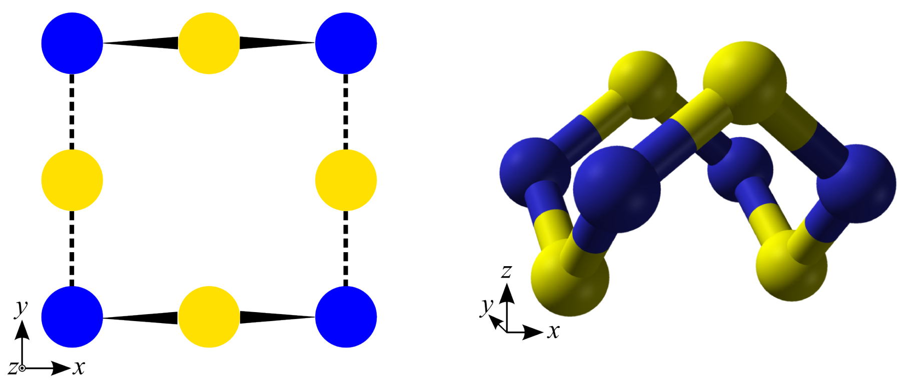
Problem Sheet 1

Michaelmas 2016

1. Consider the molecule in the figure below, comprised of four nitrogen atoms (blue) and four sulphur atoms (yellow).



   (a) Identify the highest-order rotation or rotation-inversion symmetry element and mark it on the left hand figure with the appropriate symbol.

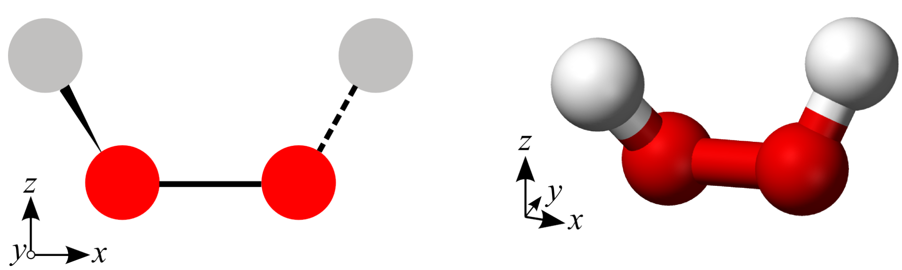
   (b) Draw any lower order rotation axes on the left hand figure with the appropriate symbols.

   (c) Draw any mirror planes on the left hand figure with the appropriate symbol.

   (d) Using the decision tree provided in the handouts, or otherwise, identify the point group of the molecule.

   (e) List all symmetry operators of the point group, divided into classes (*n.b.* a class can contain a single symmetry operation, for example $\{1\}$).

2. **Normal modes of hydrogen peroxide**



   (a) How many normal modes do you expect for a hydrogen peroxide molecule, and how many of these are vibrational normal modes?

   (b) The point group of hydrogen peroxide is 2, which contains just two symmetry operators, E and 2. Identify the position of the two-fold axis of the molecule.

   (c) Systematically construct displacement modes of the hydrogen and oxygen atoms that are either *symmetric* or *antisymmetric* under the two-fold rotation operation. *Hint* Choose hydrogen displacements that are either *parallel* or *perpendicular* to the H-O bonds and oxygen displacements that are either *parallel* or *perpendicular* to the O-O bond.

(d) Only modes that transform "in the same way" can be mixed together to form normal modes. Determine the linear combinations of modes that form the translational normal modes, the rotational normal modes, and the vibrational normal modes named "symmetric O-H stretch", "antisymmetric O-H stretch", "O-O stretch", "symmetric OOH bend", "antisymmetric OOH bend", and "torsion".

(e) Explain which of the vibrational normal modes are infra-red active, and with which polarisation?

3. A monoclinic crystal has lattice parameters $a = 0.6nm$, $b = 0.7nm$ and $c = 0.8nm$ and β=110°.

(a) Find the magnitude of the length denoted by the direction $[31\overline{2}]$.

(b) Find the magnitude of the reciprocal lattice vector $(31\overline{2})$.

(c) Find the angle between the $[31\overline{2}]$ direction and the normal to the plane $(31\overline{2})$.

(d) The crystal has space group $C2/m$ ($2 \parallel \mathbf{b}$). Determine the extinction condition (in terms of h, k, and l) for the reciprocal lattice due to the centring of the direct lattice.

(e) Draw to scale the *hk0* and *h0l* planes of the reciprocal lattice for $-2 < h < 2$, $-2 < k < 2$, and $-2 < l < 2$. What is the centring type of the reciprocal lattice?

4. Consider the orthorhombic space group $Pba2$.

(a) Explain the meaning of all symbols in the space group notation.

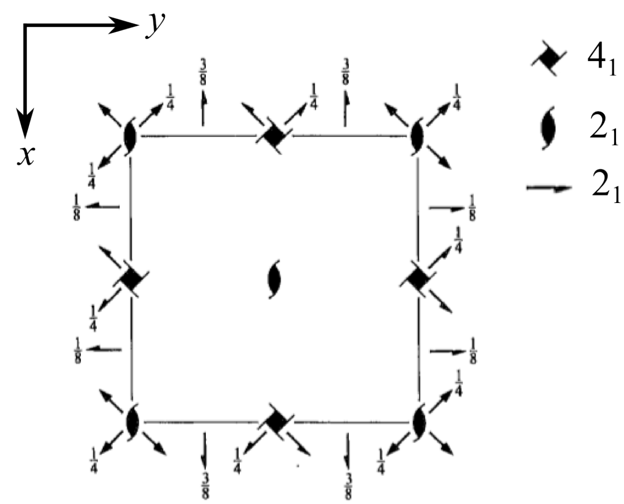
(b) Derive the point group and explain your reasoning. How many symmetry operators does the point group have?

(c) Derive the multiplicity of a general site x, y, z in this space group. What would change in your derivation if the lattice were I-centred (*e.g.* space group $Iba2$)?

(d) A special Wyckoff position in space group $Pba2$ is $[0, 0, z]$ with site symmetry ..2 . Derive the site multiplicity by comparing the number of symmetry elements in the crystal point group with the number of elements in the site symmetry group.

(e) Write the symmetry operators 2 [0,0,z], a [x,1/4,z], and b [1/4,y,z] as a rotation or rotation-inversion matrix about the origin *followed* by a translation, and show explicitly that the line of points [0,0,z] are invariant by the operation 2, and that both operators a and b generate the same, symmetry equivalent line of points, consistent with the site multiplicity found in part d.

5. Below shows a diagram of tetragonal space group $P4_12_12$, looking down the 4_1 axis.



(a) Explain the meaning of all symbols in the space group notation, $P4_12_12$.

The coordinates of the general equivalent positions of $P4_12_12$ are:

(1) x, y, z	(2) $-x, -y, z + \frac{1}{2}$
(3) $-y + \frac{1}{2}, x + \frac{1}{2}, z + \frac{1}{4}$	(4) $y + \frac{1}{2}, -x + \frac{1}{2}, z + \frac{3}{4}$
(5) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{4}$	(6) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{3}{4}$
(7) $y, x, -z$	(8) $-y, -x, -z + \frac{1}{2}$

(b) Suppose an atom is located directly on a 2-fold axis of symmetry. Write out its equivalent positions.

(c) Derive the systematic absences (extinction conditions) due to

- The 4_1 axis in the z direction
- The 2_1 axis in the x direction.