Accurate Crystal Structures of Ices from X-Ray And ED With Hirshfeld Atom Refinement

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Background. Water is an essential chemical compound for living organisms, and twenty of its different crystal solid forms (ices) are known. Still, there are many fundamental problems with these structures such as establishing the correct positions and thermal motions of hydrogen atoms. The list of ice structures is not yet complete as DFT calculations and spectroscopic measurements have suggested existence for additional as of yet unknown phases. In many ice structures, neither neutron diffraction nor DFT calculations nor X-ray diffraction methods can easily solve the problem of hydrogen atom disorder or accurately determine their atomic displacement parameters.

Methods. We applied a new way of refinement of single crystal high pressure X-ray synchrotron and laboratory X-ray and electron diffraction data called Hirshfeld Atom Refinement. This method utilizes aspherical atomic scattering factors (X-rays), and aspherical atomic electrostatic potentials (ED), based on so called stockholder (Hirshfeld) partition and is especially effective in the case of refinement of crystals of H-rich compounds.

Results. Here we present accurate crystal structures of H2O, D2O and mixed (50%H2O/50%D2O) ice VI and ice VII obtained by Hirshfeld Atom Refinement (HAR) against high pressure single crystal synchrotron and laboratory X-ray diffraction data as well as results of refinement of hexagonal ice obtained by HAR against electron diffraction data. It was possible to obtain O-H bond lengths and anisotropic atomic displacement parameters for disordered hydrogen atoms which are in good agreement with the corresponding results of single crystal neutron diffraction data.[1]

Conclusions. Our results show that Hirshfeld atom refinement against X-ray diffraction and electron diffraction data is a tool which can compete with neutron diffraction in detailed studies of polymorphic forms of ice and crystals of other hydrogen rich compounds. As neutron diffraction is relatively expensive, requires larger crystals which might be difficult to obtain, and access to neutron facilities is restricted, cheaper and more accessible X-ray measurements combined with HAR can facilitate the verification of the existing ice polymorphs and the quest for the new ones.[1]

References

[1] Chodkiewicz, M. L., Gajda, R., Lavina, B., Tkachev, S., Prakapenka, V. B., Dera, P. & Woźniak, K. (2022). Accurate crystal structure

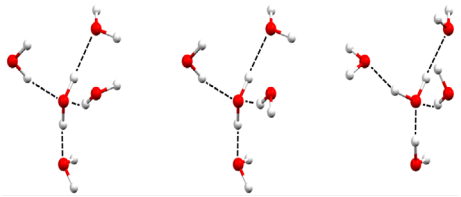

Figure 1

Financial support of this work by the National Science Centre, Poland, through OPUS 21 grant number DEC-2021/41/B/ST4/03010 is gratefully acknowledged. The work was accomplished at the TEAM TECH Core Facility for crystallographic and biophysical research to support the development of medicinal products sponsored by the Foundation for Polish Science (FNP) and at the Cryoelectron Microscopy and Electron Diffraction Core Facility at CENT (University of Warsaw, Poland). The synchrotron radiation experiments were performed at the APS (Proposal No. GUP-71134) and DESY (Proposal I-20200083 EC). of ice VI from X-ray diffraction with Hirshfeld Atom Refinement, IUCRJ, 9, 573-579.