

# Spontaneous Formation of Tetrahydrofuran Hydrate in Ultrahigh Vacuum

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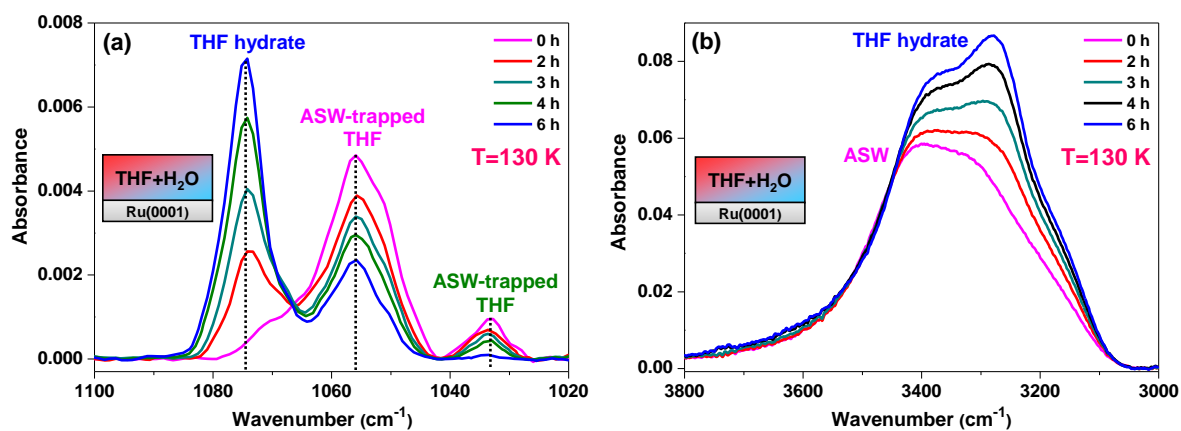
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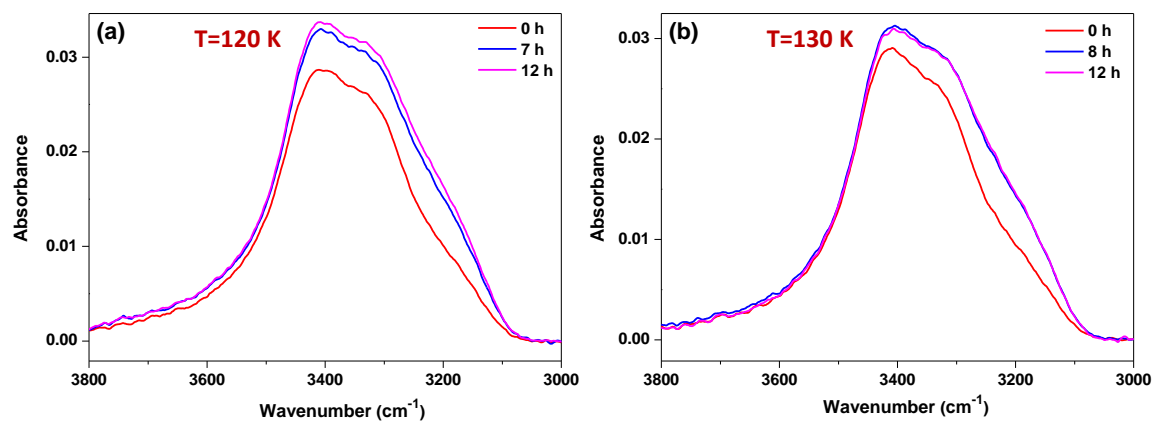
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## Supporting Information 1:



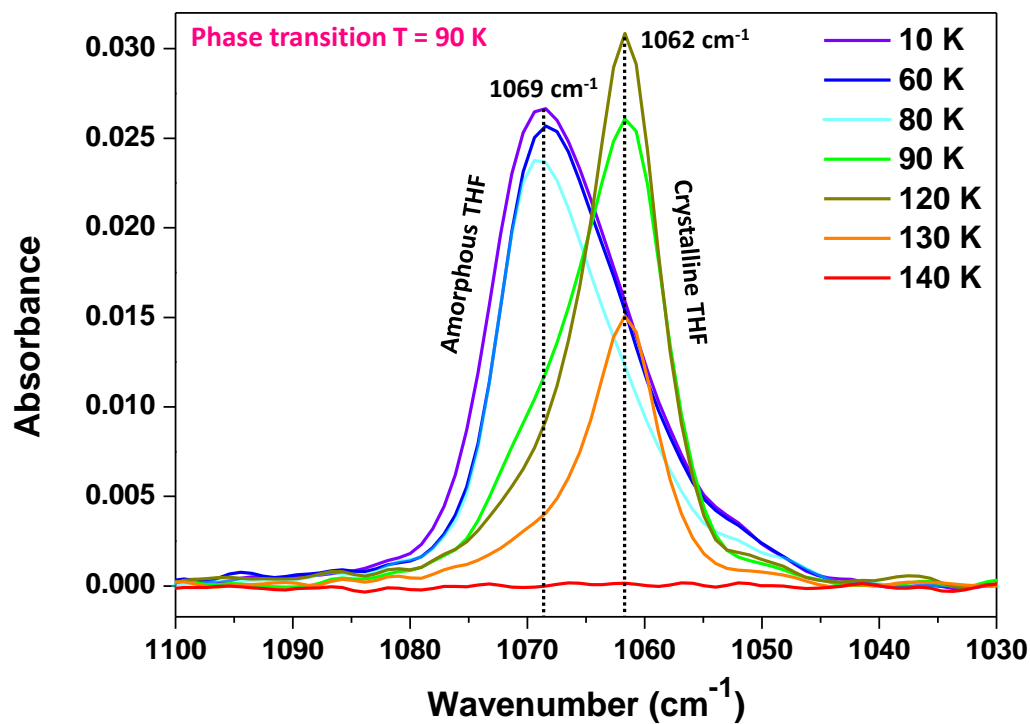
**Figure S1.** Time-dependent RAIR spectra of 300 MLs of a THF+H<sub>2</sub>O (1:5) mixture, (a) in the asymmetric C-O stretching region, and (b) O-H stretching region at 130 K, which was co-deposited on Ru(0001) substrate. This mixture was annealed at 2 K.min<sup>-1</sup> rate after co-deposition at 10 K.

## Supporting Information 2:



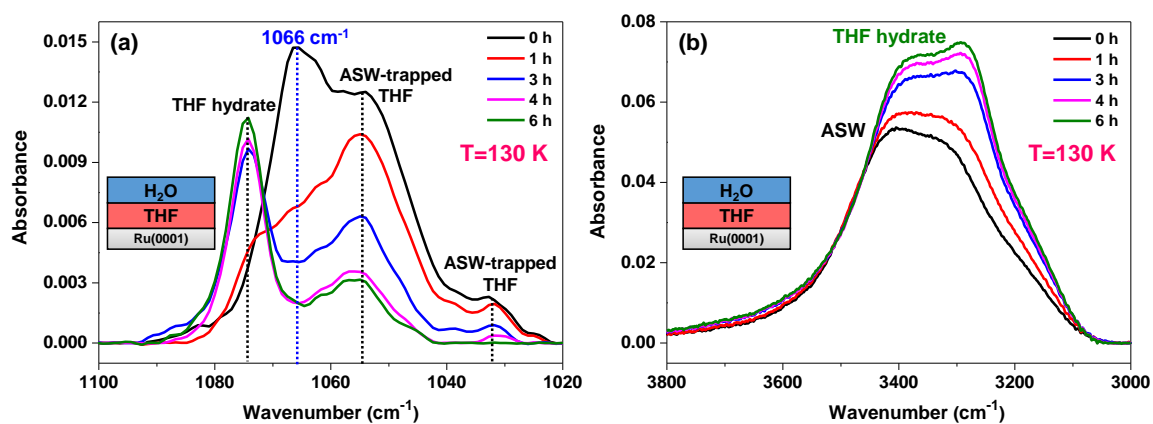
**Figure S2.** Time-dependent RAIR spectra of 150 MLs of solid H<sub>2</sub>O film at (a) 120 K, and (b) at 130 K in the O-H stretching region. Water vapor was deposited at 10 K on Ru(0001) substrate. The ice films were annealed at 2 K.min<sup>-1</sup> to the respective temperatures.

### Supporting Information 3:



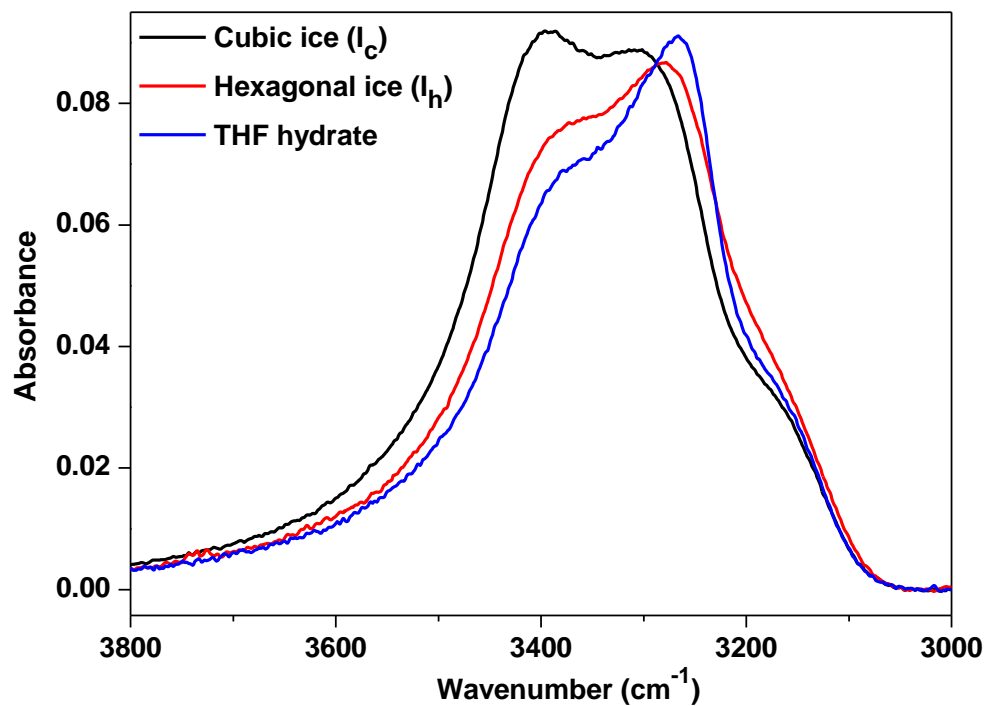
**Figure S3.** Temperature-dependent RAIR spectra of 150 MLs THF in the C-O antisymmetric stretching region.

## Supporting Information 4:



**Figure S4.** Time-dependent RAIR spectra of 300 MLs of a THF@H<sub>2</sub>O mixture (1:1) in the (a) asymmetric C-O stretching region, and (b) O-H stretching region, at 130 K, which was sequentially deposited at 10 K on the Ru(0001) substrate. The sequential deposition was carried out by condensing 150 MLs of H<sub>2</sub>O film over the same coverage of THF film, thus making it a (1:1) mixture.

## Supporting Information 5:



**Figure S5.** Comparison of the O-H stretching region of THF clathrate hydrate, hexagonal ice ( $I_h$ ), and cubic ice ( $I_c$ ), respectively. The cubic and hexagonal ices were formed by annealing at 145 K and 150 K, in separate sets of experiments.

**Table S1:**

Comparison of the computational and experimental vibrational shifts of THF clathrate hydrate. Computations were performed using B3LYP level of theory with 6-311++G (d, p) basis set.

<b>THF clathrate hydrate</b>	<b>5<sup>12</sup> cage</b>	<b>5<sup>12</sup> 6<sup>2</sup> cage</b>	<b>5<sup>12</sup> 6<sup>4</sup> cage</b>
<b>Experimental shift</b>	-	-	19.0 cm <sup>-1</sup>
<b>Computational shift</b>	3.2 cm <sup>-1</sup>	-10.3 cm <sup>-1</sup>	27.4 cm <sup>-1</sup>



**Table S2:**

Cartesian coordinates of THF clathrate hydrate in  $5^{12}$ ,  $5^{12}6^2$ , and  $5^{12}6^4$  cages. The structure is optimized by using B3LYP level of theory and 6-311G (d, p) basis set.

**1. Cartesian coordinates of THF hydrate,  $5^{12}$  cage:**

O	-3.682521000	-0.998104000	1.763573000
H	-3.035226000	-0.866700000	2.493269000
H	-3.787980000	-0.125330000	1.357865000
O	1.092542000	0.493839000	-3.575893000
H	1.897690000	0.640201000	-3.054436000
H	0.474915000	1.208872000	-3.339951000
O	-1.753901000	-0.564608000	3.717801000
H	-0.973431000	-1.139036000	3.608164000
H	-1.426274000	0.350172000	3.754553000
O	3.583155000	0.832824000	-2.011474000
H	3.477089000	1.618489000	-1.433649000
H	4.267523000	1.064619000	-2.648603000
O	-2.832497000	-1.723020000	-2.736829000
H	-2.921351000	-2.207747000	-1.901940000
H	-1.914391000	-1.904385000	-3.025289000
O	4.036332000	-0.971622000	1.988747000
H	4.064214000	-1.289603000	1.048157000
H	4.785790000	-1.390619000	2.424046000
O	-3.114222000	1.074563000	-2.444422000
H	-3.077202000	0.098716000	-2.573281000
H	-3.462663000	1.225904000	-1.551249000
O	3.713657000	1.780980000	2.123808000
H	3.846474000	0.805937000	2.093262000
H	4.278076000	2.106624000	2.829439000
O	-0.212405000	-4.020313000	0.848483000
H	-0.955025000	-3.459804000	0.549144000
H	-0.592718000	-4.887638000	1.020599000
O	-1.875847000	3.790030000	1.234954000
H	-1.167130000	3.906182000	0.555602000
H	-2.172461000	4.679308000	1.454394000
O	1.743833000	-3.501371000	-1.221326000
H	1.099801000	-3.667754000	-0.502284000
H	1.953027000	-4.367289000	-1.585556000
O	0.065712000	4.035256000	-0.728876000
H	-0.231608000	3.556994000	-1.529874000
H	0.975581000	3.746184000	-0.568324000
O	-2.980279000	-3.041229000	0.086454000

H	-3.253841000	-2.322069000	0.710272000
H	-3.674674000	-3.704312000	0.149076000
O	-0.905037000	2.502464000	-2.929182000
H	-1.125770000	2.994788000	-3.727157000
H	-1.715669000	1.949055000	-2.737951000
O	-0.824732000	2.274383000	3.571853000
H	-1.226351000	2.783847000	2.845832000
H	0.123157000	2.336428000	3.412413000
O	4.046819000	-1.743644000	-0.613860000
H	3.902412000	-0.944146000	-1.148277000
H	3.318659000	-2.352082000	-0.837987000
O	3.146063000	3.034295000	-0.264299000
H	3.725911000	3.799127000	-0.337928000
H	3.338697000	2.642617000	0.620929000
O	0.453212000	-2.442898000	3.283852000
H	1.363023000	-2.148701000	3.165436000
H	0.247925000	-2.965510000	2.487698000
O	-0.067074000	-2.095789000	-3.355735000
H	0.356275000	-1.224553000	-3.489714000
H	0.468764000	-2.534740000	-2.678443000
O	-3.872901000	1.773582000	0.366165000
H	-3.232419000	2.446605000	0.668611000
H	-4.743357000	2.162701000	0.503637000
O	-0.229599000	-1.387018000	0.174729000
C	1.049016000	-0.762497000	0.285623000
C	-1.091334000	-0.390740000	-0.379463000
C	0.788151000	0.725497000	0.600987000
C	-0.729759000	0.878050000	0.375433000
H	-0.894706000	-0.294494000	-1.450036000
H	1.573350000	-0.862942000	-0.668174000
H	1.358063000	1.359681000	-0.073686000
H	1.613562000	-1.283815000	1.054053000
H	1.081783000	0.980812000	1.619193000
H	-0.979368000	1.775688000	-0.181565000
H	-1.252852000	0.894968000	1.329844000
H	-2.114216000	-0.713939000	-0.233812000

**2. Cartesian coordinates of THF hydrate, 5<sup>12</sup>6<sup>2</sup> cage:**

O	1.929592000	4.354383000	-0.376871000
H	2.583637000	3.709538000	-0.075880000
H	3.244250000	1.643202000	2.222184000
O	-3.738463000	-2.747541000	0.743398000
H	1.630871000	4.036352000	-1.247940000

H	3.019328000	1.696461000	3.760801000
O	3.963034000	2.444642000	0.765006000
H	-3.161875000	-3.190937000	0.090795000
H	5.444451000	0.481098000	-1.502423000
O	-1.945693000	-3.933105000	-1.123039000
H	-4.461991000	-3.356545000	0.918765000
H	4.436923000	-0.345387000	-0.641034000
O	-3.996757000	1.808552000	1.410355000
H	4.721514000	3.025979000	0.895256000
H	0.761431000	-5.374600000	0.267486000
O	4.212199000	-1.823495000	0.135620000
H	4.232479000	1.795743000	0.071592000
H	1.208654000	-4.063308000	-0.445225000
O	-2.610990000	3.918551000	-0.340372000
H	-1.083769000	-4.042440000	-0.653159000
H	-1.686389000	-2.662606000	-2.552414000
O	2.470481000	-3.374829000	-1.470234000
H	-2.166310000	-4.809228000	-1.453735000
H	-1.840312000	-2.376571000	-4.070420000
O	3.107315000	-1.627117000	2.844445000
H	-3.453350000	1.443799000	2.139872000
H	1.793880000	-0.919340000	-3.366039000
O	-2.117427000	-1.974056000	3.104682000
H	-4.717208000	2.288008000	1.830360000
H	0.451490000	-1.756662000	-3.277248000
O	-4.642170000	-0.138271000	-0.628747000
H	3.621648000	-2.409938000	-0.375879000
H	-2.318832000	2.304183000	-3.091174000
O	-2.364303000	0.663374000	3.449744000
H	3.890928000	-1.834442000	1.053587000
H	-2.137006000	3.467567000	-2.077696000
O	2.824358000	1.170290000	2.975197000
H	-3.092423000	3.244319000	0.160178000
H	-0.239546000	3.788749000	1.987660000
O	4.569420000	0.528558000	-1.098690000
H	-1.850078000	4.156615000	0.231134000
H	0.426663000	4.480452000	0.764564000
O	0.495045000	-4.463526000	0.107556000
H	2.048936000	-2.743001000	-2.140060000
H	0.694175000	2.173912000	-1.879927000
O	-1.469618000	-2.020244000	-3.255586000
H	2.965741000	-4.006611000	-2.003690000
H	-0.055942000	3.013721000	-2.892717000
O	1.422969000	-1.825412000	-3.266166000

H	3.018922000	-0.657413000	2.966084000
H	1.255650000	-2.681441000	2.868155000
O	-1.798929000	3.111630000	-2.928088000
H	3.672408000	-1.930030000	3.561744000
H	0.433335000	-3.517125000	1.869680000
O	-0.396208000	4.447130000	1.289874000
H	-1.233926000	-2.393023000	3.040154000
H	2.060859000	1.470962000	-3.339107000
O	0.868978000	2.791245000	-2.603149000
H	-2.635825000	-2.295862000	2.347107000
H	3.250652000	0.740192000	-2.649311000
O	0.439462000	-3.200912000	2.787689000
H	-4.434551000	-0.980871000	-0.197710000
H	-3.766835000	0.350188000	-2.285992000
O	2.603542000	0.660732000	-3.367075000
H	-4.479140000	0.537124000	0.052888000
H	-2.617276000	-0.213365000	-3.144778000
O	-3.200721000	0.551175000	-3.058259000
H	-2.250086000	-0.318521000	3.325262000
H	-0.740722000	1.696467000	3.285104000
O	0.024802000	2.295073000	3.228665000
H	-2.669944000	0.770551000	4.357250000
H	0.795421000	1.741727000	3.041060000
O	-0.389915000	-1.440042000	0.123165000
C	-1.442628000	-0.491306000	-0.125858000
C	0.687268000	-0.716911000	0.711511000
C	-0.783677000	0.896898000	-0.248461000
C	0.717231000	0.610694000	-0.039290000
H	0.501091000	-0.558483000	1.781734000
H	-2.155863000	-0.527934000	0.700448000
H	-1.150387000	1.577443000	0.518784000
H	-1.944714000	-0.800599000	-1.036871000
H	-1.007852000	1.355940000	-1.209640000
H	1.220294000	1.401126000	0.518531000
H	1.228354000	0.478653000	-0.995576000
H	1.588989000	-1.314320000	0.597059000

### 3. Cartesian coordinates of THF hydrate, $5^{12}6^4$ cage:

O	-0.103165000	4.250630000	2.013985000
H	-1.010632000	3.897222000	2.103611000
H	-3.954335000	-1.899726000	1.007892000
O	-2.760565000	3.159732000	2.108663000
H	0.438447000	3.795651000	2.683189000

H	-3.764804000	-2.746669000	-0.289587000
O	0.482979000	4.758000000	-0.692579000
H	-2.784980000	2.281026000	2.526130000
H	4.612246000	1.184297000	-0.631358000
O	-4.026818000	2.809424000	-0.549887000
H	-3.109698000	3.046544000	1.206684000
H	5.197015000	2.444382000	0.097129000
O	1.443374000	2.740930000	4.013149000
H	-0.328884000	4.412200000	-1.099753000
H	0.753897000	1.813369000	-3.762424000
O	-2.799460000	0.750351000	3.729814000
H	0.369520000	4.619567000	0.273151000
H	2.083033000	2.431063000	-3.086984000
O	-1.981510000	3.963680000	-2.126636000
H	-4.241885000	1.873278000	-0.764557000
H	-3.360689000	0.133004000	-2.803356000
O	-0.078709000	0.481846000	4.680014000
H	-4.880825000	3.262203000	-0.473880000
H	-2.573297000	-0.827507000	-3.744297000
O	2.692620000	3.563741000	-1.914580000
H	2.198498000	2.332995000	3.501986000
H	2.762516000	-1.484156000	3.224998000
O	-4.690968000	0.198416000	-1.302924000
H	1.836316000	3.313739000	4.681926000
H	3.755960000	-1.698073000	2.023859000
O	-3.353984000	-1.849788000	2.808972000
H	-3.085535000	-0.152188000	3.477171000
H	-0.782613000	-3.658785000	1.823182000
O	3.351729000	1.578834000	2.590257000
H	-3.321722000	1.014632000	4.497448000
H	-0.956868000	-4.101956000	3.310763000
O	-0.919333000	2.021878000	-3.965619000
H	-2.746105000	3.623931000	-1.614240000
H	3.864583000	-0.480651000	-2.241145000
O	1.204545000	-1.839353000	3.990945000
H	-2.255400000	4.800034000	-2.522747000
H	5.402290000	-0.541916000	-2.177851000
O	-4.319070000	-2.050858000	0.115163000
H	-0.968847000	0.624573000	4.313072000
H	-1.824975000	-4.343466000	-0.643528000
O	4.376910000	1.982627000	-0.113822000
H	0.427219000	1.304956000	4.514007000
H	-3.028847000	-4.840579000	-1.512415000
O	1.736954000	1.720850000	-3.686565000

H	1.957507000	4.068505000	-1.498653000
H	2.376242000	0.421508000	-3.681967000
O	-2.898702000	0.090845000	-3.658276000
H	3.176902000	3.133504000	-1.190161000
H	3.310956000	-0.658521000	-4.439057000
O	3.618626000	-1.185115000	2.836948000
H	-4.565352000	-0.630736000	-0.764180000
H	-1.991414000	-2.944921000	-2.675597000
O	-1.054898000	-3.348319000	2.717394000
H	-5.473727000	0.050597000	-1.852647000
H	-0.744626000	-2.533536000	-3.500637000
O	4.629299000	-0.494334000	-1.595288000
H	-2.540631000	-2.409799000	2.842727000
H	4.459282000	-1.842821000	-0.435709000
O	-2.625995000	-4.048086000	-1.116566000
H	-4.058427000	-2.351644000	3.245330000
H	5.138244000	-2.907215000	0.493621000
O	2.849681000	-0.507449000	-3.605429000
H	3.561427000	0.633073000	2.772308000
H	0.570459000	-4.433154000	-0.049018000
O	-1.722843000	-2.511598000	-3.503519000
H	3.368164000	1.668790000	1.624868000
H	-0.073776000	-5.633630000	0.698402000
O	4.279237000	-2.586415000	0.190868000
H	-1.571220000	1.288816000	-3.923808000
H	1.298706000	-2.925655000	-2.366232000
O	-0.267554000	-4.745821000	0.369450000
H	-1.302563000	2.740599000	-3.429950000
H	1.624538000	-1.897512000	-3.464965000
O	1.119589000	-2.721537000	-3.295528000
H	0.534098000	-2.324305000	3.485480000
H	2.958020000	-3.680318000	-0.417450000
O	2.192532000	-4.179664000	-0.780671000
H	0.761410000	-0.999255000	4.266811000
H	2.531880000	-4.734138000	-1.495062000
O	-0.181008000	-1.564217000	0.009575000
C	-1.263763000	-0.674542000	-0.327519000
C	0.909735000	-0.771949000	0.504473000
C	-0.671964000	0.743275000	-0.505184000
C	0.838565000	0.565692000	-0.233486000
H	0.814390000	-0.625885000	1.588327000
H	-2.011141000	-0.710016000	0.474675000
H	-1.122841000	1.413821000	0.231271000
H	-1.721628000	-1.059897000	-1.240640000

H	-0.871096000	1.149366000	-1.498680000
H	1.227037000	1.377745000	0.386830000
H	1.407912000	0.570729000	-1.168216000
H	1.827279000	-1.335770000	0.315711000