

Reply to Comment on "Ferroelectricity in Water Ice"

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Whitworth claims that the central, incontrovertible proof of the proton-ordered nature of ice XI comes from its neutron diffraction, i.e., the fact that it shows a C-centered 8-molecule unit cell, instead of the usual 2-molecule unit cell of hexagonal ice I³. True, one of the simplest possible proton-ordered ferroelectric ice structures has this unit cell. But consider: Ice Ih shows clear neutron diffraction, despite being proton disordered. The oxygens still have translational symmetry and provide diffraction whether the protons are ordered. Ice XI's neutron diffraction requires only a distortion of the usual oxygen lattice locations. The protons can remain disordered. Whitworth ignored this possibility completely. Thus the neutron diffraction is consistent with both proton-ordered and proton-disordered ice XI. Clearly not a proof of proton ordering!

Why might ice XI's lattice distort? (1) Near the 72 K transition, much of the high-amplitude hydrogen librations should be freezing out to their zero-point limits. (2) Uniform distribution of the 0.08 M concentration of KOD used to create ice XI puts all water molecules less than six water molecules away from an ion. (3) Ice Ih is fragile, transforming to ices II, III, and IX at less than 2 kbar.⁴ The KOD doping should create internal stresses near this level.

The neutron diffraction data actually suggests proton disorder. The neutron diffraction of ice Ih is similar in intensity to that of ice XI.⁵ In ice Ih the proton disorder should attenuate the diffraction peaks, via destruction of much of the phase coherence in the Ewald sum of the scattering amplitudes, similar to Debye-Waller attenuation.⁶ Any proton ordering of the unit cell of ice I should greatly reduce the disorder and strongly increase the intensity of all diffraction peaks. Similar diffraction intensities for ice XI and ice I implies no significant proton order difference.

There is no other compelling evidence for proton order in ice XI. The dielectric studies of Whitworth⁷ show that the heterogeneous ice XI + ice Ih mix had a dielectric constant above 72 K within a factor of 2 of that expected from the simple 27000 K/T behavior seen at higher temperatures for ice I.⁷ Ferroelectrics have a $1/(T - T_0)$ dielectric dependence on either side of their Curie temperatures.⁸ Whitworth sees no such large changes approaching 72 K from above, and below 72 K the material is no longer dielectrically active (nor is ice I). So Whitworth hypothesizes that the ice I Curie temperature is very much lower than 72 K and the first order transition at 72 K preemptively forces the ice's proton order. So no, or very faint, evidence of a ferroelectric state need be dielectrically visible above 72 K. This is like saying that not hearing anything is evidence for an explosion too far away to hear. And beware: ice routinely shows artifacts in dielectric measurements, especially when heterogeneous.⁹

Regarding the residual entropy argument (see Tajima et al.¹⁰): Proponents of proton-ordered ice XI point out that at 72 K, 2.33 J/K of entropy is lost, which is 2/3 of the famous 3.4 J/K residual proton disorder entropy of ice I at 0 K.¹¹ However, 2.33 J/K is the maximum observed. They measured from 0.28 to 2.33 J/K, with various dopings and annealings. This is not compellingly equal to 3.4 J/K. Additionally, at 73 K, the total entropy of the doped ice I (0.1 M KOH) should be at least 12.6 J/K.¹⁰ Is the 0.28 to 2.33 J/K entropy loss at 72 K from the 3.4 J/K (proton disorder) portion or from the 9.2 J/K (thermal disorder) portion of the total 12.6 J/K that could be lost? Without justification they conclude that it all came from the proton disorder. They did not measure the 0 K residual entropy of ice XI, only the 72 K transition entropy.

Thus we conclude that ice XI may not be proton ordered and more experiments are needed.

Whitworth comments that it "would be misleading" to consider the vapor-grown ices of Iedema et al.¹ and Su et al.² relevant to bulk ice phases. Su et al. and Iedema et al. hoped that either the ice-substrate or ice-vacuum interface would act as a template for proton-ordered bulk ice growth. This is analogous to the routine growth of oriented diamond films from the vapor phase near room temperature.¹³ Preferred kinetics of growth and templating effects are well known to allow vapor deposition of standard *bulk* forms of either thermodynamically "unstable" solids (like diamond) or "stable" forms that other methods might not produce.

We (and Su et al.) found that these templating effects failed to produce strongly proton-ordered ices. Pt *might* strongly orient the protons of the first monolayer of ice. This net proton orientation would force a bulk proton order, if the standard hydrogen-bonding rules¹⁴ hold as the ice grows. We showed that either there is no net orientation of that first layer or that the rules are broken. This was beautifully confirmed by a recent theory paper by Witek and Buch.¹⁵ They showed that the rules are broken in the second "bilayer", to minimize the electrostatic energy, producing nonoriented protons.

References and Notes

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