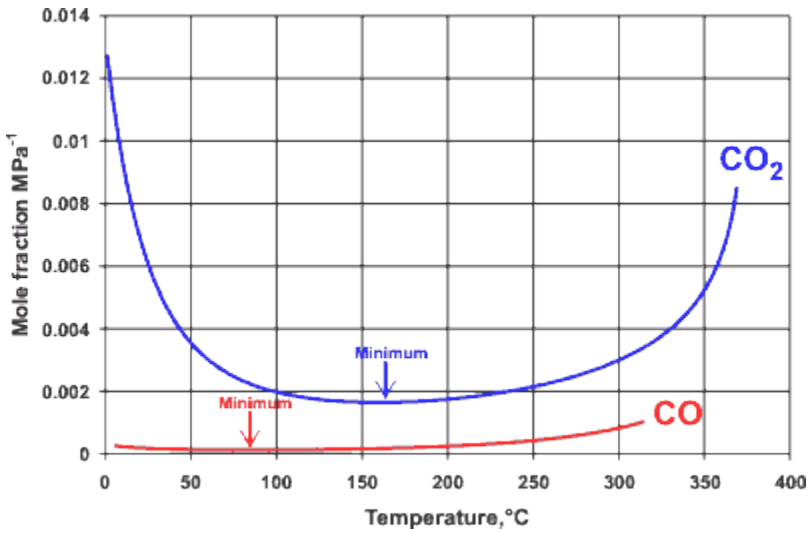
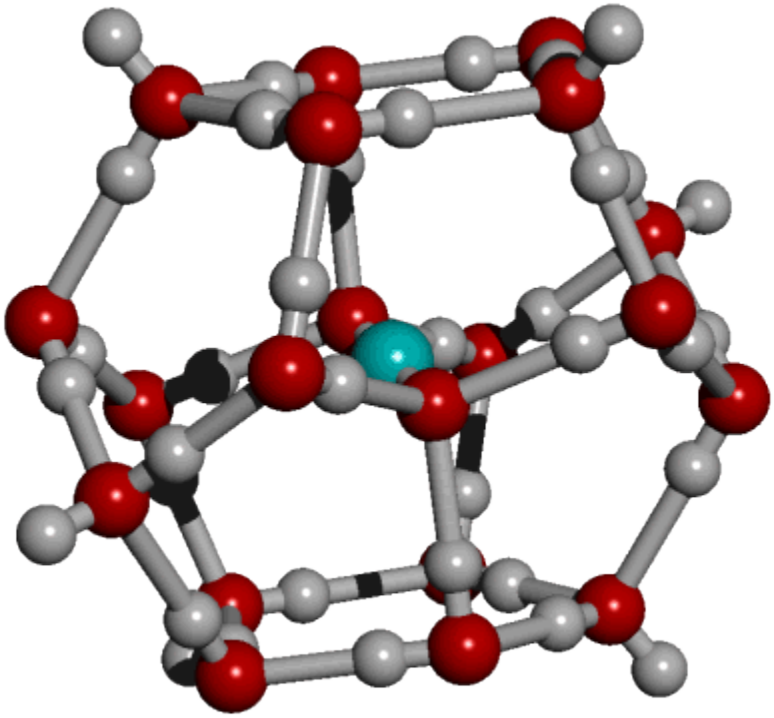
The CO_2-Water Cluster



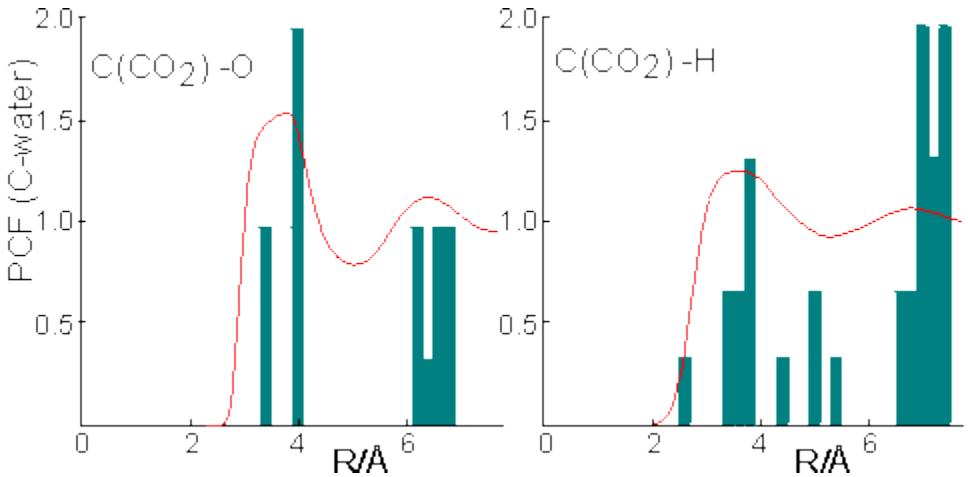
CO_2 is more soluble in water[a] than CO [IAPWS], which is strange as it is both larger and without a dipole moment. This has been explained [166] by specific hydrogen bonding between the oxygen atoms in $CO_2$and water molecules. CO has a partial positive charge on the oxygen that inhibits hydrogen bonding.



The CO_2 may form a hydration shell from a symmetrical dodecahedral arrangement of 18 water molecules where each CO_2 oxygen atom is hydrogen bonded to three water molecules. This allows

some cooperation between the hydrogen bonding at both ends of the CO_2 molecule. Such a cluster can form the central part of an icosahedral water cluster ($CO_2(H_2O)_{278}$) possessing just two defects (water molecules with only 3 rather than 4 hydrogen bonds). In this model, there are six water molecules closest to the CO_2 in agreement with many studies [499].

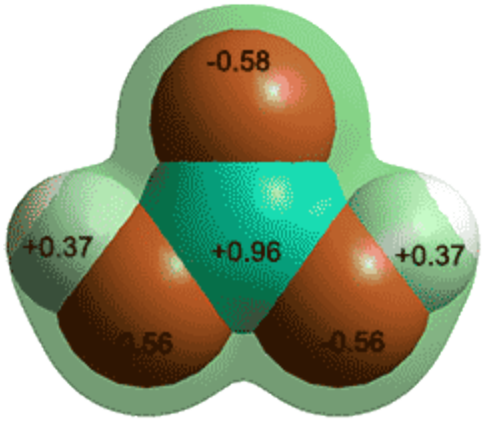
The calculated [166] carbon-oxygen and carbon-hydrogen pair correlation functions (PCF) are remarkably similar to those predicted by the icosahedral model.



The red lines are the calculated pair correlation functions, between the carbon atom in CO_2 and water, and the bars are the predictions from the model. Note that a similarly good fit is apparent if the central cluster is tetrakaidecahedral rather than dodecahedral. Such occupied $5^{12}6^2$ inner-shell clusters are found to be more stable using theoretical modeling [876].

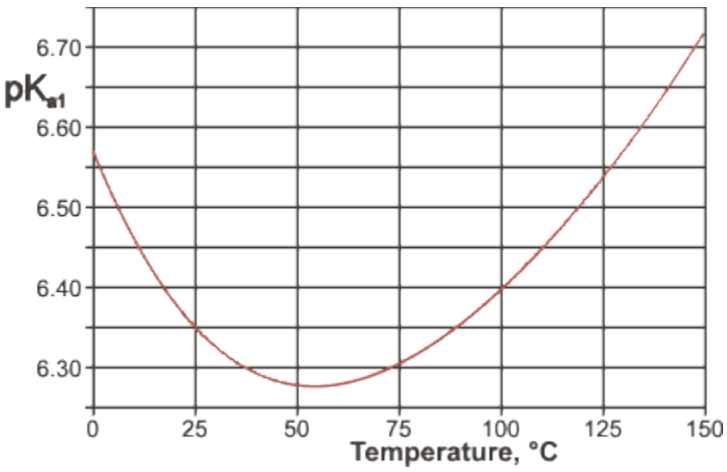
It is notable that calculated pair correlation functions between CO and water [166] are consistent with the CO molecules sitting centrally (clathrate-like) in expanded icosahedral water clusters; CO only forming extremely weak complexes to water (major, HOH---CO; minor H_2O---OC). For interactive Figures of the central dodecahedral cluster, see Jmol.

At high pressures (for example, >2 MPa) and low temperatures (for example, <4 °C) CO_2 forms crystalline clathrates(type-I clathrate, 46 H_2O:8 CO_2 maximum), within a cubic arrangement of two dodecahedral (5^{12}) and six tetrakaidecahedral ($5^{12}6^2$) cages. In these structures there is no hydrogen bonding between the CO_2 guest molecules and the water clathrate lattice and the CO_2 molecules occupy both cages but prefer the tetrakaidecahedral cages.



Footnotes

[a] CO_2 undergoes a slight hydration (~ 0.26 %) to H_2CO_3 (see right) in solution with the resulting weakly acidic H_2CO_3 ionizing slightly.



The $pK_{a1} = -\mathrm{Log}_{10}\left\{\frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]+[CO_2(aq)]}\right\}$ varies with temperature ([1862]see left) due to the higher CO_2 solubility at low temperatures and as described elsewhere.

The following equilibria occur (data at 25 °C) with some confusion over the value of the constants [1852].

CO_2 (g) + H_2O ⇌ CO_2 (aq) (slow)	$K_H = \frac{pCO_2\,(g)}{[CO_2\,(aq)]}$	$K_H \sim 31$ [1]
CO_2 (aq) + H_2O ⇌ H_2CO_3 (slow)	$K_D = \frac{[CO_2\,(aq)]}{[H_2CO_3]}$	$K_D \sim 400$
$H_2CO_3 + H_2O$ ⇌ $H_3O^+ + HCO_3^-$ (fast)	$K_1 = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]}$	$pK_1 \sim 3.45$ (theoretical)
	$K_{a1} = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3] + [CO_2\,(aq)]}$	$pK_{a1} = 6.349$ (apparent)
$HCO_3^- + H_2O$ ⇌ $H_3O^+ + CO_3^{2-}$ (fast)	$K_{a2} = \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]}$	$pK_{a2} = 10.337$

[1] $[CO_2]$ is dissolved CO_2, mol L^{-1};pCO_2 is partial pressure of CO_2 in the gas phase, atm

Thus water in equilibrium with our atmosphere (pCO_2 = 0.00039 atm) forms a 12.5 μM CO_2 (aq) solution of pH 5.6.
[Back]

Source:http://www1.lsbu.ac.uk/water/co2.html