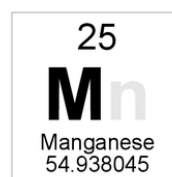
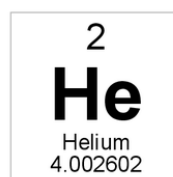
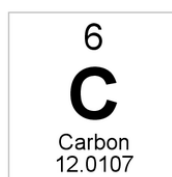
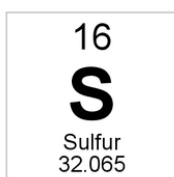
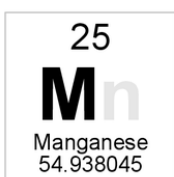


# Structure 2.2 HL

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IB CHEMISTRY HL



### Structure 2.2.11

#### Understandings:

- Resonance structures occur when there is more than one possible position for a double bond in a molecule.

#### Learning outcomes:

- Deduce resonance structures of molecules and ions.

#### Additional notes:

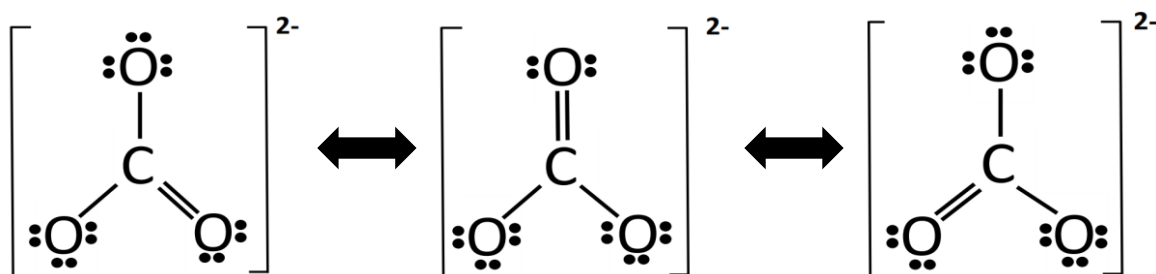
- Include the term “delocalisation”.

#### Linking questions:

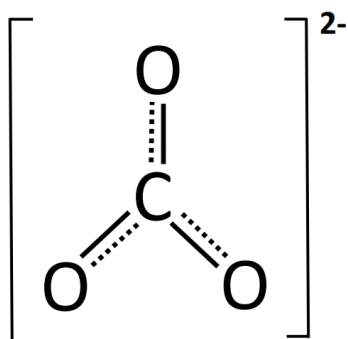
- Structure 1.3 Why are oxygen and ozone dissociated by different wavelengths of light?

### Resonance structures

- Resonance structures occur when there is more than one position for a double (or triple) bond in a molecule.
- The three resonance structures for the carbonate ion ( $\text{CO}_3^{2-}$ ) are shown below.



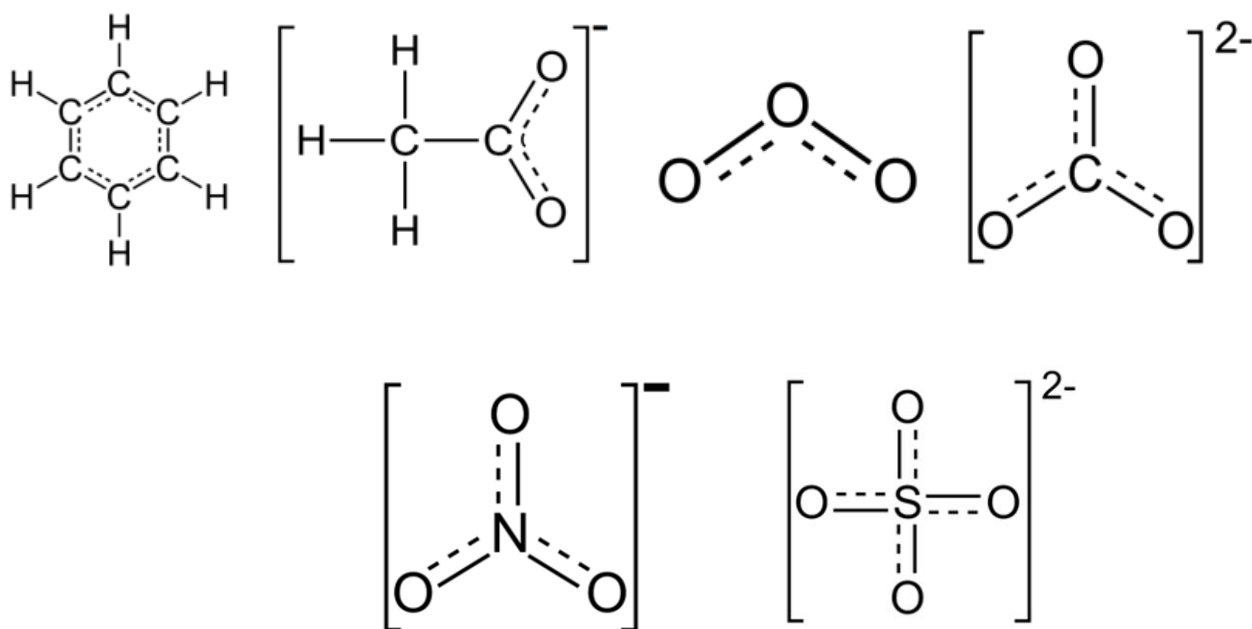
- The actual structure is a resonance hybrid structure.



The C-O bond lengths and bond strengths are identical - intermediate between a single and a double bond.

### Molecules and ions with delocalised $\pi$ electrons

- Delocalised  $\pi$  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 (known as 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  $\pi$  electrons exist in  $\pi$  bonded regions.



### Bond length and strength in molecules with delocalised $\pi$ electrons

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

### **Structure 2.2.12**

#### **Understandings:**

- Benzene, C<sub>6</sub>H<sub>6</sub>, is an important example of a molecule that has resonance.

#### **Learning outcomes:**

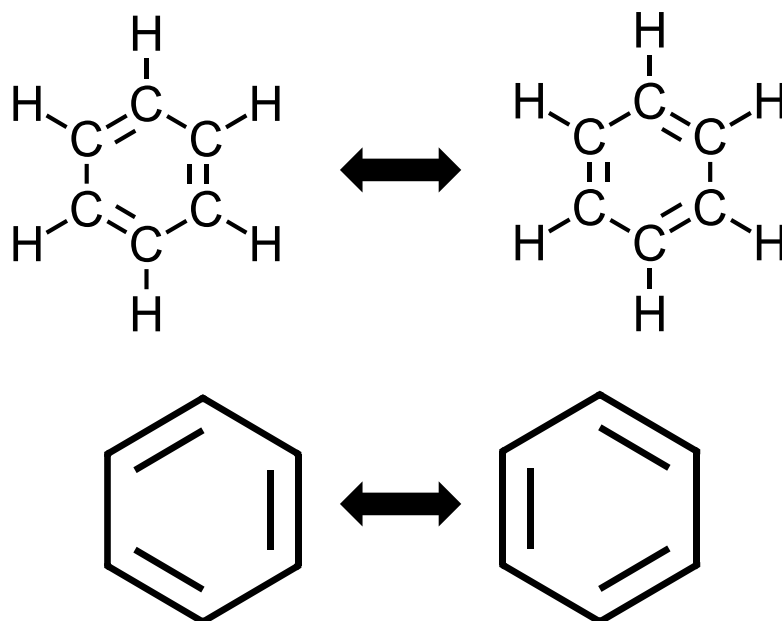
- Discuss the structure of benzene from physical and chemical evidence.

#### **Linking questions:**

- Reactivity 2.1, 2.2 How does the resonance energy in benzene explain its relative unreactivity?
- Reactivity 3.4 What are the structural features of benzene that favour it undergoing electrophilic substitution reactions?

### Evidence for the structure of benzene

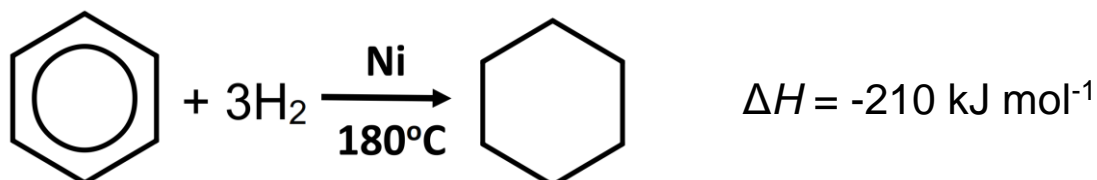
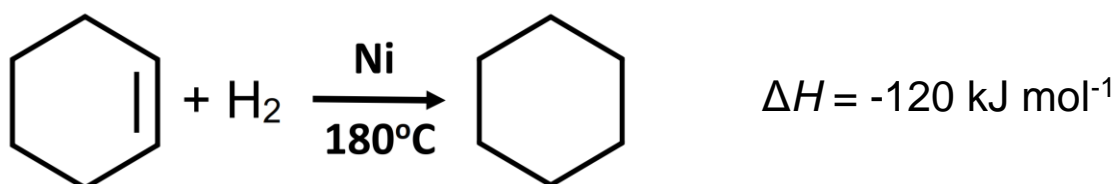
- Benzene is an aromatic unsaturated hydrocarbon.
- The molecular formula of benzene is  $C_6H_6$ .
- The Kekulé structure of benzene consists of alternating single and double bonds.



What evidence is there that the structure of benzene does not consist of alternating single and double bonds?

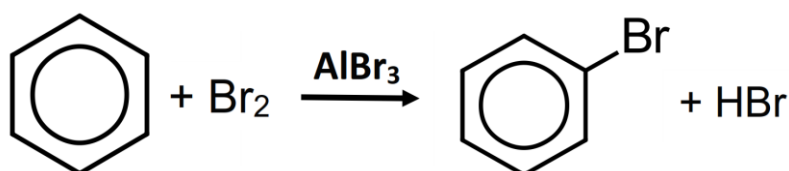
1. The length and strength of the carbon-to-carbon bonds (physical evidence).
- The carbon-to-carbon bonds in benzene are of equal length and equal strength.
  - The length and strength of the carbon-to-carbon bonds in benzene are intermediate between a carbon-to-carbon single bond and a carbon-to-carbon double bond.

2. The enthalpy of hydrogenation of benzene is less exothermic than predicted (chemical evidence).



- The delocalization of the  $\pi$  electrons minimizes the repulsion between the electrons, lowering the internal energy by  $150 \text{ kJ mol}^{-1}$  (resonance energy).

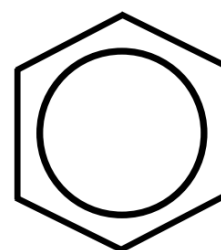
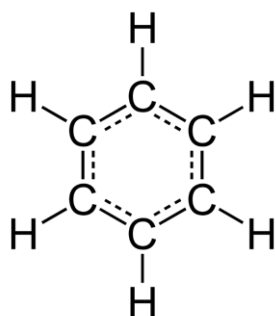
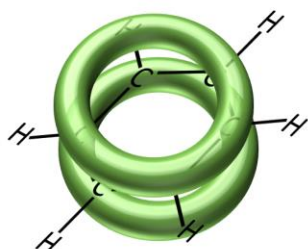
3. Benzene undergoes substitution reactions, rather than addition reactions (chemical evidence).



### The actual structure of benzene

- The actual structure of benzene is a planar regular hexagon (bond angles of  $120^\circ$ ).

#### $\pi$ bonded region



- The ring represents the delocalised electrons within the benzene molecule.

### **Structure 2.2.13**

#### **Understandings:**

- Some atoms can form molecules in which they have an expanded octet of electrons.

#### **Learning outcomes:**

- Represent Lewis formulas for species with five and six electron domains around the central atom.
- Deduce the electron domain geometry and the molecular geometry for these species using the VSEPR model.

#### **Linking questions:**

- Structure 3.1 How does the ability of some atoms to expand their octet relate to their position in the periodic table?

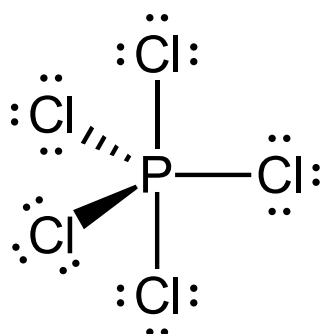
## Molecular geometry of molecules and ions with expanded octets (to six electron domains)

### Molecules and ions 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°

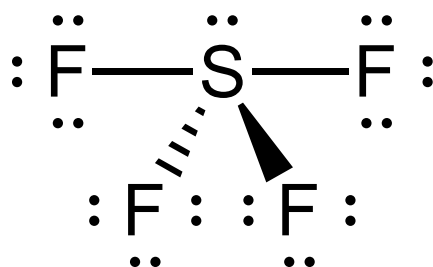
Example:  $\text{PCl}_5$



- 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:  $\text{SF}_4$

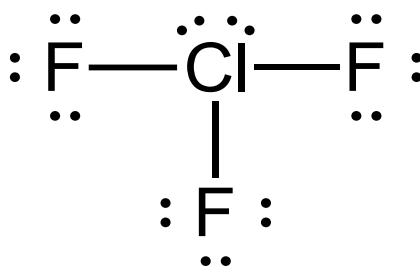




- Three bonding domains, two non-bonding domains

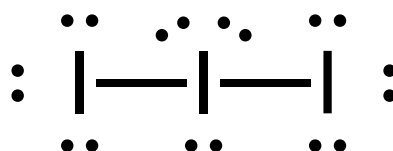
electron domains	bonding domains	non-bonding domains	electron domain geometry	molecular geometry	bond angle
5	3	2	trigonal bipyramidal	T-shaped	$<90^\circ$

Example:  $\text{ClF}_3$



- Two bonding domains, three non-bonding domains

Example:  $\text{I}_3^-$



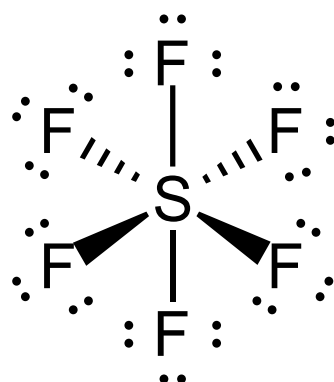
electron domains	bonding domains	non-bonding domains	electron domain geometry	molecular geometry	bond angle
5	2	3	trigonal bipyramidal	linear	$180^\circ$

## Molecules and ions with 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°

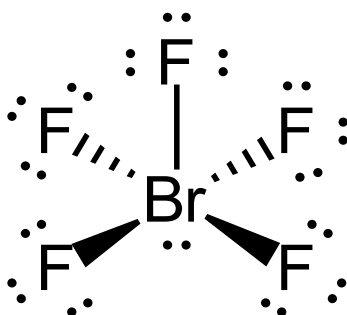
Example: SF<sub>6</sub>



- 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°

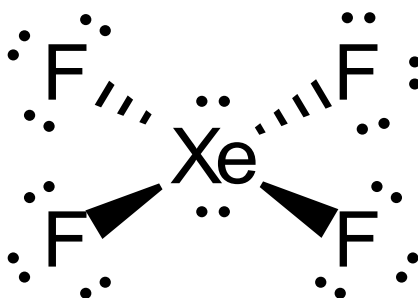
Example: BrF<sub>5</sub>



- 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<sub>4</sub>



### **Structure 2.2.14**

#### **Understandings:**

- Formal charge values can be calculated for each atom in a species and used to determine which of several possible Lewis formulas is preferred.

#### **Learning outcomes:**

- Apply formal charge to determine a preferred Lewis formula from different Lewis formulas for a species.

#### **Linking questions:**

- Structure 3.1, Reactivity 3.2 What are the different assumptions made in the calculation of formal charge and of oxidation states for atoms in a species?

## Formal charge

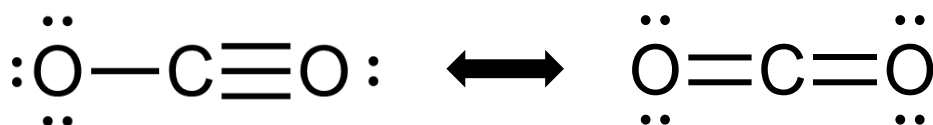
- Formal charge is used to determine which Lewis structure is preferred when more than one is possible.
- The formal charge is the charge an atom would have if all the atoms in a molecule had the same electronegativity.
- The preferred Lewis structure is the one where the individual atoms have the lowest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

$$\text{Formal charge} = \# \text{ of valence } e^- - \# \text{ of non-bonding } e^- - \frac{1}{2} \# \text{ of bonding } e^-$$

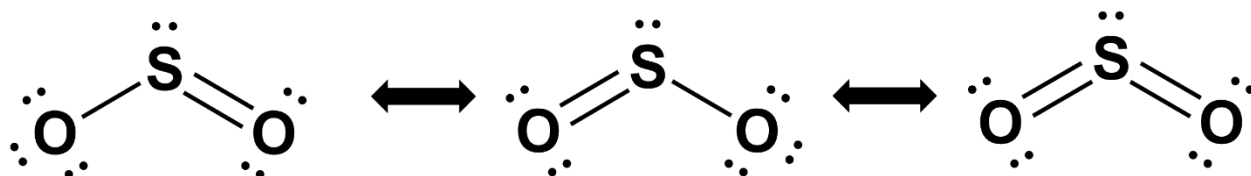
$$\text{FC} = \text{V} - \text{N} - \frac{1}{2} \text{B}$$

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

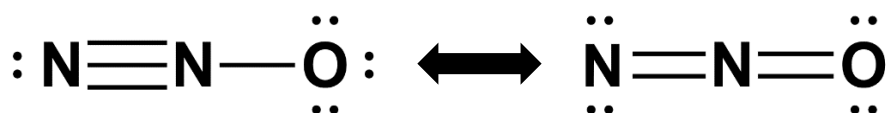
1. CO<sub>2</sub>



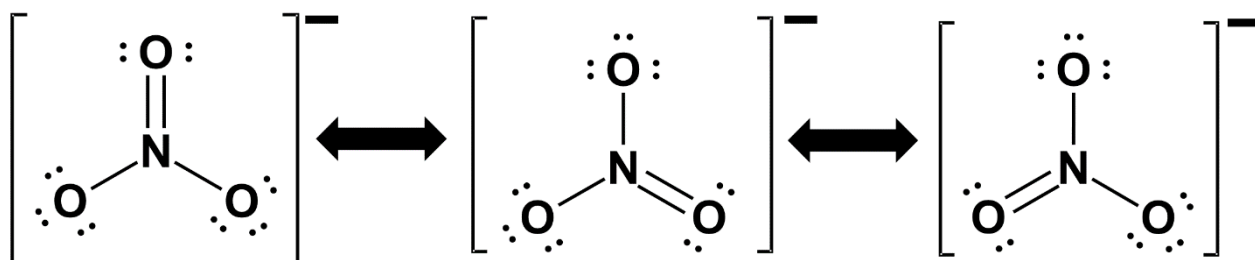
2. SO<sub>2</sub>



3. N<sub>2</sub>O



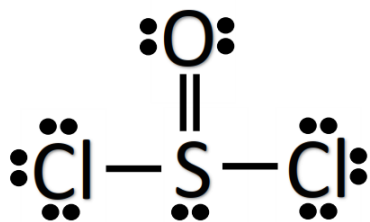
4. NO<sub>3</sub><sup>-</sup>



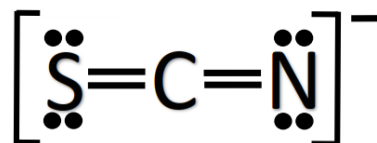
### Exercises:

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

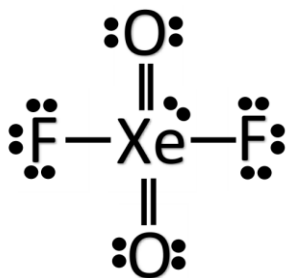
a)  $\text{SOCl}_2$  (thionyl chloride)



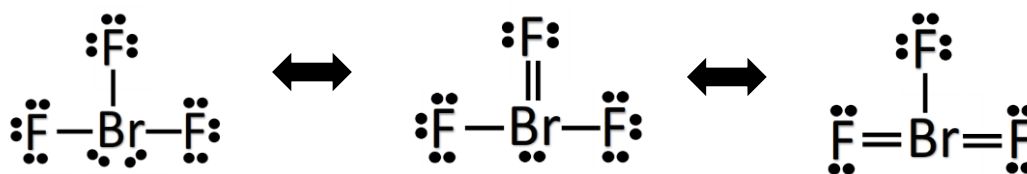
b)  $\text{SCN}^-$  (thiocyanate ion)



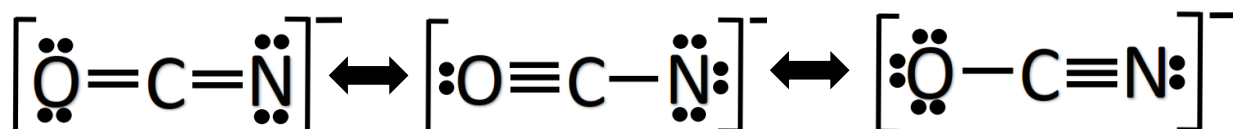
c)  $\text{XeO}_2\text{F}_2$  (xenon dioxodifluoride)



2. Assign formal charges and determine the preferred Lewis structure of  $\text{BrF}_3$



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



## Structure 2.2.15

### Understandings:

- Sigma bonds  $\sigma$  form by the head-on combination of atomic orbitals where the electron density is concentrated along the bond axis.
- Pi bonds  $\pi$  form by the lateral combination of p-orbitals where the electron density is concentrated on opposite sides of the bond axis.

### Learning outcomes:

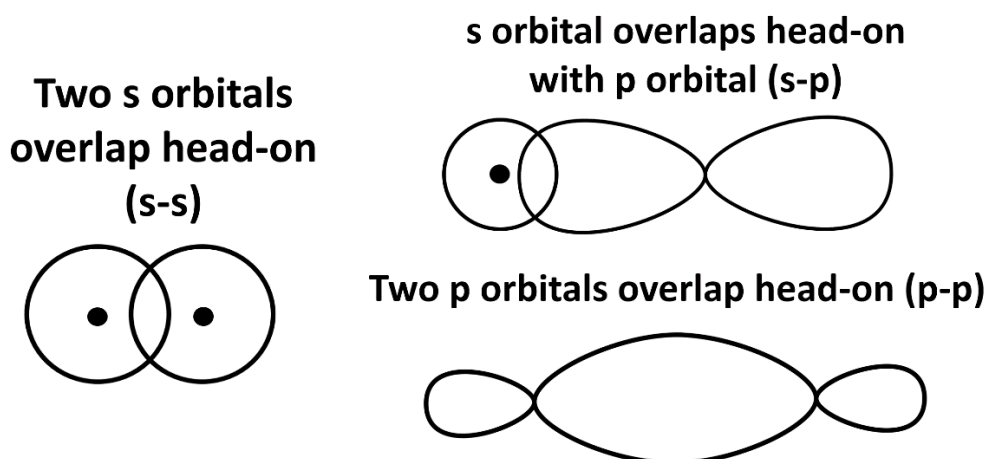
- Deduce the presence of sigma bonds and pi bonds in molecules and ions.

### Additional notes:

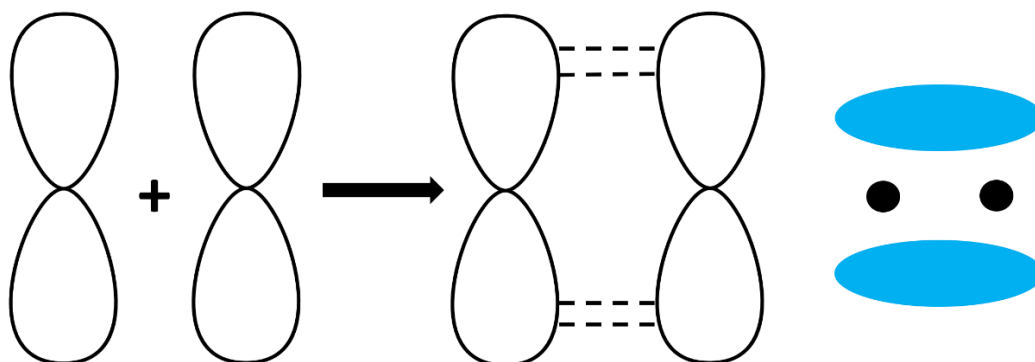
- Include both organic and inorganic examples.

## Sigma ( $\sigma$ ) and pi bonds ( $\pi$ )

- Covalent bonds result from the overlap of atomic orbitals.
- A sigma bond ( $\sigma$ ) 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 ( $\pi$ ) 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 ( $C_2H_4$ ).





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

Type of bond	sigma ( $\sigma$ )	pi ( $\pi$ )
Single covalent		
Double covalent		
Triple covalent		

**Exercises:**

1. Describe the formation of a sigma ( $\sigma$ ) bond.

2. Describe the formation of a pi ( $\pi$ ) 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 ( $\sigma$ ) and pi ( $\pi$ ) bonds in the following molecules:

a)  $\text{Cl}_2$

b)  $\text{O}_2$

c)  $\text{N}_2$

## Structure 2.2.16

### Understandings:

- Hybridisation is the concept of mixing atomic orbitals to form new hybrid orbitals for bonding.

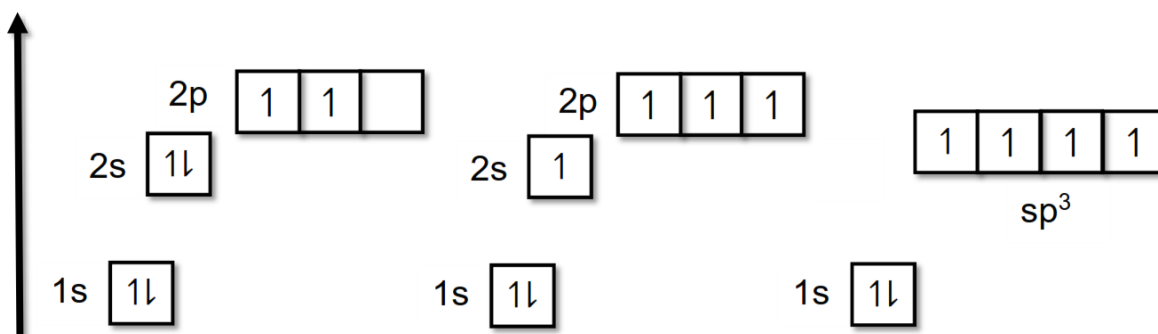
### Learning outcomes:

- Analyse the hybridization and bond formation in molecules and ions.
- Identify the relationships between Lewis formulas, electron domains, molecular geometry and type of hybridization.
- Predict the geometry around an atom from its hybridization, and vice versa.
- Additional notes:
- Include both organic and inorganic examples. Only  $sp$ ,  $sp^2$  and  $sp^3$  hybridisation need to be covered.

## 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

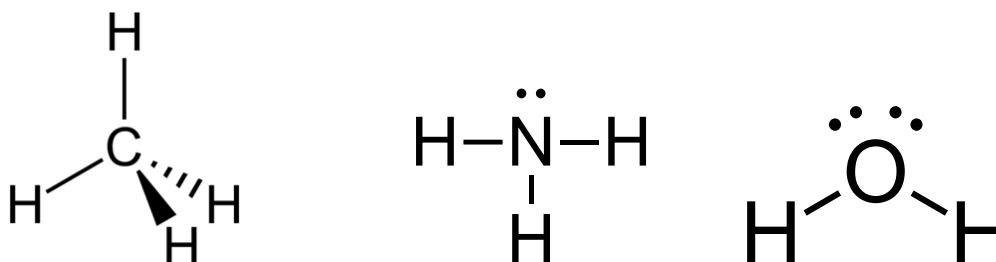


Carbon atom in ground state

C atom in excited state

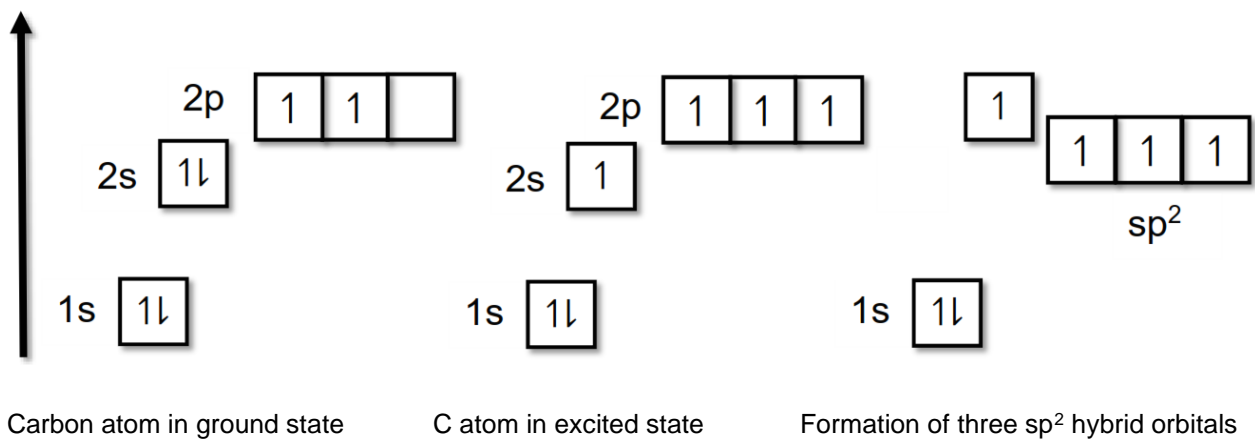
Formation of four  $sp^3$  hybrid orbitals

### Molecules with $sp^3$ hybridisation

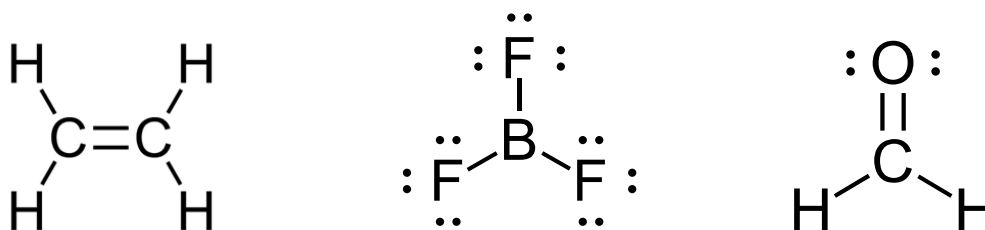


- The electron domains in the above molecules have a tetrahedral geometry.
- The molecular geometries are tetrahedral, trigonal pyramidal and bent (v-shaped) respectively.

## sp<sup>2</sup> hybridisation

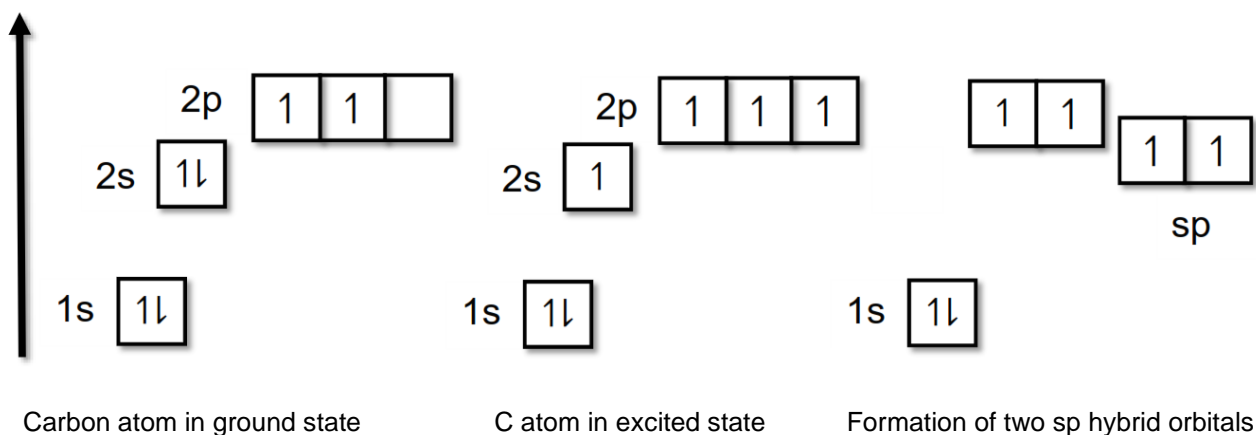


## Molecules with sp<sup>2</sup> hybridisation

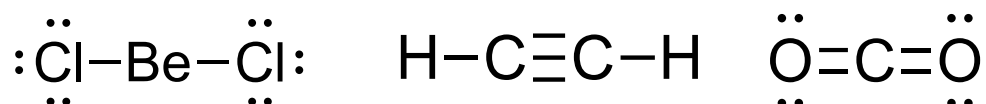


- The electron domains in the above molecules have a trigonal planar geometry with a bond angle of 120°.

## sp hybridisation



## Molecules with sp hybridisation



- The electron domains in the above molecules have a linear geometry with a bond angle of  $180^\circ$ .

## Exercises:

- Complete the following table:

Number of electron domains	Hybridisation	Molecular geometry	Bond angle
2			
3			
4			

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

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

