric phase (ice Ih) has been observed at a critical temperature of $T_c = 72$ K$^{13,14}$. Therefore, our results for the epitaxial growth of proton ordered ice at 140 K on Pt(111) and CO/Pt(111) (Figs. 1d, 1e) suggest that the critical temperature of the disordering transition of these protons is much higher than that of the proton-ordered bulk ice XI$^{21,22}$, due to the configurational pinning of H-down-ordered protons imposed by the substrates. Note that the configurational order of protons on the CO-precovered Pt(111) surface is approximately 50% weaker than that on the pristine Pt(111) surface, as estimated from the slope of the $|\chi^{(2)}|^2$-SFG
intensity (Fig. 1e, see also Supplementary Section IV for details). The modulation of the interfacial proton order may have crucial consequences for the thermodynamic behaviours of protons in multi-layered ice films.

To demonstrate the impact of the interface modification, we conducted temperature-programmed SFG measurements for 100-BL thick ice films grown on the CO-precovered and pristine Pt(111) substrates with a heating rate of 0.1 K/s. Above ~150 K, the $|\chi^{(2)}|^2$ SFG intensity starts to decrease substantially on both substrates (Figs. 4, S4a, and S4b). Reversible temperature dependence was also confirmed, indicating that the observed changes occur under thermodynamic equilibrium conditions. Interestingly, the thermal decay profiles are significantly different for these substrates, as clearly shown in the normalized plot of the SFG intensity (Figs. 4c and S4c); the SFG signal from the ice film on the CO-precovered surface decays more gently and remains more persistent up to higher temperatures compared to that on the pristine Pt(111) surface.

Generally, the SFG intensity reflects both the number of water molecules (i.e., the thickness of the ice film) and the net orientational order$^{21,22,26}$. As shown in Fig. 4d and S4d, sublimation of water molecules from ice surfaces and the resultant decrease in the total thickness of ice films become significant above 160 K$^{35,37,43}$ but is almost the same on both substrates up to ~167 K. In this temperature range, the decay profiles of the SFG intensity are notably different (Fig. 4c). Therefore, the interfacial CO layer significantly alters the thermal disordering behaviours of the many-body protons in ice.

To deal with the thickness dependence of the SFG intensity and focus on the disordering phase transition quantitatively, we introduce a thickness-normalized order-parameter $\eta$, assuming that $\chi^{(2)}$ is separable from the thickness-dependent term and the temperature-dependent term $\eta$ (see Supplementary Section III). On both substrates, the ferroelectric proton order is approximately constant below ~150 K (Fig. 5a). As the temperature
is increased further, the crystalline-ice film on the pristine Pt(111) substrate exhibits a
second-order-like disordering transition and loses ferroelectricity at $T_c = 168$ K. As will be
discussed in detail in our forthcoming paper, the slight difference between the $T_c$ values
observed in this study and our previous study$^{21}$ is ascribed to the size effects (~100 BL thick in
the present study and ~300 BL thick in Ref. 21). On the CO-precovered Pt(111) substrate, a
two-step sequential transition is clearly observed; approximately 20\% of the proton order is
gradually lost with the second-order-like disordering transition at ~160 K, whereas ~80\% of the
proton order remains unaltered at this temperature and suddenly decays at $T_c = 173$ K upon a
first-order-like transition. Notably, the single CO intercalated layer between ice and Pt(111)
further increases $T_c$ by ~5 K in comparison to the high-$T_c$ ferroelectric ice grown directly on the
Pt(111) substrate (Fig. 5a), although the absolute extent of the proton order is weakened (Fig. 1).
Our results thus clearly demonstrate the possibility of interface engineering for modulating
configurational order and the thermal stability of strongly correlated many-body protons in ice
beyond the thermodynamic limit of bulk ice$^{10,11}$.

The temperature profiles of the order-disorder transition were analysed by a statistical
model$^{15}$ explicitly taking account of the multiple proton configurations under the ice rules and
their partial violation$^{9,10}$ in the HB network. As shown in the inset of Fig. 5a, the transition
curves can be described in terms of (1) the H-down orientational preference energies $E_0$ from
the H-up proton configurations and (2) the formation energy $E_{LD}$ of orientational defects that
break the ice rules by unimolecular reorientation (Figs. 5b and 5c)$^{15}$. In particular, $E_{LD}/E_0$ is
indicative of the cooperativity of protons in configurational disordering. As shown in the inset
of Fig. 5a, the ice rules are almost rigidly satisfied and the ferro-to-paraelectric phase transition
suddenly takes place as a first-order transition at $T_c \sim 1.4E_0/k_B$ at the suitably large $E_{LD} (E_{LD}/E_0 >
10)$, whereas $T_c$ substantially decreases from $1.4E_0/k_B$ and proton disordering occurs as a
second-order transition at smaller $E_{LD} (E_{LD}/E_0 < 10)$. 


The transition curve for the pristine Pt(111) surface is well described by $E_0 = 11.8 \pm 0.8$ meV and $E_{LD} = 79 \pm 11$ meV (Table 1, blue curve in Fig. 5a). The local proton rearrangements that violate the ice rules (Fig. 5b) are partially allowed at the smaller $E_{LD}/E_0$ value of ~7, and thus, as shown in the inset of Fig. 5a, the ferroelectric proton order gradually decays in the ice films, resulting in the second-order like transition. In contrast to the pristine Pt(111) surface, two $E_{LD}$ components are necessary to describe the two-step transition on the CO-precovered surface. The curve fitting result coloured in red in Fig. 5a shows that the second-order-like first disordering component at ~160 K is expressed by $E_0 = 10.4 \pm 0.4$ meV and $E_{LD,1} = 90 \pm 9$ meV ($E_{LD,1}/E_0 \sim 9$), whereas the first-order-like second disordering component at ~173 K is expressed by $E_0 = 10.4 \pm 0.4$ meV and $E_{LD,2} = 163 \pm 8$ meV ($E_{LD,2}/E_0 \sim 16$). The sudden transition at ~173 K characterized by the relatively larger defect formation energy $E_{LD,2}/E_0 \sim 16$ is induced by cooperative proton rearrangement (Fig. 5c) rather than unimolecular proton rearrangement (Fig. 5b), as also described in the inset of Fig. 5a. The two representative values of $E_{LD}$ for the ice films on the CO-precovered Pt(111) substrate (Table 1) can be ascribed to the two different local environments of first-layer water molecules adsorbed on the on-top and bridge CO molecules on the Pt(111) surface (Fig. 1b).30

The orientational preference energy $E_0$ for the CO-precovered Pt(111) ($E_0^{(CO/Pt)}=10.4 \pm 0.4$ meV), which is smaller than that on the pristine Pt(111) ($E_0^{(Pt)}= 11.8 \pm 0.8$ meV), is qualitatively consistent with the feature observed in the film growth processes under which the degree of proton order on the CO-precovered Pt(111) is smaller than that on the pristine Pt(111) (Figs. 1d and 1e). Although the H-down orientational pinning is slightly weaker on the CO/Pt(111) surface than on the pristine Pt(111) surface, as suggested by $E_0$, the observed thermal decay profile (Figs. 4 and 5) indicates that the proton ordering in the ice films on the CO-precovered surface persists up to higher temperature than that on the pristine Pt(111). This difference originates from the larger $E_{LD}/E_0$ values on the CO-precovered surface ($E_{LD}^{(CO/Pt)}$).
\( I_{E_0}^{(CO/Pt)} = 9 \text{ and } 16 \) than on the pristine Pt(111) \( (E_{LD}^{(Pt)} / I_{E_0}^{(Pt)} = 7) \) (Table 1), which indicates that the ice rules are more rigidly satisfied and more thermal energy is required for proton rearrangement on the CO-precovered Pt(111) (inset of Fig. 5a). These results suggests that the intercalated CO interfacial layer has crucial consequences for both lowering the magnitude of orientational pinning and enhancing the collectiveness of proton rearrangement in the H-bond network of ice films.

In summary, we demonstrated for the first time that angstrom-scale interface modification has critical impacts on the nano- to mesoscopic-scale structures and properties of strongly correlated protons in heteroepitaxial ice, by leveraging SFG spectroscopy for sensitive monitoring of proton configurations in the H-bond network. The intercalation of a single O layer between ice and Pt(111) completely suppressed the proton ordering inherent to crystalline ice films epitaxially grown on Pt(111)\(^{21,22}\), whereas more high-\(T_c\) net-H-down proton ordering emerges with the intercalation of a single CO layer. The balance between the configurational pinning at the heterointerface and cooperativity of many-body protons is key to altering both the magnitude and thermodynamic stability of the proton ordering significantly. Our experimental approach and concept are also applicable to other H-bonded systems in which strongly correlated protons have the potential to exhibit a variety of emergent properties\(^{17,18}\).

Therefore, this work provides a new interface engineering strategy for fabricating functional nanomaterials composed of strongly correlated many-body protons, paving the way for pioneering mesoscopic physics of H-bonded systems beyond the thermodynamic constraints of bulk materials.

Finally, it is worth remarking that the orientation of the interfacial water molecules has crucial consequences in the transfer processes of protons, electrons, and ions in an electric double layer\(^{21,44}\). Therefore, our concept of surface engineering of the orientation of water molecules would also have profound implications for designing and controlling various
interfacial phenomena occurring at solid-liquid interfaces such as in electrochemistry, catalysis, atmospheric chemistry, and biology.\textsuperscript{24,45–49}
**Table 1.** Thermodynamical energy parameters of water molecules in ice films

<table>
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<tr>
<th>Substrate</th>
<th>Pt(111)</th>
<th>CO/Pt(111)</th>
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<tr>
<td>$E_0$ (meV)</td>
<td>11.8 ± 0.8</td>
<td>10.4 ± 0.4</td>
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<tr>
<td>$E_{LD1}$ (meV)</td>
<td>79 ± 11</td>
<td>90 ± 9</td>
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<tr>
<td>$E_{LD1}/E_0$</td>
<td>6.7</td>
<td>8.6</td>
</tr>
<tr>
<td>$E_{LD2}$ (meV)</td>
<td>---</td>
<td>163 ± 8</td>
</tr>
<tr>
<td>$E_{LD2}/E_0$</td>
<td>---</td>
<td>15.7</td>
</tr>
</tbody>
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Fig. 1 | Experimental scheme of SFG and impact of angstrom-scale interface termination on the emergent ferroelectric proton order in the mesoscopic-scale H-bond network of ice.

(a) Schematic illustration of in situ SFG spectroscopy in the heteroepitaxial growth process of HDO crystalline ice films on a surface-precovered Pt(111) substrate. (b, c) (4×2) saturated structure of CO molecules, and (c) (2×2) saturated structure of O atoms on Pt(111). The unit cells of the adsorbed molecules are shown with the black solid lines. In (b), the CO molecules adsorbed on the top and bridge sites of the Pt(111) substrate are coloured purple and brown, respectively. (d) $|\chi^{(2)}|^2$ SFG vibrational spectra in the OH stretching region of isotope-diluted ~100 BL thick HDO crystalline ice films grown on pristine, CO-precovered, and O-precovered Pt(111) substrates. (e) $|\chi^{(2)}|^2$ peak intensity as a function of ice thickness. The solid lines represent the linear fits to the data.
Fig. 2| IRAS measurement of ice films on pristine and surface-modified Pt(111) substrates. Peak-normalized IRAS spectra of isotopically diluted HDO crystalline ice films (50 BL) on pristine, CO-precovered and O-precovered Pt(111) substrates. The vertical dashed line shows the peak position of the transmission absorption spectrum of bulk HDO hexagonal ice. (Inset) Thickness dependence of the peak height. The blue triangle, red circle, and grey square correspond to the ice films on the pristine, CO-precovered, and O-precovered Pt(111) substrates, respectively.
Fig. 3 | Phase-sensitive heterodyne-detected SFG spectroscopy of ice films on surface modulated Pt(111). a, Imχ(2) spectra of H-down-ordered ferroelectric HDO ice film (40 BL) on CO-precovered Pt(111) and b, proton-disordered paraelectric HDO ice film (40 BL) on O-precovered Pt(111).
Fig. 4 | Effect of thermal heating on the $|\chi^{(2)}|^2$ SFG vibrational spectra of HDO ice films. a, Two-dimensional plots of the $|\chi^{(2)}|^2$ spectra for ice films on the pristine Pt(111) surface and b, CO-precovered Pt(111) surface as a function of temperature. The initial thickness of the ice samples is ~100 BL, and a heating rate of 0.1 K/s is applied after precooling to 120 K. White dotted lines represent the peak position. c, Comparison of the temperature profiles of $|\chi^{(2)}|^2$ on these substrates and d, ice thickness. The data in (c) and (d) are normalized to the corresponding data at ~150 K. The SFG decay profiles on the two surfaces deviate from each other, whereas the thickness profiles are similar in the region between the vertical dashed lines.
Fig. 5 | Thermal disordering of the emergent proton order in the ice films on pristine and CO-precovered Pt(111) surfaces. a, Ferroelectric order parameters obtained from the experimental data (Fig. 4) normalized to those at 120 K as a function of temperature. The solid lines are ferroelectric–paraelectric behaviour curves fitted with the statistical model taking into account the ice rules and their partial violation\(^1\(^5\). (Inset) Effect of ice rule breaking on the temperature dependence of the ferroelectric order parameters simulated by the statistical model\(^1\(^5\) at \(E_{LD}/E_0\) = 20 (red), 10 (brown), 4 (green), and 2 (blue). The horizontal axis is the temperature scaled by \(E_0/k_B\). See the text for nomenclatural details. b, Schematic illustration of water reorientation in the H-bond network by unimolecular reorientation, accompanying the formation of orientational defects which have no proton (\(L\)-defect) and two protons (\(D\)-defect) between the nearest-neighbour O atoms. c, Schematic illustration of cooperative molecular reorientation under the ice rules.
Methods

Sample preparation

The experiments were conducted in an ultrahigh vacuum (UHV) chamber with a base pressure below $5\times10^{-8}$ Pa. The Pt(111) single-crystal substrate surface was cleaned by repeated cycles of Ar$^+$ sputtering ($-5\times10^{-3}$ Pa, beam energy 500 eV), annealing at 800 K under an O$_2$ pressure of $-5\times10^{-5}$ Pa, and flushing at 1050 K in the UHV environment. A CO layer with c(4×2) symmetry was adsorbed by exposing the clean Pt(111) surface to CO gas ($-5\times10^{-7}$ Pa) at 100 K, followed by annealing at 260 K$^{34}$. An O layer with p(2×2) symmetry was adsorbed by exposing the clean Pt(111) surface to O$_2$ gas ($-1\times10^{-5}$ Pa) at 150 K, where dissociative adsorption of O$_2$ gas to atomic O occurs$^{31}$. Ice was grown by physical vapor deposition of isotope diluted HDO (HDO:D$_2$O ~ 1:2 mixing ratio) on Pt(111) at 140 K. Using isotope-diluted water minimizes inter- and intra-molecular vibrational coupling of the water molecules$^{50}$ and facilitates interpretation of the SFG spectra$^{33}$. The isotopic concentration of OH chromophore in this study ([OH]/[OD] = 1/4) is half of that in our previous report ([OH]/[OD] = 1/2)$^{21}$, which enables more precise analysis and interpretation of the spectral shape because smaller concentration of OH leads to more sharpening of the H-bonded OH stretching band$^{51}$. The amount of adsorbed water molecules is expressed in the BL unit; 1 BL corresponds to the amount of water molecules in a bilayer of bulk ice Ih ($-1.1\times10^{19}$ m$^{-2}$), which is nearly equivalent to the amount of water molecules in the saturated first layer on Pt(111).

Setup for SFG measurement

The details of experimental setup for SFG spectroscopy have been described elsewhere$^{21,22}$. Briefly, the output pulse of Ti:sapphire regenerative amplifier (Spectra Physics, 1 kHz, $\sim$1.6 mJ/pulse) was split into two to generate a narrow band “visible” pulse ($\sim$1.0 μJ/pulse, 800 nm)
and a broadband infrared pulse (150-fs duration, \(\sim 4 \mu \text{J/pulse, } 3150-3450 \text{ cm}^{-1}\)). SFG measurements were conducted in the reflection geometry by coaxially aligning the visible and infrared pulses with \(p\) polarization at an incident angle of 61.5°. In this setup, the coherence length is estimated to be \(\sim 4.7 \mu \text{m}^{21,22}\), which is much longer than the thickest ice samples with \(~100\) water layers. In the case of ice nanofilms on metal substrates, \(ppp\)-SFG signals are dominated by the \(ZZZ\) component of \(\chi^{(2)}\) \(22,26,32\), where the three polarization states and components are expressed in the order of the SFG, VIS, and IR; the \(Z\)-axis of the lab frame is defined to be parallel to the \(c\)-axis of hexagonal crystalline ice (see Supplementary Section IV). In this setup, the OH oscillators parallel to the surface normal dominantly contribute to the SFG signal intensity. We focus on isotopically diluted HDO molecules to simplify the spectral shape of the OH stretching mode\(^{33}\). The absolute value of \(|\chi^{(2)}|\) was deduced by the procedure described in detail in Ref. \(22\).

**Setup for IRAS measurement**

IRAS measurement was conducted using a Fourier transform infrared spectrometer (Brucker IFS 66v/S) with a resolution of 4 cm\(^{-1}\). The IR light was focused on the sample by a concave mirror through a BaF\(_2\) view port at an incident angle of 84°. The reflected light from the sample was detected with a mercury cadmium telluride detector (Teledyne Judson Technologies). The light path outside the UHV chamber was evacuated below 1 Pa to avoid unfavourable IR absorption by H\(_2\)O and CO\(_2\) gas in air.
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Competing Interests

The authors declare no competing interests.

Additional Information

Supplementary information is available at https://xxx
References


