Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Structure Prediction of the Solid Forms of Methanol: An Ab Initio Random Structure Searching Approach

Supporting Information

by

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Fig. S1. Relative enthalpy–pressure diagrams obtained by different dispersion-corrected functionals. The horizontal axis is pressure (GPa), and the vertical axis is relative enthalpy with respect to the β phase (meV/molecule). The trend for the change of the relative enthalpy with pressures is the same by these four functionals. The range of phase transition pressure for α–δ′ and α–γ transitions by the PBE-D3 functional is 1.0–1.5 GPa higher than that by the optB86b functional. A similar trend was also observed on PBE-D2 and optB88 functionals. In summary, Grimme-type dispersion-corrected functionals predicted slightly higher phase transition pressure than vdW-DF functionals did.

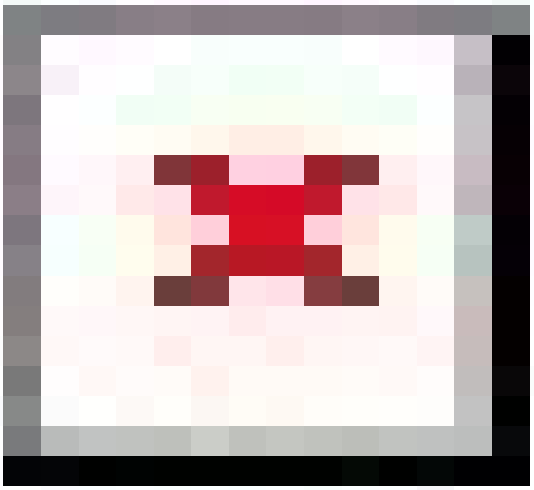


Fig. S2 The first 200 structures from AIRSS constrained by (a) the lattice parameter of the α phase with four methanol molecules and (b) The lattice parameter of the γ phase with six methanol molecules. P1 and $\bar{P}1$ space groups were implemented during the search. The vertical axis is the energy in meV per molecule relative to the structure with the lowest energy on each search.

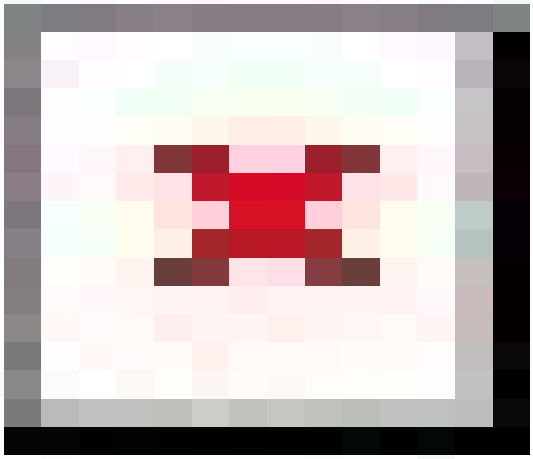


Fig. S3. Energy-unfavorable packing (dashed green circle) of methanol molecules in 4R2S. The OH···O hydrogen bond is depicted using blue dashed lines.

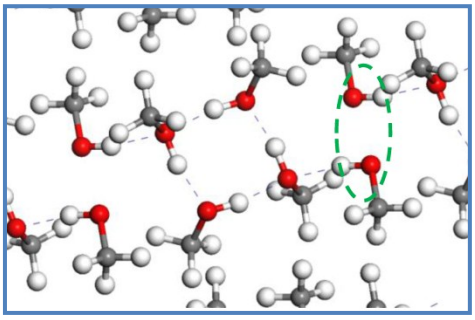
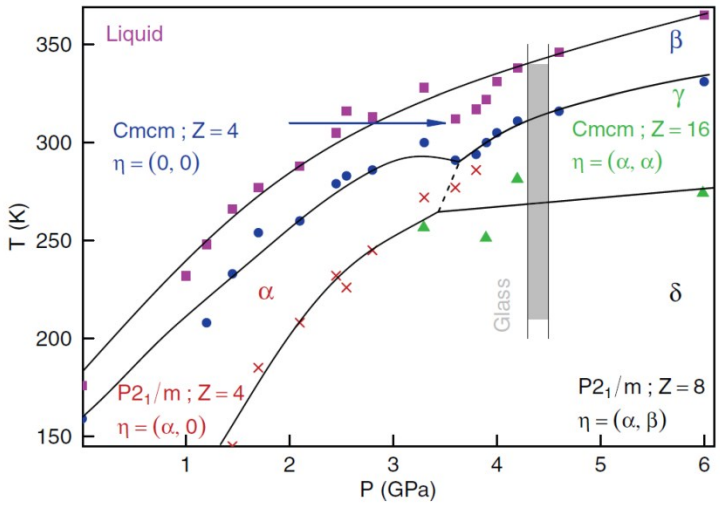


Fig. S4. Photocopy of the phase diagram of methanol based on the anomalies of the static dielectric constant by Kondrin (*The Journal of Chemical Physics* 139, 084510, 2013). The points correspond to experimental data, and the solid lines are drawn by eye observations of the data. The gray area indicates the region of methanol glass formation, and the blue arrow represents the "β–β" phase transition suggested by the author. The dashed line between α and γ phases is used because the author could not determine the phase boundary through the experiment. The phase diagram also displays the unit cell information of different phases such as symmetry, molecule number, and isotropy order parameter. However, some information differs from that in other studies, and the author did not explain the discrepancies in the article. To avoid confusion among readers, this phase diagram is placed in the supporting information. Reprinted with permission from [*The Journal of Chemical Physics* 139, 084510, 2013]. Copyright [2013], American Institute of Physics



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H23	H	0.82035	0.61717	0.03285	0.01267	Uiso	1.00
H24	H	0.87545	0.70394	0.51082	0.01267	Uiso	1.00
H25	H	0.26022	0.60008	0.23106	0.01267	Uiso	1.00
H26	H	0.33175	0.77371	0.01953	0.01267	Uiso	1.00
H27	H	0.59280	0.54517	0.93299	0.01267	Uiso	1.00
H28	H	0.89454	0.79059	0.82259	0.01267	Uiso	1.00
H29	H	0.09689	0.53973	0.63820	0.01267	Uiso	1.00
H30	H	0.34478	0.92825	0.48670	0.01267	Uiso	1.00
H31	H	0.80956	0.46231	0.56640	0.01267	Uiso	1.00
H32	H	0.05713	0.85108	0.41496	0.01267	Uiso	1.00