

Molecules Module – Lecture 4: VSEPR Theory and Bond Order, Length, and Energy

Learning Objective	Openstax 2e Chapter
VSEPR and multiple bonds	<u>7.6</u>
Molecular Shape and Dipole Moments	<u>7.6</u>
Bond Order, Length, Energy	<u>7.5, 7.6, 8.4</u>

Suggested Practice Problems

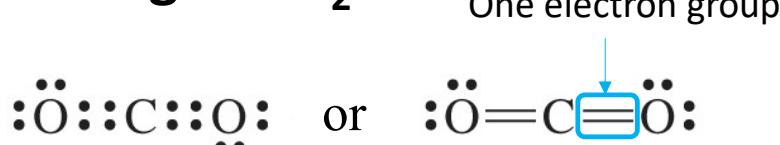
[Chapter 7 Exercises](#) – Questions: 89, 97, 99, 101, 65, 67, 69, 73

Answers can be found in the [Chapter 7 Answer Key](#)

How do we deal with multiple covalent bonds?

Each multiple covalent bond constitute one group of electrons as all bond pairs are confined to the same region.

Looking at CO_2 :

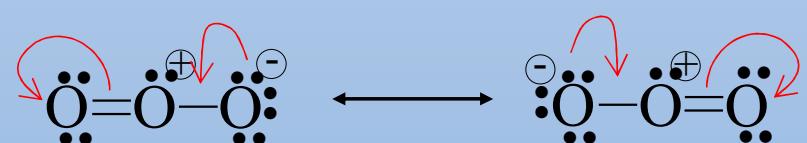


VSEPR notation: AX_2

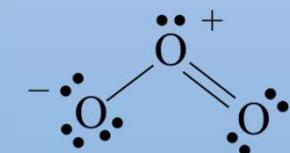
Electron-group geometry: linear

Molecular geometry: linear

What about ozone, O_3 ?



AX_2E
(molecule is bent)

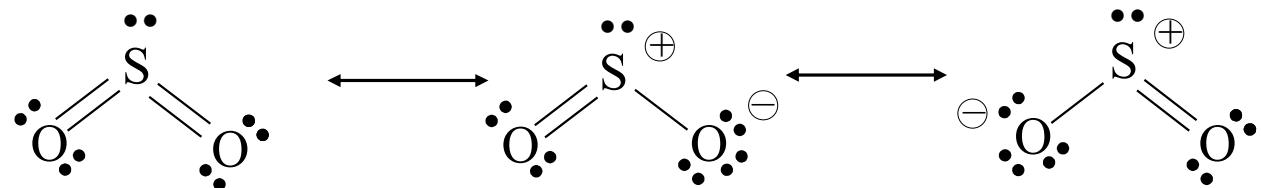


Looking at SO_2 :

VSEPR notation: AX_2E

Electron-group geometry:
trigonal planar

Molecular geometry: bent

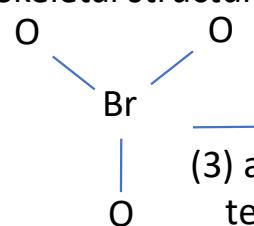


Example 1

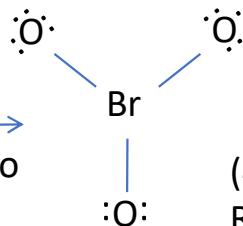
Determine the electron-group geometry and molecular geometry of bromate ion, BrO_3^- .

(1) Total number of valence electrons (7 for Br, 6 for each O, plus 1 for negative charge) = $7 + 3 \times 6 + 1 = 26$

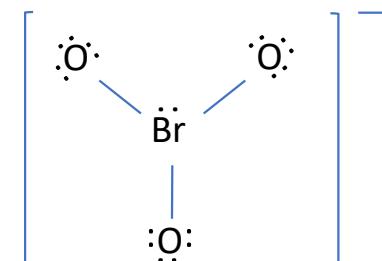
(2) Skeletal structure



(3) add electrons to terminal atoms

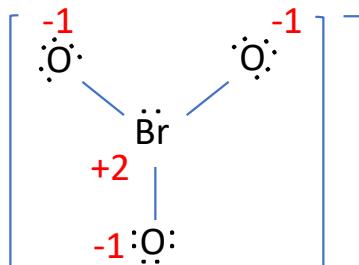


(4) 3 bond pairs + 9 lone pairs = 24 electrons
Remaining V.E.= $26 - 24 = 2$ on central atom

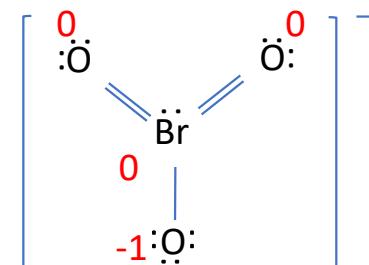


(5) At first glance, it appears to satisfy the octet rule. Now need to check formal charges.

Br atom (fourth row) valence shell can be expanded to remove some unfavorable formal charges.



(6) add multiple bonds to reduce formal charges



Expanded valence shell on Br

Electron group: AX_3E

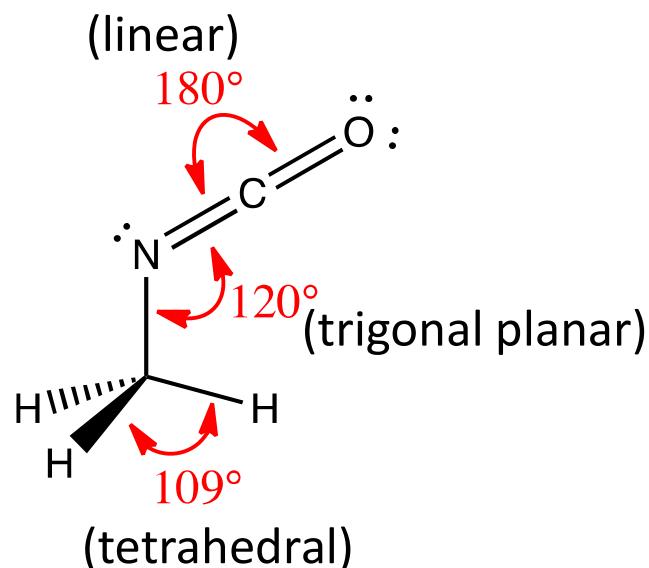
Electron group geometry is tetrahedral, but the molecular geometry is trigonal pyramidal.

Note: get AX_3E for both of these, so don't need to correct formal charges to get correct geometry

Molecules with More Than One Central Atom

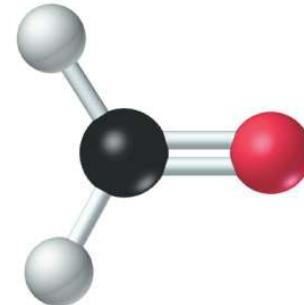
The geometric distribution of terminal atoms around each central atom must be determined and the results then combined into a single description of the molecular shape around that central atom.

Methyl isocyanate
 CH_3NCO

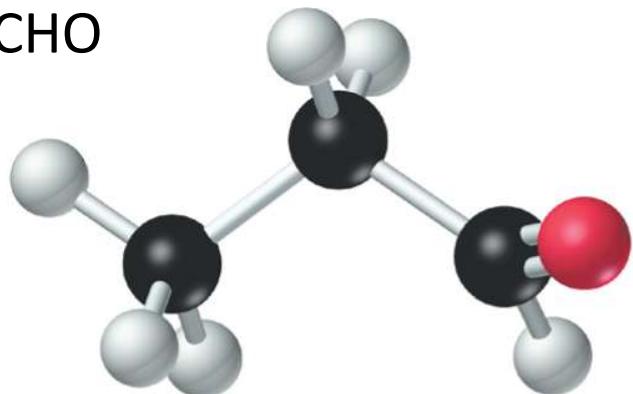


VSEPR Theory & Organic Molecules

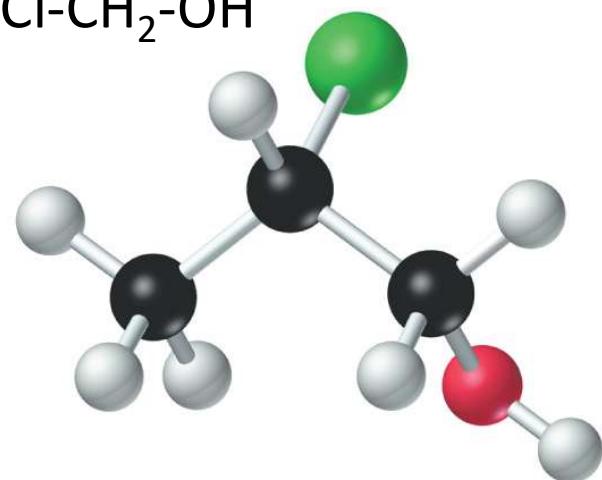
CH_2O



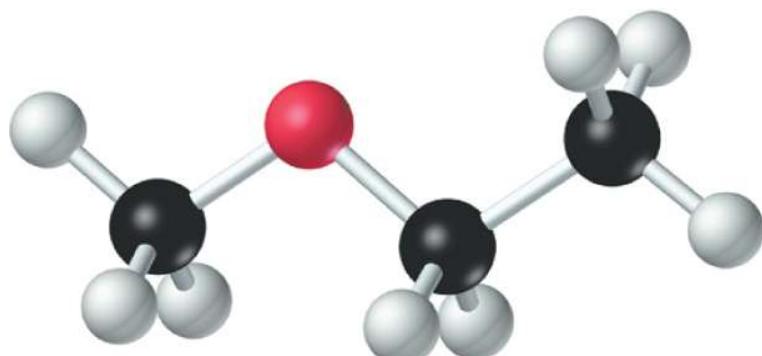
$\text{CH}_3\text{-CH}_2\text{-CHO}$



$\text{CH}_3\text{-CHCl-CH}_2\text{-OH}$



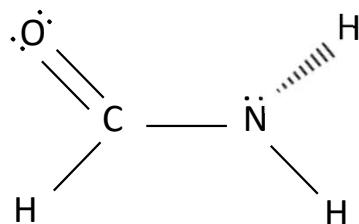
$\text{CH}_3\text{-O-CH}_2\text{-CH}_3$



Example 2

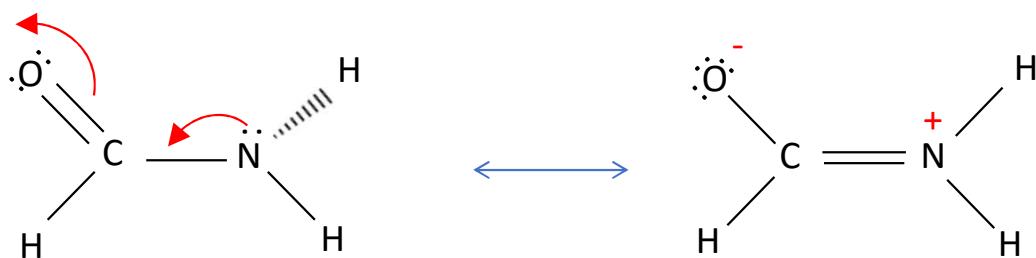
Determine the molecular shape of formamide, HC(O)NH_2

(1) Recall the functional group in Orgo. Draw the Lewis structure



(2) So, on the C, it is AX_3 (so trigonal planar). On the N, it is AX_3E (so trigonal pyramidal). This is the correct answer for Lewis structure-based geometry.

In reality, the molecule is more planar than expected. Can you explain?

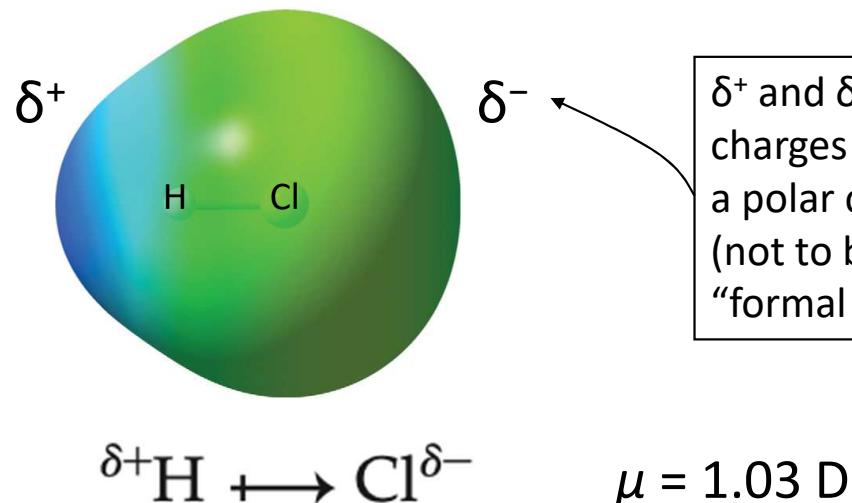


One resonance structure has both C and N with AX_3 (planar). Overall molecule is closer to planar!

Molecular Shape and Dipole Moments

In the HCl molecule, Cl is more electronegative, so pulls more electron density toward it causing a polar covalent bond.

We use the cross-base arrow to indicate a polar covalent bond.



δ^+ and δ^- are the partial charges on the atoms across a polar covalent bond (not to be confused with “formal charges”)

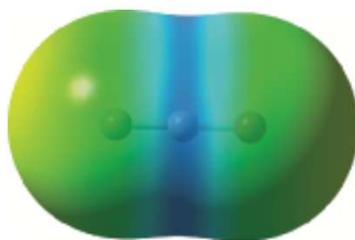
Dipole moment, μ , describes the extent of charge displacement in a polar covalent bond:

$$\mu = \delta \times d$$

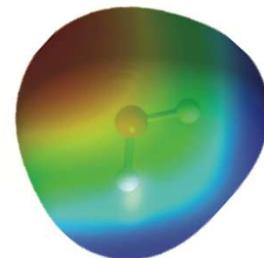
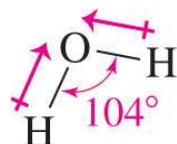
Unit = Coulomb • meter
 $3.34 \times 10^{-30} \text{ C} \cdot \text{m} = 1 \text{ D (Debye)}$

Molecular Dipole Moment Depends on Shape

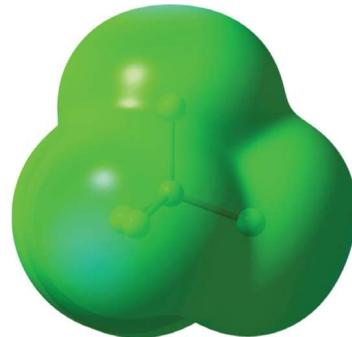
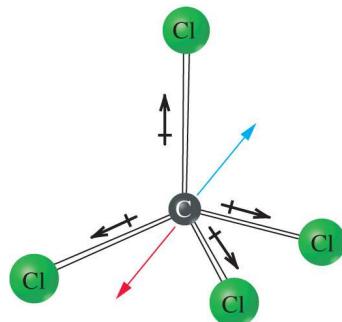
Treat individual bond dipole moments as vectors.



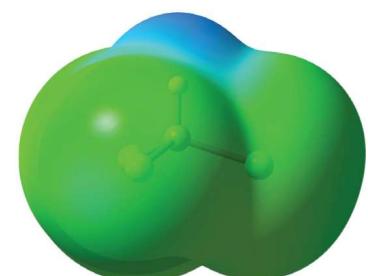
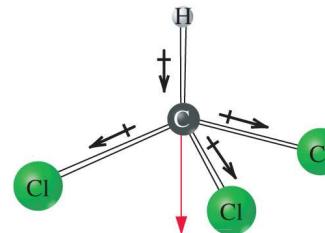
CO_2 is non-polar. $\mu = 0 \text{ D}$



H_2O is polar. $\mu = 1.84 \text{ D}$



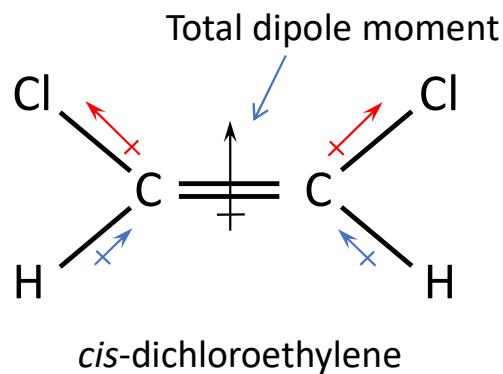
CCl_4 is non-polar.



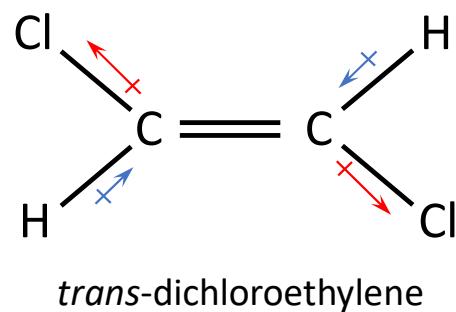
CHCl_3 is polar.

Example 1

Draw structures for both *cis* and *trans*-dichloroethylene and determine the position of the molecular dipole.



$$\mu = 1.89 \text{ D}$$



$$\mu = 0 \text{ D}$$

Detect and Measure Molecular Dipole

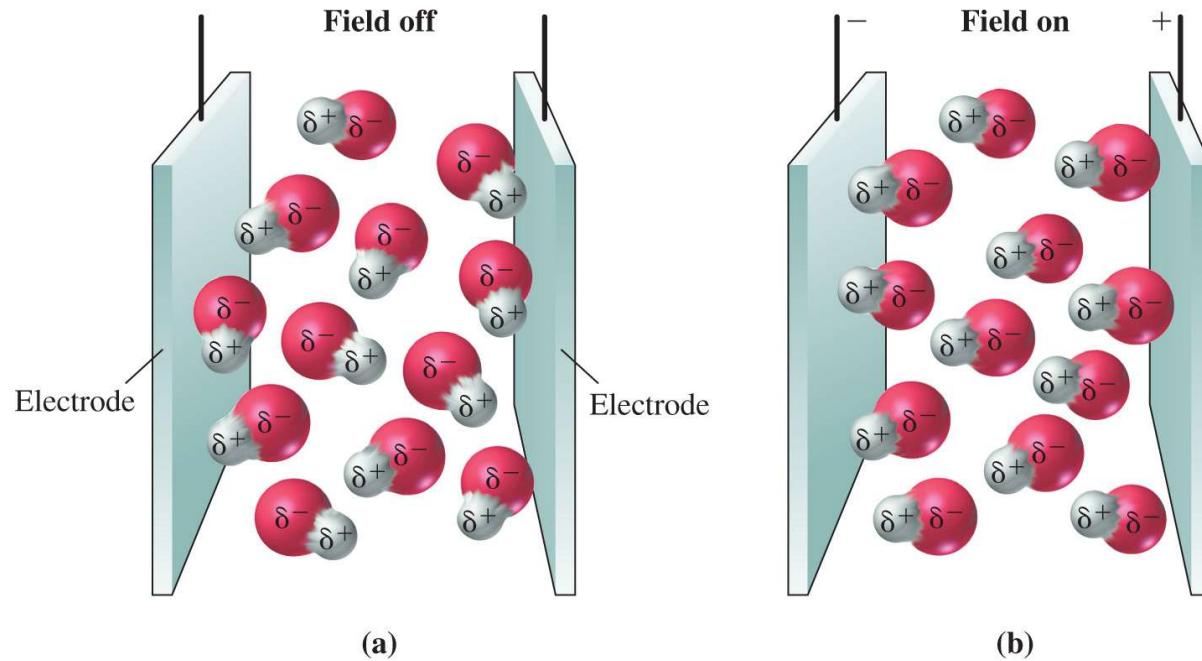
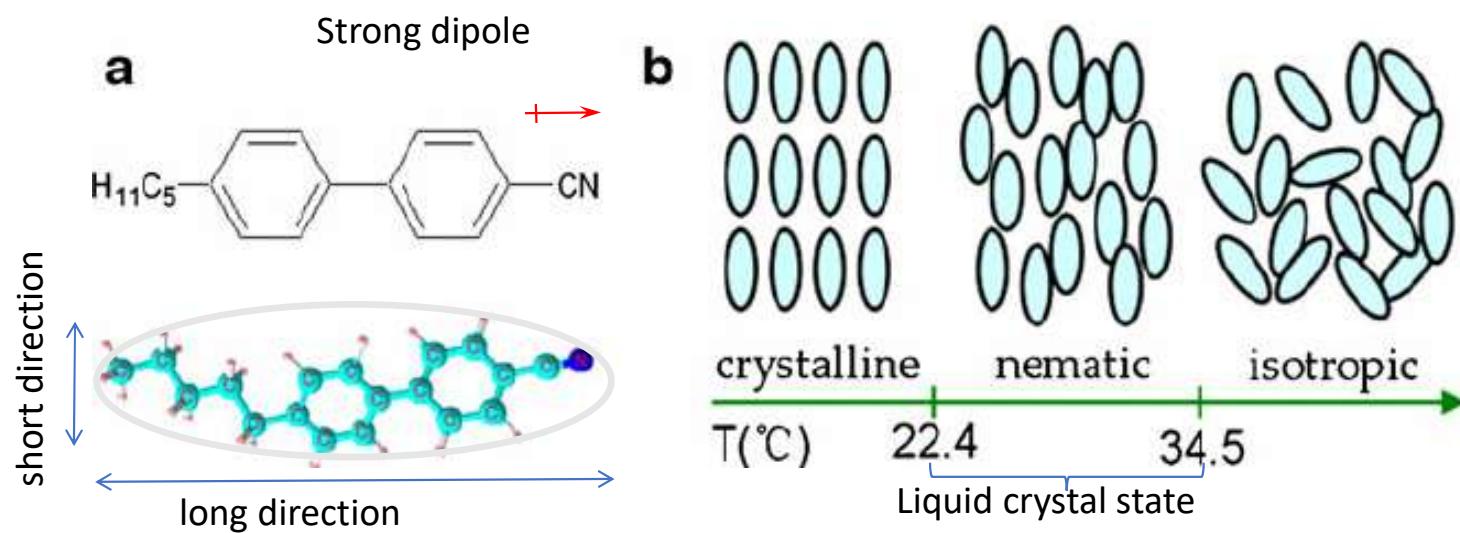


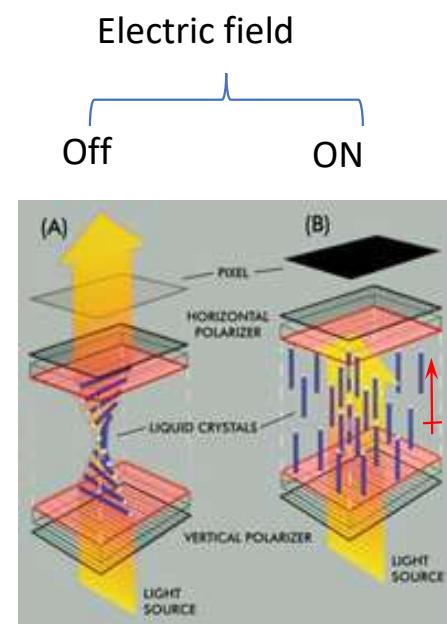
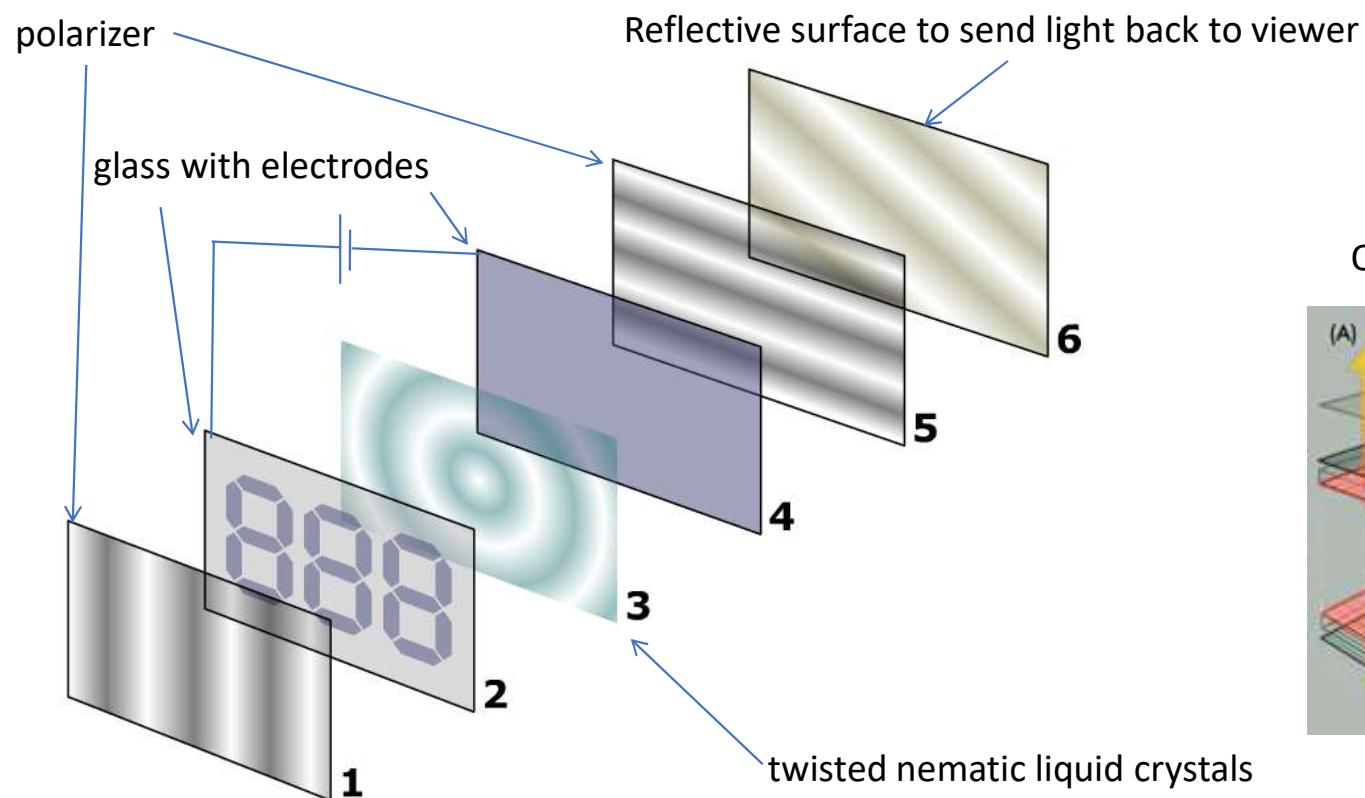
Figure 1: Polar molecules in an electric field.

- When the field is off, the molecules orient randomly.
- When the field is on, the molecules orient so that the negative ends of the molecules are toward the positive plate and vice versa.

Liquid Crystal Display (LCD) Screens

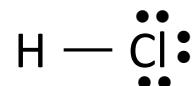


Liquid Crystal Display (LCD) Screens



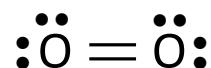
Bond Order

- **Bond Order** describes whether a covalent bond is single, double, or triple. This is denoted by the # of shared electron pairs in a chemical bond.
 - Single bond, bond order = 1
 - Double bond, bond order = 2
 - Triple bond, bond order = 3
- In some unusual molecules, it is also possible to have bond order greater than 3 (e.g., transition metals.)

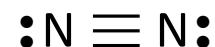


Bond Order =

1



2



3

Bond Length

- **Bond length** is the distance between the centres of two atoms joined by a covalent bond.
- The length of covalent bond between two atoms can be approximated as the sum of their covalent radii.
- In general for bond length:
single bond > double bond > triple bond
- Related to bond energy (Module 4)

TABLE 10.2 Some Average Bond Lengths^a

Bond	Bond Length, pm	Bond	Bond Length, pm	Bond	Bond Length, pm
H—H	74.14	C—C	154	N—N	145
H—C	110	C=C	134	N=N	123
H—N	100	C≡C	120	N≡N	109.8
H—O	97	C—N	147	N—O	136
H—S	132	C=N	128	N=O	120
H—F	91.7	C≡N	116	O—O	145
H—Cl	127.4	C—O	143	O=O	121
H—Br	141.4	C=O	120	F—F	143
H—I	160.9	C—Cl	178	Cl—Cl	199
				Br—Br	228
				I—I	266

^aMost values (C—H, N—H, C—H, and so on) are averaged over a number of species containing the indicated bond and may vary by a few picometers. Where a diatomic molecule exists, the value given is the actual bond length in that molecule (H₂, N₂, HF, and so on) and is known more precisely.

Typical units:

- pm, picometer (10^{-12} m)
- Å, Angstrom (10^{-10} m)

Recall Average Bond Energies

Bond-dissociation energies from Module 4. Note connection to bond order and bond length.

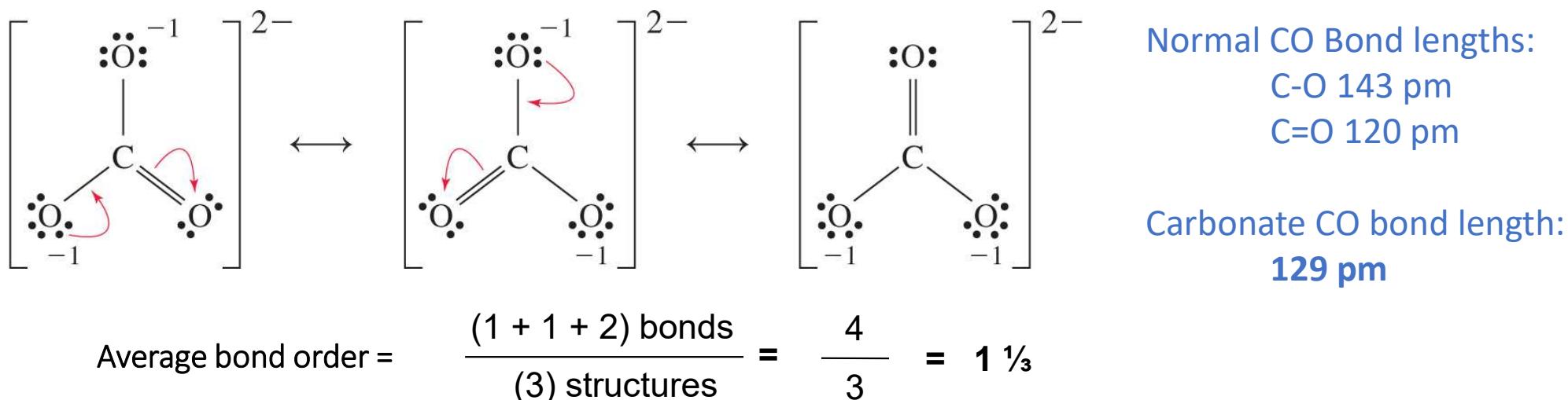
TABLE 10.3 Some Average Bond Energies^a

Bond	Bond Energy, kJ mol ⁻¹	Bond	Bond Energy, kJ mol ⁻¹	Bond	Bond Energy, kJ mol ⁻¹
H—H	436	C—C	347	N—N	163
H—C	414	C=C	611	N=N	418
H—N	389	C≡C	837	N≡N	946
H—O	464	C—N	305	N—O	222
H—S	368	C=N	615	N=O	590
H—F	565	C≡N	891	O—O	142
H—Cl	431	C—O	360	O=O	498
H—Br	364	C=O	736 ^b	F—F	159
H—I	297	C—Cl	339	Cl—Cl	243
				Br—Br	193
				I—I	151

- Values are approximate measures of the strength of a particular type of chemical bond.
- In general, for bond energy : **single bond < double bond < triple bond**

Bond Order/Length and Resonance

- When molecules display resonance, fractional bond orders are possible.
- The bond order becomes the average of the bonds between the atoms from each resonance structure.



Note: formal charge is also shared across resonance structures – average charge on each O atom = $-2/3$