

LECTURE 4. MOLECULAR VIBRATIONS

4.1 Introduction

In general the vibration of a polyatomic molecule does not involve deformation of an individual bond or bond angle.

Instead molecular vibration involves excitation of normal modes of vibration of a molecule. A normal mode of vibration involves a synchronous deformation of the molecule in which the displacement vectors describing the motion of individual atoms combine so as to belong to one of the irreducible representations of the molecule. The atoms all undergo their displacements at the same frequency and all pass through the equilibrium configuration at the same time.

4.2 Basis sets for molecular vibrations

* A set of $3N$ displacement vectors with 3 vectors attached to each of the N atoms in a polyatomic molecule will form the basis for construction of $3N$ symmetry adapted functions. However, 3 of these must correspond to translation of the molecule as whole in three orthogonal directions. In non-linear molecules a further 3 correspond to molecular rotation about three mutually perpendicular axes. For linear molecules there are only 2 rotational degrees of freedom. Thus we find $3N-6$ modes of normal modes of vibration for non-linear molecules and $3N-5$ for linear molecules. In high symmetry molecules some of these modes may be grouped together in degenerate sets.

* For polyatomic molecules of the sort AB_n or AB_nC_m with a unique central atom (e.g. XeF_4 , XeO_3F_2 but not B_2Cl_4) it may often be advantageous to work with a basis set of $3N-3$ vectors, omitting the 3 vectors on the central atom: these will always correspond simply to the translation of the molecule, so that with this basis set we generate vibrations plus rotations.

* Finally in many situations (especially on General Papers!) a problem will focus only on stretching vibrations. In particular we often want to know about stretching vibrations in AB_n polyatomics or about carbonyl stretches or cyanide stretches in $M(CO)_n$ or $M(CN)_n$ complexes. In these cases we can use a much simpler basis set which consists simply of a set of n vectors along the bond directions. (In the AB_n species these vectors must be taken to have their origins on the B atoms, not on the A atom). This basis set will generate the n stretching vibrations without any redundancy.

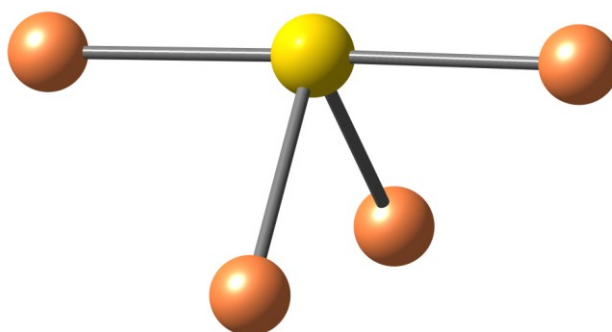
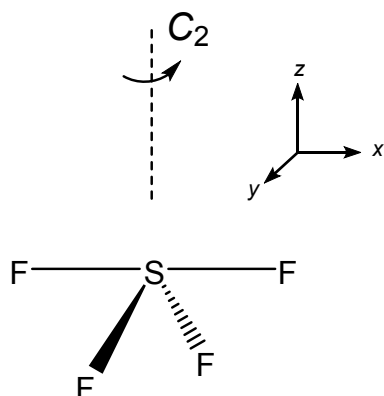
4.3 Using bond stretching basis sets

In general we need to write down the characters of the transformation matrices which describe the effects of each symmetry operation in the group on the chosen basis set. **Vectors on a given atom only contribute to the diagonal sum if the atom is unshifted.** When we are dealing with the set of n bond stretching vectors in an AB_n molecule this gives us the simple rule:

Character under operation $R = \chi(R) = \text{Number of B atoms unshifted under the operation.}$

We can now apply these ideas to deduce the irreducible representations spanned by bond stretching vectors in SF₄, CF₄ and XeF₄.

4.3.1 SF₄ point group C_{2v}



C _{2v}	E	C ₂	σ _v (xz)	σ' _v (yz)		
A ₁	1	1	1	1	z	x ² , y ² , z ²
A ₂	1	1	-1	-1	R _z	xy
B ₁	1	-1	1	-1	x, R _y	xz
B ₂	1	-1	-1	1	y, R _x	yz
Γ _{stretch}	4	0	2	2		

Applying the reduction formula:

$$n(A_1) = 1/4(4+0+2+2) = 2$$

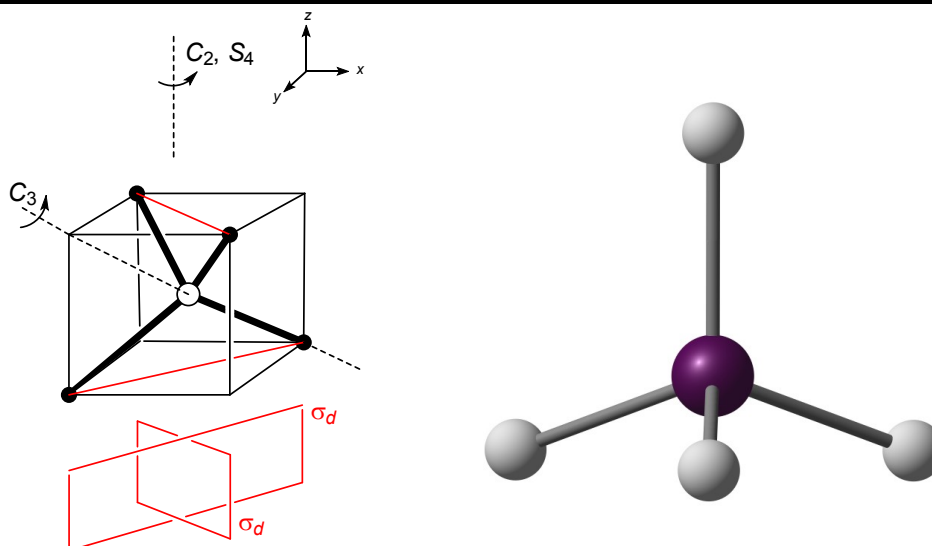
$$n(A_2) = 1/4(4+0-2-2) = 0$$

$$n(B_1) = 1/4(4+0+2-2) = 1$$

$$n(B_2) = 1/4(4+0-2+2) = 1$$

$$\Gamma_{\text{stretch}} = 2A_1 + B_1 + B_2$$

All 4 modes are both IR and Raman active. We can derive the same result by recognising that there are two different sorts of F atom. For each pair an in phase combination of stretches gives an A₁ mode, whilst the out of phase combinations generate the B₁ and B₂ modes. This simple consideration allows us to sketch out the displacement vectors in the stretching modes.

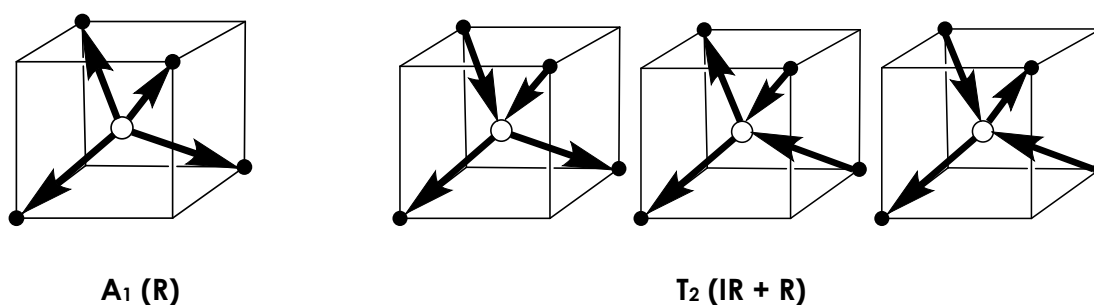
4.3.2 CF₄ point group T_d

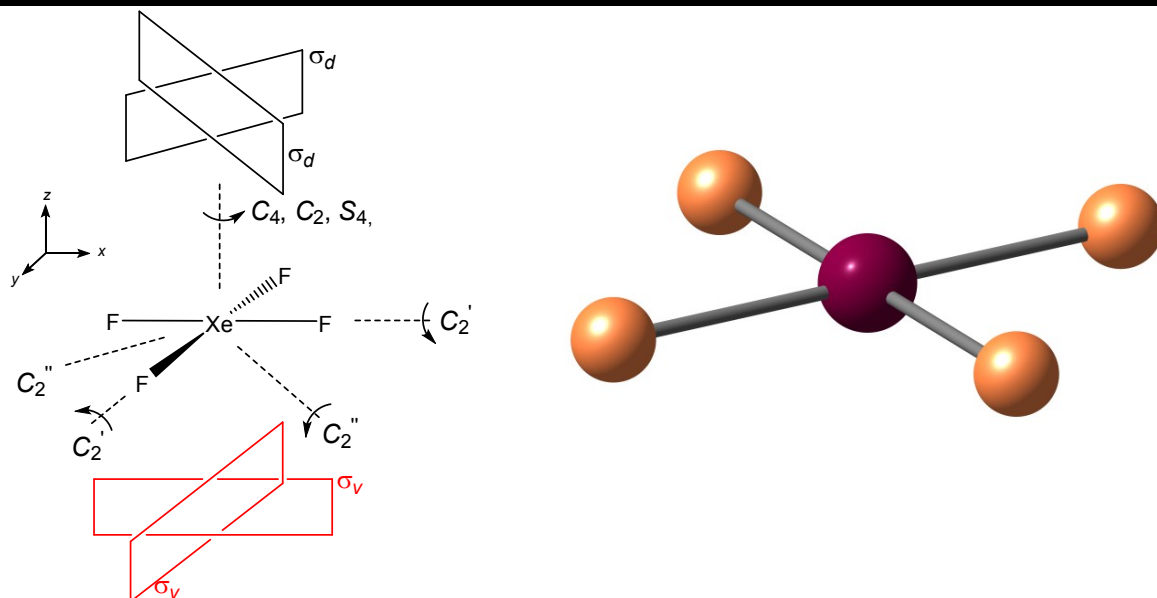
T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	
A_1	1	1	1	1	1	$x^2+y^2+z^2$
A_2	1	1	1	-1	-1	
E	2	-1	2	0	0	$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)
T_2	3	0	-1	-1	1	(x, y, z) (xy, xz, yz)
Γ_{stretch}	4	1	0	0	2	

$$\begin{aligned}
 n(A_1) &= 1/24 \{ (4 \times 1 \times 1) + (1 \times 1 \times 8) + 0 + 0 + (2 \times 1 \times 6) \} = 1 \\
 n(A_2) &= 1/24 \{ (4 \times 1 \times 1) + (1 \times 1 \times 8) + 0 + 0 - (2 \times 1 \times 6) \} = 0 \\
 n(E) &= 1/24 \{ (4 \times 2 \times 1) - (1 \times 1 \times 8) + 0 + 0 + 0 \} = 0 \\
 n(T_1) &= 1/24 \{ (4 \times 3 \times 1) + 0 + 0 + 0 - (2 \times 1 \times 6) \} = 0 \\
 n(T_2) &= 1/24 \{ (4 \times 3 \times 1) + 0 + 0 + 0 + (2 \times 1 \times 6) \} = 1
 \end{aligned}$$

$$\Gamma_{\text{stretch}} = A_1 + T_2$$

A_1 is only Raman active; T_2 is both IR and Raman active. The form of the A_1 mode is trivially obvious. We can sketch the form of the T_2 modes by noting that they are of the same symmetry as p orbitals on the central atom. We use a convention that the displacement vector points toward a + sign on the orbital and a way from a - sign.



4.3.3 XeF₄ point group D_{4h}

D _{4h}	E	2C ₄	C ₂	2C _{2'}	2C _{2''}	i	2S ₄	σ _h	2σ _v	2σ _d	
A _{1g}	1	1	1	1	1	1	1	1	1	1	x ² +y ² , z ²
A _{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R _z
B _{1g}	1	-1	1	1	-1	1	-1	1	1	-1	x ² -y ²
B _{2g}	1	-1	1	-1	1	1	-1	1	-1	1	xy
E _g	2	0	-2	0	0	2	0	-2	0	0	(R _x , R _y)
A _{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A _{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z
B _{1u}	1	-1	1	1	-1	-1	1	-1	-1	1	
B _{2u}	1	-1	1	-1	1	-1	1	-1	1	-1	
E _u	2	0	-2	0	0	-2	0	2	0	0	(x, y)
Γ _{stretch}	4	0	0	2	0	0	0	4	2	0	

Application of the reduction formula is tedious in this case but we simplify the calculation somewhat by recognising that the in-plane stretch vector cannot possibly generate any irreducible representations that change sign under the σ_h operation. Hence we ignore E_g and the ungerade A and B representations.

$$n(A_{1g}) = 1/16\{(4 \times 1 \times 1) + 0 + 0 + (2 \times 1 \times 2) + 0 + 0 + 0 + (4 \times 1 \times 1) + (2 \times 1 \times 2) + 0\} = 1$$

$$n(A_{2g}) = 1/16\{(4 \times 1 \times 1) + 0 + 0 - (2 \times 1 \times 2) + 0 + 0 + 0 + (4 \times 1 \times 1) - (2 \times 1 \times 2) + 0\} = 0$$

$$n(B_{1g}) = 1/16\{(4 \times 1 \times 1) + 0 + 0 + (2 \times 1 \times 2) + 0 + 0 + 0 + (4 \times 1 \times 1) + (2 \times 1 \times 2) + 0\} = 1$$

$$n(B_{2g}) = 1/16\{(4 \times 1 \times 1) + 0 + 0 - (2 \times 1 \times 2) + 0 + 0 + 0 + (4 \times 1 \times 1) - (2 \times 1 \times 2) + 0\} = 0$$

$$n(E_u) = 1/16\{(4 \times 2 \times 1) + 0 + 0 + 0 + 0 + 0 + 0 + (4 \times 2 \times 1) + 0 + 0\} = 1$$

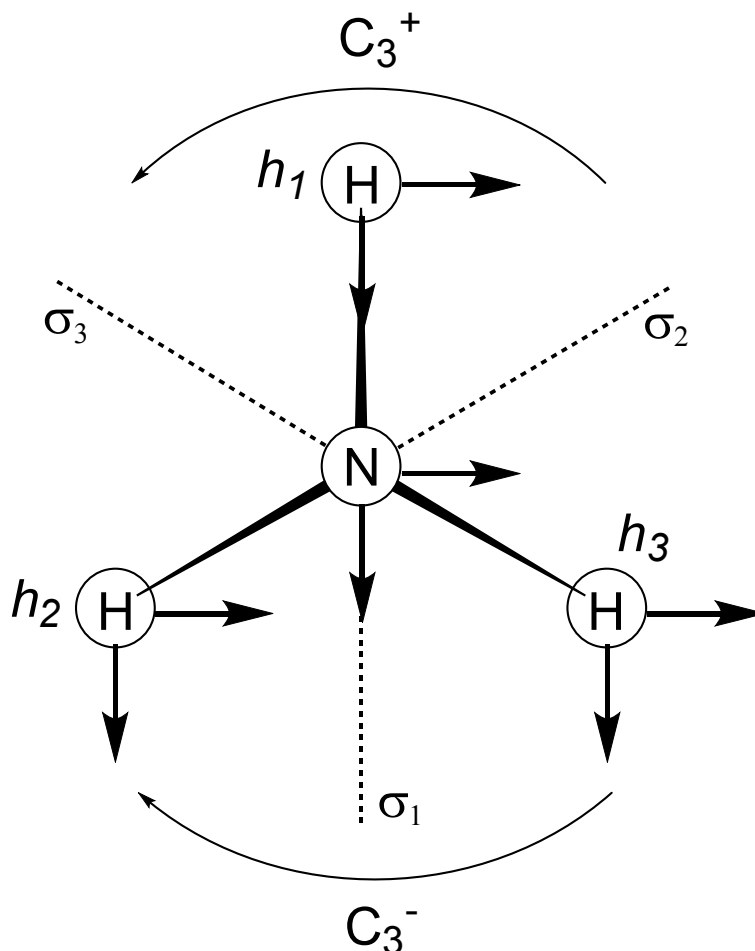
$$\Gamma_{\text{stretch}} = A_{1g} + B_{1g} + E_u$$

Of these modes A_{1g} and B_{1g} are Raman active and E_u is IR active. The **mutual exclusion rule** applies, as in all centrosymmetric systems. Because the dipole moment operator is u and the components of the polarisability tensor are g , no mode can be both Raman and IR active in a molecule with a centre of symmetry.

Exercise: Sketch out the form of the modes.

4.4 The vibrations of NH₃

NH₃ belongs to the point group C_{3v} and we can tackle the problem of deriving the symmetry of its normal modes of vibration using a “complete” basis set with 3 vectors on each of the 4 atoms.



Plan view of the NH₃ molecule with a complete basis set of 3 displacement vectors on each atom. Besides the two vectors seen for each atom, a “z” vector points upward from each atomic centre.

The major new problem encountered with this basis set is the effect of the 3-fold rotation on the vectors (x,y,z) on the N atom. In general if we use $R(\alpha)$ to indicate rotation by an angle α :

$$R(\alpha) \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos \alpha & -\sin \alpha & 0 \\ \sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Thus the character for a trio of vectors (x,y,z) under rotation by α is $1+2\cos\alpha$. (If we are dealing with an S type improper rotation, the z vector changes direction so that the character is instead $-1+2\cos\alpha$)

For C_3^+ , $\alpha = 120^\circ$ so that $\cos \alpha = -1/2$ and the trace of the transformation matrix for C_3^+ is $\chi(120^\circ) = 0$. Similarly for C_3^- $\alpha = 240^\circ$ and again $\cos \alpha = -1/2$ and $\chi(240^\circ) = 0$. This illustrates the general point that the character is always the same for two operations of the same class. Thus when dealing with reflections we can choose for convenience the σ_1 mirror plane where two vectors on H_1 and the N atom are unshifted under σ and one changes sign so that the contribution from each atom to $\chi(\sigma)$ is +1. Thus we derive the set of characters shown below:

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	$(x, y) (R_x, R_y)$	$(x^2-y^2, xy) (xz, yz)$
Unshifted atoms	4	1	2		
$\chi(3N)$	12	0	2		

Application of the reduction formula gives:

$$\begin{aligned}
 n(A_1) &= 1/6\{(12 \times 1 \times 1) + 0 + (2 \times 1 \times 3)\} = 3 \\
 n(A_2) &= 1/6\{(12 \times 1 \times 1) + 0 + (2 \times -1 \times 3)\} = 1 \\
 n(E) &= 1/6\{(12 \times 2 \times 1) + 0 + 0\} = 4
 \end{aligned}$$

hence:

$$\begin{aligned}
 \Gamma(3N) &= 3A_1 + 1A_2 + 4E \\
 \Gamma(\text{trans}) &= 1A_1 + 1E \\
 \Gamma(\text{rot}) &= 1A_2 + 1E \\
 \Gamma(\text{vib}) &= 2A_1 + 2E
 \end{aligned}$$

Using a set of 3 stretching vectors it can be quickly shown that:

$$\Gamma(\text{Stretch}) = A_1 + E$$

therefore:

$$\Gamma(\text{Bend}) = A_1 + E$$

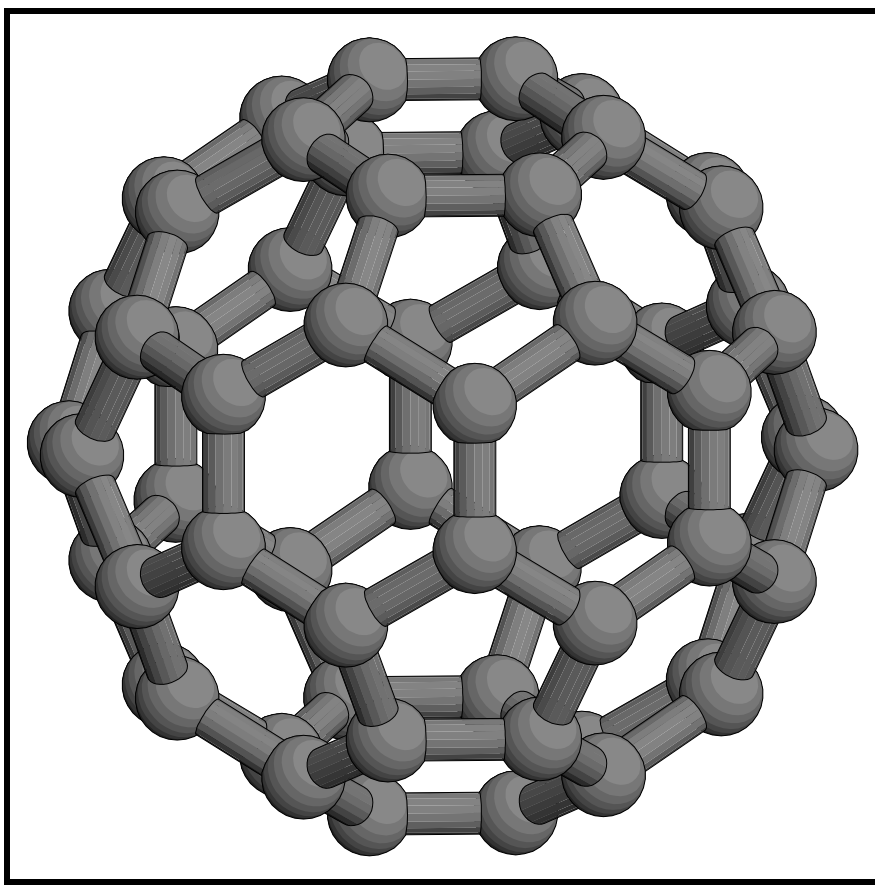
Where stretching and bending modes are of the same symmetry, mixing between them is allowed.

4.5 The vibrations of C_{60}

C_{60} is a remarkable molecule built up from 20 hexagonal rings and 12 pentagonal rings. Group theory played an important part in the discovery of C_{60} by making the simple prediction that the molecule should have only 4 infrared active vibrations.

C_{60} is a very rare example of a molecule belonging to the icosahedral point group I_h . The $3N-6$ rule tells us that there are no less than 174 modes of vibration and on the face of it the problem of deriving the symmetry of these modes is formidable. The character table looks particularly unfriendly and contains characters such as $\frac{1}{2}(1 \pm \sqrt{5})$! The group order is $h=120$ and there are 10 irreducible representations including 4-fold degenerate G representations and five fold degenerate H representations. These degeneracies are not encountered in other molecular point groups.

Nonetheless it turns out to be very easy to derive the normal modes of vibration. This is because **none** of the rotational symmetry axes passes through an atomic position and the character of the basis set of 180 displacement vectors under the rotational operations is zero. The character under inversion i is also zero. The 15 mirror planes each contain 4 atoms so that the character under σ is $(4 \times 2 - 4 \times 1) = 4$. The only other operation where a non-zero character appears is under the identity operation, where $\chi(E)=180$. Application of the reduction formula is therefore much less problematic than expected. It transpires that there are only 4 infrared active T_{1u} modes and 8 Raman active H_g modes.



I_h	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	i	$12S_{10}$	$12S_{10}^3$	$20S_6$	15σ	$\eta^\pm = 1/2(1 \pm \sqrt{5})$	
A_g	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
T_{1g}	3	η^+	η^-	0	-1	3	η^-	η^+	0	-1	(R_x, R_y, R_z)	
T_{2g}	3	η^-	η^+	0	-1	3	η^+	η^-	0	-1		
G_g	4	-1	-1	1	0	4	-1	-1	1	0		
H_g	5	0	0	-1	1	5	0	0	-1	1		$(2z^2-x^2-y^2, x^2-y^2, xy, yz, xz)$
A_u	1	1	1	1	1	-1	-1	-1	-1	-1		
T_{1u}	3	η^+	η^-	0	-1	-3	$-\eta^-$	$-\eta^+$	0	1	(x, y, z)	
T_{2u}	3	η^-	η^+	0	-1	-3	$-\eta^+$	$-\eta^-$	0	1		
G_u	4	-1	-1	1	0	-4	1	1	-1	0		
H_u	5	0	0	-1	1	-5	0	0	1	-1		
Γ_{3N}	180	0	0	0	0	0	0	0	0	4		

$$n(A_g) = 1/120\{(1 \times 180) + (4 \times 15)\} = 2$$

$$n(T_{1g}) = 1/120\{(3 \times 180) - (4 \times 15)\} = 4$$

$$n(T_{2g}) = 1/120\{(3 \times 180) - (4 \times 15)\} = 4$$

$$n(G_g) = 1/120\{(4 \times 180) + (0 \times 15)\} = 6$$

$$n(H_g) = 1/120\{(5 \times 180) + (4 \times 15)\} = 8$$

$$n(A_u) = 1/120\{(1 \times 180) - (4 \times 15)\} = 1$$

$$n(T_{1u}) = 1/120\{(3 \times 180) + (4 \times 15)\} = 5$$

$$n(T_{2u}) = 1/120\{(3 \times 180) + (4 \times 15)\} = 5$$

$$n(G_u) = 1/120\{(4 \times 180) + (0 \times 15)\} = 6$$

$$n(H_u) = 1/120\{(5 \times 180) - (4 \times 15)\} = 7$$

$$\text{No. of } g \text{ functions} = 2 + 4 \times 3 + 4 \times 3 + 6 \times 4 + 8 \times 5 = 90$$

$$\text{No. of } u \text{ functions} = 1 + 5 \times 3 + 5 \times 3 + 6 \times 4 + 7 \times 5 = 90$$

$$\Gamma_{3N} = 2A_g + 4T_{1g} + 4T_{2g} + 6G_g + 8H_g + A_u + 5T_{1u} + 5T_{2u} + 6G_u + 7H_u$$

$$\Gamma_{\text{trans}} = T_{1u}$$

$$\Gamma_{\text{rot}} = T_{1g}$$

$$\Gamma_{\text{vib}} = 2A_g + 3T_{1g} + 4T_{2g} + 6G_g + 8H_g + A_u + 4T_{1u} + 5T_{2u} + 6G_u + 7H_u$$

PROBLEMS

1. Use the reduction formula to show that the bond stretching vibrations in SF_6 belong to irreducible representations $a_{1g} + e_g + t_{1u}$. By matching the displacement vectors to atomic orbitals on S of the same symmetry (or otherwise), sketch out the atomic displacements in these normal modes. Which of these modes is IR active? Which are Raman active?
2. Derive the irreducible representations of the C–H stretching vibrations in benzene (C_6H_6) and sketch out the displacements in these normal modes of vibration. (Hint: the working given in handout 1 relating to the π MOs in benzene and the solution to problem 2 should both be useful to you.)
3. A useful shortcut to deriving the stretching modes of vibration in an AB_n polyatomics is to recognise that the set of irreducible representations spanned by the n bond stretching vectors is the same as that spanned by the atomic wavefunctions on A which are used to construct hybrid orbitals along the bond directions. Verify that this approach gives the same answers as those derived from application of the reduction formula for bond stretching vibrations in SF_6 (sp^3d^2), CF_4 (sp^3) and XeF_4 (sp^2d). What is the symmetry of the stretching vibrations in BF_3 (sp^2) and PF_5 (sp^3d). (Hints. Remember that a central atom s orbital is always totally symmetric, and that transformation properties of p and d orbitals are always given in the character table. Be careful that the irreducible representations you choose correspond to the correct number of atomic orbitals.)
4. Use a full set of displacement vectors to derive the normal modes of vibration of *cis* and *trans* isomers of N_2F_2 . Discuss the pattern of infrared and Raman activity for the two isomers and show how vibrational spectroscopy can be used to distinguish the two isomers.
5. Use a basis set with 3 vectors on each H atom but no vectors on N to derive the complete set of vibrations for NH_3 . Compare your calculation with that given in the handout, where a “full” basis set was used.
6. Derive the normal modes of vibration of BF_3 (D_{3h}) and discuss the activity of these modes in IR and Raman spectroscopy. Compare these results with those for NH_3 . Which overtone and combination bands would be active in IR spectroscopy of BF_3 ?