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

Supporting Information

Thermodynamic and structural features of chlorodifluoromethane (a sI-sII dual hydrate former) + external guest (N_2 or CH_4) hydrates and their significance for greenhouse gas separation

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Table S1. Atomic coordinates and site occupancies for $CHClF_2$ hydrate at 133 K. Space group: $Pm\bar{3}n$, Lattice parameter: a = 11.9268(6) Å (R_{wp} = 12.3 % and χ^2 = 24.8) (background subtracted)

Atom	x	y	z	B (Å²)	g
O1	0.1844(2)	0.1844	0.1844	1.025(2)	1
O2	0	0.3082(3)	0.1158(3)	2.520(1)	1
O3	0	0.5	0.25	2.156(3)	1
H1	0.2317(3)	0.2317(3)	0.2317(3)	1.537(2)	0.5
H2	0	0.438(3)	0.191(3)	3.234(4)	0.5
H3	0	0.388(4)	0.151(5)	3.781(2)	0.5
H4	0	0.327(2)	0.0321(6)	3.781	0.5
H5	0.0535(19)	0.2484(14)	0.146(4)	3.781	0.5
H6	0.105(3)	0.234(3)	0.176(3)	1.537(2)	0.5
C_L1	0.24958	0.49168	0.02334	0.289(2)	0.1247(5)
F_L1	0.19174	0.57577	0.07071	0.289	0.1247
F_L2	0.20538	0.39387	0.05711	0.289	0.1247
Cl_L1	0.23936	0.50211	-0.1265	0.289	0.1247
H_L1	0.33779	0.49654	0.04686	0.433(4)	0.1247

Table S2. Atomic coordinates and site occupancies for $CHClF_2$ (5%) + N_2 (95%) hydrate at 133 K. Space group: $Fd\bar{3}m$, Lattice parameter: a = 17.0843(5) Å (R_{wp} = 10.1% and χ^2 = 13.1) (background subtracted)

Atom	x	y	z	B (Å^2)	g
O1	0.125	0.125	0.125	0.584(4)	1
O2	0.2175(2)	0.2175	0.2175	1.328(2)	1
O3	0.1823(2)	0.1823	0.3709(2)	0.226(2)	1
H1	0.1841(2)	0.1841	0.1841	1.993(4)	0.5
H2	0.1584(2)	0.1584	0.1584	0.877(6)	0.5
H3	0.208(3)	0.208	0.2742(12)	1.993	0.5
H4	0.198(2)	0.198	0.3168(13)	0.338(2)	0.5
H5	0.1407(3)	0.1407	0.375(4)	0.338	0.5
H6	0.233(5)	0.165(6)	0.395(5)	0.338	0.5
N_S1	0.9863	0.01166	0.02777	0.485	0.0595(5)
N_S2	0.01367	0.9883	0.9722	0.485	0.0595
C_L1	0.34566	0.37748	0.41507	3.933(6)	0.0385(4)
F_L1	0.31099	0.44067	0.38384	3.933	0.0385
F_L2	0.31345	0.313	0.38385	3.933	0.0385
Cl_L1	0.44838	0.37945	0.39291	3.933	0.0385
H_L1	0.33859	0.37735	0.47851	5.899	0.0385
N_L1	0.38282	0.3956	0.39966	0.0001	0.0032(4)
N_L2	0.36718	0.3544	0.35034	0.0001	0.0032

*The position of the N_2 molecules was fixed at the center of the hydrate cages during the refinement.

Table S3. Atomic coordinates and site occupancies for $CHClF_2$ (5%) + CH_4 (95%) hydrate at 133 K. Space group: $Fd\bar{3}m$, Lattice parameter: a = 17.1232(2) Å (R_{wp} = 9.72% and χ^2 = 12.5) (background subtracted)

Atom	x	y	z	B (Å^2)	g
O1	0.125	0.125	0.125	0.310(4)	1
O2	0.2168(2)	0.2168	0.2168	0.470(2)	1
O3	0.1824(16)	0.1824	0.3704(2)	1.651(2)	1
H1	0.1837(2)	0.1837	0.1837	0.705(4)	0.5
H2	0.1581(2)	0.1581	0.1581	0.465(6)	0.5
H3	0.205(4)	0.205	0.2724(19)	0.705	0.5
H4	0.193(6)	0.193	0.314(3)	2.477(3)	0.5
H5	0.1407(3)	0.1407	0.373(5)	2.477	0.5
H6	0.245(3)	0.153(2)	0.379(4)	2.477	0.5
C_S1	0	0	0	0.481	0.851
H_S1	0.01212	0.01486	0.9393	0.722	0.07092
H_S2	0.9905	0.9373	0.00498	0.722	0.07092
H_S3	0.9479	0.03097	0.01943	0.722	0.07092
H_S4	0.04949	0.01689	0.03627	0.722	0.07092
C_L1	0.34883	0.36139	0.35135	5.696	0.02394
F_L1	0.39436	0.41311	0.31399	5.696	0.02394
F_L2	0.36739	0.28927	0.32695	5.696	0.02394
Cl_L1	0.36543	0.36859	0.45465	5.696	0.02394
H_L1	0.2874	0.37357	0.33982	8.543	0.02394
C_L1	0.375	0.375	0.405	4.274	0.07092
H_L1	0.42315	0.40171	0.4369	6.411	0.01773
H_L2	0.33511	0.34728	0.44611	6.411	0.01773

H_L3	0.39784	0.33125	0.36483	6.411	0.01773
H_L4	0.3439	0.41976	0.37216	6.411	0.01773

*The position of the CH_4 molecules in the small (5^{12}) cages was fixed at the center of the hydrate cages during the refinement.

Table S4. Phase fractions of hydrate and hexagonal ice in the hydrate samples

	Fraction of hydrate (wt%)	**Fraction of hexagonal ice (wt%)**
$CHClF_2$ hydrate	95.2	4.8
$CHClF_2$ + N_2 hydrate	51.8	48.2
$CHClF_2$ + CH_4 hydrate	46.8	53.2

*The higher ice fraction in the binary hydrates was attributable to the smaller driving force for binary hydrate formation.

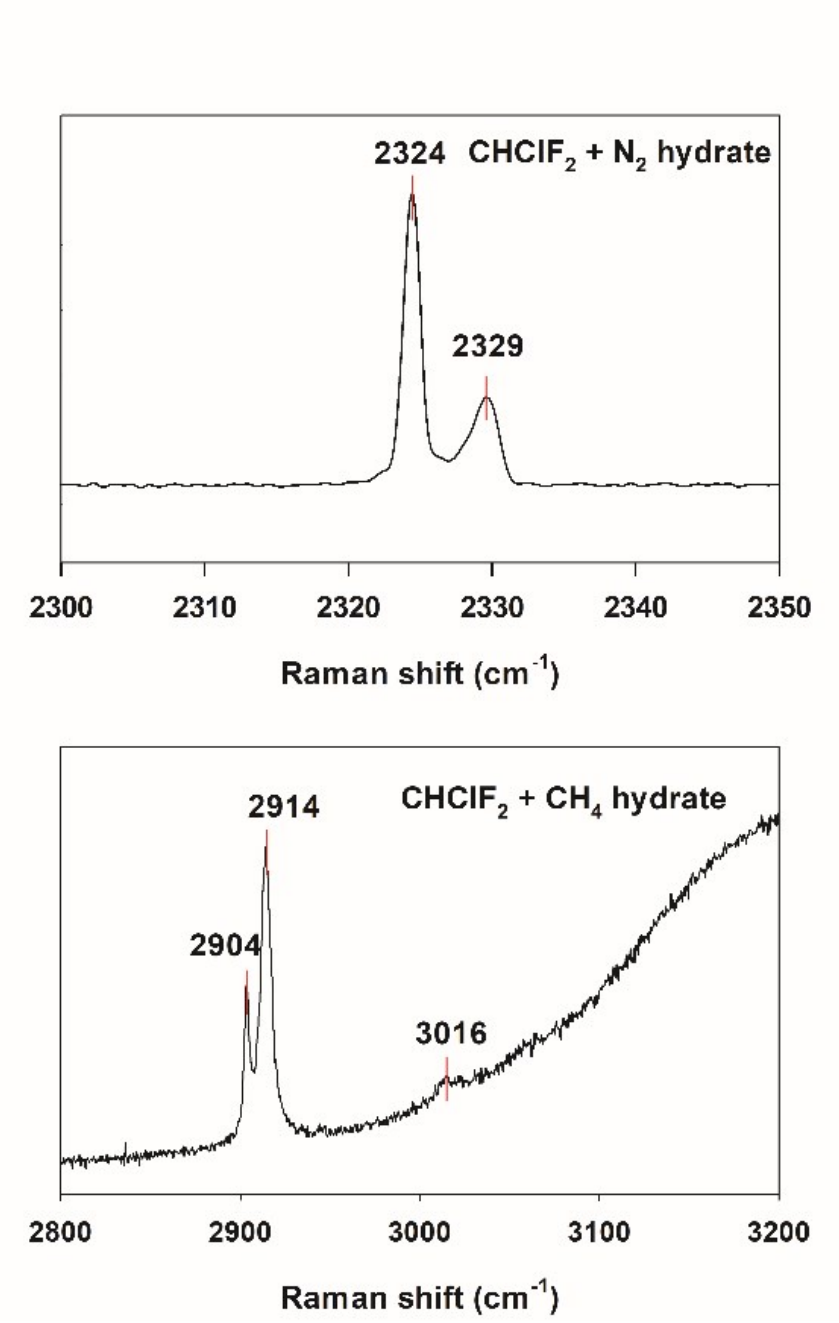

Fig. S1. *In situ* Raman spectra of binary $CHClF_2$ (5%) + N_2 (95%) hydrate (2300 – 2350 cm^{-1}) and binary $CHClF_2$ (5%) + CH_4 (95%) hydrate (2800 – 3200 cm^{-1}). The peak at 2329 cm^{-1} originated from residual air in the Raman probe.