

Supplementary Information

Similarities between Tetrahydrofuran Clathrate Hydrate After Pressure-Induced Amorphization and Aqueous Tetrahydrofuran Solution: An in-situ Raman and Infrared Spectroscopic Study

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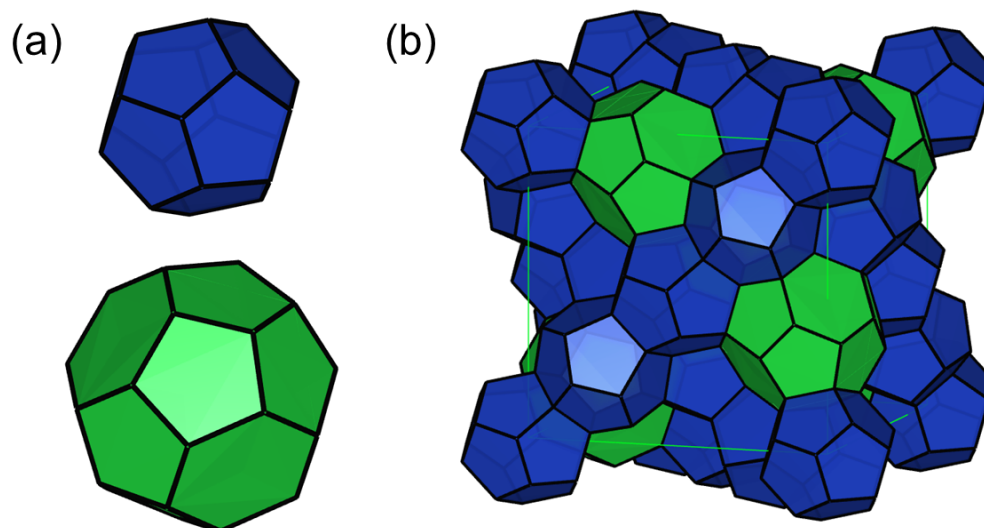


Fig. S1 Crystal structure of the type II clathrate hydrate.^{S1} (a) Two cages in the type II clathrate hydrate: small (pentagonal dodecahedron, 5¹², S1) cage (blue) and large (hexakaidecahedron, 5¹²6⁴, L) cage (green). (b) Unit cell composed of sixteen small cages and eight large cages.

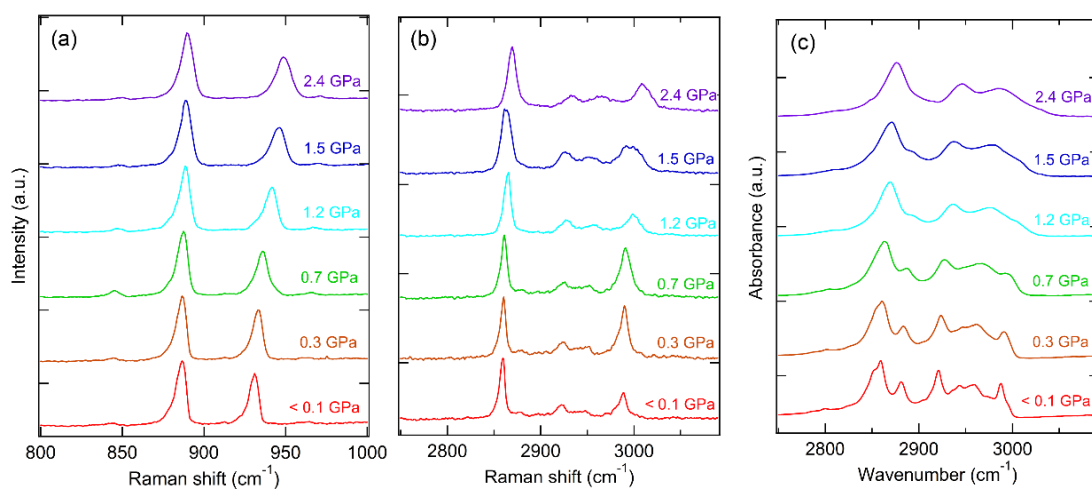


Fig. S2 Raman and IR spectra of solid THF measured on the isothermal compression at 100 K.

(a) Raman spectra in the THF ring stretching region. (b) Raman and (c) IR spectra in the CH stretching region.

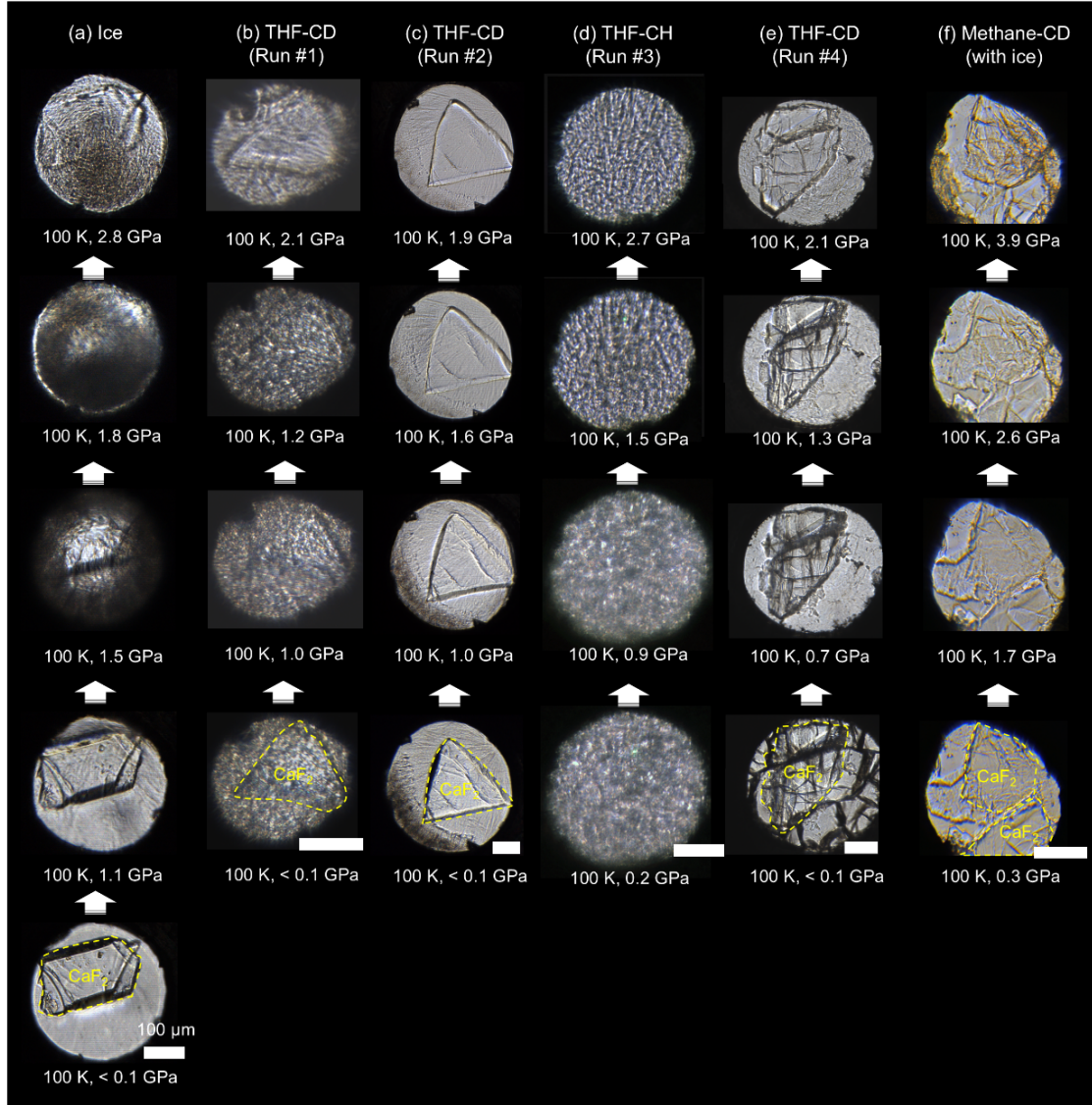


Fig. S3 Photomicrographs for THF-CD/CH (Runs #1 – 4), deuterated ice and methane clathrate deuterate (methane-CD) in the DAC sample chamber on the isothermal compression at 100 K. Methane-CD underwent PIA at 2.5 – 3 GPa. ^{S2}

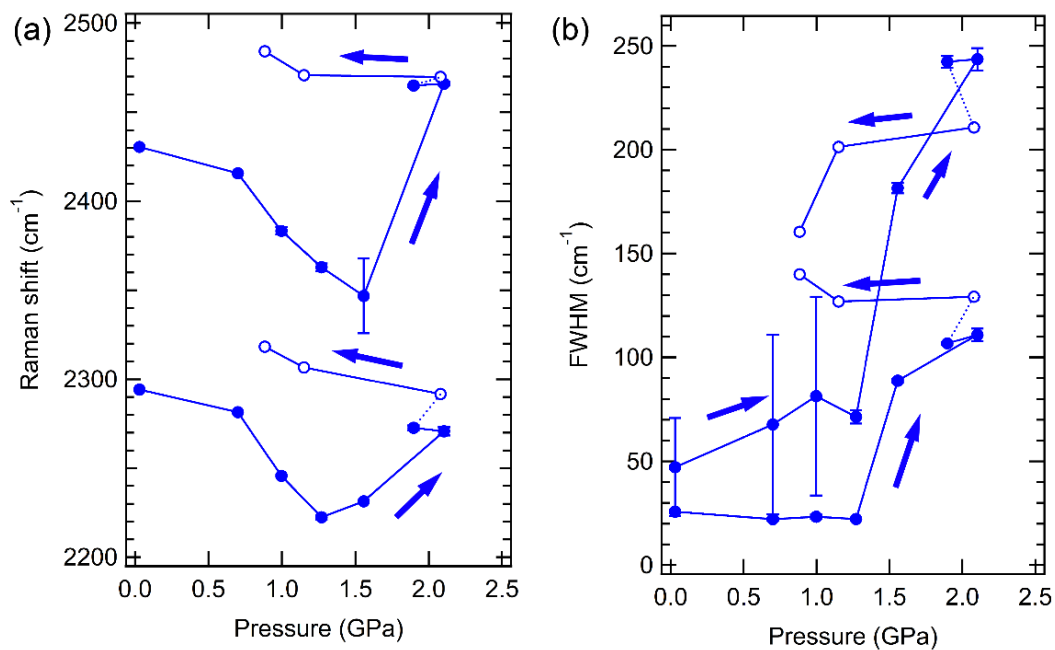


Fig. S4 Peak wavenumbers (a) and FWHM (b) of the Raman bands due to coupled OD stretching modes of THF-CD as a function of pressure at 100 K (Run #4). Filled and open symbols show data before and after annealing, respectively. Error bars in each graph indicate the variation in the values depending on the position in the sample hole.

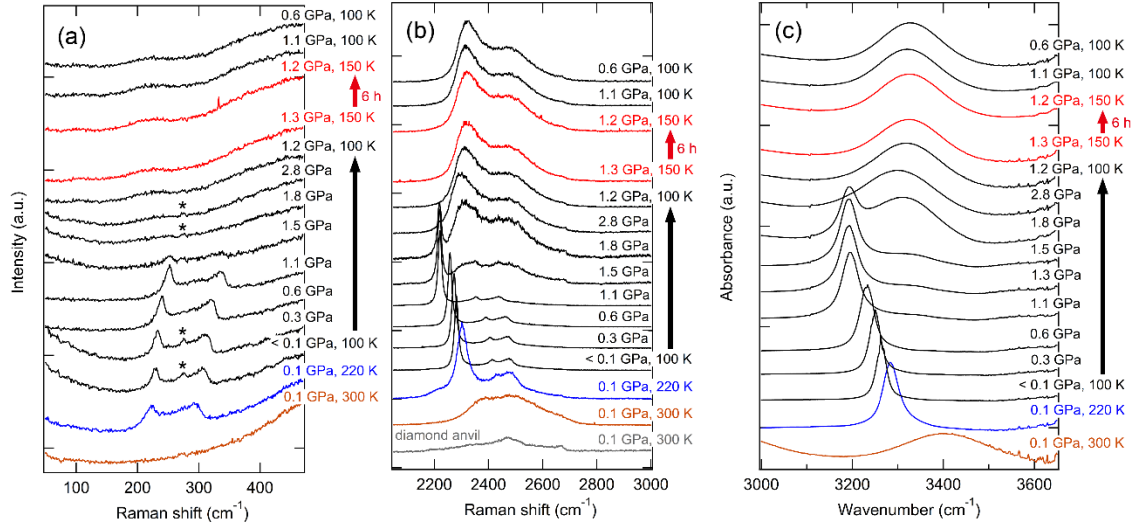


Fig. S5 Changes in Raman and IR spectra of D₂O with small amount of HDO (0.1 %) along the experimental P–T path shown in **Fig. 1**. (a) Raman spectra of the phonon/intermolecular mode. The peaks marked with an asterisk are an artifact due to stray light. (b) Raman spectra of the coupled OD stretching modes. (c) IR spectra of the uncoupled OH stretching modes.

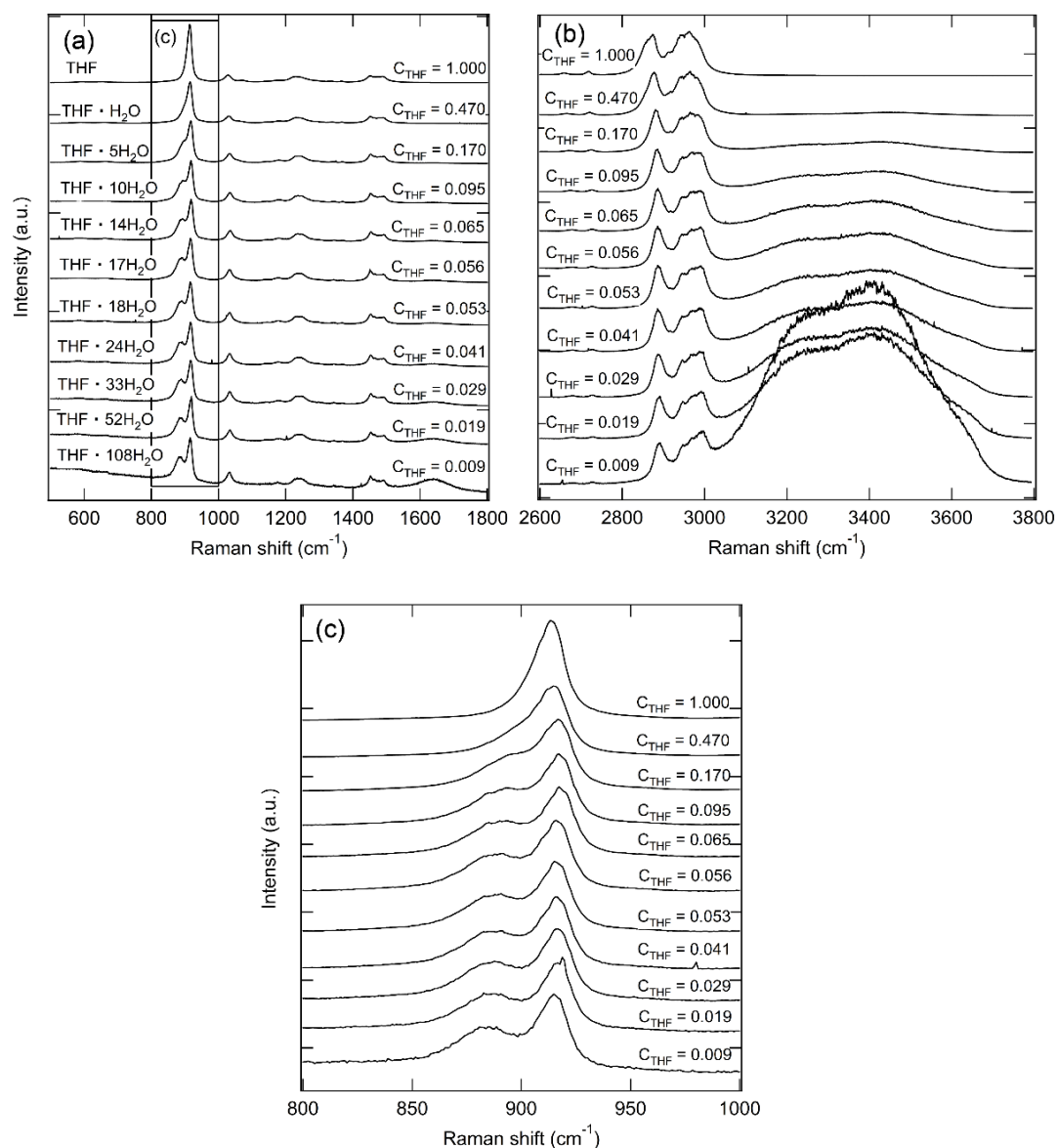


Fig. S6 Raman spectra of the aqueous solutions of THF measured at ambient pressure and room temperature. (a) the THF ring stretching, CH_2 rocking and CH bending region, (b) the CH and OH stretching region and (c) magnified view around the THF ring stretching region. C_{THF} indicates molar fractions of THF.

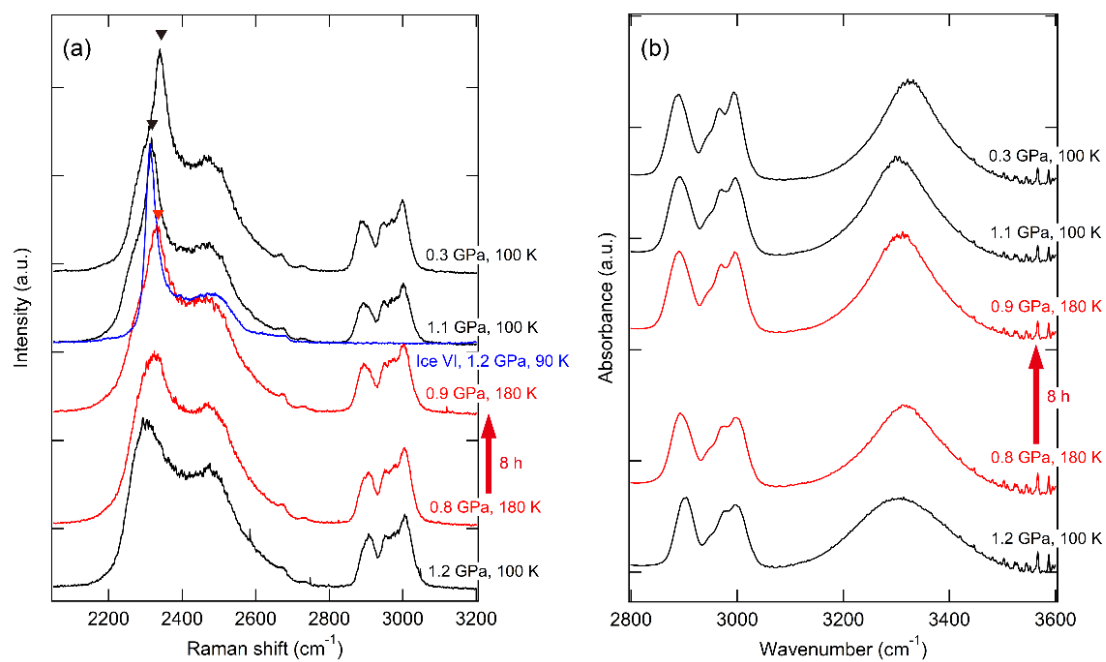


Fig. S7 Raman spectra (a) and IR spectra (b) of the amorphous THF-CD before, during (red curves), and after annealing (Run #2). The Raman spectrum of ice VI is also shown.

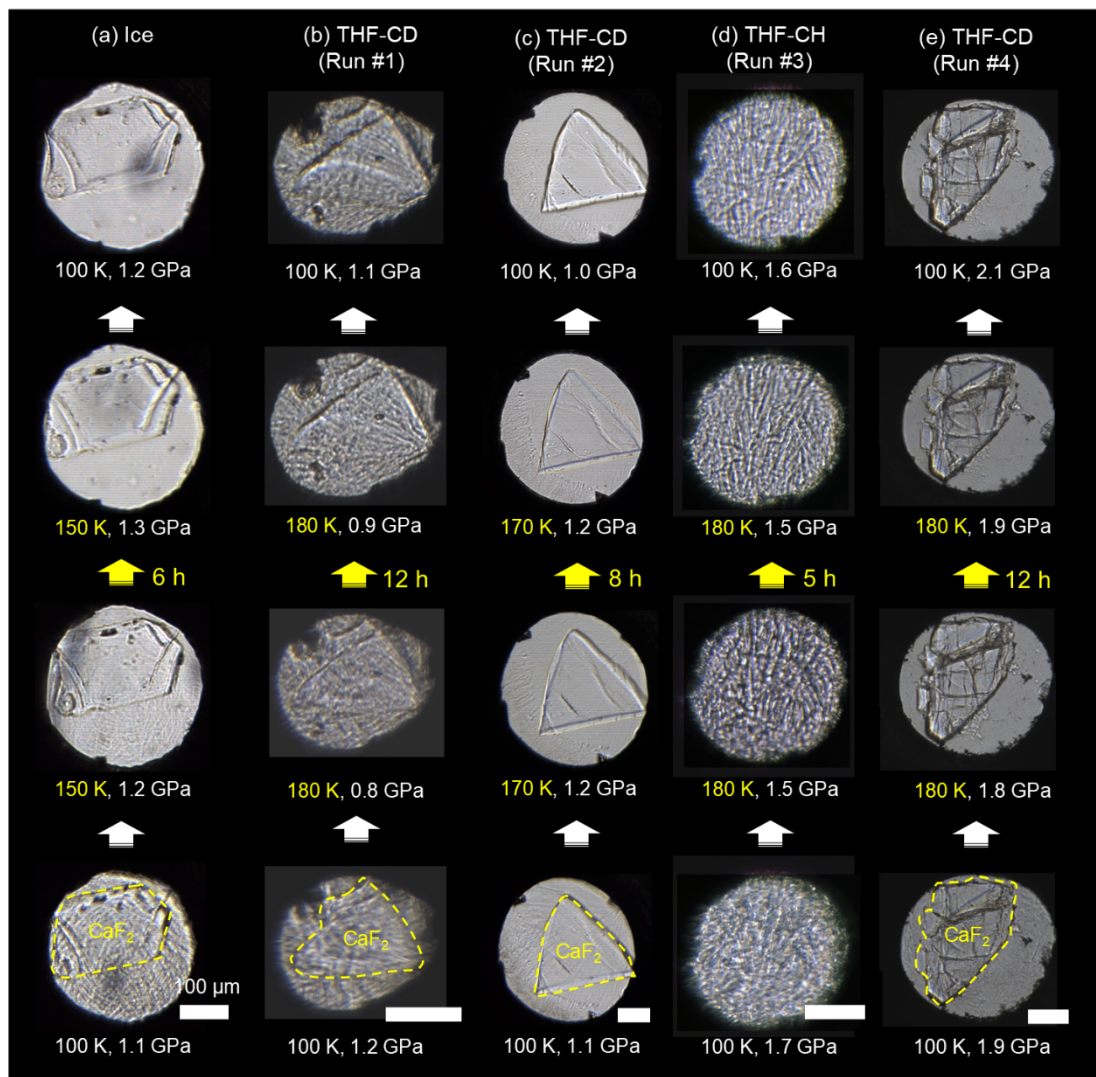


Fig. S8 Photomicrographs for THF-CD/CH (Runs #1 – 4) and deuterated ice before, during, and after annealing.

References

- S1 K. Momma and F. Izumi, *J. Appl. Crystallogr.*, 2011, **44**, 1272–1276.
- S2 N. Noguchi, Y. Shiraishi, M. Kageyama, Y. Yokoi, S. Kurohama, N. Okada and H. Okamura, *Phys. Chem. Chem. Phys.*, 2023, **25**, 22161-22170.