



Benha university
Faculty of science
Chemistry department

4th year students
Applied inorganic chemistry
(Double course)

Date : 9.6.2019
Time: 2 hours
Code: Ch424

Answer the following Questions:

Section A

1. Answer only **Two** questions from the following:

Q1: Calculate Γ_{vib} , Γ_{str} and Γ_{bend} for SO_2 molecule and predict the number of IR bands expected. (20 Marks)

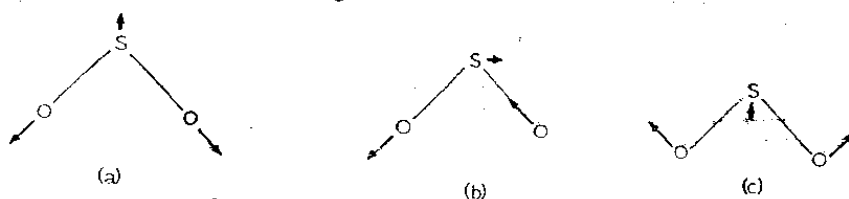
Q2: Calculate Γ_{σ} and clarify the type of hybridization take place in the bond formation of PF_5 molecule (20 Marks)

Q3: How can you deduce Γ_{σ} , $\Gamma_{\Pi(11)}$ and $\Gamma_{\Pi(\perp)}$ in BF_3 molecule? (20 Marks)

With Best Wishes, Dr. Ayman Abdel Razik

Vibrational Spectroscopy

An N-atomic molecule possesses $3N$ dynamical degrees of freedom, i.e. there are $3N$ different independent ways in which the atoms in the molecule can move. For non-linear molecule, there are three *translational* (i.e. translation of the whole molecule along any three perpendicular axes) and three *rotational* (i.e. rotation about these three axes) degrees of freedom. These leave $(3N-6)$ independent *vibrational* degrees of freedom. For linear molecule there are only two rotational degrees of freedom (no rotation can occur about the molecular axis) leaving $(3N-5)$ vibrational degrees of freedom. Each of these $(3N-6)$ or $(3N-5)$ are called vibrational modes of the molecule. For example for a bent tri-atomic molecule such as SO_2 we can see the three vibrational modes as in figure



It will be seen that two of the vibrations involve stretching of the S-O bonds while one is chiefly an angle deformation. In each of the vibrational modes the atomic displacement occur at a characteristic frequency which depends upon the restoring forces acting against the molecular displacements (force constants) and the atomic masses of the atoms. Now to obtain theoretically the number of vibrational modes we use the fact that

$$\Gamma_{3N} = \Gamma_{\text{vibration}} + \Gamma_{\text{translation}} + \Gamma_{\text{rotation}} = \Gamma_V + \Gamma_T + \Gamma_R$$

In each case we can find Γ_{T+R} from the character table then by subtraction we can find Γ_{vib} . Let us now return to the example of SO_2 , we found that:

$$\Gamma_{3N} = 3A_1 + A_2 + 2B_1 + 2B_2 \quad \text{and from } C_{2v} \text{ character table we find}$$

$$\Gamma_{T+R} = A_1 + A_2 + 2B_1 + 2B_2 \quad \text{then}$$

$$\Gamma_{\text{vib}} = 2A_1 + B_2 = \quad \text{three vibrational bands.}$$

Now we need to classify these bands into stretching or bending (deformation).

To do this a set of vectors is drawn to represent the bonds in molecule and the characters of Γ_{stretch} are generated using the following rules

a- vectors shifted to a new position by a symmetry operation R contribute 0 to $X(R)$.

b- unshifted vectors contribute +1 to $X(R)$

c- vectors unshifted in position but reversed in direction contribute -1 to $X(R)$

thus for SO_2 molecule stretching vectors:

C_{2v}	E	C_2	$\sigma(xz)$	$\sigma(yz)$
Γ_{str}	2	0	0	2



This gives $\Gamma_{\text{str}} = A_1 + B_2$ (two bands) and $\Gamma_{\text{bend}} = A_1$ (only one band)

Thus the IR spectra of SO_2 molecule show three vibrational bands, two of them ($A_1 + B_2$) are stretching and the third (A_1) is bending deformation. All of the three bands are IR active (see character table). The observed infra-red spectral bands of SO_2 molecule are listed in the following table

Band (cm^{-1})	assignment
518	A_1 ; O-S-O deformation
1151	A_1 ; symmetric S-O stretch
1362	B_2 ; antisymmetric S-O stretch

Example (5): predict the number of IR bands expected to be found in POCl_3 , H_2O , PtCl_4^{2-} and CO_3^{2-} molecules then show which of them is IR inactive.

II-Construction of Hybrid Orbitals

It frequently happens that maximum bonding energy in a certain molecule may not be achieved by using pure s, p, d, ... atomic orbitals to form bonds. A better overlap, and hence a stronger bond, can be achieved by employing hybrid atomic orbitals. These are constructed from the s, p, d, ... orbitals of the atom to give orbitals concentrated along the observed bond directions. In many cases, the use of group theory can show which combination of atomic orbitals must be used to construct hybrid orbitals.

A simple case which can be obtained is the planer trigonal molecule BF_3 , which belongs to D_{3h} point group. We need to find the combination of boron atomic orbitals which will be most appropriate for the formation of B-F σ -bonds. It necessary to construct three orbitals pointing along the B-F bond directions and a suitable set of vectors which can be used as bases for the representations as shown in Fig.1



Fig.1. B-F σ -bonding vectors for the BF_3 molecule

Using the methods developed before we can obtain the representation Γ_σ :

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_σ	3	0	1	3	0	1

This is a reducible representation which can be decomposed into the following irreducible representations:

$$\Gamma_\sigma = a_1' + e'$$

Thus, a set of three B-atomic orbitals must be used of which one has a_1' symmetry in the D_{3h} point group (s-orbital) and two degenerate have e'

symmetry (p_x, p_y). Hence, the boron atomic orbitals which must be used to produce hybridization are the $2s, 2p_x$ and $2p_y$ and the type of hybridization is sp^2 .

Let us take further examples, considering in each case the type of hybridization necessary for most efficient σ -bonding

(a) NH_4^+

The relevant vectors are shown in Fig.2



Fig.2. N-H σ -bonding vectors for the NH_4^+ ion (T_d)

This gives rise to a reducible representation of the point group T_d

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Γ_σ	4	1	0	0	2

which can be reduced to

$$\Gamma_\sigma = a_1 + t_2$$

The only nitrogen orbitals which are energetically available for the bonding are the $2s$ and $2p$, and from the character table we see that the p -orbitals can be used as a bases for the t_2 irreducible representation. The s -orbital is as usual totally symmetric (a_1) and therefore an s and three p -orbitals are required forming sp^3 -hybrids.

(b) PF_5

This molecule belongs to D_{3h} and atomic orbitals of P atom must be hybridized to give orbitals in the directions are shown in Fig.3. The five vectors give the following representation of D_{3h}

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_σ	5	2	1	3	0	3

which is reducible to

$$\Gamma_\sigma = 2a_1' + a_2'' + e'$$

The phosphorus atom can use 3s, 3p and 3d-orbitals for bonding and of these the following have the correct symmetry properties:

$$a_1' : s, d_{z^2}$$

$$a_2'' : p_z$$

$$e' : (p_x, p_y) \text{ and } (d_{xy}, d_{x^2-y^2})$$

the following combinations would be equally good from the symmetry point of view:

$$(i) s, d_{z^2}, p_z, (p_x, p_y) \text{ i.e. } sp^3d \text{ or}$$

$$(ii) s, d_{z^2}, p_z, (d_{xy}, d_{x^2-y^2}) \text{ i.e. } spd^3$$

for phosphorus atom, the 3-d orbitals are somewhat higher in energy than the 3-s and 3-p and therefore it seems that the hybrid orbitals can be described as sp^3d .

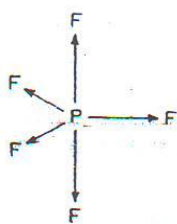


FIG. 3. P-F σ -bonding vectors for the PF_5 molecule (D_{3h}).

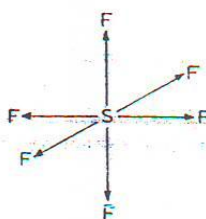


FIG. 4. S-F σ -bonding vectors for the SF_6 molecule (O_h).

(c) SF_6

This is an octahedral (O_h) molecule, and the vectors in fig.4 will generate a σ -bonding hybrid orbital representation

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$3\sigma_d$
Γ_σ	6	0	0	2	2	0	0	0	4	2

Thus, $\Gamma_\sigma = a_{1g} + e_g + t_{1u}$

Sulphur atom can use 3s, 3p and 3d-orbitals for bonding and of these the following have the correct symmetry properties:

$$a_{1g} : s$$

$$e_g : d_{z^2}, (d_{x^2-y^2})$$

$$t_{1u} : (p_x, p_y, p_z)$$

there is no choice, and the only set of hybrid orbitals which could give an octahedral arrangement can be described as sp^3d^2

Hybrid Orbitals for π -Bonding

So far we have dealt with the formation of σ -bond only. Similar principles are involved in the construction of hybrid orbitals suitable for π -bonding. We will consider for example the BF_3 molecule (D_{3h}). The orbitals on the fluorine atoms which can overlap to form π B-F bonds will be p-orbitals, either in the molecular plane (Fig.5-a) or perpendicular to it (Fig.5-b). We need to find which boron orbitals can overlap with these to form $\pi(\parallel)$ and $\pi(\perp)$ bonds (parallel or perpendicular to the molecular plane)

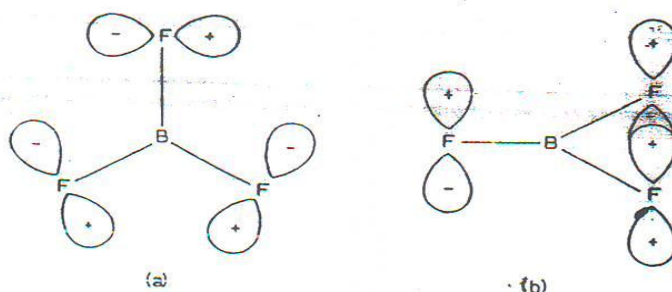


Fig.5. B-F π -bonding for BF_3 molecule; a- parallel and b- perpendicular

Thus we can easily obtain the following representations of D_{3h}

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\Gamma_{\pi(\parallel)}$	3	0	-1	3	0	-1
$\Gamma_{\pi(\perp)}$	3	0	-1	-3	0	1

which is reducible to

$$\Gamma_{\pi(\parallel)} = a_2' + e'$$

$$\Gamma_{\pi(\perp)} = a_2'' + e''$$

The following B orbitals could be used to construct sets suitable for $\pi(\parallel)$ -bonding

a_2' : none; e' : (p_x, p_z) and ($d_{x^2-y^2}, d_{xy}$)