

Bond dipoles, molecular dipoles, quadrupoles

Bond dipole- local momentum associated with polar covalent bond

$$\mu = q \times r$$

Units- Debye (D)

$$1 \text{ D} = 10^{-18} \text{ esu} \times \text{cm}$$

esu- electrostatic unit, $1e = 4.80 \times 10^{-10} \text{ esu}$

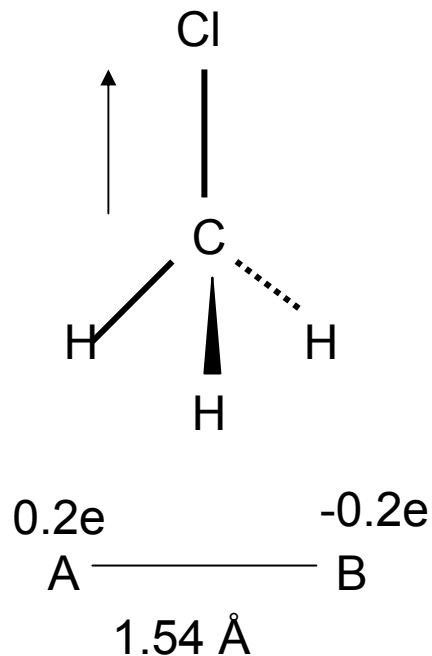
$q = 0.2$, $r = 1.54$ – watch for units!

$$\mu = 0.2 e \times 4.80 \times 10^{-10} \text{ esu/e} \times 1.54 \text{ \AA} \times 10^{-8} \text{ cm/\AA} =$$

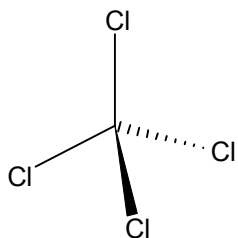
$$1.47 \times 10^{-18} \text{ esu} \times \text{cm} = 1.48 \text{ D}$$

$$1 \text{ D} = 0.39 \text{ au (atomic unit)}$$

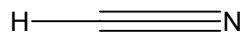
au: unit of mass- electron mass, unit of charge- proton charge, unit of angular momentum- \hbar



Molecular dipole moments- watch for symmetry!

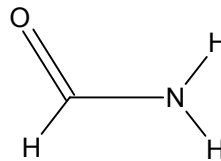
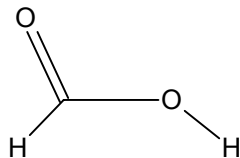
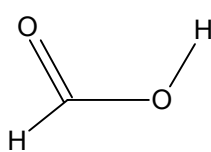


$\mu=0$



$\mu \neq 0$

Compare μ (D)



Quadrupole, octupole,.. (multipoles)

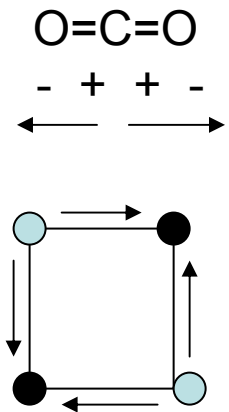
Multipoles- interaction of arrays of point charges

n-pole- an array of n point charges with an n-pole moment but NO lower moments

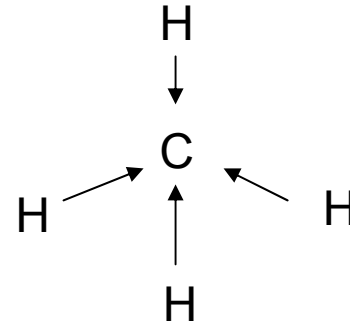
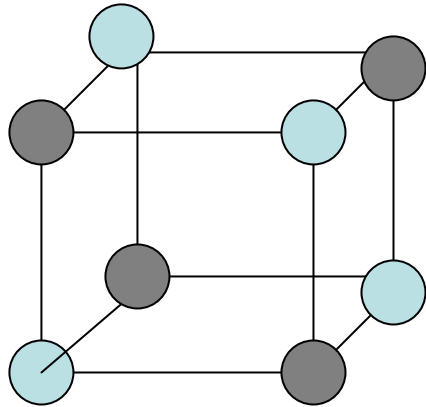
Monopole: point charge, monopole moment- the overall charge

Dipole- array of two point charges with no net charge (no monopole moment)

Quadrupole: array of 4 charges, no dipole moment, no net charge



Octupole- 8 point charges, no quadrupole



For inter-molecular forces:

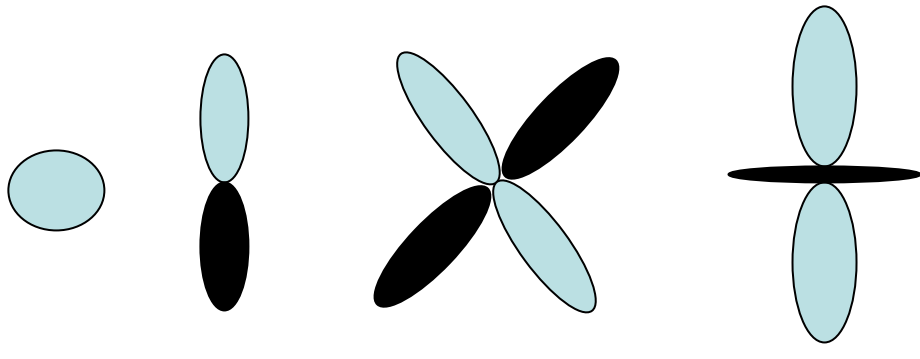
The interaction falls off more rapidly with higher order of n-poles

Dipole-dipole interaction: r^{-3} (usually about 2 kJ/mol)

2^n -pole with 2^m pole : $1/(r^{n+m-1})$

Quadrupole-quadrupole: $1/r^{4+4-1} = r^{-7}$

n-poles and molecular orbitals



s

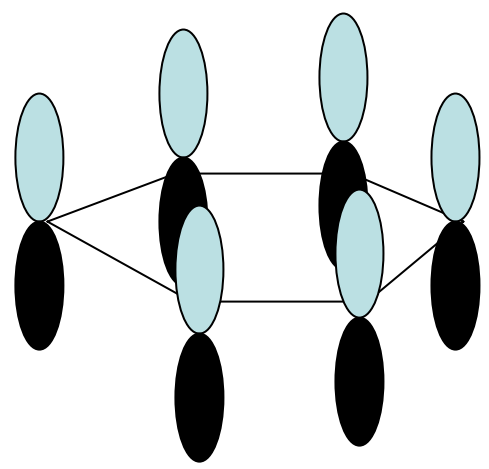
p

d

monopole

dipole

quadrupole



Benzene- no dipole moment



Benzene has quadrupole moment

Bond lengths

Standard bond angles are known for organic systems. Standard bond lengths?

Typical bond lengths, in Å, for some covalent bonds:

Single bonds:

C(sp³)-C(sp³)		1.53-1.55
C(sp³)-C(sp²)		1.49-1.52
C(sp²)-C(sp²)		
conjugated		1.45-1.46
nonconjugated		1.47-1.48
C(sp)-C(sp)		1.37-1.38
C(sp³)-O(sp³)	ethers	1.42-1.44
C(sp³)-N(sp³)	amines	1.46-1.48
C-F		1.39-1.43
C-Cl		1.78-1.85
C-Br		1.95-1.98
C-I		2.15-2.18
C(sp³)-H		1.09-1.10
C(sp²)-H		1.075-1.085
C(sp)-H		1.06
N-H		1.00-1.02
O-H		0.96-0.97

Double bonds:

C(sp²)-C(sp²)	alkenes	1.31-1.34
C(sp²)-C(sp²)	arenes	1.38-1.40
C(sp²)-O(sp²)	aldehydes and ketones	1.19-1.22
C(sp²)-O(sp²)	esters	1.19-1.20
C(sp²)-O(sp²)	amides	1.225-1.24
C(sp²)-N(sp²)	imines	1.35
Triple bonds		
C(sp)-C(sp)	alkynes	1.17-1.20

Covalent, Ionic, and van der Waals radii (in Å) of Selected Atoms

Atom	Covalent	vdW	ion	Ionic
C	0.77	1.68	-	-
H	0.30	1.11	H ⁻	2.08
N	0.70	1.53	-	-
O	0.66	1.50	-	-
F	0.64	1.51	F ⁻	1.36
Cl	0.99	1.84	Cl ⁻	1.81
Br	1.14	1.96	Br ⁻	1.95
I	1.33	2.13	I ⁻	2.16

Polarizability: the ability of the electron cloud to distort in response to an external electric field

As a result, the induced dipole appears in addition to permanent dipole (if present)

Polarizability= magnitude of the dipole induced by one unit of field gradient (in units of volume, cm³)

Atomic polarizabilities (α , Å³ = cm³x10⁻²⁴)

H	0.6668							He	0.205
	C	1.76	N	1.10	O	0.802	F	0.557	
			P	3.13	S	2.90	Cl	2.18	
							Br	3.05	
							I	≈5.0	

Selected molecular polarizabilities

CH ₄	2.6	NH ₃	2.21	H ₂ O	1.45	H ₂ S	3.8
CO ₂	2.91	CS ₂	8.8	CF ₄	3.84	CCl ₄	11.2
C ₂ H ₂	3.6	C ₂ H ₄	4.25	C ₂ H ₆	4.45	CH ₃ OH	3.23
Benzene	10.32	Cyclohexene	10.7	Cyclohexane	11.0		

Symmetry of molecular systems

Symmetry elements: plane, axis and point (center of inversion)

Symmetry operations:

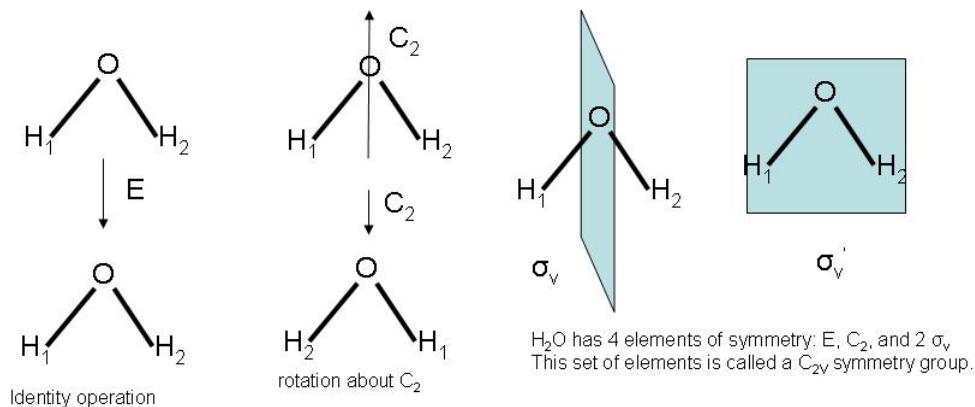
1. rotation about a proper axis. For example, C_2 means rotation about $360^\circ/2$ (180°), C_3 – rotation about $360^\circ/3$ (120°), where n is an *order* of the axis.
2. reflection in a plane of symmetry, σ . there are 3 types of planes. σ_h is perpendicular to C_n (main axis); σ_v contains the main axis, σ_d divides in half the angle between the two C_2 which are perpendicular to C_n .
3. inversion of all atoms through a center of symmetry, (center of inversion) denoted as i . $C_2 \times \sigma_h = i$
4. identity operation **E**- position of atoms do not change- corresponds to the rotation about 360° .

All other operations is just a combination of the symmetry operations described above.

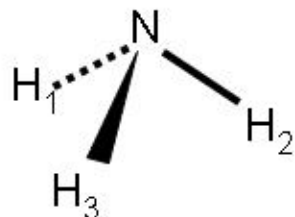
Of particular importance is rotation about an axis, C_n , followed by reflection through the plane perpendicular to the axis, σ_h . This operation is called a rotation about an **improper axis**, denoted as S_n .

A necessary and sufficient criterion for chirality is an absence of S_n axes. If any S_n exists the structure is achiral

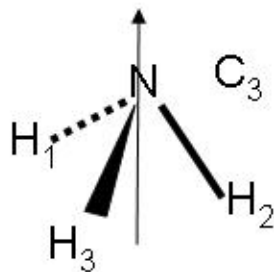
Symmetry elements of H₂O



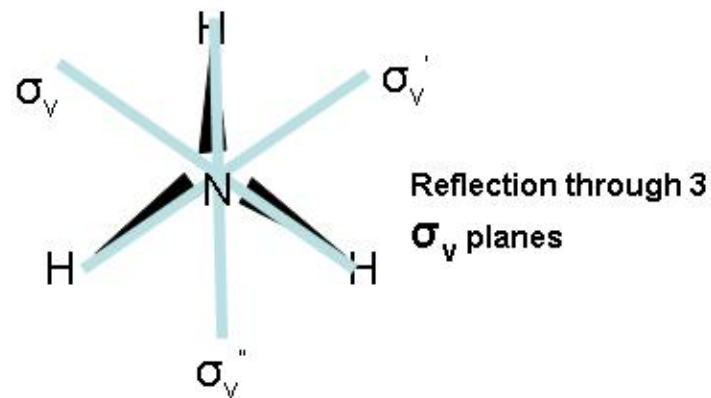
Symmetry elements of NH_3 :



Trigonal pyramidal



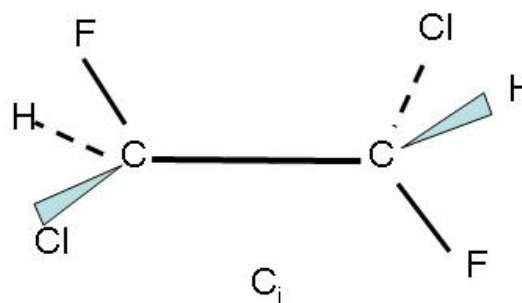
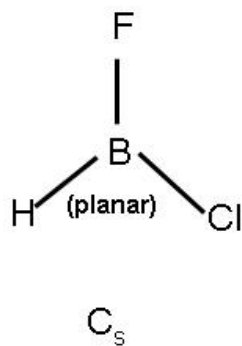
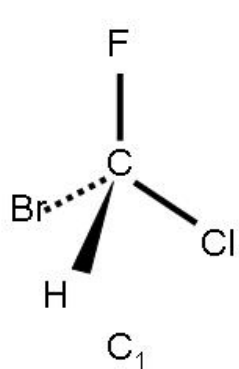
Rotation about 120°



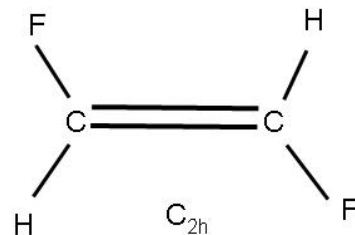
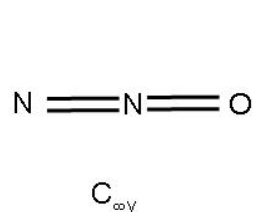
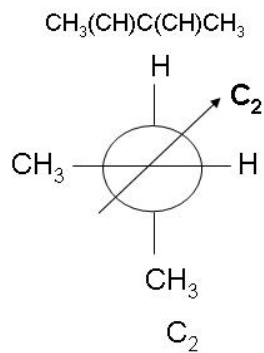
NH_3 has 5 elements of symmetry: E, C_3 , and 3 σ_v .
This set of elements is called a C_{3v} symmetry group.

Symmetry groups:

No axis other than C_1 : C_1 (no symmetry), C_s , C_i

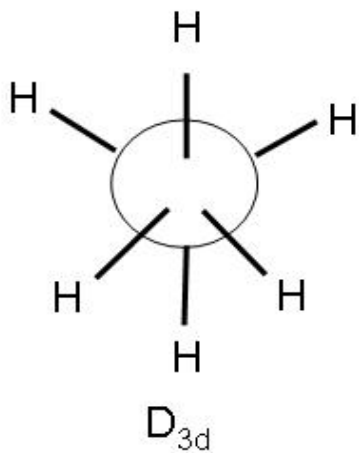


2. Only one axis with $n > 1$: C_n , S_n , C_{nv} , C_{nh}



dihedral groups, D: contain C_n and $n C_2$ perpendicular to C_n .

D_n , D_{nh} , D_{nd}



The cubic groups: T_d (E, 8 C_3 , 3 C_2 , 6 S_4 , 6 σ_d), O_h

