Infrared Spectra of Gas Hydrates from First-Principles

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SI 1. Non-convoluted IR spectra at equilibrium

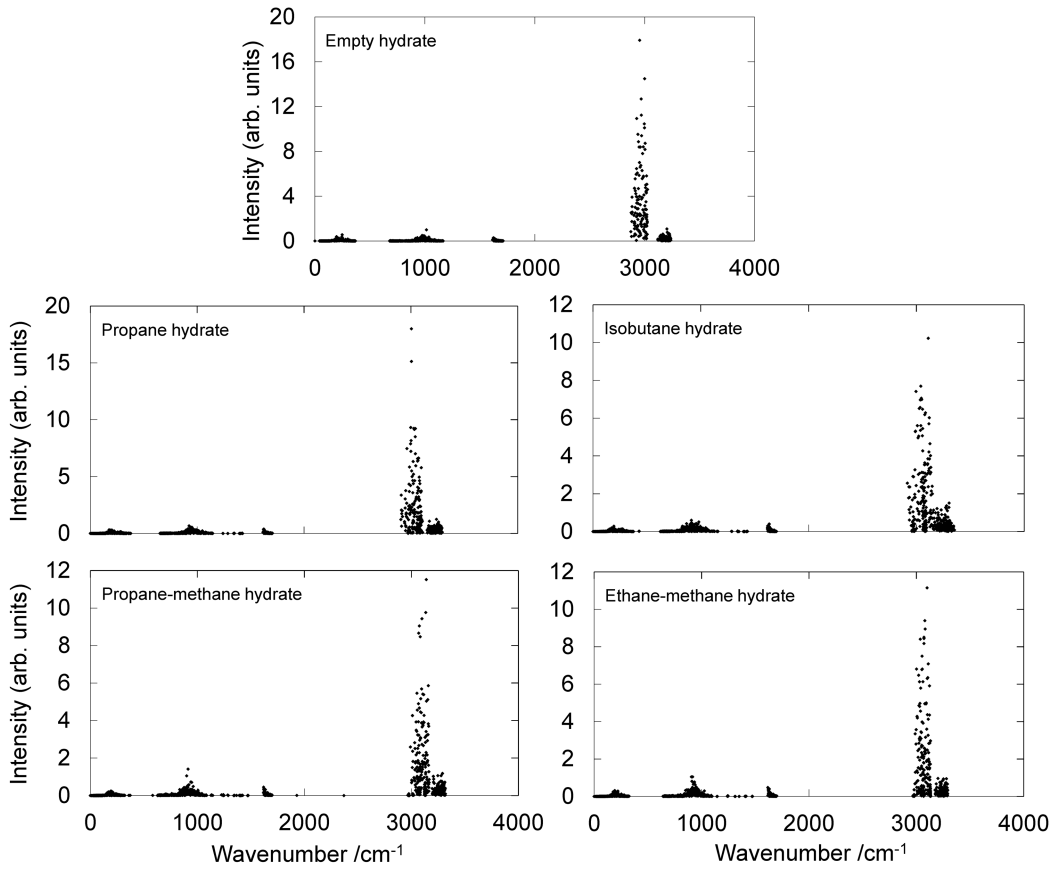

Figure S1. Raw IR data of empty, propane, isobutane, propane-methane, and ethane-methane sII gas hydrates at equilibrium (0 K and 0 GPa).

SI 2. Hydrogen bond angles in sII gas hydrates

Table S1. Hydrogen bond angles in sII gas hydrates

Guest molecule(s)	H-bond angle (°)	Standard deviation (°)
Empty	176.76	2.023
Propane	176.70	2.000
Isobutane	176.57	2.066
Ethane-methane	176.72	1.971
Propane-methane	176.72	2.031

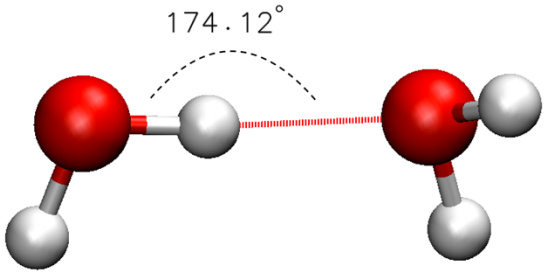

Figure S2. Schematic illustrating a hydrogen bond angle between two water molecules in sII propane-methane hydrates.

SI 3. IR spectra under pressure

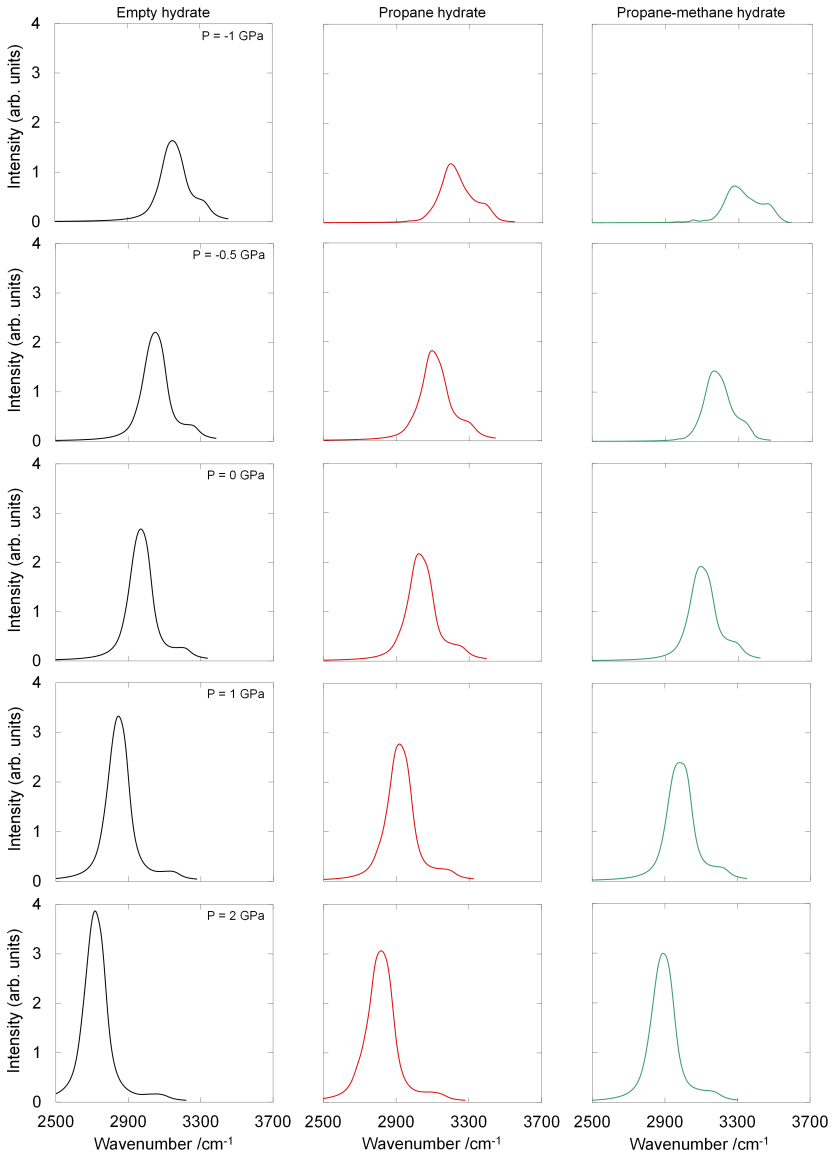

Figure S3. OH stretching region under pressure in empty, propane, and propane-methane sII hydrates.

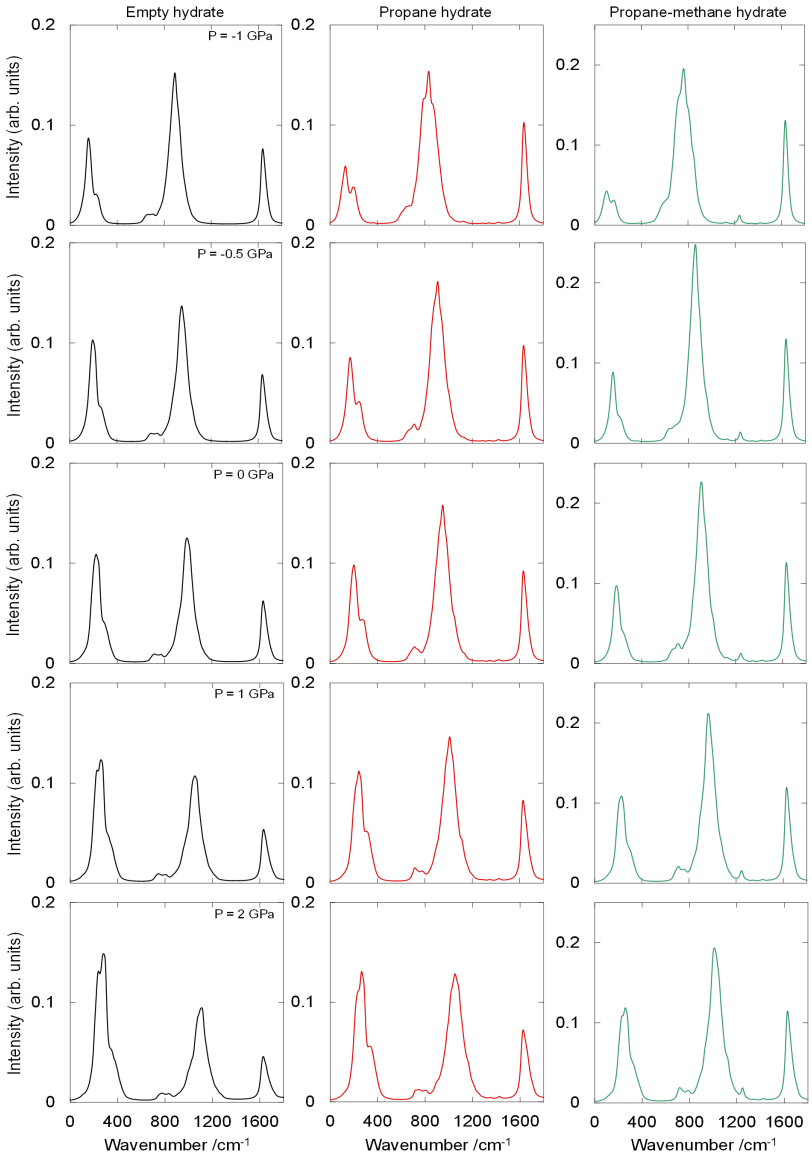

Figure S4. Low frequency region under pressure in empty, propane and propane-methane sII hydrates.

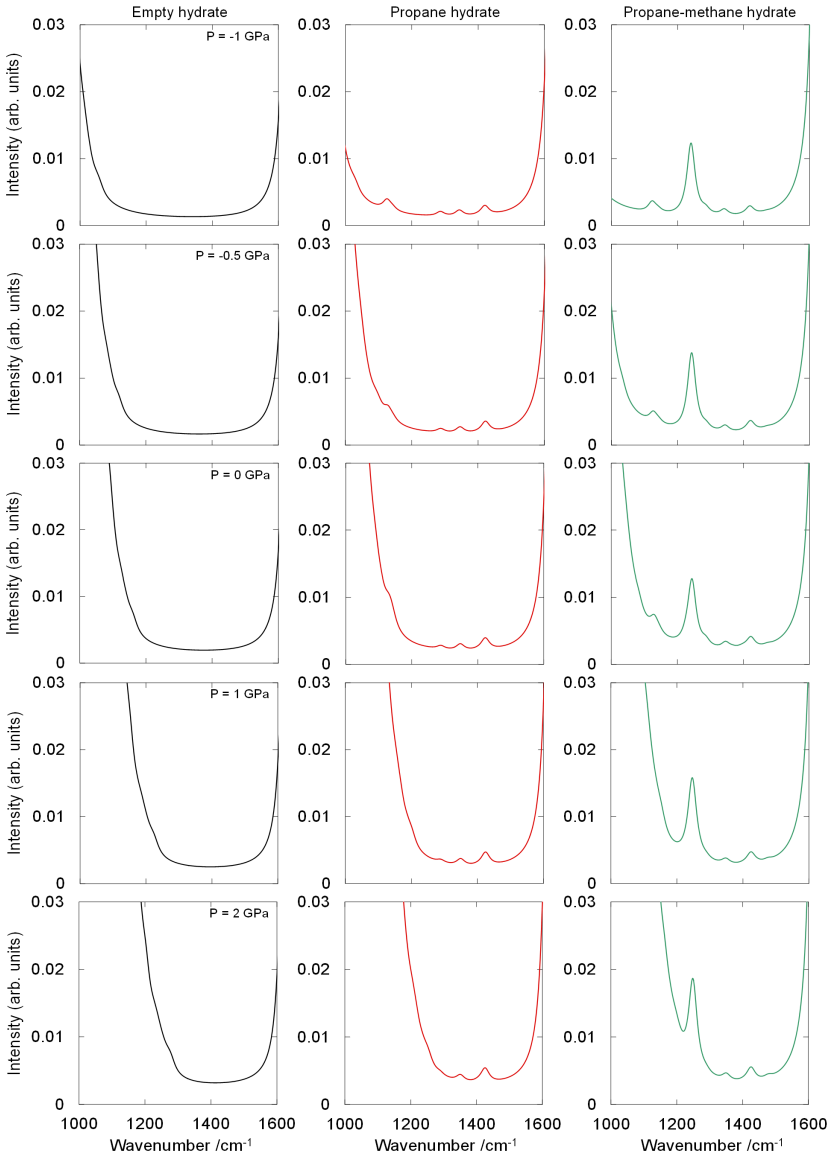

Figure S5. Guest molecule bending region under pressure in empty, propane, and propane-methane sII hydrates.

SI 4. sII gas hydrate vibrational mode peak frequency data

Table S2. Vibrational mode peak frequency summary of the H_2O molecules for empty, propane, and propane-methane hydrates under pressure.

Pressure (GPa)	H-bond stretch /cm^{-1}			Libration mode /cm^{-1}			Bending mode /cm^{-1}		
	Empty	Propane	Propane-methane	Empty	Propane	Propane-methane	Empty	Propane	Propane-methane
-1.0	155.23	128.80	100.95	890.23	832.80	761.95	1637.23	1635.80	1633.95
-0.5	193.94	169.46	154.96	950.94	908.46	857.96	1634.94	1633.46	1631.96
0.0	220.94	201.14	184.30	988.94	951.14	907.30	1633.94	1632.14	1631.30
1.0	258.94	243.14	226.35	1050.94	1009.14	963.35	1630.94	1629.14	1629.35
2.0	279.98	264.65	257.98	1110.98	1052.65	1008.98	1628.98	1626.65	1627.98

Pressure (GPa)	OH symmetric stretch /cm^{-1}			OH asymmetric stretch /cm^{-1}		
	Empty	Propane	Propane-methane	Empty	Propane	Propane-methane
-1.0	3149.23	3195.80	3275.95	3310.23	3377.80	3453.95
-0.5	3049.94	3096.46	3165.96	3249.94	3286.46	3333.96
0.0	2968.94	3024.14	3094.30	3199.94	3240.14	3285.30
1.0	2844.94	2917.14	2980.35	3126.94	3180.14	3214.35
2.0	2715.98	2817.65	2890.98	3054.98	3108.65	3166.98

SI 5. Hydrogen bond force constants under pressure

Table S3. The effect of pressure on the hydrogen bond strength and Young's modulus of empty, propane, and propane-methane sII hydrates.

Pressure (GPa)	H-bond length /Å[a]			H-bond force constant /N·m^{-1}			Young's modulus (IR) /GPa		
	Empty	Propane	Propane-methane	Empty	Propane	Propane-methane	Empty	Propane	Propane-methane
-1.0	1.839	1.909	2.018	1.345	0.926	0.569	7.32	4.85	2.82
-0.5	1.759	1.804	1.858	2.100	1.604	1.341	11.94	8.89	7.22
0.0	1.710	1.749	1.793	2.726	2.259	1.897	15.94	12.92	10.58
1.0	1.644	1.679	1.714	3.744	3.301	2.861	22.77	19.66	16.69
2.0	1.593	1.628	1.661	4.377	3.911	3.716	27.48	24.03	22.37

[a]Reference 34.

SI 6. Vertical shifting as a predictive tool

The reference point for the vertical shifting was taken to be empty sII hydrates, as it is the simplest case, and it is the base sII hydrate crystal structure without any guest molecules.

Propane sII hydrate shifting:

$$\omega_{new} = \omega_{old} + \left(\omega_{0,\ ref} - \omega_0\right) - 5.5 * P$$

$$\omega_{new} = \omega_{old} + 19.8 - 5.5 * P$$

Propane-methane sII hydrate shifting:

$$\omega_{new} = \omega_{old} + 36.65 - 5.5 * P$$

where ω_{new} is the shifted H-bond stretching frequency in cm^{-1}, ω_{old} is the original H-bond stretching frequency in cm^{-1}, $\omega_{0,\ ref}$ is the H-bond stretching frequency of the reference structure (in this case empty sII gas hydrates) at equilibrium in cm^{-1}, ω_0 is the H-bond stretching frequency at equilibrium in cm^{-1}, and P is the pressure in GPa. The '-5.5*P' term makes the overlap slightly better and was obtained from fitting 2nd degree polynomials to the three original frequency versus pressure data (the difference between the linear terms, see Figure S6). The quadratic terms were ignored as they are very similar among the three hydrates.

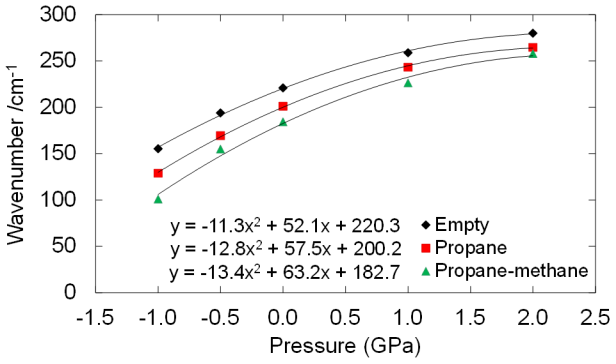

Figure S6. Second degree polynomial fittings of the H-bond stretching frequency data as a function of pressure for empty, propane and propane-methane sII hydrates.

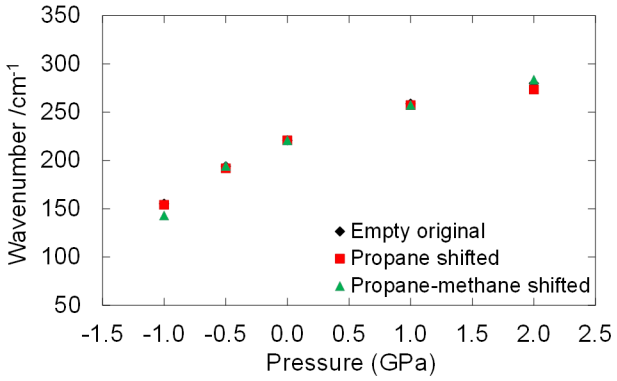

Figure S7. Vertically-shifted H-bond stretching frequency data sets for propane and propane-methane sII hydrates overlapping with empty sII hydrates.

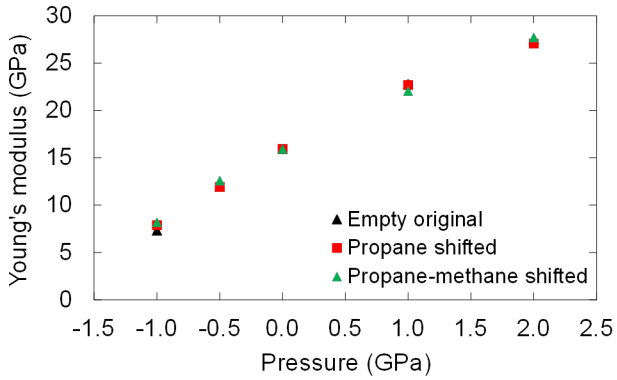

Figure S8. Vertically-shifted Young's modulus data sets for propane and propane-methane sII hydrates overlapping with empty sII hydrates.

Once we know that vertical shifting scales the data, we can use the frequency versus pressure data of our reference structure along with our equilibrium data for other structures to then create a frequency versus pressure curve over the same pressure range for the other structures. Since we have computed the equilibrium H-bond stretching frequencies for isobutane and ethane-methane sII gas hydrates (183.8 cm^{-1} and 194.6 cm^{-1}, respectively), we can estimate their H-bond stretching frequencies at other pressures using empty hydrates as a reference point, shown in Figure S9 as dashed lines.

Ethane-methane sII hydrate H-bond stretching frequency data extrapolation:

$$\omega = \omega_{ref} - \left(\omega_{0,\ ref} - \omega_0\right) + 5.5 * P$$

$$\omega = \omega_{ref} - 26.4 + 5.5 * P$$

Isobutane sII hydrate H-bond stretching frequency data extrapolation:

$$\omega = \omega_{ref} - 37.2 + 5.5 * P$$

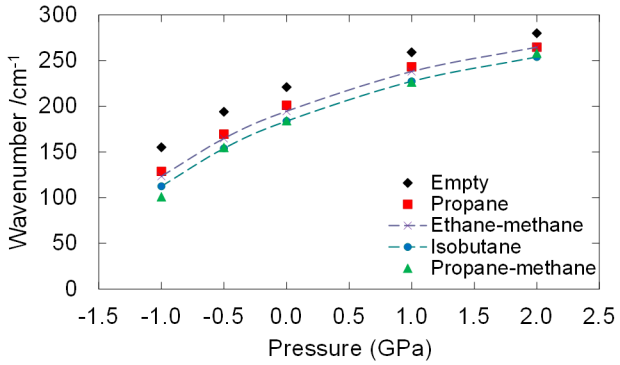

Figure S9. Extrapolation of the hydrogen bond stretching frequencies as a function of pressure in isobutane and ethane-methane sII hydrates using vertical shifting.

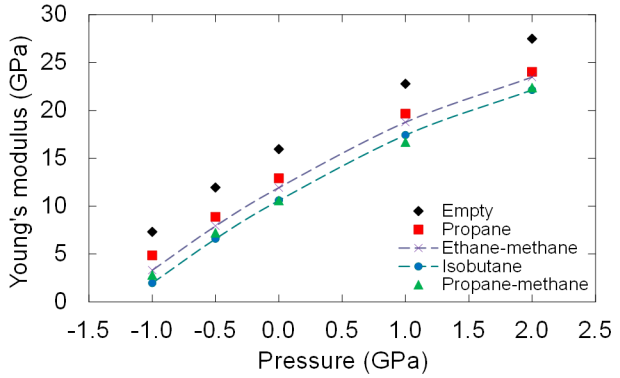

Figure S10. Extrapolation of Young's modulus as a function of pressure in isobutane and ethane-methane sII hydrates using vertical shifting.