Supplementary information

Direct observation of pressure-induced amorphization of methane/ethane hydrates using Raman and infrared spectroscopy

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Fig. S1 Crystal structure of the type I clathrate hydrate. (a) Two cages in the type I clathrate hydrate: small (pentagonal dodecahedron, $5^{12}$) cage (blue) and large (tetrakaidecahedron, $5^{12}6^2$) cage (brown). (b) Unit cell composed of two small cages and six large cages.
**Fig. S2** Normal modes of the methane (a) and ethane molecules (b). The frequencies for the free molecules and Raman and IR activity are shown. In the figures “Raman” and “IR” indicate Raman and IR activity, respectively.
Fig. S3 Raman spectra of MH on the isothermal compression at 10 K. (a) Selected spectra of the OD and CH stretching ($\nu_1$, $\nu_3$) modes. The OD stretching bands of MH are marked with reverse triangles. (b) Magnified view around the $\nu_1$ mode. (c) Peak wavenumbers of the $\nu_1$ Raman bands as a function of pressure at 10 K. (d) FWHM of the $\nu_1$ Raman bands of the methane molecule in the small cage as a function of pressure at 10 K. In (c) and (d), gray points show the dataset at 100 K (Fig. 3).
Fig. S4 IR spectra of MH and EH at 2000–4000 cm$^{-1}$. 
Fig. S5 IR spectra of the CH stretching modes of MH (a) and EH (b) on cooling.
Fig. S6 IR spectra showing the CH stretching mode of EH on the isothermal compression at 100 K. The spectrum of solid ethane is also shown.
References
