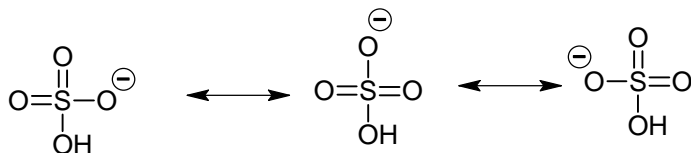
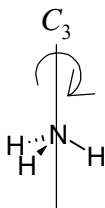


Section 4 – pre-midterm solutions

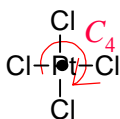
- 2.1 (a) bent (b) tetrahedral (c) tetrahedral
- 2.2 (a) trigonal planar (b) trigonal pyramidal (c) square-based pyramid
- 2.3 (a) T-shaped (b) square planar (c) linear
- 2.5 PCl_4^- is see-saw shape, PCl_4^+ is tetrahedral, PCl_6^- is octahedral
- 4.13 The acids are shown in Table 4.3, the oxoanions are loss of one H^+ from one of the OH groups. As you can see, there are increasing number of resonance structures for the conjugate bases as the $\text{p}K_a$ increases. For example, for the acid H_2SO_4 , there are three resonance structures:



- 6.1 (a) σ_v in the plane of the paper.

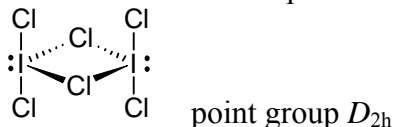


- (b) σ_h in the plane of the paper.

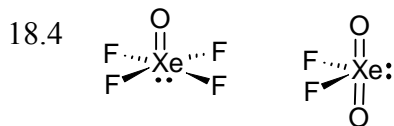


- 6.2 (i) i (ii) i (iii) neither (iv) S_4
- 6.3 (see the point groups in the appendix Resource Section 4 for a full list of the symmetry elements for each point group)
- (a) C_s (b) D_{3h} (c) T_d (d) $C_{\infty v}$ (e) C_1 (f) T_d
- 6.4 Benzene is D_{6h} , therefore has 7 mirror planes (three along a pair of C-H bonds, three between the bonds, and the plane of the molecule itself).
1,3,5- $\text{C}_6\text{H}_3\text{Cl}_3$ has 4 planes of symmetry (D_{3h} point group)
- 15.7 (a) and (b) as in 2.5 (c) trigonal bipyramidal
- 17.9 SbCl_5 is trigonal bipyramidal, FCIO_3 (Cl is the central atom) is tetrahedrally oriented at the Cl.
- 17.11 MCl_4F_2 has *cis* and *trans* as discussed in class. Both have 1 ^{19}F NMR signal.
 MCl_3F_3 has *mer* and *fac* isomers. The *fac* has 1 ^{19}F NMR signal. The *mer* has two (the two Fs that are *trans* to each other will have a separate signal from the F that is *trans* to a Cl atom)

17.13 I have omitted 3 lone pairs on each Cl for clarity:



17.14 A trigonal pyramidal structure (like NH_3 , with $\text{Cl}=\text{O}$ bonds), point group C_s



Section 4 – post-midterm solutions

6.10 We are looking for rows in the point group table that contain both a linear term (x , y , or z) and a quadratic term (x^2 , y^2 , z^2 , xy , xz , yz).

- (a) SF_6 is in the O_h point group; there are no irreducible representations that allow both IR and Raman activity
- (b) In BF_3 , point group D_{3h} , the irreducible representation E' allows both IR and Raman activity

6.11 A_2 , B_1 , and B_2

- 6.13 (a) Planar PF_3 is D_{3h} , pyramidal is C_{3v} . In the latter, all vibrations that are IR active are also Raman active (and *vice versa*). In planar PF_3 , this is not the case (while vibrations with E' symmetry are active in both, the other IR stretch is not Raman active (A_2'') and the other Raman-active stretches are not IR active (A_1' and E'')).
- (b) In D_{2h} , no IR-active vibrations are Raman active. In D_{2d} , all IR-active stretches will also show up in the Raman spectrum.