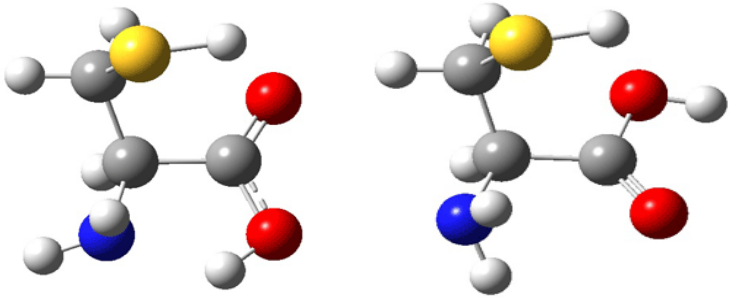
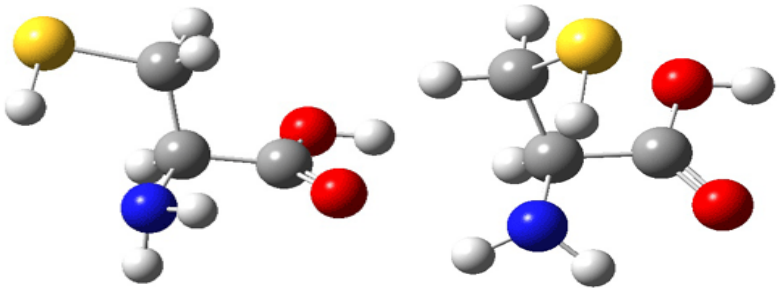
CYSTEINE CONFORMATIONS REVISITED

Schaefer, Csaszar, and Allen have applied the focal point method towards predicting the energies and structures of cysteine.[1] This very high level method refines the structures that can be used to compare against those observed by Alonso[2] in his laser ablation molecular beam Fourier transform microwave spectroscopy experiment (see this post). They performed a broad conformation search, initially examining some 66,664 structures. These reduced to 71 unique conformations at MP2/cc-pvTZ. The lowest 11 energy structures were further optimized at MP2(FC)/aug-cc-pV(T+d)Z. The four lowest energy conformations are shown in Figure 1 along with their relative energies.



I
(0.0)

II
(4.79)



III (5.81) IV (5.95)

Figure 1. MP2(FC)/aug-cc-pV(T+d)Z optimized geometries and focal point relative energies (kJ mol^{-1}) of the four lowest energy conformers of cysteine.[1]

The three lowest energy structures found here match up with the lowest two structures found by Alonso and the energy differences are also quite comparable: 4.79 kJ and 5.81 mol^{-1} with the focal point method 3.89 and 5.38 kJ mol^{-1} with MP4/6-311++G(d,p)// MP2/6-311++G(d,p). So the identification of the cysteine conformers made by Alonso remains on firm ground.

Source: http://comporgchem.com/blog/?p=242