Supplementary Material

Table S1. Initial and final structures of the water molecules in all samples studied in this work. *mon* is used to represent unbound water molecules and W…W to indicate water molecules linked by a H-bond with O…H ≤ 2.2 Å. The O…H distance of the H-bond is quoted in Å.

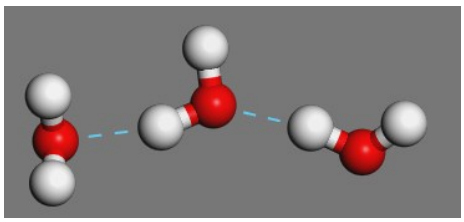
	Initial	Final
	Structure (H-bond distance/Å)	Structure (H-bond distance/Å)
large-matrix (from 32 CO matrix)		
30CO-2W-a	mon,mon	mon,mon
30CO-2W-b	mon,mon	mon,mon
30CO-2W-c	W…W (1.9)	W…W (1.9)
29CO-3W-a	mon,W…W (2.0)	mon,W…W (2.2)
29CO-3W-b	W…W…W (1.9,1.9)	W…W…W (1.9,1.9)
28CO-4W	mon,mon,W…W (2.0)	mon,W…W…W (2.1,2.1)
small-matrix (from 16 CO matrix)		
14CO-2W-a	W…W (2.1)	W…W (1.9)
14CO-2W-b	mon,mon	W…W (1.9)
14CO-2W-c	mon,mon	mon,mon
14CO-2W-d	mon,mon	mon,mon
13CO-3W-a	mon,W…W (1.9)	mon,W…W (1.9)
13CO-3W-b	mon,W…W (2.0)	mon,W…W (1.9)
13CO-3W-c	mon,W…W (2.2)	mon,W…W (2.0)
13CO-3W-d	mon,W…W (2.2)	W…W…W (1.9,1.9)
12CO-4W-a	mon,mon,mon,mon	mon,W…W…W (1.8,1.9)
12CO-4W-b	mon,mon,mon,mon	mon,mon,mon,mon
12CO-4W-c	mon,mon,W…W (1.9)	mon,mon,W…W (1.9)
12CO-4W-d	W…W,W…W (2.0,2.0)	W…W…W…W (1.9,1.9,2.0)
H2O clusters		
29CO-triW-lin[a]	W…W…W (1.8,1.9)	W…W…W (1.8,1.8)
29CO-triW-ang[a]	W…W…W (1.9,1.9)	W…W…W (1.8,1.8,2.0[b])
28CO-tetraW-lin[a]	W…W…W…W (1.9,2.0,2.0)	W…W…W…W (1.8,1.8,1.9)

28CO-tetraW-ang[a]	W…W…W…W (1.8,1.8,1.8)	W…W…W…W (1.8,1.8,1.8)
25CO-triW-tetraW-lin	W…W…W;W…W…W…W	W…W…W…W…W…W…W
	(1.8,1.9;1.9,1.9,2.0)	(1.7,1.8,1.8,1.8,1.8,2.0[b])
13CO-triW-lin[a]	W…W…W (1.8,1.9)	W…W…W (1.7,1.7)[c]
13CO-triW-ang[a]	W…W…W (1.9,1.9,1.9[b])	W…W…W (1.9,1.9,2.0[b])
12CO-tetraW-lin[a]	W…W…W…W (1.9,2.0,2.0)	W…W…W…W (1.8,1.8,1.9)
12CO-tetraW-ang[a]	W…W…W…W (1.8,1.8,1.8)	W…W…W…W (1.8,1.8,1.8)
11CO-pentaW-lin[a]	W…W…W;W…W (1.7,1.8;1.8)	W…W…W…W…W (1.8,1.8,1.8,1.9)
Amorphous		
13CO-triW-lin-amorp[a]	mon,mon,mon	mon,W…W (1.8)
13CO-triW-ang-amorp [a]	mon,mon,mon	W…W…W (1.9,2.0)

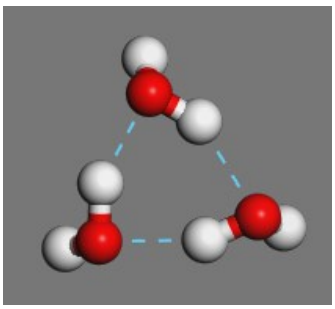
[a]Initial structure of clusters calculated for the isolated species

[b]Closed ring structure

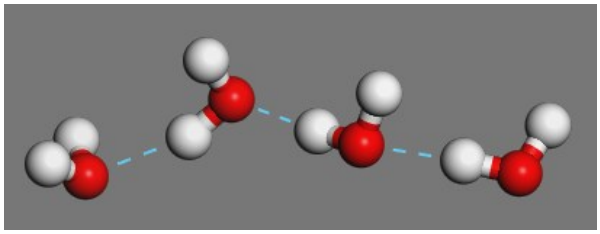
triW-lin



triW-ang



tetraW-lin



tetraW-ang

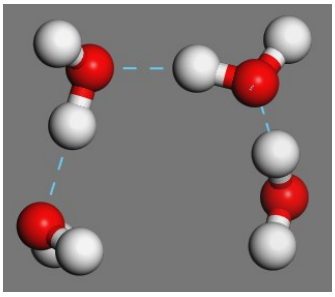


Fig. S1. Water clusters with 3 and 4 molecules. Optimized structures adopt quasi-linear and quasi-closed (angular) configurations.