Contribution ID: **28** Type: **Plenary Lecture**

High Pressure Phase Transitions in Molecular Crystals

Tuesday, 13 September 2022 08:45 (1 hour)

In the organic solid state, high pressure to 10 GPa leads to compression of intermolecular interactions and phase transitions. Pressure is therefore a very useful means for studying polymorphism in molecular solids. We have investigated hydrogen-bonded materials (*e.g.* amino acids) as well as very simple compounds (*e.g.* pyridine), and the talk will show how experimental structures of organic solids can be interpreted using semi-empirical and *ab initio* volume and energy calculations to develop an understanding of phase stability. Volume minimisation is the dominant driving force in almost all high-pressure phase transitions, although the relief of unfavourably compressed contacts can also play a role. Analysis of volume changes are therefore critical in the interpretation of phase transitions at high pressure, and we have developed a Monte Carlo algorithm for calculation of occupied ('network') and unoccupied ('void') space in crystal structures [1]. The variation of the volumes of the voids and the network of intermolecular contacts with pressure sensitively reveals discontinuities associated with first and second order phase transitions, providing insight into the effect of compression. The method is shown to be especially useful for the correlation of high-pressure crystallographic and spectroscopic data, illustrated for naphthalene, where a phase transition previously detected by vibrational spectroscopy, and debated in the literature for over 80 years, has been revealed unambiguously in crystallographic data for the first time.

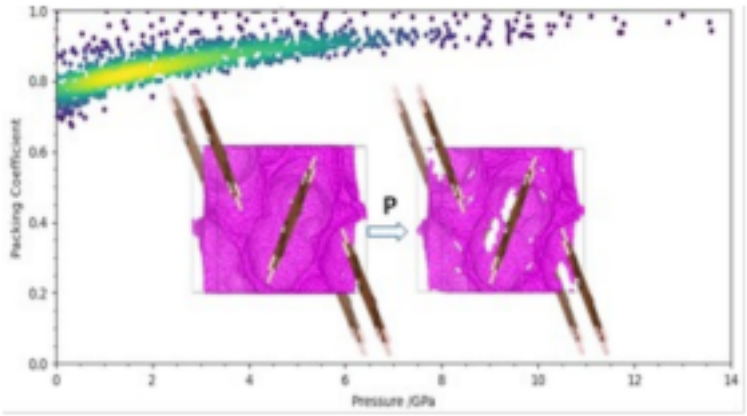

Figure 1:

Figure 1. Variation of packing coefficient with pressure. Inset: loss of interstitial void space in naphthalene at high pressure.

[1] C.J.G. Wilson, T. Cervenka, P.A. Wood, S. Parsons, Cryst. Growth Des., 2022, 22, 2328-2341.

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