Bonding HL (answers)

IB CHEMISTRY HL

14.1 Further aspects of covalent bonding and structure

Understandings:

- Covalent bonds result from the overlap of atomic orbitals. A sigma bond (σ) is formed by the direct head-on/end-to-end overlap of atomic orbitals, resulting in electron density concentrated between the nuclei of the bonding atoms. A pi bond (π) is formed by the sideways overlap of atomic orbitals, resulting in electron density above and below the plane of the nuclei of the bonding atoms.
- Formal charge (FC) can be used to decide which Lewis (electron dot) structure is preferred from several. The FC is the charge an atom would have if all atoms in the molecule had the same electronegativity. FC = (Number of valence electrons)-½(Number of bonding electrons)-(Number of non-bonding electrons). The Lewis (electron dot) structure with the atoms having FC values closest to zero is preferred.
- Exceptions to the octet rule include some species having incomplete octets and expanded octets.
- Delocalization involves electrons that are shared by more than two nuclei in a molecule or ion as opposed to being localized between a pair of atoms.
- Resonance involves using two or more Lewis (electron dot) structures to represent a particular molecule or ion. A resonance structure is one of two or more alternative Lewis (electron dot) structures for a molecule or ion that cannot be described fully with one Lewis (electron dot) structure alone.

Applications and skills:

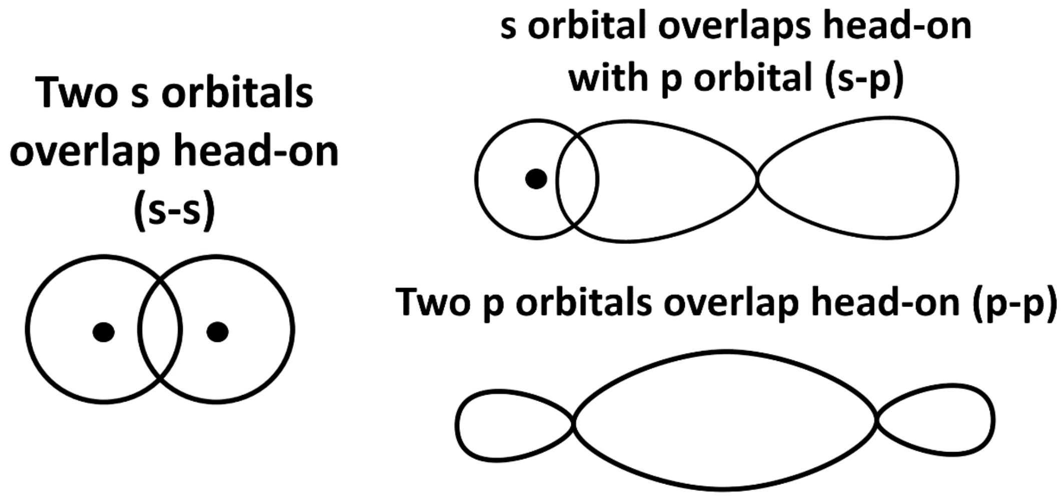
- Prediction whether sigma (σ) or pi (π) bonds are formed from the linear combination of atomic orbitals.
- Deduction of the Lewis (electron dot) structures of molecules and ions showing all valence electrons for up to six electron pairs on each atom.
- Application of FC to ascertain which Lewis (electron dot) structure is preferred from different Lewis (electron dot) structures.
- Deduction using VSEPR theory of the electron domain geometry and molecular geometry with five and six electron domains and associated bond angles.
- Explanation of the wavelength of light required to dissociate oxygen and ozone.
- Description of the mechanism of the catalysis of ozone depletion when catalysed by CFCs and NO_x.

Syllabus checklist

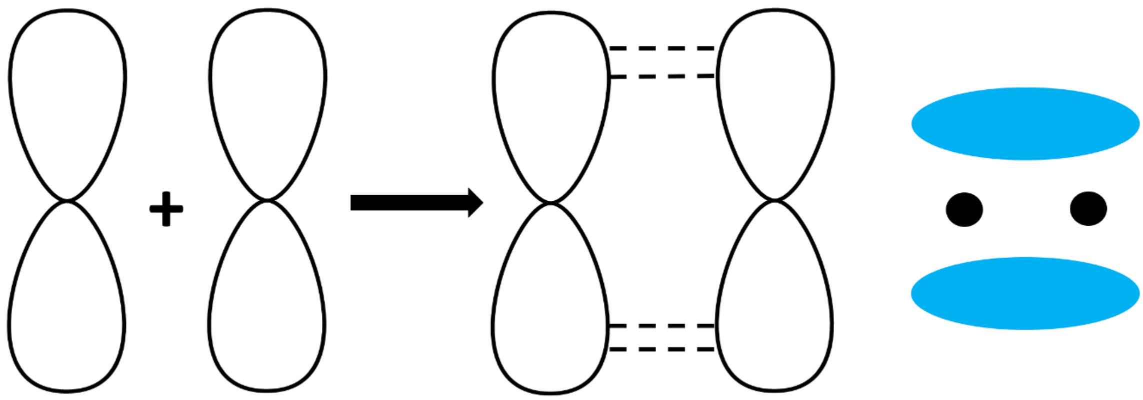
Objective	I am confident with this	I need to review this	I need help with this
Explain the formation of sigma and pi bonds			
Draw Lewis structures for molecules and ions with up to 6 electron domains around the central atom.			
Determine the formal charge on an atom.			
Use the concept of formal charge to deduce the preferred Lewis structure for a molecule.			
Explanation of the wavelength of light required to dissociate oxygen and ozone.			
Describe the mechanism of the catalysis of ozone depletion by CFCs and NO_x			

Sigma (σ) and pi bonds (π)

- Covalent bonds result from the overlap of atomic orbitals.
- A sigma bond (σ) is formed by the direct head-on (axial) overlap of atomic orbitals, resulting in electron density concentrated between the nuclei of the bonding atoms.
- Sigma bonds are formed by head-on overlap of s orbitals, head-on overlap of s and p orbitals and head-on overlap of p orbitals, as shown below.



- A pi bond (π) is formed by the sideways (lateral) overlap of atomic orbitals, resulting in electron density above and below the plane of the nuclei of the bonding atoms.
- The diagram below shows the formation of a pi bond between the two carbon atoms in ethene (C_2H_4).



Number of sigma and pi bonds in a single, double, and triple covalent bond.

Type of bond	sigma (σ)	pi (π)
single	1	0
double	1	1
triple	1	2

Exercises

1. Describe the formation of a sigma (σ) bond.
   A sigma (σ) bond is formed by head-on overlap of atomic orbitals. The electron density is concentrated between the nuclei of the bonding atoms.

2. Describe the formation of a pi (π) bond.
   A pi (π) bond is formed by sideways overlap of atomic orbitals. The electron density is concentrated above and below the plane of the nuclei of the bonding atoms.

3. Complete the following table:

Type of overlap	Type of bond formed
s and s head on	sigma
s and p head on	sigma
p and p head on	sigma
p and p sideways	pi

4. Determine the number of sigma (σ) and pi (π) bonds in the following molecules:

a) Cl_2 single bond between atoms– one sigma (σ) bond

b) O_2 double bond between atoms– one sigma (σ), one pi (π) bond

c) N_2 triple bond between atoms – one sigma (σ), two pi (π) bonds

Formal charge

- Formal charge is used to determine which Lewis structure is preferred when more than one is possible.
- The formal charge is the charge an atom would have if all the atoms in a molecule had the same electronegativity.
- The preferred Lewis structure is the one where the individual atoms have the lowest possible formal charge (closest to zero).

Formal charge = # of valence e⁻ – # of non-bonding e⁻ – ½ # of bonding e⁻

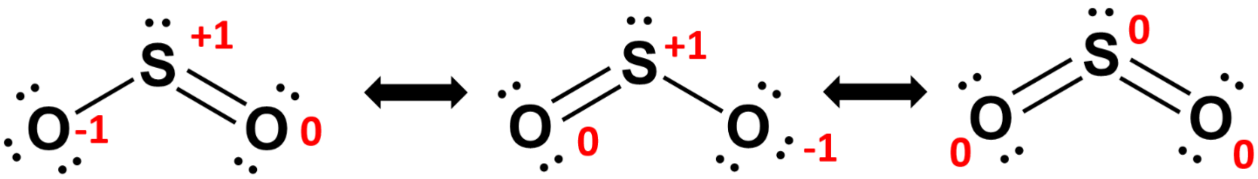
$$FC = V - N - \tfrac{1}{2} B$$

Example: Deduce the formal charge on each atom and determine which structure is the preferred Lewis structure.

1. CO_2

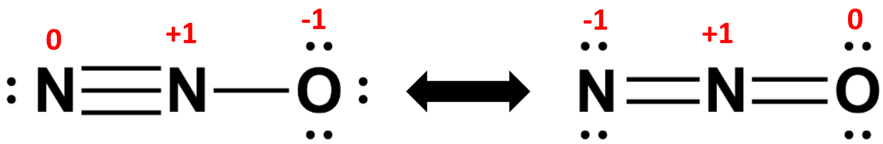
Lewis structure on the right is the preferred one as all formal charges are zero.

2. SO_2



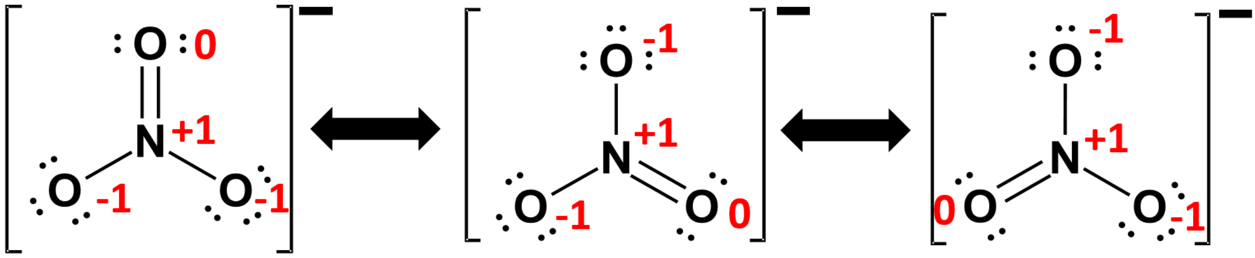
Lewis structure on the right is the preferred one as all formal charges are zero.

3. N_2O



The Lewis structure on the left has the negative formal charge on the more electronegative atom (oxygen), therefore it is the preferred Lewis structure.

4. NO_3^-

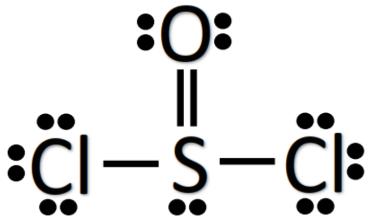


The three Lewis structures are equivalent Lewis structures (same formal charges on each atom). Note that the sum of the formal charges equals the charge on the ion.

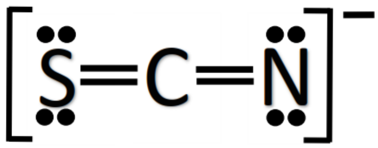
Exercises:

1. Identify the formal charge on each atom in the following molecules:

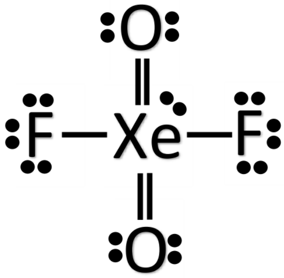
a) $SOCl_2$ (thionyl chloride)



b) SCN^- (thiocyanate ion)

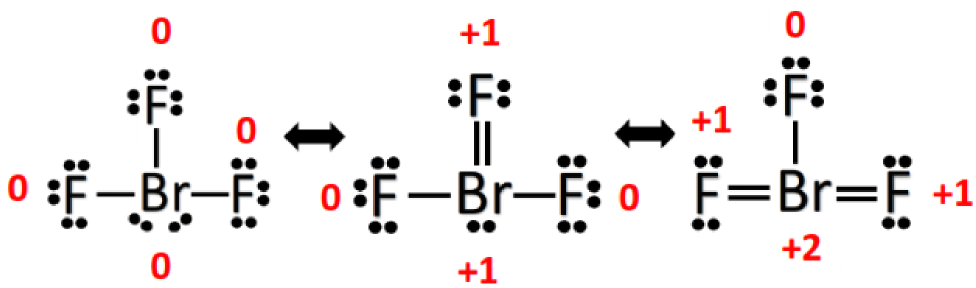


c) XeO_2F_2 (xenon dioxodifluoride)



1)
a) S: 0 Cl: 0 O: 0
b) S: 0 C: 0 N: -1
c) Xe: 0 F: 0 O: 0

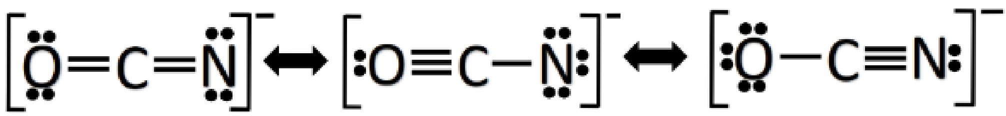
2. Assign formal charges and determine the preferred Lewis structure of BrF_3



The Lewis structure on the left is the preferred Lewis structure – the formal charges on each atom is zero.

3. Assign formal charges and determine the preferred Lewis structure of the cyanate ion:

3) A B C



0 0 -1 +1 0 -2 -1 0 0

Lewis structure C is the preferred Lewis structure. Even though Lewis structures A and C have the same overall formal charge (the same as the charge on the ion), structure C has the negative formal charge assigned to the most electronegative atom (O).

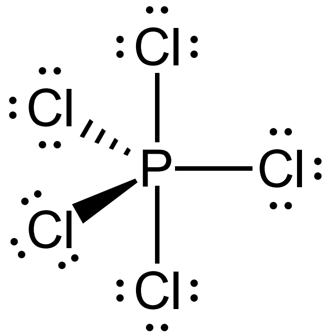
Molecular geometry (molecules and ions with up to six electron domains)

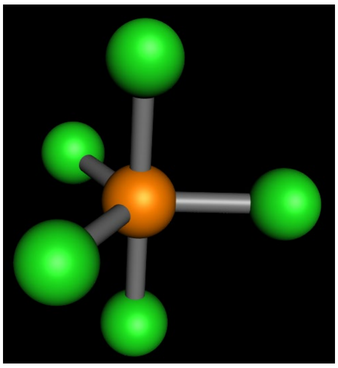
Molecules with five electron domains

- **Five bonding domains and zero non-bonding domains**

electron domains	**bonding domains**	**non-bonding domains**	**electron domain geometry**	**molecular geometry**	**bond angle**
5	5	0	trigonal bipyramidal	trigonal bipyramidal	90º 120º

Example: PCl_5

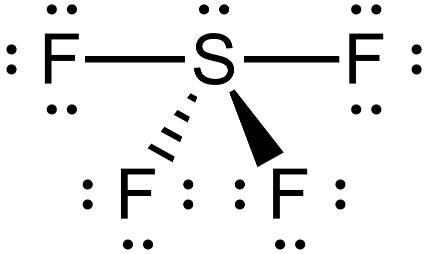


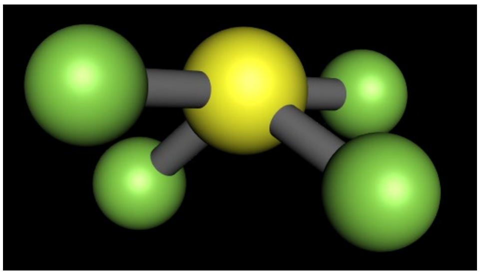


- **Four bonding domians and one non-bonding domain**

electron domains	**bonding domains**	**non-bonding domains**	**electron domain geometry**	**molecular geometry**	**bond angle**
5	4	1	trigonal bipyramidal	see-saw	90º <120º

Example: SF_4

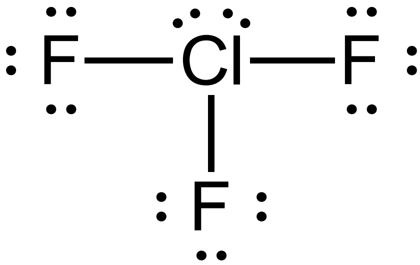
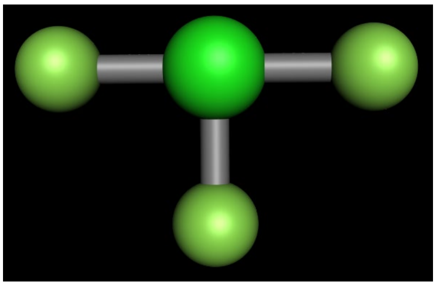




- **Three bonding domains, two non-bonding domains**

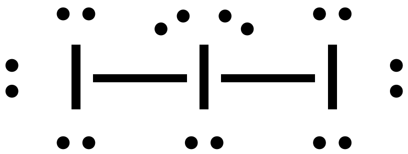
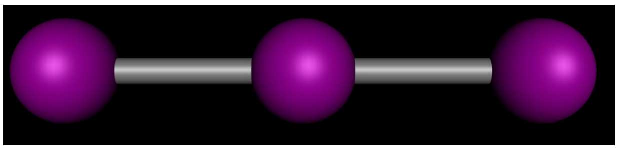
electron domains	bonding domains	non-bonding domains	electron domain geometry	molecular geometry	bond angle
5	3	2	trigonal bipyramidal	T-shaped	<90°

Example: ClF_3

- **Two bonding domains, three non-bonding domains**

Example: I_3^-

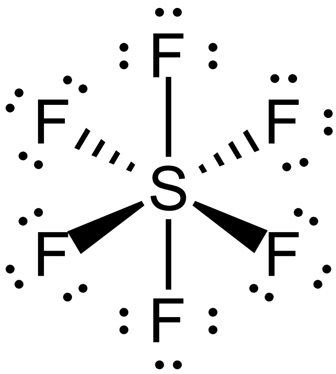
electron domains	bonding domains	non-bonding domains	electron domain geometry	molecular geometry	bond angle
5	2	3	trigonal bipyramidal	linear	180°

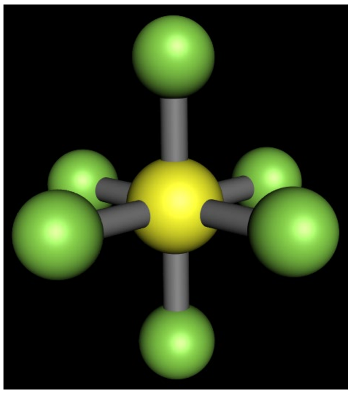
Six electron domains

- **Six bonding domains, zero non-bonding domains**

electron domains	bonding domains	non-bonding domains	electron domain geometry	molecular geometry	bond angle
6	6	0	octahedral	octahedral	90°

Example: SF_6

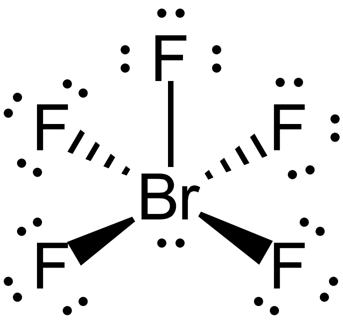


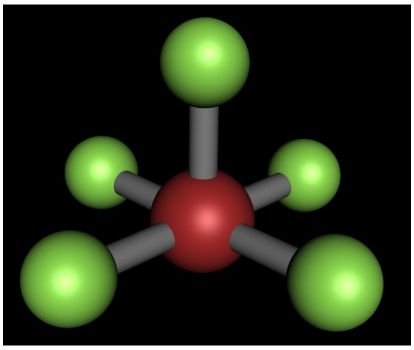


- **Five bonding domains, one non-bonding domain**

electron domains	bonding domains	non-bonding domains	electron domain geometry	molecular geometry	bond angle
6	5	1	octahedral	square pyramidal	<90°

Example: BrF_5

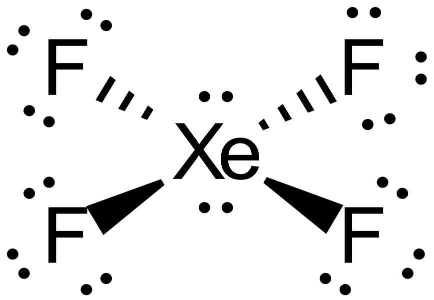


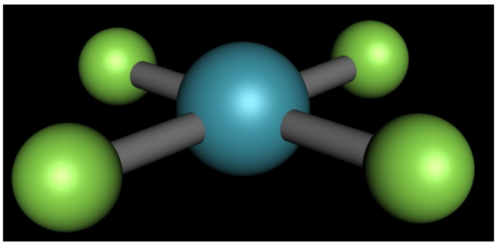


- **Four bonding domains, two non-bonding domains**

electron domains	**bonding domains**	**non-bonding domains**	**electron domain geometry**	**molecular geometry**	**bond angle**
6	4	2	octahedral	square planar	90°

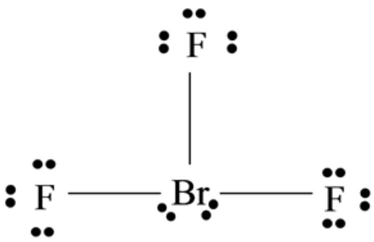
Example: XeF_4



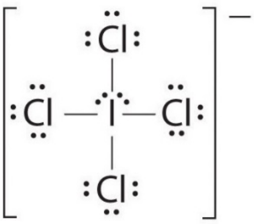


Exercise: predict the shape and bond angle for the following molecules and ions.

a) BrF_3 b) ICl_4^-



T-shaped (<90°)



Square planar (90°)

Catalytic destruction of ozone

Nitrogen monoxide (NO)

- NO is produced in internal combustion engines by the direct combination of nitrogen and oxygen at high temperatures.

$$N_{2(g)} + O_{2(g)} \rightarrow \cdot NO_{(g)} + \cdot NO_{(g)}$$

- The mechanism for the reaction with ozone is as follows:

$$\cdot NO_{(g)} + O_{3(g)} \rightarrow \cdot NO_{2(g)} + O_{2(g)}$$

$$\cdot NO_{2(g)} + O_{3(g)} \rightarrow \cdot NO_{(g)} + 2O_{2(g)}$$

Overall equation:

$$O_{3(g)} + O\bullet_{(g)} \longrightarrow 2O_{2(g)}$$

Chlorofluorocarbons (CFCs)

- CFCs were widely used as refrigerants.

$$Cl\bullet_{(g)} + O_{3(g)} \longrightarrow ClO\bullet_{(g)} + O_{2(g)}$$

$$ClO\bullet_{(g)} + O\bullet_{(g)} \longrightarrow O_{2(g)} + Cl\bullet_{(g)}$$

Overall equation:

$$O_{3(g)} + O\bullet_{(g)} \longrightarrow 2O_{2(g)}$$

Exercises:

1. CFCs and NO_X are pollutants responsible for the depletion of the ozone layer. Discuss the role of NO_X in this process and include equations for a stepwise mechanism.

   NO acts as a catalyst

   $NO\bullet_{(g)} + O_{3(g)} \longrightarrow NO_{2(g)} + O_{2(g)}$

   $NO_{2(g)} + O\bullet_{(g)} \longrightarrow NO\bullet_{(g)} + O_{2(g)}$

2. (i) State the equations for the depletion of ozone by the CFC, dichlorodifluoromethane, CCl_2F_2

   $CCl_2F_{2(g)} \rightarrow CClF_2\bullet_{(g)} + Cl\bullet_{(g)}$

   $Cl\bullet_{(g)} + O_{3(g)} \rightarrow ClO\bullet_{(g)} + O_{2(g)}$

   $ClO\bullet_{(g)} + O\bullet_{(g)} \rightarrow O_{2(g)} + Cl\bullet_{(g)}$

   (ii) Use your answer to part (i) to explain why CFCs are so effective at ozone depletion.

   Cl• is regenerated and can deplete further ozone molecules.

Calculating wavelength from bond enthalpy values

$$E = hv \qquad\qquad c = v\lambda$$

E **– energy (J)**
h **– Planck's constant**
6.63×10^{-34} J•s
v **– frequency (s^{-1})**

c **– speed of light**
3.00×10^{8} m s^{-1}
λ **– wavelength (m)**
v **– frequency (s^{-1})**

$$\lambda = \frac{hc}{E}$$

Example: Calculate the wavelength of light required to break the bonds in O_2 and O_3.

O_2

$$\boldsymbol{\lambda = \frac{(6.63 \times 10^{-34}\, J\, s)\,(3.00 \times 10^{8}\, m\, s^{-1})}{\frac{498\, kJ\, mol^{-1} \times 1000}{6.02 \times 10^{23}\, mol^{-1}}}}$$

λ = $\mathbf{2.40 \times 10^{-7} m = 240\ nm}$

O_3

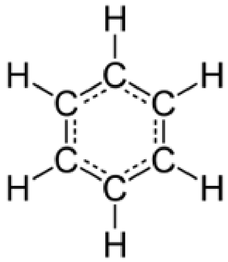
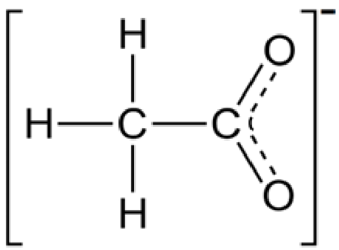
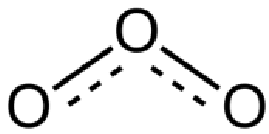
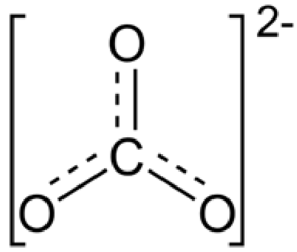
$$\boldsymbol{\lambda = \frac{(6.63 \times 10^{-34}\, \mathrm{J}\, s)\,(3.00 \times 10^{8}\, m\, s^{-1})}{\frac{364\ \mathrm{kJ\ mol^{-1}} \times 1000}{6.02 \times 10^{23}\ \mathrm{mol^{-1}}}}}$$

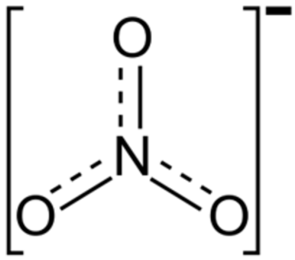
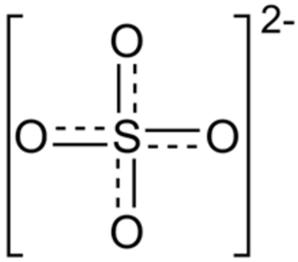
λ = $\mathbf{3.30 \times 10^{-7} m = 330\ nm}$

The stronger double bond in O_2 absorbs shorter wavelength UV radiation.
The weaker bonds in O_3 absorb longer wavelength UV radiation.

Molecules and ions with delocalised π electrons

- Delocalised π electrons are electrons that are shared between more than two nuclei.
- They exist in all molecules or ions for which there is more than one Lewis structure (resonance structures).
- Delocalisation involves electrons that are shared by more than two nuclei in a molecule or ion as opposed to being localised between a pair of atoms.
- Rather than the electrons being contained in specific bonds, delocalised π electrons exist in π bonded regions.

Bond length and strength in molecules with delocalised π electrons

- The bond lengths and strengths in molecules with delocalised π electrons are equal.
- They are intermediate in length and strength between a single and a double bond.

14.2 Hybridisation

Understandings:

- A hybrid orbital results from the mixing of different types of atomic orbitals on the same atom.

Applications:

- Explanation of the formation of sp^3, sp^2 and sp hybrid orbitals in methane, ethene and ethyne.
- Identification and explanation of the relationships between Lewis (electron dot) structures, electron domains, molecular geometries and types of hybridization.

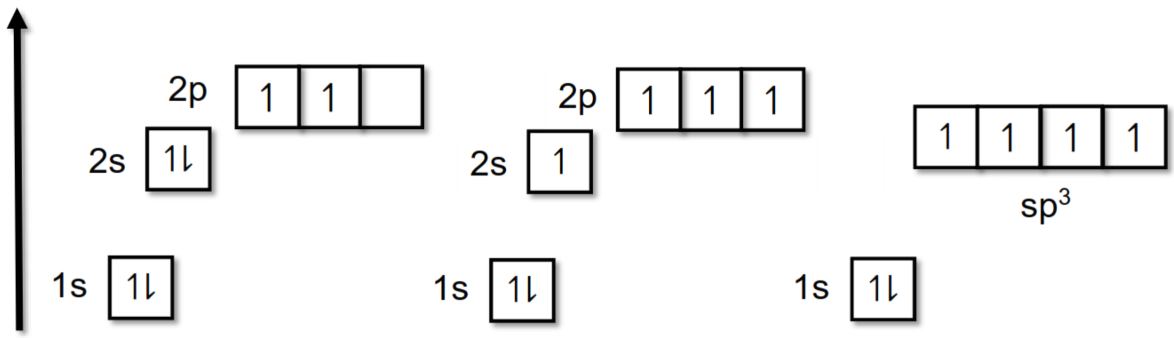
Syllabus checklist

Objective	**I am confident with this**	**I need to review this**	**I need help with this**
Explain the formation of sp^3, sp^2 and sp hybrid orbitals in methane, ethene and ethyne.			
Identify and explain the relationship between the number of electron domains, molecular geometry and type of hybridisation.			

Hybridisation

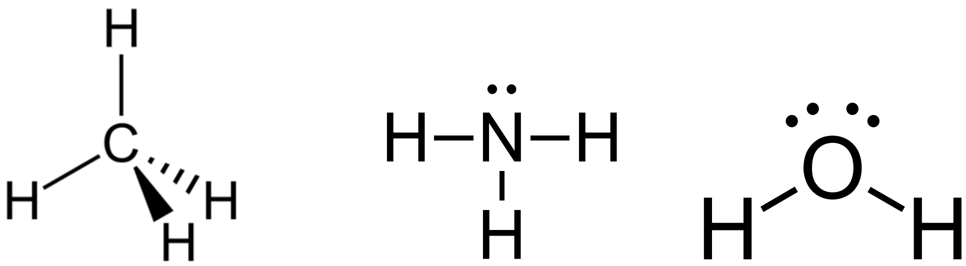
- Hybridisation is the mixing of atomic orbitals to form hybrid orbitals that are used for bonding.
- Hybrid orbitals result from the mixing of different types of atomic orbitals (s and p) on the same atom.

sp^3 hybridisation



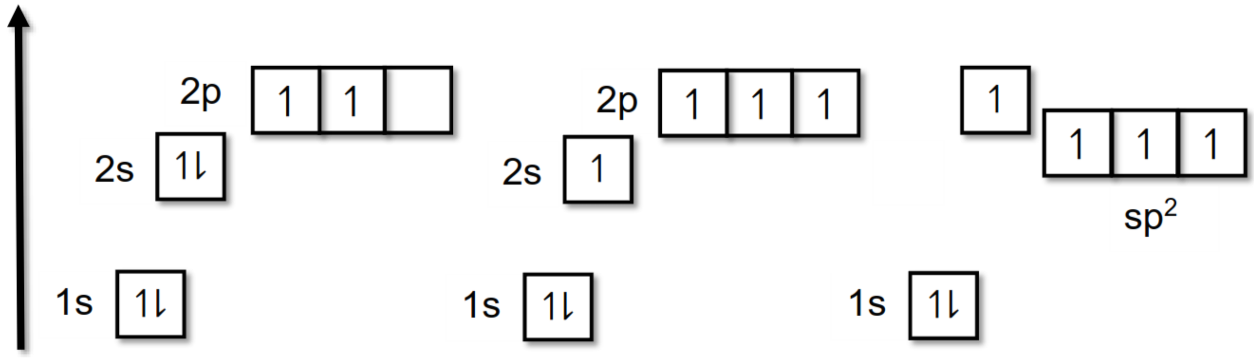
Carbon atom in ground state | C atom in excited state | Formation of four sp^3 hybrid orbitals

Molecules with sp^3 hybridisation



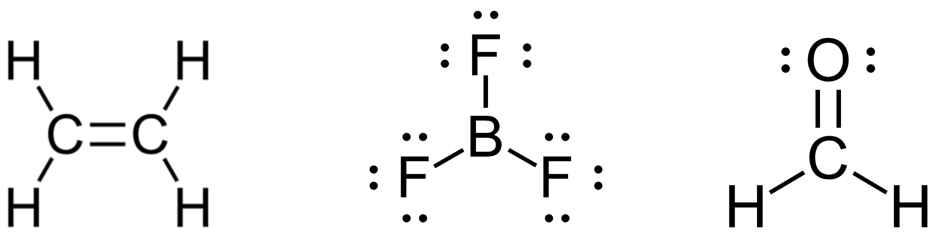
- The electron domains in the above molecules have a tetrahedral geometry.
- The molecular geometries are tetrahedral, trigonal pyramidal and bent (v-shaped) respectively.

sp² hybridisation



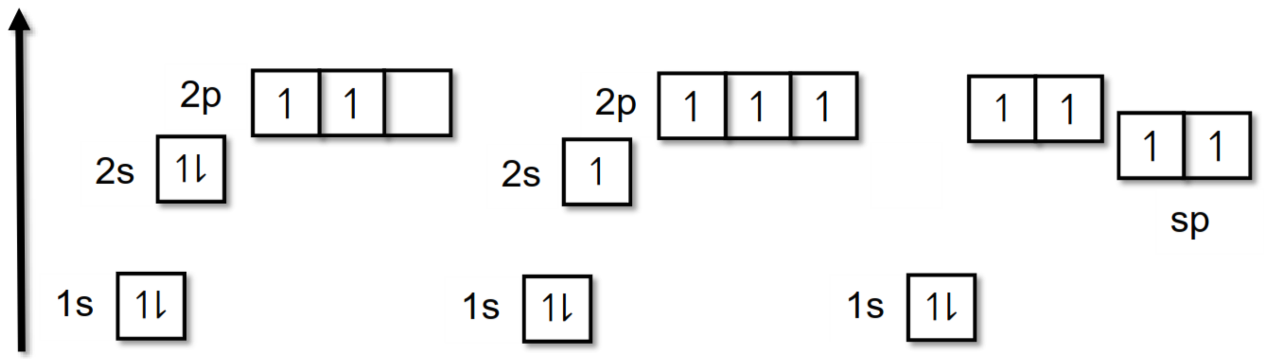
Carbon atom in ground state C atom in excited state Formation of three sp^2 hybrid orbitals

Molecules with sp^2 hybridisation



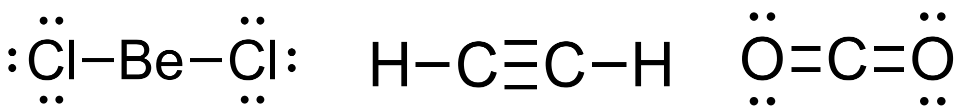
- The electron domains in the above molecules have a trigonal planar geometry with a bond angle of 120°.

sp hybridisation



Carbon atom in ground state | C atom in excited state | Formation of two sp hybrid orbitals

Molecules with sp hybridisation



- The electron domains in the above molecules have a linear geometry with a bond angle of 180°.

Exercises:

1) Complete the following table:

number of electron domains	hybridisation	molecular geometry	bond angle
2	sp	linear	180°
3	sp^2	trigonal planar	120°
4	sp^3	tetrahedral/trigonal pyramidal/bent	109.5° / 107.8° / 104.5°

2) Describe the hybridisation of the carbon atom in ethane, ethane and ethyne.

Ethane: the carbon atom in ethane is sp^3 hybridised. One 2s orbital and three 2p orbitals mix to form four sp^3 hybrid orbitals.
Ethene: the carbon atom in ethane is sp^2 hybridised. One 2s orbital and two 2p orbitals mix to form three sp^2 hybrid orbitals.
Ethyne: the carbon atom in ethyne is sp hybridised. One 2s orbital and one 2p orbital mix to form two sp hybrid orbitals.

3) Determine the hybridisation of the atom and the bond angle around the atoms in bold in the following molecules:

a) H_2**S** **sp^3**

b) **P**H_3 **sp^3**

c) **N**H_4^+ **sp^3**

d) H_3**O**$^+$ **sp^3**

e) **C_2**F_4 **sp^2**

f) **N_2**H_4 **sp^3**

g) HC**O**OH **sp^3**

h) H_2**O_2** **sp^3**

i) **C**O_3^{2-} **sp^2**

j) H**C**N **sp**