CYSTEINE CONFORMERS

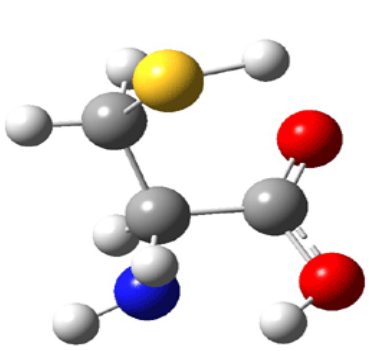
Alonso and coworkers have developed the technique of laser ablation molecular beam Fourier transform microwave spectroscopy to detect biomolecules. In a recent paper[1] they determined the structure of the glycine: one water complex – it is of the neutral configuration. They have now examined the conformations of cysteine[2]. The presence of the thiol side group adds considerable complexity to the problem due to the many conformations possible.

The experiment detected six conformers. Determining the structures responsible for each set of signals was made possible by comparing the experimental results with those determined by computation. Alonso computed 11 low energy conformations of cysteine at MP2/6-311++G (d, p). Then comparing the computed rotational constants and ^{14}N nuclear quadrupole coupling tensor components with the experiment, they were able to match up all six experimental conformers with computed structures. The experimental and computed constants for the three most abundant structures are listed in Table 1. The geometries of all six conformers are drawn in Figure 1.

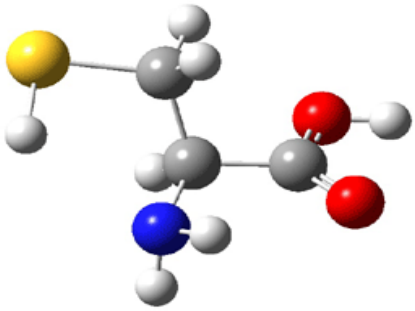
Table 1.Experimental and computed spectroscopic constants (MHz) for the three most abundant conformers of cysteine.[2]

	II_b		**I_a**		**I_b**	
	Expt	MP2	Expt	MP2	Expt	MP2
A	3071.14	3040	4235.63	4221	2889.45	2855
B	1606.54	1623	1187.28	1185	1623.00	1664
C	1331.80	1347	1003.11	1013	1367.83	1386
χ_{aa}	-3.12	-3.14	-4.26	-4.67	-0.14	-0.01
χ_{bb}	2.44	2.59	2.78	2.86	0.44	0.25
χ_{cc}	0.68	0.55	1.49	1.80	-0.30	-0.24
ΔE^a		0		450		325

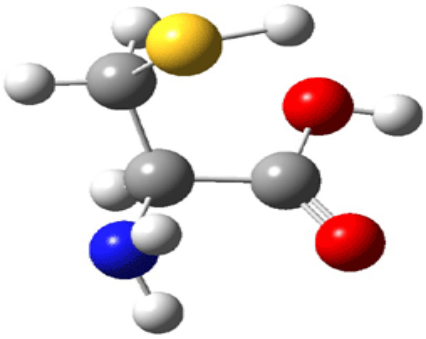
[a]Relative energy in cm^{-1} computed at MP4/6-311++G(d,p)// MP2/6-311++G(d,p).



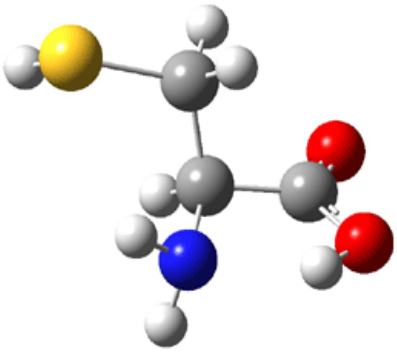
IIb (0.0)



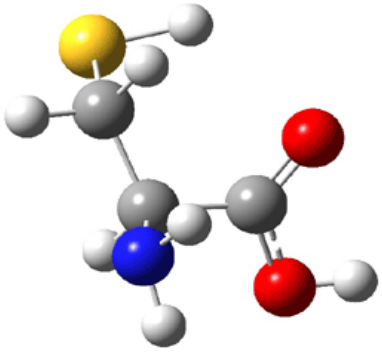
Ia (450)



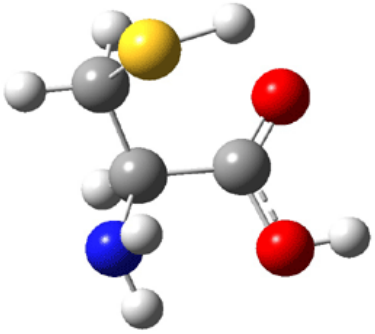
Ib (325)



IIa (527)



III$_\beta$c (765)



III$_\beta$b (585)

Table 1. Optimized structures of the six observed conformers of cysteine. Relative energies in cm^{-1}computed at MP4/6-311++G(d,p)//MP2/6-311++G(d,p). (Note – the geometries shown were optimized at PBE1PBE/6-311+G(d,p) since they MP2 structures are not available!)

This study demonstrates the nice complementary manner in which computation and experiment can work together in structure determination.

Source: http://comporgchem.com/blog/?p=83