

**Determining suitable periodic DFT methods for modelling Titan-relevant molecular minerals**N.D Stapleton<sup>1</sup>, H.E. Maynard-Casely<sup>2</sup>, S.A Moggach<sup>1</sup>, D. Spagnoli<sup>1</sup>

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Saturn's largest moon, Titan, has geological features similar to those found on Earth, with seas, lakes and sweeping dunes. Unlike the Earth, however, the temperature hardly varies from around 92 K and the surface composition is dominated by molecular materials composed of H, C and N. The presence of liquid hydrocarbon seas and an active weather system on Titan could allow for deposited 'pure' compounds from the atmosphere to mix and form molecular co-crystals. No comprehensive computational chemical methods have been applied to all currently known Titan co-crystals. Determination of co-crystal structures could lead to more complete understandings of how geological processes affect and interact with minerals on the surface of Titan, as currently little is known of such phenomena [1].

A thorough periodic density functional theory (DFT) study of the set of structurally determined Titan-relevant molecular co-crystals and the single-component crystals of their respective co-formers was completed. A range of different exchange-correlation functionals were tested along with various dispersion correction methods. This included a combination of post-hoc corrected and inherent van der Waals dispersion functionals, including the cutting edge D4 correction, which has been shown to accurately reproduce unit cell volumes and lattice energies of a generic benchmark set [2]. To ensure structures converged as accurately as possible, a multi-step geometry optimisation was performed on all systems. This method has been previously used by Taylor and Day [3] on a large set of molecular crystals whose structures were obtained from diffraction data. The more accurate DFT dispersion corrected methods calculate lattice parameters and cell volumes closer to experimental data. Many of the functionals consistently underestimated cell volumes, which has been observed in previous work by Moellmann and Grimme [4]. Overall, we found the RPBE-D4 functional performed the best on average for recreating experimental cell volumes. Co-crystallisation was generally seen to be a thermodynamically unfavourable process, however, the magnitude of decrease in stability was usually relatively small.

[1] Cable, M. L., Runčevski, T., Maynard-Casely, H. E., Vu, T. H. & Hodyss, R. (2021). *Acc Chem Res.*, 54, 3050.

[2] Caldeweyher, E., Mewes, J.-M., Ehlert, S. & Grimme, S. (2020). *Phys. Chem. Chem. Phys.*, 22, 8499.

[3] Taylor, C. R. & Day, G. M. (2018). *Crst. Growth Des.* 18, 892.

[4] Moellmann, J. & Grimme, S. (2014). *J. Phys. Chem. C.*, 118, 7615.

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