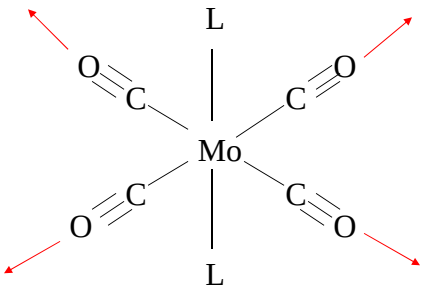
Chem 104A, UC, Berkeley



Carbonyl stretch

Four vectors as Basis

D_{4h}	E	$2C_4$	C_2	$2C_2$	$2C_{2''}$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ	4	0	0	2	0	0	0	4	2	0

$$\Gamma_{CO.stretch} = A_{1g} + B_{1g} + E_u$$

$IR: E_u$

$Raman: A_{1g} + B_{1g}$

Two degenerate mode
One absorption peak

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D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2\ z^2$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		x^2-y^2
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	

Exclusion rule:

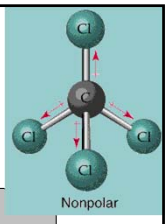
In centrosymmetric molecules, no IR-active vibration can also be Raman active and vice versa.

Point group containing the inversion operation i have two sets of irreducible representation, g and u.

Set u: -→ x, y, z
Set g: → xy, xz, yz, z^2, x^2-y^2

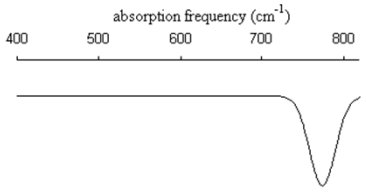
C_{2h}	E	C_2	i	σ_h		
A_g	1	1	1	1	R_z	x^2, y^2, z^2, xy
B_g	1	−1	1	−1	R_x, R_y	xz, yz
A_u	1	1	−1	−1	z	
B_u	1	−1	−1	1	x, y	

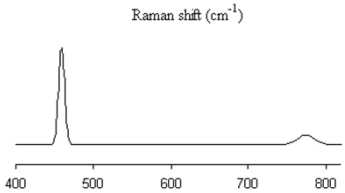
The C-Cl stretching modes of CCl_4 have $A_1 + T_2$ symmetry



Γ 4 1 0 0 2

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	_	_
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0	$(R_x; R_y; R_z)$	$(2z^2-x^2-y^2; x^2-y^2)$
T_1	3	0	-1	1	-1		
T_2	3	0	-1	-1	1	(x; y; z)	(xy;xz;yz)





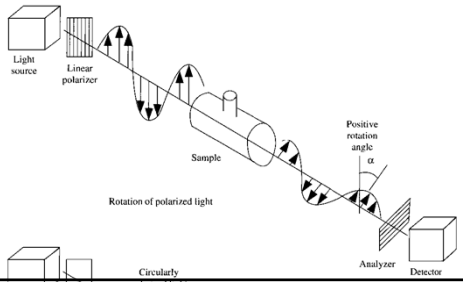
Optical activity:

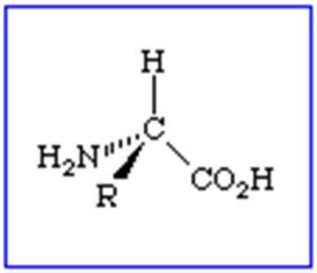
an optical active molecule is one that rotates the plane of the polarized light.

A molecule is optically active only if it cannot be superimposed on its mirror image(chiral or dissymmetric):

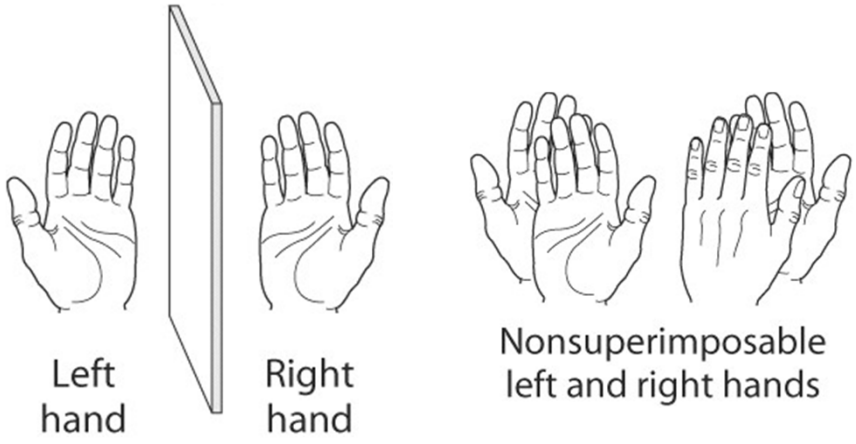
(1) if it does not contain an S_n axis;

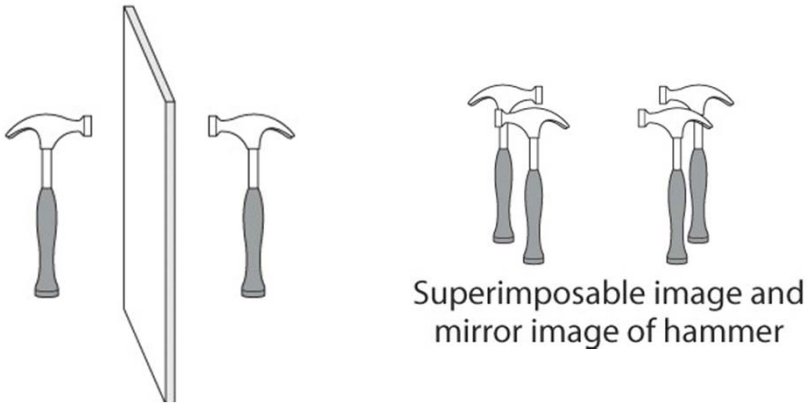
(2) if it belongs to a point group C_1, C_n or D_n.



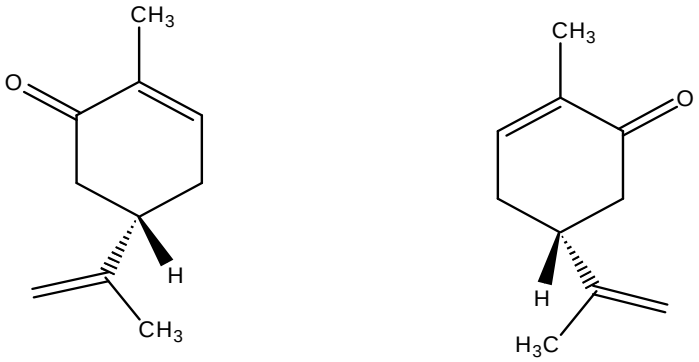


6.1.1 Superimposable and Nonsuperimposable

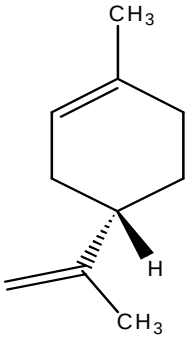


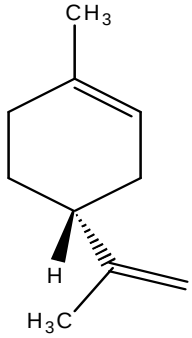

Superimposable image and
mirror image of hammer

Carvone

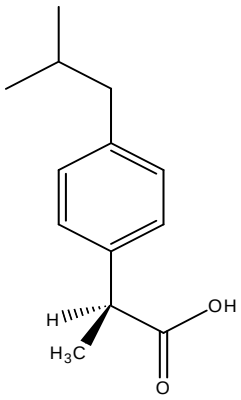

CH3
O
H
CH3
CH3
O
H
H3C

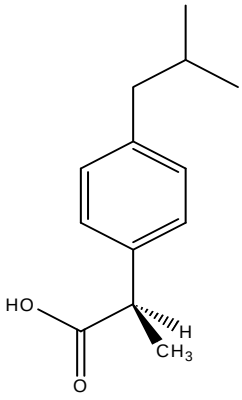
Limonene

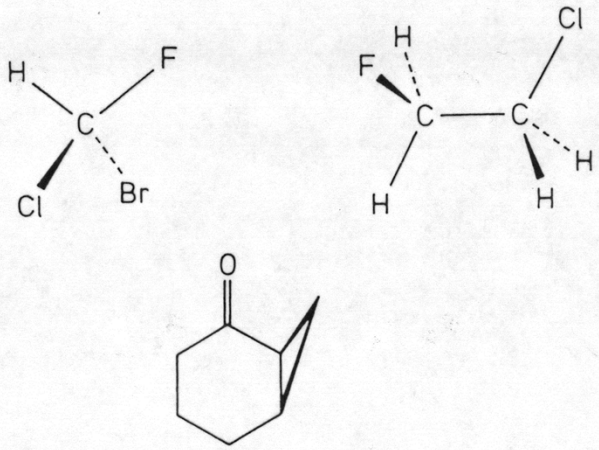




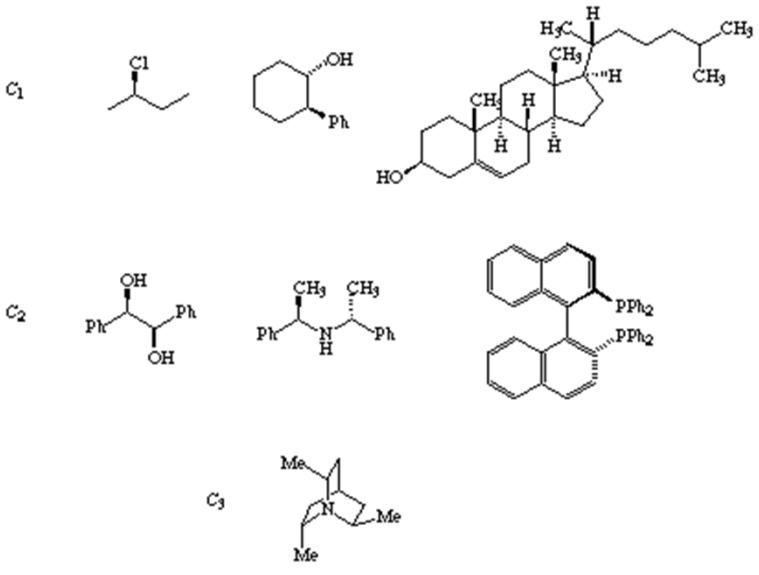
Ibuprofen

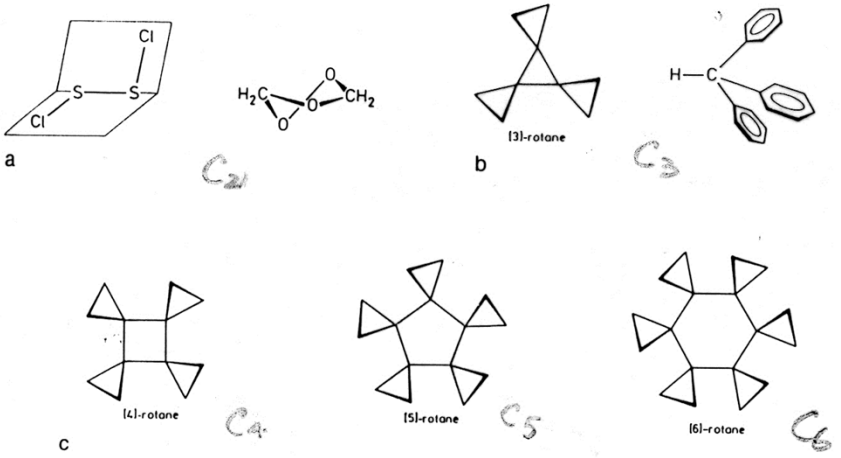


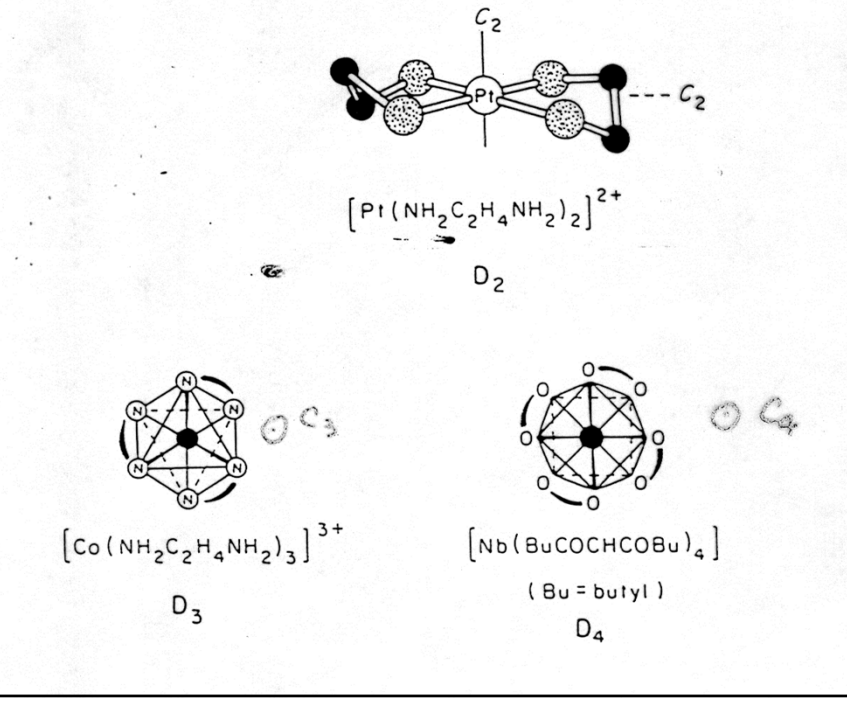




Examples with C_1 symmetry: no symmetry elements except the onefold rotation metry is asymmetry).




Cl
S
S
Cl
a
C_{2v}
H_2C
O
O
CH_2
[3]-rotane
b
C_3
H—C
[4]-rotane
C_4
[5]-rotane
C_5
[6]-rotane
C_6
c


C_2
Pt
C_2
$[Pt(NH_2C_2H_4NH_2)_2]^{2+}$
D_2
C_3
$[Co(NH_2C_2H_4NH_2)_3]^{3+}$
D_3
C_4
$[Nb(BuCOCHCOBu)_4]$
(Bu = butyl)
D_4

Symmetry & Group Theory

✓ Predict vibrational spectra

✓ Determine optical activity

Construct bonding based on atomic orbitals

Access reaction pathway