Oral Contributions

[MS30-03] Looking beyond the harmonic approximation. Insights from ab initio molecular orbital calculations. Carole A. Morrison,[a] Anthony M. Reilly,[b]

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We could be forgiven for thinking of molecules as static, rigid entities, just like the models we build from plastic kits, but it is quite misleading to do so. They are dynamic. They vibrate, they twist and they turn. In a crystallographic refinement procedure this dynamic (or thermal) motion is captured in the Debye-Waller factor, which when described within the confines of the harmonic approximation gives us the thermal ellipsoid.

But do molecular crystals really vibrate in an harmonic way? Is the thermal ellipsoid, devised over 50 years ago, still fit for purpose? Answers to these questions can be obtained from molecular dynamics (MD) simulations, but these come with their own challenges. This talk will focus on the issues faced by ab initio MD simulations to be able to faithfully reproduce the sizes and orientations of thermal ellipsoids for molecular crystalline systems. Once confidence has been obtained, the rewards can be great: we can look beyond the harmonic approximation and devise new generic anharmonic Debye-Waller factors based on simple distortions of the much-loved thermal ellipsoid. This talk we will also present results based on ab initio MD simulations that highlight the knock-on impact on bond distances if the thermal motion is described anharmonically.

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