

Bonding

IB CHEMISTRY HL

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14.1 Further aspects of covalent bonding and structure

Understandings:

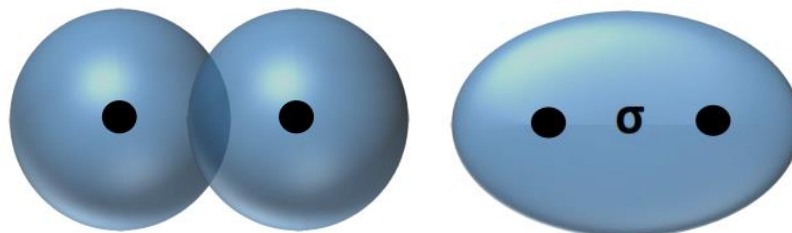
- Covalent bonds result from the overlap of atomic orbitals. A sigma bond (σ) is formed by the direct head-on/end-to-end overlap of atomic orbitals, resulting in electron density concentrated between the nuclei of the bonding atoms. A pi bond (π) is formed by the sideways overlap of atomic orbitals, 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. $FC = (\text{Number of valence electrons}) - \frac{1}{2}(\text{Number of bonding electrons}) - (\text{Number of non-bonding electrons})$. 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 .

sigma (σ) and pi bonds (π)

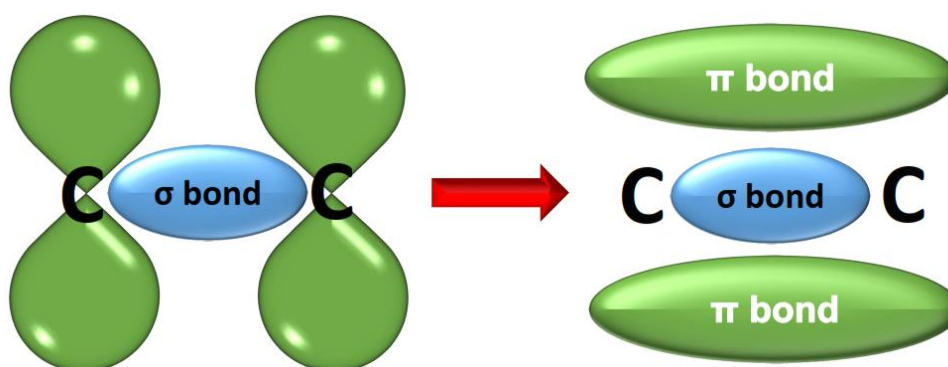
- Covalent bonds result from the overlap of atomic orbitals.
- A sigma bond (σ) is formed by the direct head on overlap of atomic orbitals, resulting in electron density concentrated between the nuclei of the bonding atoms.
- Sigma bonds are formed by head-on overlap of s orbitals, head-on overlap of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



s orbital overlaps with p orbital two p orbitals overlap head on



- 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.
- 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.

2. Describe the formation of a pi (π) bond.

3. Complete the following table:

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

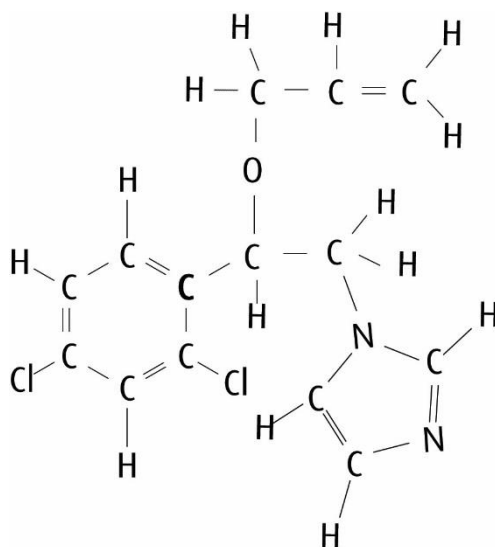
4. Determine the number of sigma (σ) and pi (π) bonds in the following molecules:

a) Cl_2

b) O_2

c) N_2

5. Determine the number of sigma (σ) and pi (π) bond in a molecule of imazalil (pictured below).



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 valance e^- – # of non-bonding e^- – $\frac{1}{2}$ # of bonding e^-

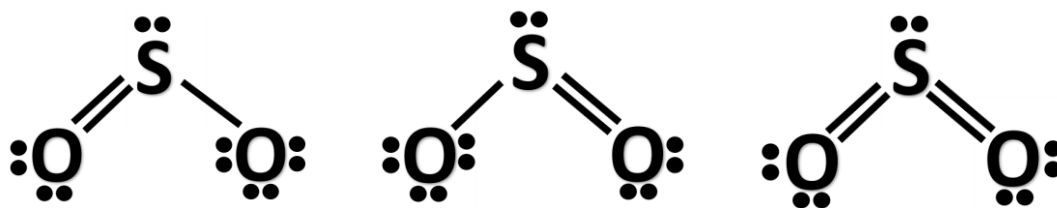
$$FC = V - N - \frac{1}{2} B$$

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

1. CO_2



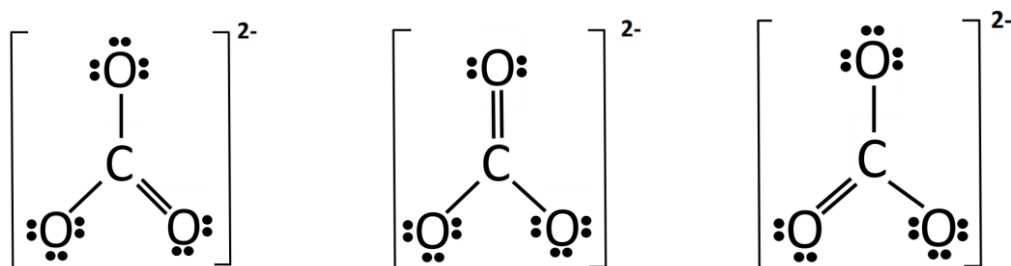
2. SO₂



3. N₂O



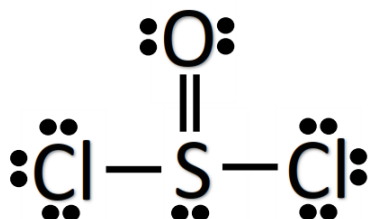
4. CO₃²⁻



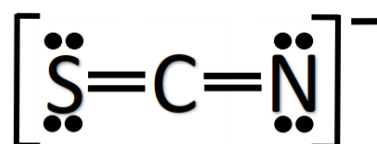
Exercises:

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

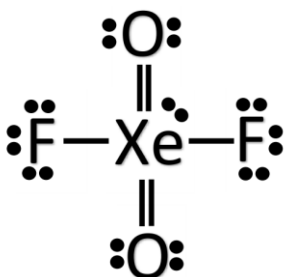
a) SOCl₂ (thionyl chloride)



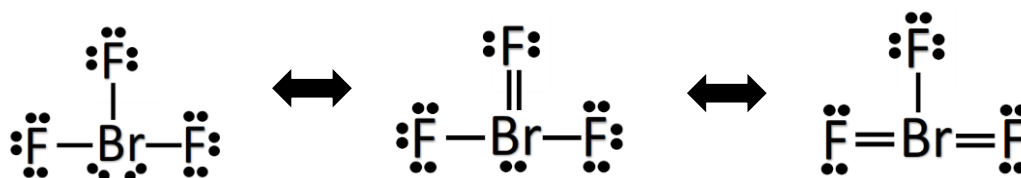
b) SCN⁻ (thiocyanate ion)



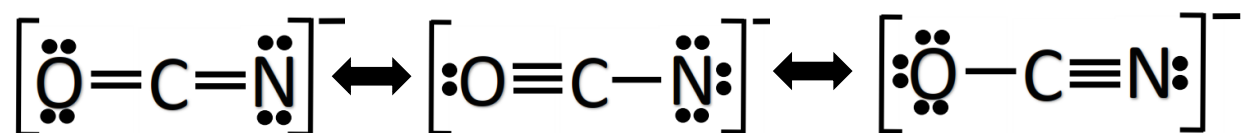
c) XeO_2F_2 (xenon dioxodifluoride)



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



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



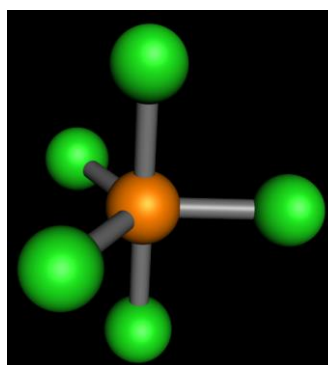
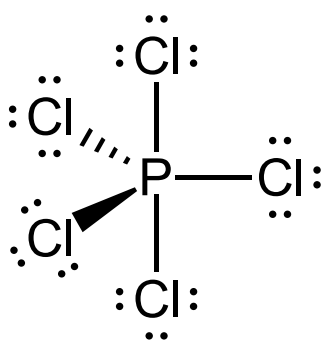
Molecular geometry (up to six electron domains)

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	90° 120°

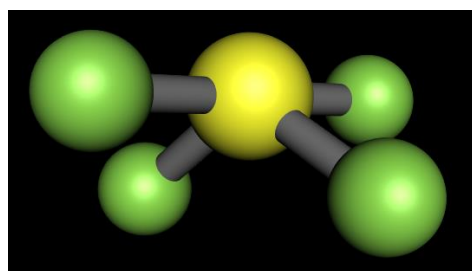
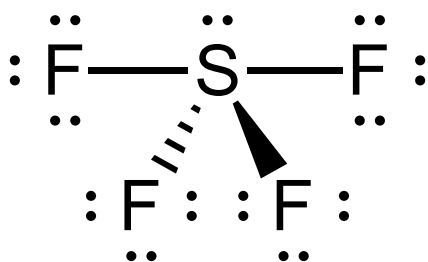
Example: PCl_5



- Four bonding domains 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	90° <120°

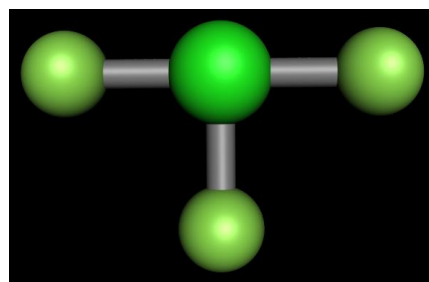
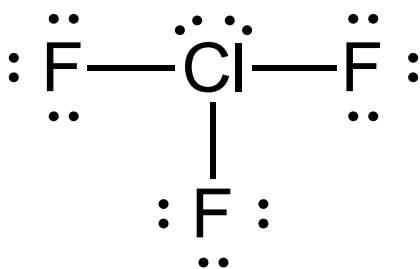
Example: SF_4



- Three bonding domains, two non-bonding domains

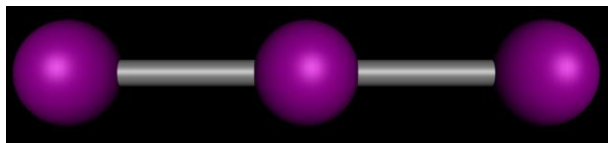
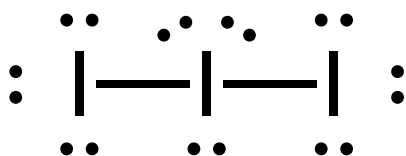
electron domains	bonding domains	non-bonding domains	electron domain geometry	molecular geometry	bond angle
5	3	2	trigonal bipyramidal	T-shaped	$<90^\circ$

Example: ClF_3



- Two bonding domains, three non-bonding domains

Example: I_3^-



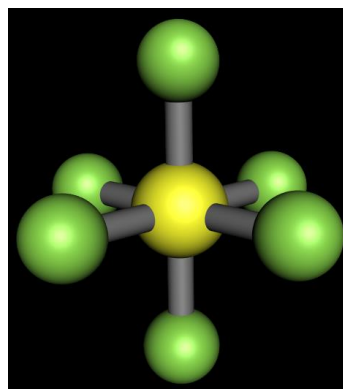
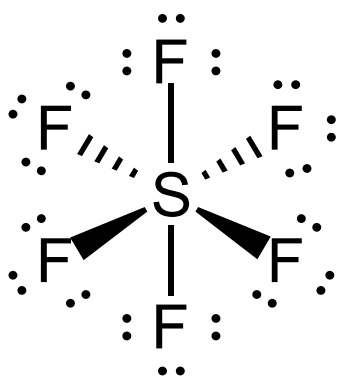
electron domains	bonding domains	non-bonding domains	electron domain geometry	molecular geometry	bond angle
5	2	3	trigonal bipyramidal	linear	180°

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°

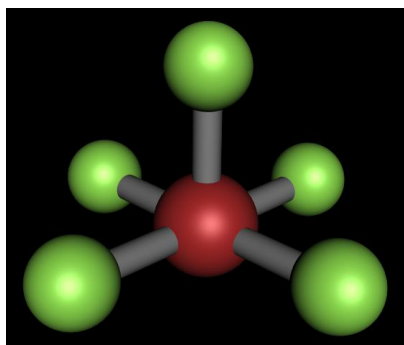
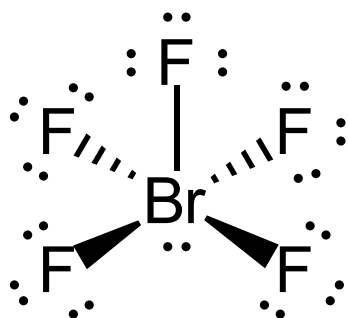
Example: SF₆



- 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°

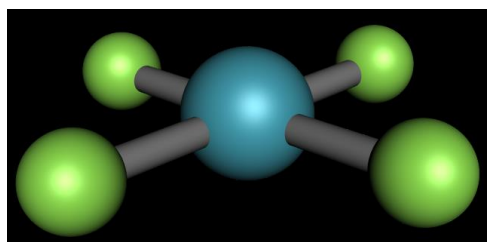
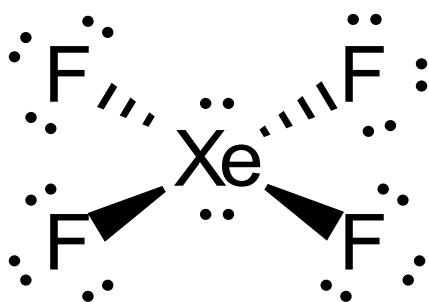
Example: BrF₅



- 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°

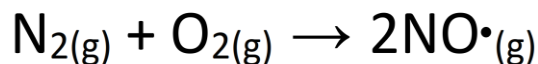
Example: XeF₄



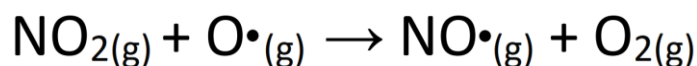
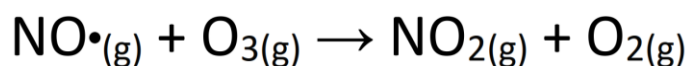
Catalytic destruction of ozone

Nitrogen monoxide (NO)

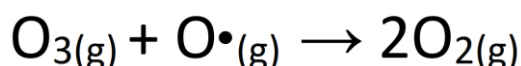
- NO is produced in internal combustion engines by the direct combination of nitrogen and oxygen at high temperatures.



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

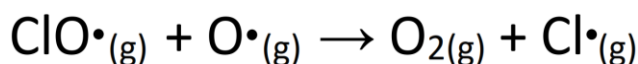
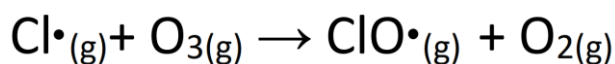


Overall equation:

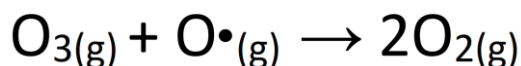


Chlorofluorocarbons (CFCs)

- CFCs were widely used as refrigerants.



Overall equation:



Exercises:

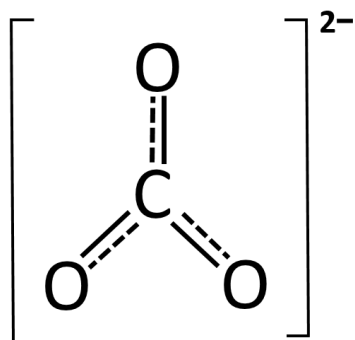
1. CFCs and NO_x are pollutants responsible for the depletion of the ozone layer. Discuss the role of NO_x in this process and include equations for a stepwise mechanism.
2. (i) State the equations for the depletion of ozone by the CFC, dichlorodifluoromethane, CCl_2F_2

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

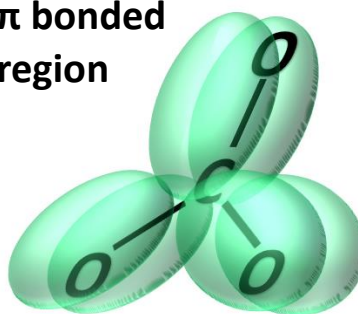
Delocalised π electrons

- 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.
- Rather than the electrons being contained in specific bonds, delocalised π electrons exist in π bonded regions.

Carbonate ion (CO_3^{2-})

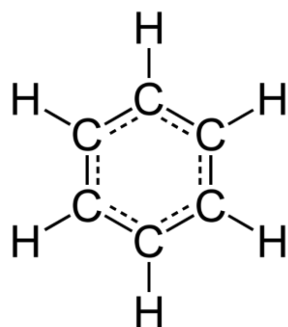


π bonded region

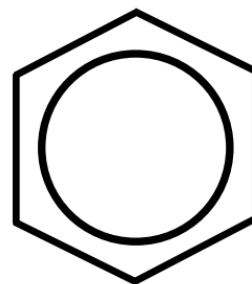
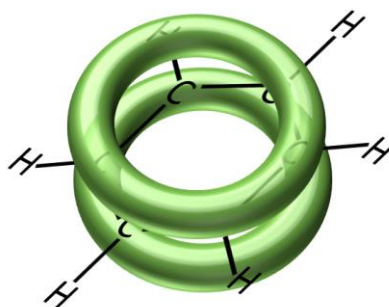


- In the carbonate ion (above) and benzene molecule (below) the delocalised π electrons in the π bonded region are spread over more than two nuclei.

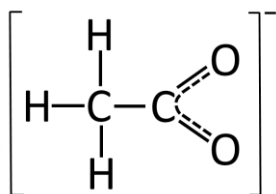
Benzene (C_6H_6)



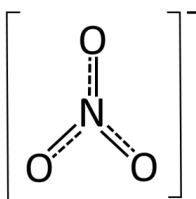
π bonded region



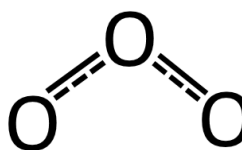
Additional molecules with delocalised π electrons



ethanoate ion CH_3COO^-



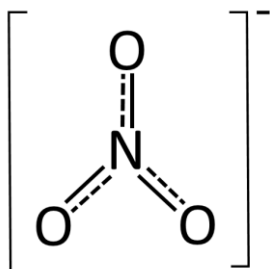
nitrate ion NO_3^-



ozone O_3

Bond length and strength in molecules with delocalised π electrons

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



The length and strength of the bonds in the nitrate ion are intermediate between a single and a double bond (bond order 1.5).

Summary

- Delocalized π electrons are shared between more than two nuclei.
- Bond lengths and bond strengths are intermediate between a single and double bond.
- Delocalized π electrons bring extra stability to a molecule (resonance energy).

14.2 Hybridization

Nature of science:

The need to regard theories as uncertain—hybridization in valence bond theory can help explain molecular geometries, but is limited. Quantum mechanics involves several theories explaining the same phenomena, depending on specific requirements.

Understandings:

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

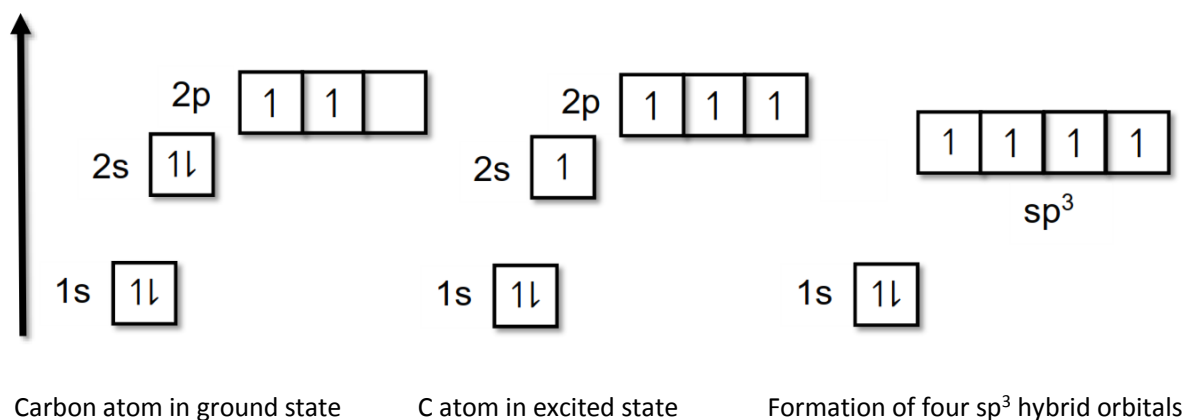
Applications:

- 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.

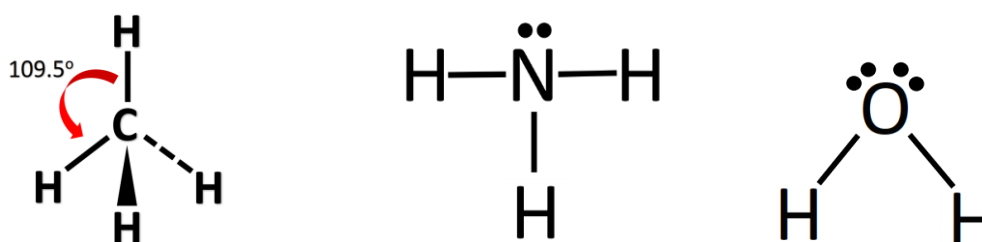
Hybridisation

- Hybridization 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

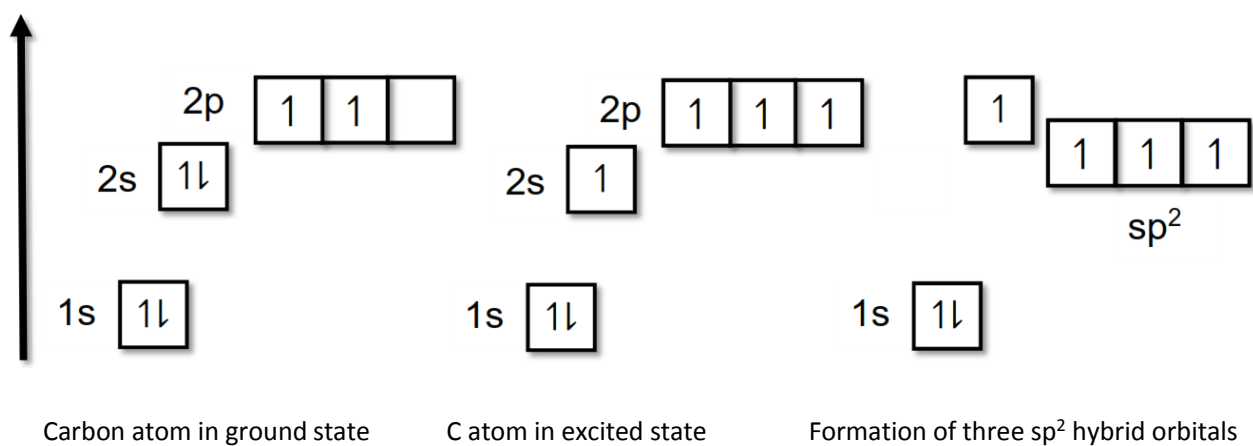


Molecules with sp^3 hybridisation

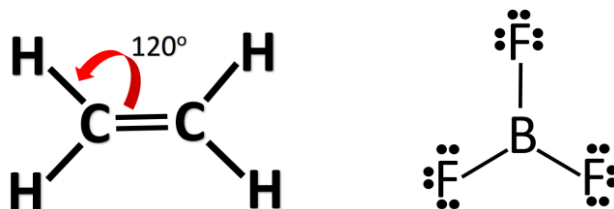


- The electron domains in the above molecules have a tetrahedral geometry.
- The molecular geometries are tetrahedral, trigonal pyramidal and bent respectively.

sp^2 hybridisation

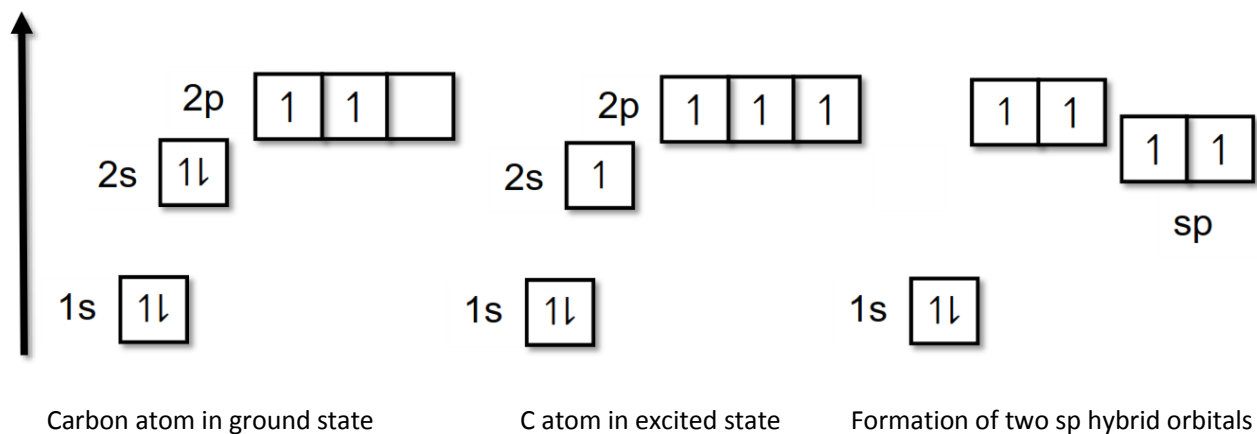


Molecules with sp^2 hybridisation

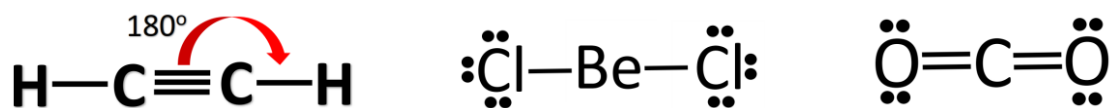


- The electron domains in the above molecules have a trigonal planar geometry with a bond angle of 120° .

sp hybridisation



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			
3			
4			

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

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

