



Supplementary Information for
Clathrate hydrates in interstellar environment

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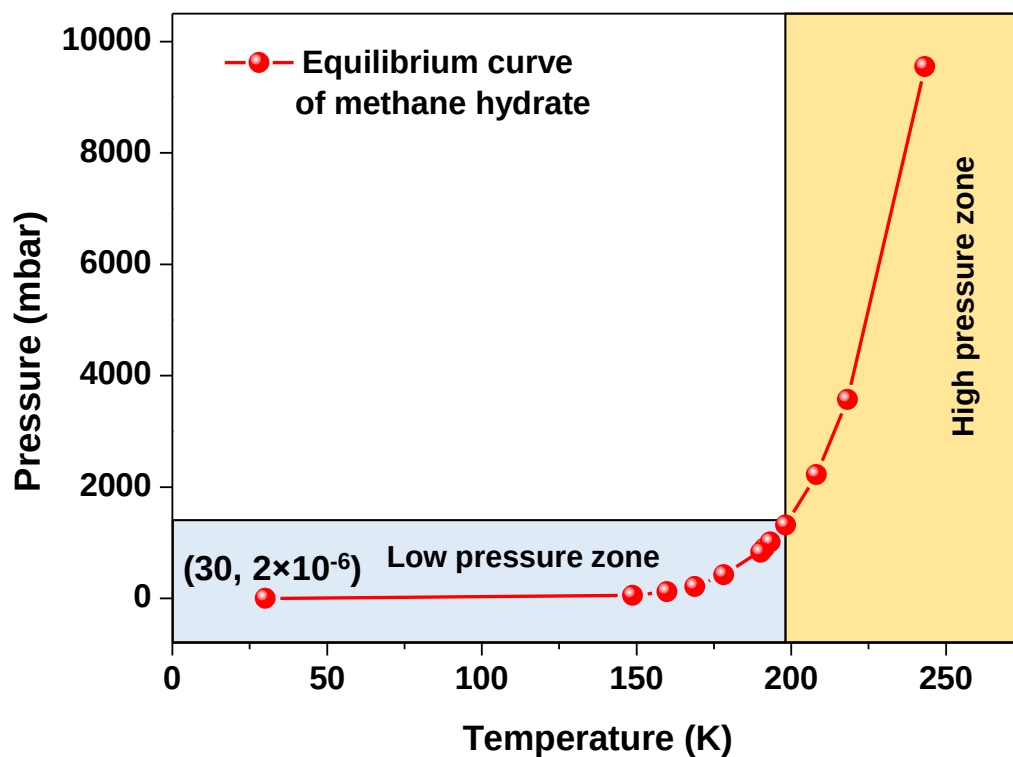


Fig. S1. Equilibrium curve for CH₄ clathrate hydrate. The curve depicts the stability of CH₄ clathrate hydrate as a function of temperature and pressure. Extrapolation of the curve to 30 K, denotes that CH₄ hydrate could be stable up to 2×10⁻⁶ mbar pressure. Two different pressure zones of the equilibrium curve are indicated with different colours.

Table S1

Comparison of the computational and experimental vibrational shift of CH₄ and CO₂ clathrate hydrate compared to free CH₄ and CO₂ using the B3LYP level of theory with 6-311++G (d, p) basis set. Optimized structures are shown.

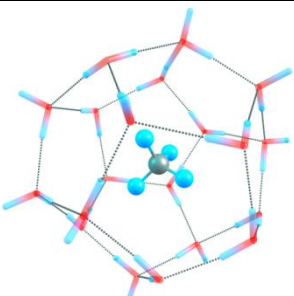
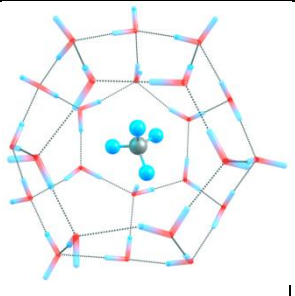
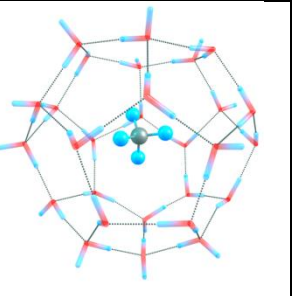
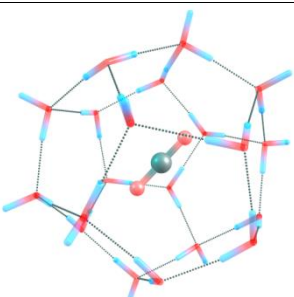
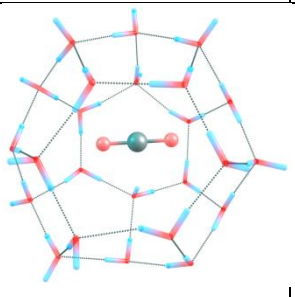
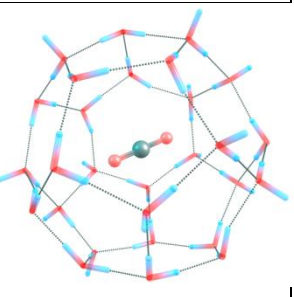
	5 ¹² cage	5 ¹² 6 ² cage	5 ¹² 6 ⁴ cage
CH₄ Clathrate hydrate			
Experimental shift	8.0 cm ⁻¹	-	-
Computational shift	9.3 cm ⁻¹	-9.2 cm ⁻¹	-9.1 cm ⁻¹
CO₂ Clathrate hydrate			
Experimental shift	-36.0 cm ⁻¹	-	-
Computational shift	-86.0 cm ⁻¹	-16.6 cm ⁻¹	15.8 cm ⁻¹

Table S2

Cartesian coordinates of CH₄ and CO₂ hydrate of 5¹², 5¹²6², and 5¹²6⁴ cages. The structure is optimized by using B3LYP level of theory and 6-311G (d, p) basis set.

1. Cartesian coordinates of CH₄ hydrate, 5¹² Cage:

O	-3.113799000	1.008215000	-2.047060000
H	-2.381895000	0.992378000	-2.714133000
H	-3.218239000	0.092361000	-1.737059000
O	0.761157000	-0.854957000	3.737123000
H	1.560278000	-0.913295000	3.191474000
H	0.148218000	-1.525272000	3.382112000
O	-1.002868000	0.947991000	-3.756640000
H	-0.309583000	1.569863000	-3.462264000
H	-0.578668000	0.068649000	-3.767502000
O	3.236217000	-0.955734000	2.135120000
H	3.165067000	-1.629113000	1.426215000
H	3.958821000	-1.235974000	2.706513000
O	-2.887629000	1.244738000	2.323347000
H	-2.864259000	1.802526000	1.528887000
H	-2.060639000	1.440855000	2.816443000
O	3.377885000	1.359687000	-1.664637000
H	3.390890000	1.479109000	-0.669870000
H	4.148373000	1.829781000	-2.000028000
O	-3.128400000	-1.415490000	1.789380000
H	-3.087569000	-0.450695000	2.003609000
H	-3.283298000	-1.476211000	0.831714000

O	2.934977000	-1.253851000	-2.282868000
H	3.114524000	-0.298037000	-2.098165000
H	3.468989000	-1.484359000	-3.050455000
O	-0.392260000	3.941626000	-0.321881000
H	-1.300177000	3.541485000	-0.260272000
H	-0.524169000	4.853345000	-0.602208000
O	-1.315789000	-3.368020000	-1.793775000
H	-0.766874000	-3.555981000	-0.981288000
H	-1.479818000	-4.222051000	-2.206772000
O	1.274060000	3.320629000	1.800109000
H	0.676657000	3.585035000	1.064246000
H	1.488010000	4.128382000	2.278270000
O	0.169003000	-3.814487000	0.364703000
H	-0.238946000	-3.488499000	1.197401000
H	1.064810000	-3.442266000	0.323879000
O	-2.826177000	2.787763000	-0.173036000
H	-2.934327000	2.091445000	-0.898850000
H	-3.618404000	3.333407000	-0.214224000
O	-1.055651000	-2.776069000	2.622687000
H	-1.388378000	-3.388609000	3.286796000
H	-1.855960000	-2.248031000	2.311115000
O	0.248875000	-1.605446000	-3.500857000
H	-0.291977000	-2.196372000	-2.949011000
H	1.080021000	-1.487073000	-3.016487000
O	3.377580000	1.642717000	0.955655000

H	3.325899000	0.801116000	1.444402000
H	2.669365000	2.221709000	1.300892000
O	2.888590000	-2.759494000	0.015226000
H	3.477233000	-3.513445000	-0.097366000
H	2.928022000	-2.253620000	-0.830955000
O	0.935500000	2.696090000	-2.620765000
H	1.742558000	2.253160000	-2.312497000
H	0.528794000	3.081979000	-1.827324000
O	-0.442940000	1.678091000	3.581632000
H	-0.011264000	0.807131000	3.705067000
H	0.163645000	2.190341000	3.026261000
O	-3.430939000	-1.707732000	-1.081963000
H	-2.720572000	-2.319774000	-1.376262000
H	-4.261351000	-2.100719000	-1.369631000
C	0.021699000	0.014389000	-0.004436000
H	0.102928000	-1.071075000	-0.064084000
H	-0.278043000	0.408448000	-0.974906000
H	0.984345000	0.437479000	0.283329000
H	-0.722369000	0.274011000	0.747594000

2. Cartesian coordinates of CO₂ hydrate, 5¹² Cage:

O	-0.868021000	3.588583000	-1.062084000
H	0.066218000	3.438070000	-1.408937000
H	-1.430117000	2.919226000	-1.508264000
O	-1.706223000	-2.946539000	2.022264000
H	-0.770471000	-3.035377000	1.755662000

H	-2.171975000	-2.696231000	1.191943000
O	1.596326000	3.122198000	-1.934612000
H	2.186276000	2.918271000	-1.169796000
H	1.624434000	2.318089000	-2.504875000
O	1.040272000	-3.445759000	1.251327000
H	1.080443000	-3.488309000	0.263060000
H	1.111111000	-4.360300000	1.563830000
O	-3.071044000	1.240215000	2.040835000
H	-2.352366000	1.862651000	1.806185000
H	-2.630359000	0.554553000	2.609979000
O	3.820642000	-0.340356000	0.262704000
H	3.423565000	-0.820900000	1.074377000
H	4.775571000	-0.307884000	0.426195000
O	-3.889176000	0.127430000	-0.240429000
H	-3.634618000	0.543466000	0.638883000
H	-3.459546000	0.689488000	-0.919834000
O	2.916361000	-1.388227000	-1.994854000
H	3.314869000	-1.004684000	-1.156094000
H	3.642988000	-1.470212000	-2.630746000
O	1.299069000	2.625576000	2.498043000
H	0.400986000	2.879855000	2.108578000
H	1.586053000	3.384128000	3.028280000
O	-1.096637000	-0.132027000	-3.637858000
H	-1.187205000	-1.051178000	-3.209203000
H	-1.310462000	-0.266456000	-4.573538000

O	1.098934000	0.151735000	3.562278000
H	1.180338000	1.088266000	3.236013000
H	1.116802000	0.201161000	4.529891000
O	-1.340796000	-2.497246000	-2.570136000
H	-1.970098000	-2.436408000	-1.803130000
H	-0.489404000	-2.775385000	-2.172927000
O	-1.038061000	3.174905000	1.441572000
H	-0.949613000	3.321711000	0.415082000
H	-1.488139000	3.970026000	1.766134000
O	-2.952018000	-2.254904000	-0.391508000
H	-3.755968000	-2.794278000	-0.446434000
H	-3.300324000	-1.285945000	-0.316151000
O	1.592742000	0.749874000	-3.423629000
H	0.652483000	0.484801000	-3.511696000
H	1.982256000	0.062811000	-2.849519000
O	2.838088000	-1.586054000	2.308754000
H	2.226577000	-2.283377000	1.979844000
H	2.258337000	-0.965752000	2.813275000
O	1.168056000	-3.356005000	-1.486938000
H	1.409354000	-4.148468000	-1.990155000
H	1.850759000	-2.664779000	-1.716536000
O	3.117526000	2.443550000	0.301684000
H	3.315088000	1.486219000	0.258949000
H	2.488449000	2.526490000	1.047734000
O	-1.694213000	-0.618757000	3.500779000

H	-1.766148000	-1.490403000	3.035732000
H	-0.754396000	-0.372599000	3.401749000
O	-2.559414000	1.650173000	-2.227732000
H	-2.050242000	1.012432000	-2.796781000
H	-3.187348000	2.092683000	-2.818208000
C	-0.236975000	-0.022832000	-0.055102000
O	0.569452115	0.641156553	0.470020419
O	-1.043403816	-0.686813492	-0.580231437

3. Cartesian coordinates of CH₄ hydrate, 5¹²6² Cage:

O	-1.670912000	-4.226009000	-1.082352000
H	-2.375524000	-3.766957000	-0.603643000
H	-2.959334000	-2.320575000	1.911485000
O	3.529092000	2.803767000	1.029338000
H	-1.351771000	-3.578305000	-1.739442000
H	-2.569391000	-2.645506000	3.386338000
O	-3.825508000	-2.802754000	0.442226000
H	2.929516000	3.374599000	0.509101000
H	-5.468080000	-0.476336000	-1.297831000
O	1.675003000	4.357287000	-0.462631000
H	4.288235000	3.348667000	1.261625000
H	-4.426153000	0.220910000	-0.353308000
O	4.139684000	-1.822405000	0.869087000
H	-4.547179000	-3.439336000	0.475345000
H	-0.981477000	5.165787000	1.386092000
O	-4.100843000	1.509095000	0.645082000

H	-4.152398000	-2.036879000	-0.088426000
H	-1.472644000	4.135872000	0.310204000
O	2.754696000	-3.524800000	-1.148957000
H	0.821835000	4.395381000	0.033043000
H	1.390268000	3.342589000	-2.065515000
O	-2.709958000	3.585579000	-0.704716000
H	1.911470000	5.272815000	-0.647189000
H	1.490020000	3.250005000	-3.612671000
O	-2.744559000	0.731707000	3.040679000
H	3.633583000	-1.680969000	1.697571000
H	-1.998216000	1.501647000	-2.910970000
O	2.229125000	1.390499000	3.194198000
H	4.929342000	-2.315907000	1.112625000
H	-0.744828000	2.479495000	-2.858839000
O	4.353905000	0.558668000	-0.693508000
H	-3.609881000	2.239531000	0.222207000
H	2.223599000	-1.362192000	-3.409527000
O	2.624222000	-1.238043000	3.147085000
H	-3.636143000	1.295966000	1.475066000
H	2.218476000	-2.751014000	-2.703744000
O	-2.471293000	-1.980180000	2.696660000
H	3.194764000	-2.945362000	-0.509959000
H	0.592452000	-4.140968000	1.200296000
O	-4.579206000	-0.571005000	-0.940033000
H	2.062654000	-3.995233000	-0.634114000

H	-0.123889000	-4.625560000	-0.086935000
O	-0.709102000	4.380655000	0.899103000
H	-2.306692000	3.123411000	-1.524305000
H	-0.341601000	-1.612857000	-1.657252000
O	1.122959000	2.810480000	-2.838108000
H	-3.333393000	4.233540000	-1.050255000
H	0.234227000	-2.116329000	-2.985975000
O	-1.711676000	2.439102000	-2.755956000
H	-2.632211000	-0.244876000	2.975008000
H	-1.137195000	1.788790000	3.046958000
O	1.802672000	-2.243961000	-3.435423000
H	-3.253054000	0.885301000	3.844124000
H	-0.512036000	3.000628000	2.303422000
O	0.726252000	-4.665817000	0.391856000
H	1.310371000	1.731422000	3.207575000
H	-1.890831000	-0.791522000	-3.007814000
O	-0.636408000	-1.982559000	-2.497875000
H	2.685233000	1.881333000	2.489575000
H	-3.256373000	-0.341073000	-2.411504000
O	-0.373664000	2.391835000	3.046281000
H	4.094280000	1.264692000	-0.082898000
H	3.437823000	0.428194000	-2.285335000
O	-2.577228000	-0.090461000	-3.057271000
H	4.324432000	-0.265563000	-0.174937000
H	2.208278000	1.072719000	-2.963687000

O	2.862669000	0.369477000	-3.074985000
H	2.459143000	-0.254212000	3.165096000
H	1.068282000	-2.297241000	2.811159000
O	0.330133000	-2.914756000	2.665132000
H	2.970538000	-1.460402000	4.017548000
H	-0.467690000	-2.376841000	2.566654000
C	0.273774000	0.028734000	0.124279000
H	0.247314000	-1.019981000	0.427699000
H	1.075606000	0.172601000	-0.600784000
H	0.463833000	0.641570000	1.005234000
H	-0.680662000	0.318927000	-0.319142000

4. Cartesian coordinates of CO₂ hydrate, 5¹²6² Cage:

O	0.924327000	-4.271216000	-1.002928000
H	0.117919000	-4.127666000	-0.489932000
H	-1.145871000	-3.412845000	2.055052000
O	1.485002000	4.299181000	0.902052000
H	0.860379000	-3.642443000	-1.746774000
H	-0.618827000	-3.437657000	3.517730000
O	-1.595810000	-4.312127000	0.612579000
H	0.666072000	4.439132000	0.389312000
H	-4.370677000	-3.460119000	-1.063668000
O	-0.918089000	4.510434000	-0.560126000
H	1.796279000	5.172287000	1.162723000
H	-3.810366000	-2.244442000	-0.248867000
O	4.556701000	0.834186000	0.836470000

H	-1.652190000	-5.271066000	0.548338000
H	-3.569920000	3.810540000	1.330457000
O	-4.208194000	-0.945854000	0.721561000
H	-2.330449000	-3.940048000	0.074625000
H	-3.476551000	2.664970000	0.268110000
O	4.397838000	-1.439490000	-1.099305000
H	-1.651706000	4.096084000	-0.048420000
H	-0.651556000	3.378515000	-2.082013000
O	-4.284931000	1.517126000	-0.702504000
H	-1.248593000	5.372562000	-0.835036000
H	-0.127150000	3.105896000	-3.524321000
O	-2.675457000	-0.783823000	3.139978000
H	4.061790000	0.682406000	1.669739000
H	-2.626512000	0.141540000	-2.931559000
O	1.151354000	2.440252000	3.109620000
H	5.486847000	0.891199000	1.077303000
H	-2.114796000	1.621420000	-2.927138000
O	3.371151000	2.829900000	-0.797838000
H	-4.228803000	-0.078109000	0.278439000
H	2.780148000	-0.049862000	-3.413861000
O	2.979907000	0.518745000	3.111220000
H	-3.690206000	-0.835611000	1.540206000
H	3.515440000	-1.175917000	-2.636865000
O	-0.922532000	-2.842374000	2.823957000
H	4.417246000	-0.686008000	-0.490709000

H	2.836439000	-3.029222000	1.236715000
O	-3.548801000	-3.024117000	-0.815092000
H	4.048153000	-2.189809000	-0.570516000
H	2.478621000	-3.804023000	-0.053318000
O	-2.939589000	3.282082000	0.828980000
H	-3.738088000	1.336909000	-1.540270000
H	0.214978000	-1.502215000	-2.331876000
O	-0.661011000	2.737727000	-2.811563000
H	-5.178640000	1.708922000	-1.006373000
H	1.478903000	-1.811849000	-3.163727000
O	-2.912810000	1.071654000	-2.832473000
H	-2.032597000	-1.525377000	3.089947000
H	-1.916372000	0.976551000	3.108154000
O	2.921256000	-1.013355000	-3.403145000
H	-3.242091000	-0.971337000	3.895796000
H	-2.023365000	2.277905000	2.276867000
O	3.230295000	-3.428795000	0.443017000
H	0.196768000	2.212985000	3.129825000
H	-1.449901000	-2.019742000	-3.321833000
O	0.597318000	-2.195804000	-2.880566000
H	1.263372000	3.081360000	2.389559000
H	-2.630423000	-2.186872000	-2.298298000
O	-1.584034000	1.889483000	3.046487000
H	2.792935000	3.329876000	-0.200309000
H	2.673902000	2.143459000	-2.325081000

O	-2.199404000	-1.565376000	-2.908164000
H	3.823983000	2.170298000	-0.243938000
H	1.275135000	1.685598000	-2.748633000
O	2.179542000	1.750217000	-3.075471000
H	2.283661000	1.230852000	3.111445000
H	2.254027000	-1.213976000	2.813420000
O	1.958656000	-2.131674000	2.702163000
H	3.379574000	0.547887000	3.986700000
H	0.998975000	-2.101258000	2.605737000
C	-0.299000000	-0.053692000	0.072084000
O	-0.825551000	1.023644000	-0.532867000
O	0.225129000	-1.130569000	0.675788000

5. Cartesian coordinates of CH₄ hydrate, 5¹²6⁴ Cage:

O	-1.605874000	4.327345000	1.091007000
H	-0.654904000	4.407629000	0.894300000
H	4.240880000	0.680906000	-1.253611000
O	1.233495000	4.441217000	0.673175000
H	-2.034107000	4.065372000	0.259580000
H	4.480701000	-0.767814000	-0.759697000
O	-2.056668000	2.784311000	3.368236000
H	1.513626000	4.169658000	-0.214507000
H	-4.444734000	-1.192308000	0.417931000
O	2.705554000	2.928418000	2.718463000
H	1.691220000	3.853647000	1.294587000
H	-5.572570000	-0.294812000	0.990577000

O	-2.874993000	3.695924000	-1.473950000
H	-1.163278000	2.570836000	3.676758000
H	-0.987716000	-1.466298000	4.048379000
O	1.895069000	3.860804000	-2.103425000
H	-1.935305000	3.355548000	2.579668000
H	-2.409912000	-0.948528000	3.549798000
O	0.606333000	2.048822000	4.405162000
H	3.264189000	2.163176000	2.446792000
H	3.239813000	-0.849629000	2.774491000
O	-0.745370000	3.468092000	-3.305074000
H	3.315039000	3.605709000	3.030048000
H	2.884539000	-2.358665000	2.721381000
O	-3.398682000	0.421657000	3.080969000
H	-3.397667000	2.847257000	-1.548749000
H	-2.230601000	0.163339000	-3.940207000
O	4.219506000	0.756811000	1.990518000
H	-3.505033000	4.402630000	-1.648458000
H	-2.636723000	-1.076249000	-3.096173000
O	3.469582000	1.595749000	-2.799803000
H	2.467083000	3.109831000	-2.354693000
H	1.962820000	-1.149562000	-3.893241000
O	-4.257056000	1.444682000	-1.756283000
H	2.297519000	4.648681000	-2.483857000
H	1.918542000	-0.261234000	-5.175820000
O	0.544487000	-0.874416000	4.614731000

H	1.345024000	2.393503000	3.866115000
H	-3.187659000	-3.228967000	0.896130000
O	-0.772966000	1.018254000	-4.521579000
H	0.679144000	2.472813000	5.266724000
H	-4.566967000	-3.592812000	0.253793000
O	4.717913000	0.160548000	-0.585984000
H	0.076719000	3.653591000	-2.826103000
H	3.357457000	-2.718420000	-1.839087000
O	-4.722620000	-0.265511000	0.538887000
H	-1.473930000	3.594558000	-2.664691000
H	4.681411000	-3.205331000	-1.185147000
O	-1.875353000	-1.757685000	3.727678000
H	-2.966247000	1.303071000	3.182815000
H	-1.978711000	-2.837672000	2.753840000
O	2.935260000	-1.586080000	3.323035000
H	-3.668930000	0.363306000	2.154304000
H	-2.386425000	-4.376539000	2.643973000
O	-3.001014000	-0.299826000	-3.539573000
H	4.409631000	0.574759000	1.033410000
H	3.100205000	-3.264608000	0.596776000
O	1.933968000	-0.224859000	-4.213202000
H	5.044014000	0.597337000	2.462156000
H	1.901992000	-3.990620000	1.254997000
O	-3.826361000	-2.983336000	0.160478000
H	2.926743000	0.968464000	-3.326700000

H	-3.077576000	-3.004971000	-1.461877000
O	3.961160000	-2.573327000	-1.085948000
H	4.247552000	1.782165000	-3.337163000
H	-3.358176000	-3.237996000	-2.980485000
O	-2.118740000	-3.636620000	2.087794000
H	-3.869394000	0.835977000	-2.420132000
H	1.246287000	-3.243811000	-2.866705000
O	2.798806000	-3.643142000	1.434631000
H	-4.442885000	0.900718000	-0.973779000
H	2.359088000	-3.495501000	-3.917251000
O	-2.657193000	-3.031014000	-2.352912000
H	1.374381000	-1.190133000	4.201493000
H	0.053421000	-4.193386000	-0.205613000
O	2.086042000	-2.871771000	-3.234887000
H	0.583603000	0.093715000	4.565807000
H	-0.517509000	-4.176128000	1.229564000
O	0.223361000	-4.513301000	0.691120000
H	0.042339000	0.616402000	-4.196206000
H	-1.068476000	-3.680186000	-2.349020000
O	-0.160157000	-4.048155000	-2.215880000
H	-0.785060000	1.923773000	-4.127641000
H	-0.237369000	-4.999070000	-2.351085000
C	0.381333000	-0.246902000	-0.139731000
H	0.268241000	-1.056677000	-0.863370000
H	-0.540807000	-0.144842000	0.433693000

H	0.577766000	0.689340000	-0.663475000
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H	1.199761000	-0.472262000	0.543971000
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6. Cartesian coordinates of CO₂ hydrate, 5¹²6⁴ Cage:

C	-0.550460000	0.498600000	-0.096952000
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O	-1.145201000	-0.417503000	-0.484701000
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O	0.040166000	1.425588000	0.290450000
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O	1.082845000	-3.985558000	2.360476000
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H	1.843465000	-3.387649000	2.473499000
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H	3.328391000	2.699927000	1.002441000
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O	3.323752000	-2.196294000	2.509719000
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H	0.326129000	-3.543707000	2.778462000
---	-------------	--------------	-------------

H	3.035841000	3.327263000	-0.387179000
---	-------------	-------------	--------------

O	0.826312000	-4.812167000	-0.290227000
---	-------------	--------------	--------------

H	3.109558000	-1.345108000	2.921842000
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H	-3.962353000	-2.146585000	-0.743573000
---	--------------	--------------	--------------

O	4.567539000	-1.785603000	-0.135342000
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H	3.669184000	-1.996440000	1.626401000
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H	-4.277706000	-3.636801000	-0.431233000
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O	-1.139664000	-2.767234000	3.839162000
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H	1.568986000	-4.376439000	-0.733826000
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H	-0.025539000	-2.219308000	-3.812846000
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O	2.639252000	0.163912000	4.067027000
---	-------------	-------------	-------------

H	0.906897000	-4.576584000	0.658940000
---	-------------	--------------	-------------

H	-1.112681000	-3.004221000	-2.955189000
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O	3.030826000	-3.512784000	-1.778790000
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H	4.581901000	-0.881471000	-0.529158000
H	3.302119000	0.572848000	-2.889269000
O	-0.146643000	-0.328137000	4.844819000
H	5.482998000	-2.006409000	0.065273000
H	2.308208000	1.247033000	-3.870466000
O	-1.461706000	-4.075461000	-1.600126000
H	-1.985262000	-2.543001000	3.351054000
H	-3.071568000	1.093057000	3.110235000
O	4.544150000	0.707807000	-1.262840000
H	-1.389496000	-3.417766000	4.503116000
H	-3.688675000	1.060709000	1.677818000
O	2.637483000	2.707051000	2.824773000
H	2.678808000	1.059139000	3.677278000
H	-0.201764000	4.067327000	1.813120000
O	-3.350096000	-2.089127000	2.558355000
H	3.205333000	0.178822000	4.845885000
H	-0.268389000	4.356737000	3.343362000
O	1.705636000	-2.044115000	-3.957043000
H	3.608034000	-2.962489000	-1.214814000
H	-3.707321000	-0.564164000	-2.515879000
O	-1.693658000	1.760848000	3.996086000
H	3.581157000	-4.231004000	-2.108399000
H	-5.226665000	-0.758674000	-2.228463000
O	3.712572000	2.844221000	0.121121000
H	0.785251000	-0.262441000	4.587191000

H	0.901983000	4.425392000	-0.849178000
O	-3.723820000	-2.895306000	-0.165832000
H	-0.461812000	-1.196620000	4.522802000
H	1.981672000	5.090096000	-1.747902000
O	-0.994509000	-2.361557000	-3.693403000
H	-0.662814000	-4.378186000	-1.106269000
H	-1.910035000	-1.226475000	-3.723785000
O	2.910870000	0.481866000	-3.769422000
H	-2.019727000	-3.622067000	-0.952441000
H	-3.003083000	-0.555552000	-4.667349000
O	-3.769993000	0.670732000	2.557774000
H	4.245265000	1.484324000	-0.716283000
H	1.308032000	3.153156000	-2.977356000
O	0.070176000	3.732213000	2.692267000
H	5.318336000	1.007483000	-1.751056000
H	0.222056000	2.493160000	-3.852374000
O	-4.386415000	-0.610882000	-1.779895000
H	1.723211000	3.070395000	2.803983000
H	-4.398840000	0.823809000	-0.708806000
O	1.716022000	4.249505000	-1.359645000
H	3.177952000	3.378565000	3.255465000
H	-5.243798000	1.756435000	0.223020000
O	-2.621116000	-0.454904000	-3.788458000
H	-3.546116000	-1.128619000	2.563078000
H	-1.400594000	4.200142000	-0.314769000

O	1.178534000	2.690636000	-3.816980000
H	-3.486148000	-2.399928000	1.647228000
H	-0.961360000	5.610188000	0.154543000
O	-4.366288000	1.640111000	-0.157325000
H	2.104179000	-1.149701000	-3.958760000
H	-1.915402000	2.469763000	-2.752932000
O	-0.669999000	4.691564000	0.134280000
H	2.166162000	-2.532104000	-3.257276000
H	-1.880095000	1.264675000	-3.722875000
O	-1.601040000	2.196055000	-3.625305000
H	-1.086697000	2.239357000	3.415911000
H	-3.372609000	2.878141000	-0.796480000
O	-2.727424000	3.493659000	-1.224271000
H	-1.163910000	1.013200000	4.364138000
H	-3.246424000	4.083672000	-1.781829000

Table S3

Comparison of the computational and experimental vibrational frequency of CH₄ and CO₂ Clathrate hydrate using the B3LYP level of theory and 6-311++G(d, p) basis.

B3LYP/6-311++G(d, p) Level	Free CH₄/CO₂	5¹² cage	5¹² 6² cage	5¹² 6⁴ cage
CH₄ hydrate	3129.6 (26)	3138.9 (24) 3144.1 (12) 3151.6 (10)	3120.4 (6) 3128.9 (10) 3141.3 (3)	3120.5 (22) 3132.2 (11) 3138.9 (16)
CO₂ hydrate	2420.0 (712)	2333.5 (295)	2403.4 (580)	2435.8 (546)

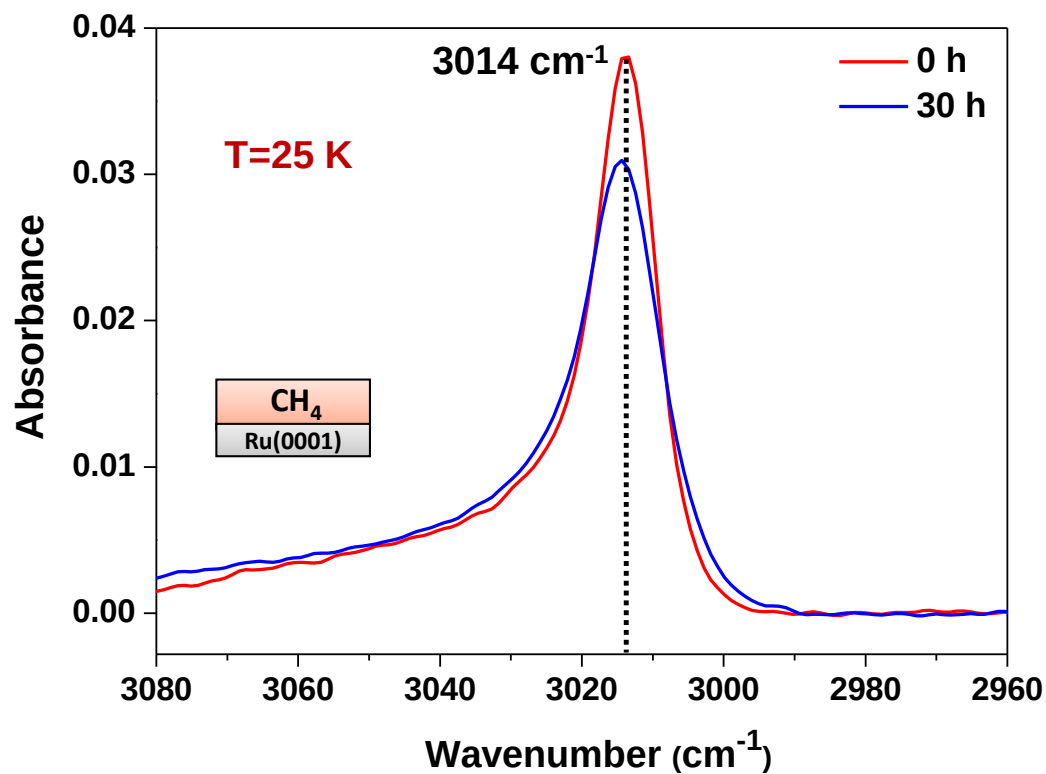


Fig. S2. Time dependent RAIR spectra of 150 MLs of solid CH₄ in the C-H antisymmetric stretching region at 25 K. The decrease in the intensity of the IR peak is due to desorption of CH₄ in UHV. This experiment was performed at 25 K instead of 30 K, as at this temperature (30 K), most of the CH₄ desorbed from the surface after 30 hours.

Table S4

Properties of (3,-1) bond critical points in CH₄ and CO₂ clathrate hydrate computed at B3LYP level of theory with 6-311++G (d, p) basis set.

Clathrate Hydrate (5¹²)	Type of bonding	Bonds	$\rho(r_C)$	$\nabla^2\rho(r_C)$
CH ₄	van der Waals interaction	-C-H of free CH ₄	0.27217	-0.89913
		-C-H of CH ₄ hydrate	0.27199	-0.89544
		-C-H $\cdots$ H ₂ O interaction	0.00598	0.01601
CO ₂	Hydrogen bonding	-C=O of free CO ₂	0.45773	-0.08650
		-C=O of CO ₂ hydrate	0.44922	-0.07620
		-C=O $\cdots$ H ₂ O interaction	0.01563	0.07161

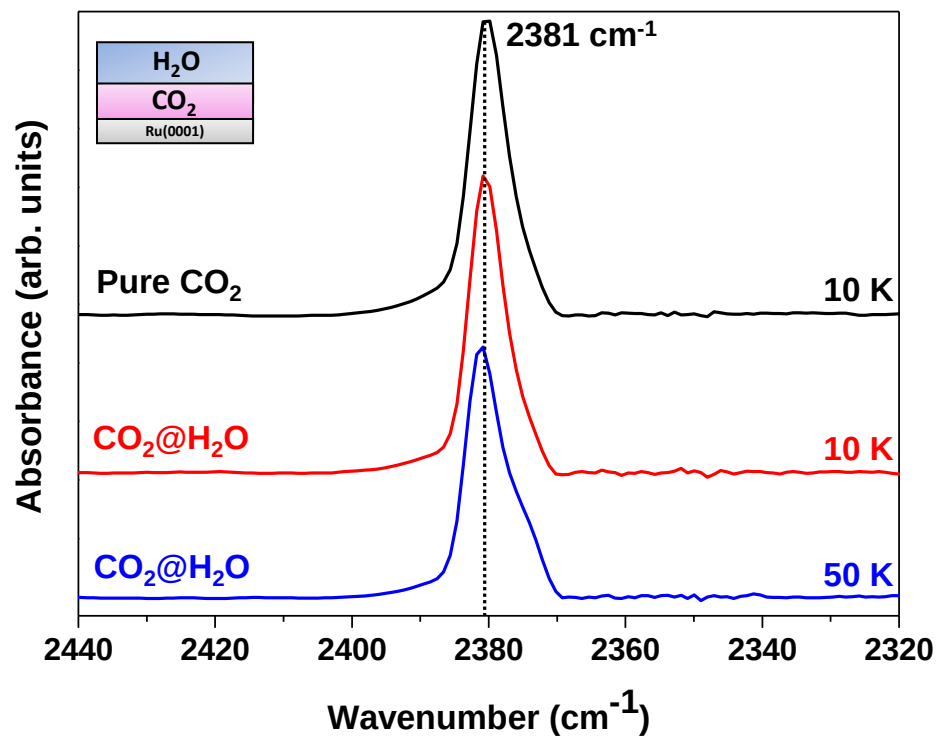


Fig. S3. Temperature dependent RAIR spectra of 300 MLs of $\text{CO}_2@ \text{H}_2\text{O}$ (1:5 ratio) in the C=O antisymmetric stretching region. Spectrum for pure solid CO_2 was added for comparison. The $\text{CO}_2@ \text{H}_2\text{O}$ symbolism implies that H_2O was deposited over CO_2 . The spectra were translated vertically for the clarity.

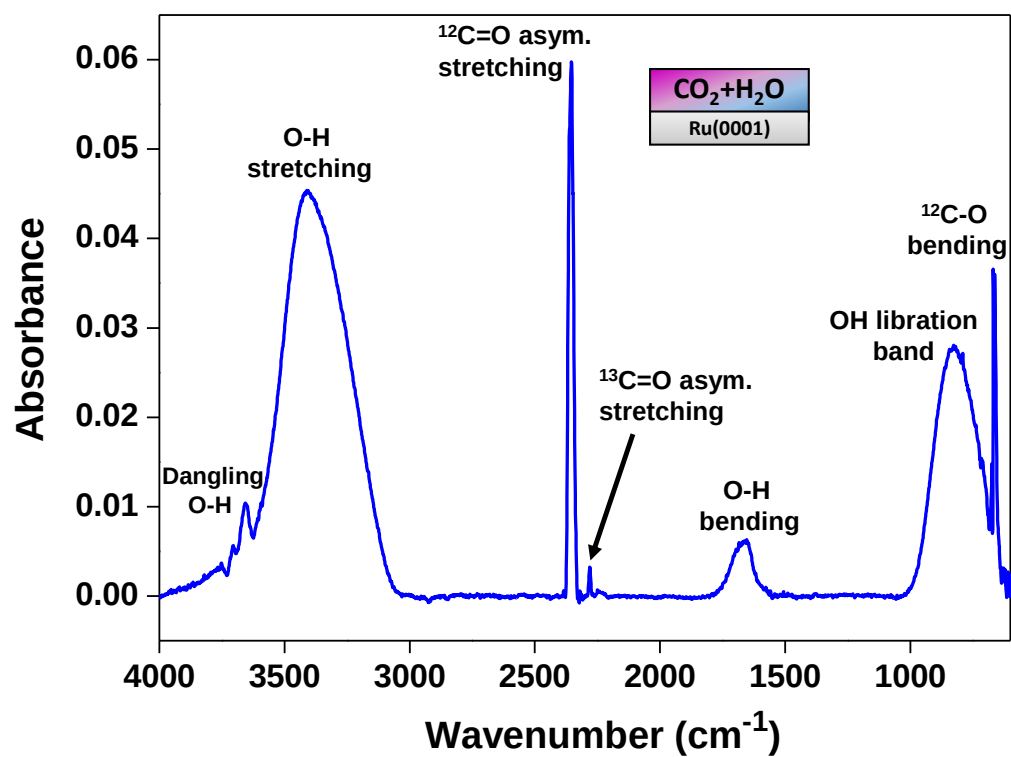


Fig. S4. Full scale RAIR spectrum of 300 MLs of $\text{CO}_2+\text{H}_2\text{O}$ (1:5 ratio) at 10 K.

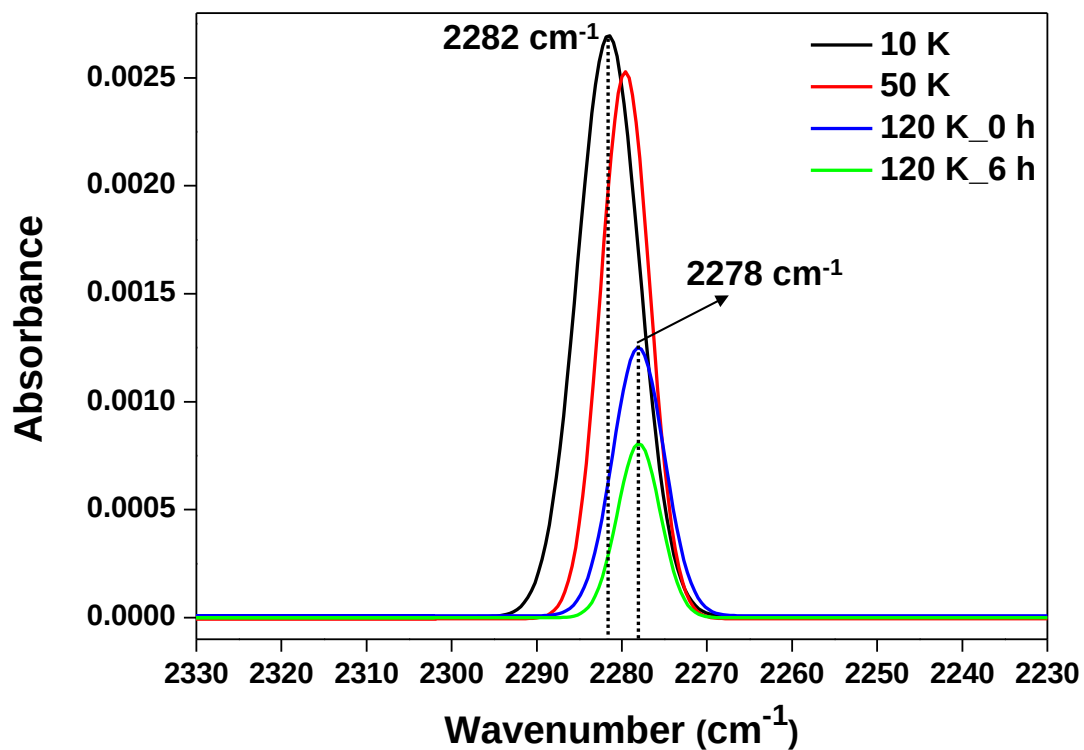


Fig. S5. Temperature dependent RAIR spectra of 300 MLs of CO₂+H₂O (1:5 ratio) in the ¹³C=O antisymmetric region. Reduction in intensity with time is due to partial desorption.

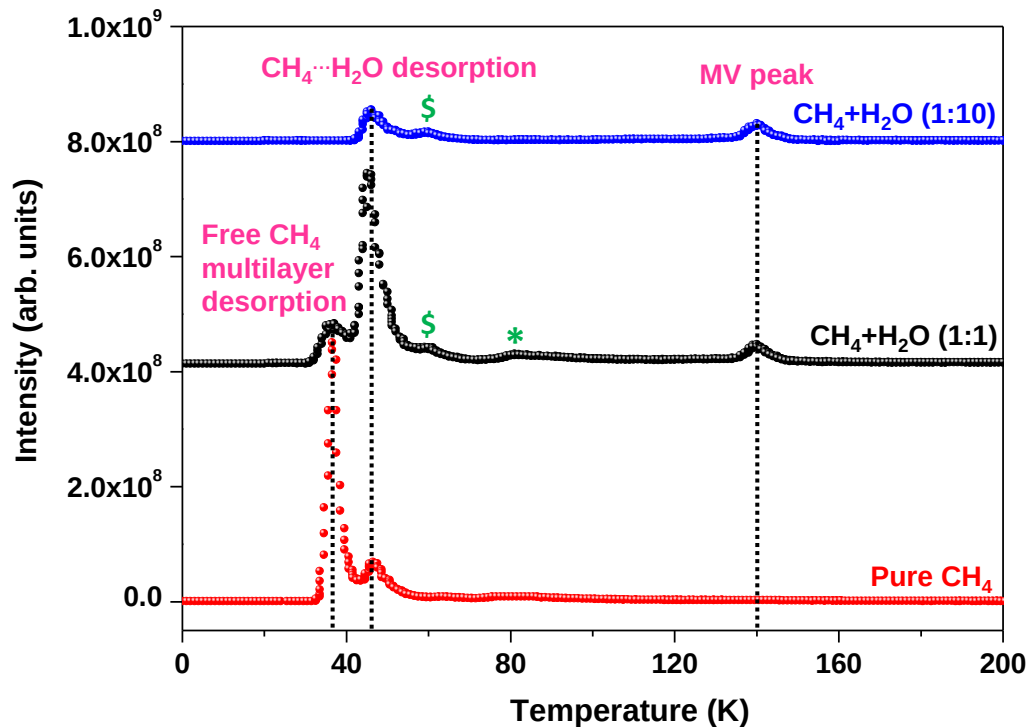


Fig. S6. TPD mass spectra of 150 MLs of solid CH_4 and $\text{CH}_4+\text{H}_2\text{O}$ co-deposited ice systems at different ratios (heating rate of $30 \text{ K}\cdot\text{min}^{-1}$). Here, the intensities of CH_3^+ ($m/z=15$) under these conditions are plotted. After the deposition at 10 K, these ice systems were annealed and simultaneously the mass spectra were recorded. The marked desorption (*, \$) peaks are due to the structural transitions of amorphous ice during annealing (1).

References:

1. Jenniskens P & Blake DF (1994) Structural transitions in amorphous water ice and astrophysical implications. *Science* 265(5173):753.