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Supplementary Information to

The Structure of Methanol at 5.09 GPa: the Fortuitous Formation of a New High-Pressure Phase

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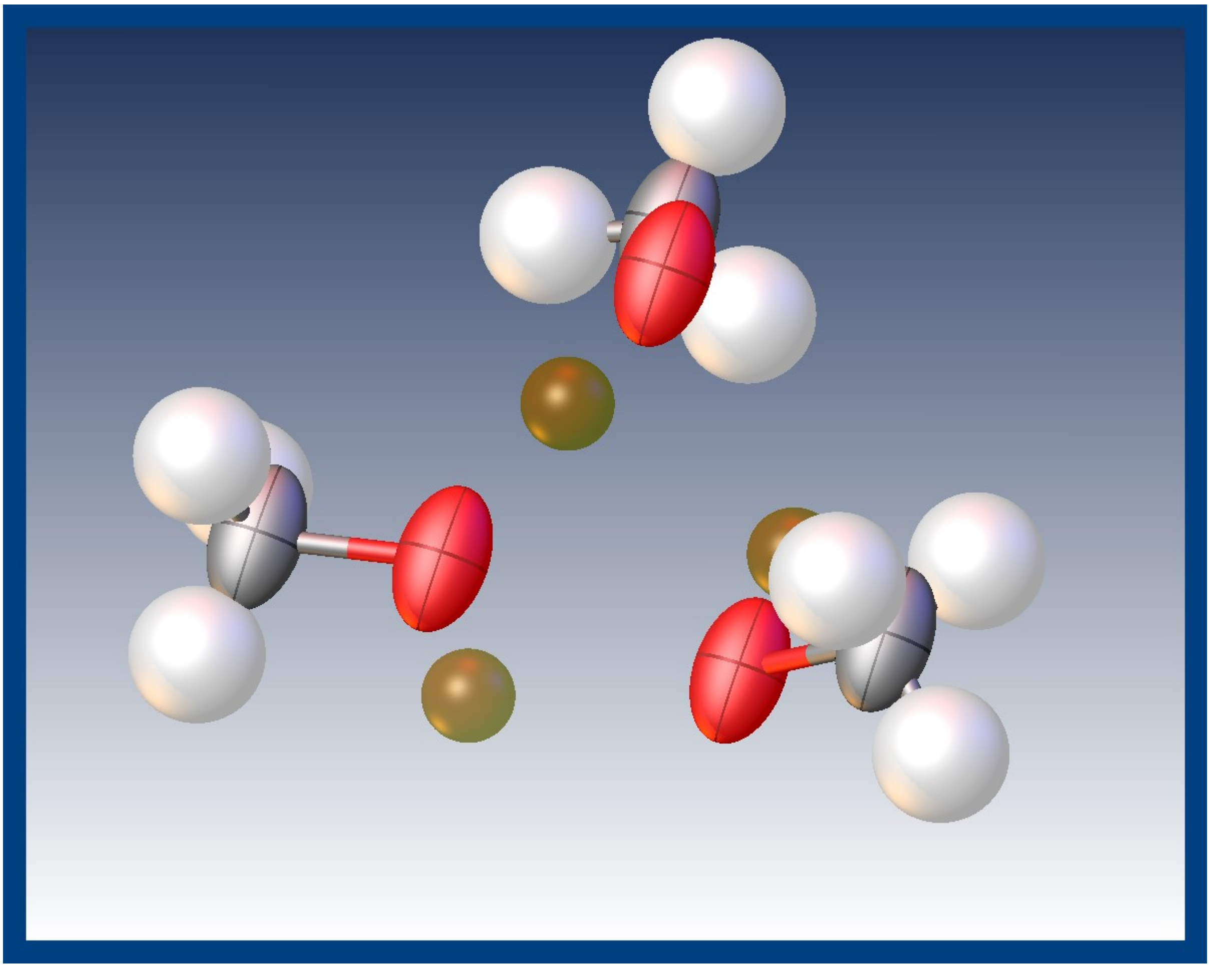

Figure S1: Difference Fourier map showing 'visible' hydroxyl O-atom positions (in orange) of the asymmetric unit in ε-methanol. Atoms are coloured as follows: C – grey, O – red, H – white.

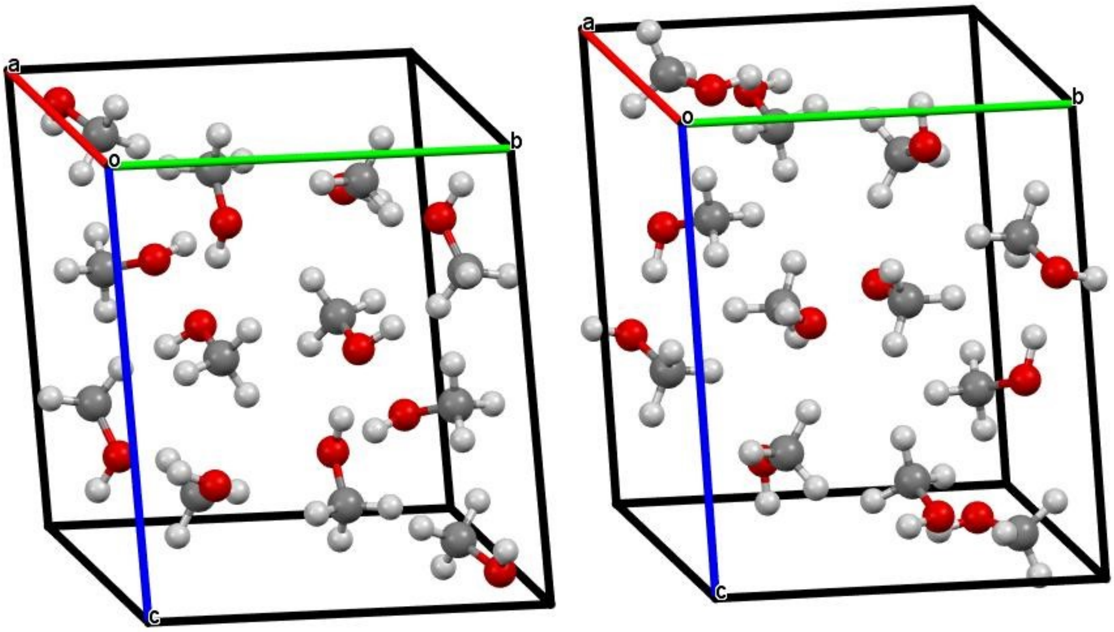

Figure S2: Unit cell contents of optimised structures of proposed orientations for the ε-phase of methanol. Left: ε_1. Right: ε_2.

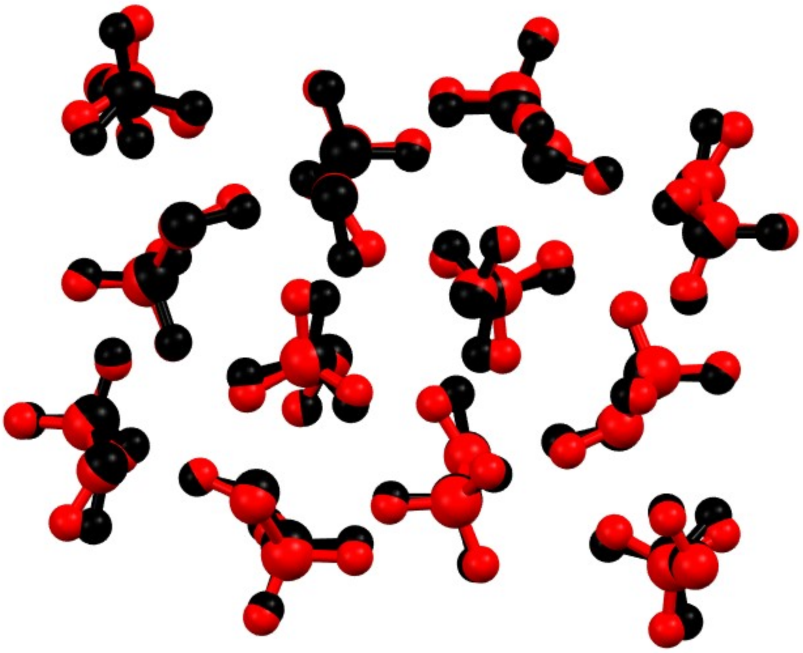

Figure S3: Overlap of the ε_2 optimised structure (black) and *ε*-methanol experimental crystal structure (red) viewed down the *a*-axis. Note, the experimental structure H-atoms positions were normalised before overlaying, with a RMSD of 0.0147 Å.

DFT Error Analysis

Complete determination of the uncertainty that arises from relative stabilities of molecular crystals with periodic DFT methods can be a difficult task.[1] A periodic DFT study of molecular crystals by Moellmann and Grimme has estimated a mean absolute error of 4.5 kJ mol^{-1} for the same level of theory used in the present study.[2] The energy difference of ε_1 and ε_2 is -5.8 kJ mol^{-1}, which is greater than the error of 4.5 kJ mol^{-1}, but this does not completely guarantee that ε_1 is lower in energy than ε_2. However, in a more recent study of molecular co-crystals, Taylor and Day noted that when comparing relative stabilities of similar crystal structures, errors that arise from how D3-corrected methods treat bonds in general sense may systematically and fortuitously cancel out.[1] This would lead to reduced uncertainty in calculations of relative energies between similar crystal structures. Therefore, our calculations very likely yielded a more accurate result that what appears from a simple comparison to a benchmark-determined error, albeit by some undetermined amount.

Crystallographic details

Crystallographic data for the structure reported in this paper has been deposited at the Cambridge Crystallographic Data Centre (2202722). Copies of the data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.KCB21EZ, UK (fax +441223336033; deposit@ccdc.cam.ac.uk).

References

[1] C. R. Taylor, G. M. Day, *Cryst. Growth Des.* **2018**, *18*, 892-904.
[2] J. Moellmann, S. Grimme, *J. Phys. Chem. C.* **2014**, *118*, 7615-7621.