MS37-P2 Transformation of α-cyclodextrin hydrates at high pressure: a combined X-ray diffraction and molecular dynamics study

Rubén Granero-García[1], Ben Corry[2], Francesca P.A. Fabbiani[1]

1. Crystallography Department, GZG, Georg-August-Universität Göttingen, Göttingen, Germany
2. Research School of Biology, Australian National University, ACT, Australia

email: ruben.granero@geo.uni-goettingen.de

The application of moderately high pressures is a powerful tool to induce structural changes in crystals of organic compounds. We are particularly interested in a detailed understanding of how and why structural transformations take place as a function of pressure. To provide a better answer to these questions we have complemented some of our single-crystal X-ray diffraction studies with molecular dynamics simulations.

One of the hydrates (form I) of α-cyclodextrin, a cyclic derivative of starch composed of six glucose units, incorporates additional water molecules in its cavity under compression up to 0.65 GPa. Concomitantly, one of the terminal hydroxyl groups becomes increasingly disordered as pressure is applied, expanding the available volume in the cavity [1]. Usually, compression of a molecular material enhances order and reduces the void volume [2-6], opposite to our experimental findings. This has motivated us to further explore the system using molecular dynamics.

First, we have performed simulations of the crystal in the absence of solvent at different pressures to study whether pressure has a direct effect on the disorder of the terminal hydroxyl groups. Second, we have carried out simulations on a cluster of unit cells immersed in water to study possible relationships between disorder, water content and pressure. From these simulations we have also been able to explore how the inclusion of water in the cavities takes place. Third, we have performed free energy calculations to better understand the rotation of the terminal hydroxyl groups and the movement of water through the crystal. Combining all our findings we propose a mechanism for the inclusion of water in α-cyclodextrin in the solid state at high pressure, which differs from the induced-fit mechanism that operates in solution at ambient pressure [7].

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MS37-P3 Radiation damage in chemical crystallography

Peter N. Horton[1], Simon J. Coles[1], Mateusz B. Pitak[1], Graham J. Tizzard[1], Claire Wilson[2]

1. UK National Crystallography Service, Chemistry, University of Southampton, Southampton, SO17 1BJ, U.K.
2. School of Chemistry, University of Glasgow, Glasgow, G12 8QQ, U.K.

email: pnh@soton.ac.uk

Although crystals suffering radiation damage is a well-known and studied phenomena for macromolecular crystallography[1], as far as we are aware there still appears to be no such published work relating to chemical crystallography. However, there are numerous anecdotal accounts of disintegrating crystals and resolution progressively dropping off that have been ascribed to radiation damage. Since the start of operations on the small molecule synchrotron beamline I19[2] at Diamond Light Source, there have been repeated comments from multiple users observing sample damage in the beam.

The UK National Crystallography Service[3] handles a wide variety of samples and a number of these have experienced radiation damage. In order to understand the causes and symptoms of this effect in greater detail some controlled experiments were performed. A series of experiments were conducted on crystals that were known to undergo radiation damage in order to determine some quantification of the effect. Additionally the aim is to understand what one might be able to do to mitigate against the damage caused and determine whether the effects observed are similar to those of macromolecular crystallography. The effects of varying the collection temperature, overall dose, dose rate and wavelength of X-ray used were all tested and normalised for each sample.

Samples where radiation damage has been observed were chosen and were also required to be air stable and preferably not suffer from solvent loss, in order to minimize problems of non-reproducibility. Those chosen to probe this effect were:

1. A gold complex – has potential to suffer heavily from absorption effects.

2. A nickel complex with significant solvent water – this could to some extent mimic the behaviour exhibited by proteins.

3. A small organic compound – an example of unexpected decay. The poster will summarise the results of these experiments and contrast them with data collected on a high intensity rotating anode laboratory source.

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