Poster Presentation

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Finding and Characterizing Commensurate Modulations in Molecular Crystals

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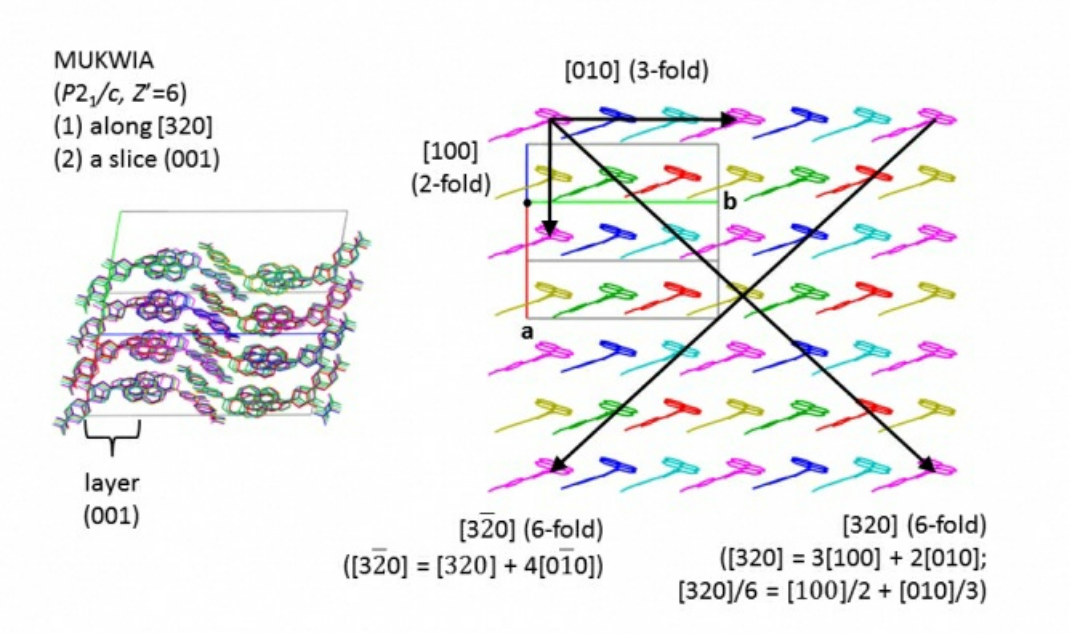
In an n-fold modulation small molecular translations, rotations, and/or conformational changes make independent n molecules that would otherwise be related by a crystallographic translation. Half of the organic structures archived in the CSD [1} that have more than four independent molecules are modulated [2]. (All were refined as commensurate.) Developing an automated method for identifying such modulations is desirable because it is easy to miss seeing them, even when a sophisticated display program like Mercury [3] is used. We also wanted to know whether translational modulations are as frequent for Z′ = 2 – 4 structures as for Z′ > 4 structures. The Z′>4 structures that had been examined individually [2] were used to develop and test the algorithm, which could then be run for the Z′ = 2, 3, and 4 structures that are too numerous to consider individually. The algorithm also quantifies the major components of the modulations, i.e., the transverse and longitudinal displacements, molecular rotations, and conformational differences.

Modulations in several directions are sometimes seen by eye because a pseudotranslation vector [m1 m2 m3]/n, mi integers, can be combined with any lattice vector [l1 l2 l3]. Furthermore, if n has an integer factor p (i.e., 2 and 3 for n =6) then there are also modulations [m1 m2 m3]/(n/p) + [l1 l2 l3] (see image). The shortest pseudotranslation that relates the most molecules is a unique choice and is usually the most visually obvious. There are some structures, however, in which that pseudotranslation seems to be the result of combining two lower-order modulations.

Because modulations extend over large distances and many molecules they are probably established during the early stages of crystal growth rather than at the time of nucleation. Modulations may also appear during the crystal contraction that accompanies cooling. Understanding how modulations are established, however, is likely to be difficult because the related molecules are often not in close contact.

[1] Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). Acta Cryst. B72, 171-179.
[2] Brock, C. P. (2016) Acta Cryst. B72, 807-821.
[3] Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., Streek, J. v. d. & Wood, P. A. (2008). J. Appl. Cryst. 41, 466-470.



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