

6. Polyatomic molecules
symmetry number
vibrations
classical partition functions
without internal rotation

POLYATOMIC MOLECULES

ELECTRONIC electronic levels $- E_i/kT$

$$g_{elec} = \sum_i (2S+1) \underbrace{(1 \text{ or } 2 \text{ or } 3)}_g e^{-E_i/kT}$$

degeneracy depends on the symmetry of the electronic state as described by the point group
 IRREDUCIBLE REPRESENTATION

A or B $g_i = 1$

E $g_i = 2$

T or F $g_i = 3$

Every electronic wavefunction of a molecule must "have the same symmetry" (or "transforms as" or "belongs to") one of the IRREDUCIBLE REPRESENTATIONS of the point group to which the nuclear configuration (i.e., the spatial arrangement of the atoms) of the molecule belongs.

Examples: H-O belongs to point group C_{2v}
H-O

Every electronic wavefunction belongs to one of the following IRREDUCIBLE REPS
 $A_1, A_2, B_1, \text{ or } B_2$

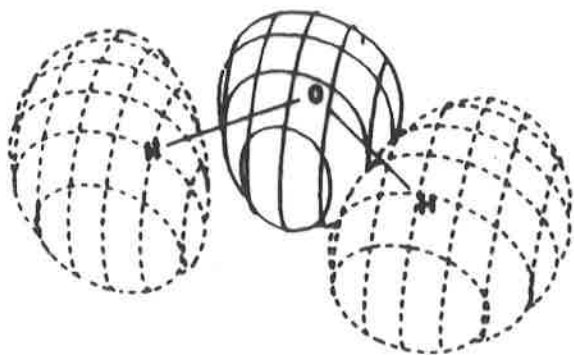
10 electrons

$$(1a_1)^2 (2a_1)^2 (1b_2)^2 (3a_1)^2 (1b_1)^2 = {}^1A_1 \text{ ground state}$$

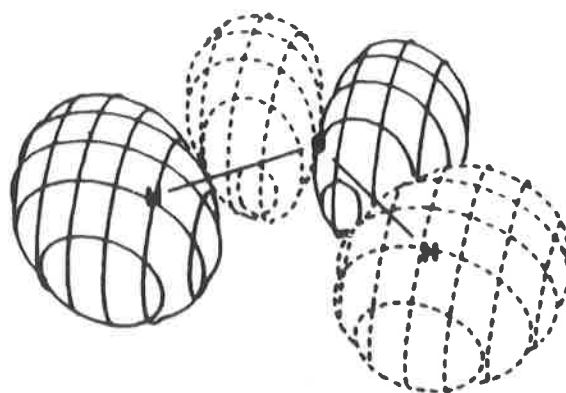
$$(1a_1)^2 (2a_1)^2 (1b_2)^2 (3a_1)^2 (1b_1)(2b_2) = {}^1A_2, {}^3A_2 \text{ excited state}$$

9. Water

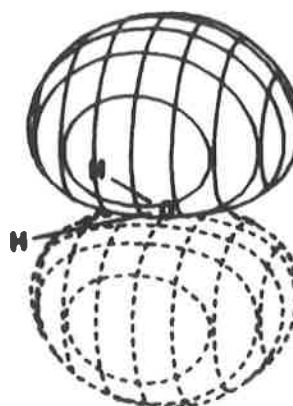
Symmetry: C_{2v}



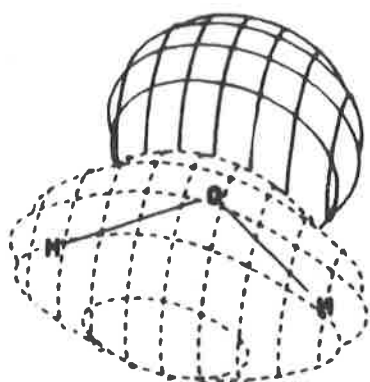
$4A_1 \quad E = 0.4056 \quad 0^* \text{OH}_2$



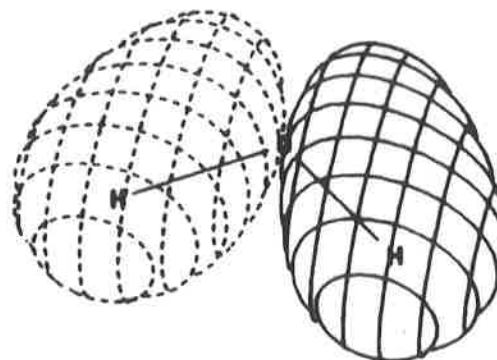
$2B_2 \quad E = 0.5812 \quad \pi^* \text{OH}_2$



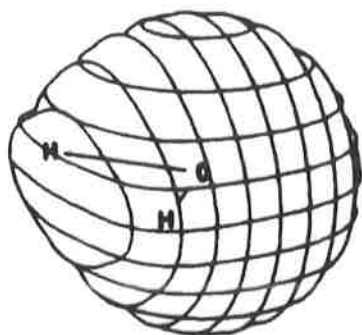
$1B_1 \quad E = -0.4294 \quad \pi$



$3A_1 \quad E = -0.4833 \quad \pi$



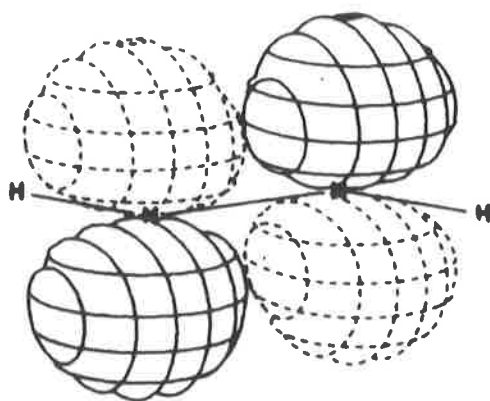
$1B_2 \quad E = -0.6313 \quad \pi \text{OH}_2$



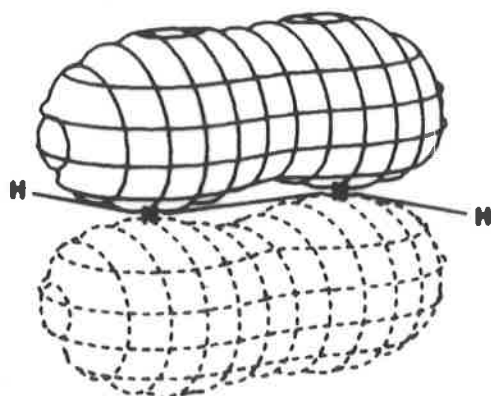
$2A_1 \quad E = -1.3049 \quad 0 \text{OH}_2$

21. Diimide

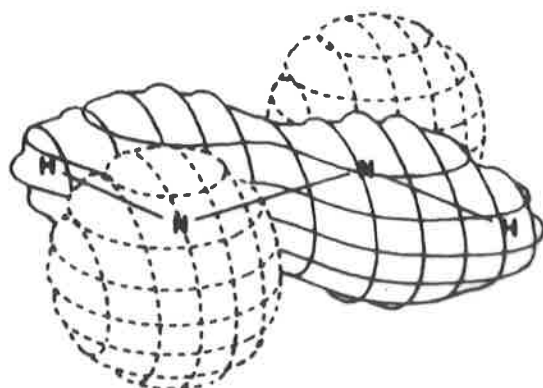
Symmetry: C_{2h}



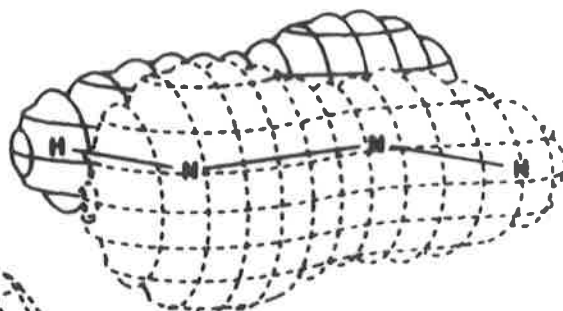
$1B_g \quad \pi^*_{NN}$



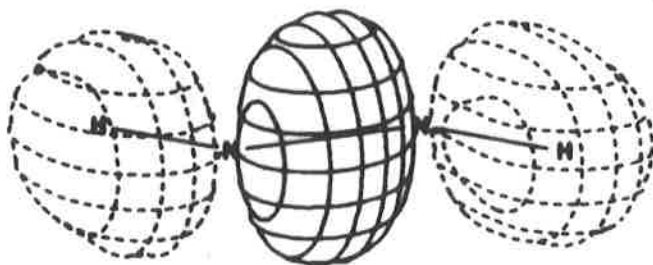
$1B_u \quad E=-0.5292 \quad \pi_{NN}$



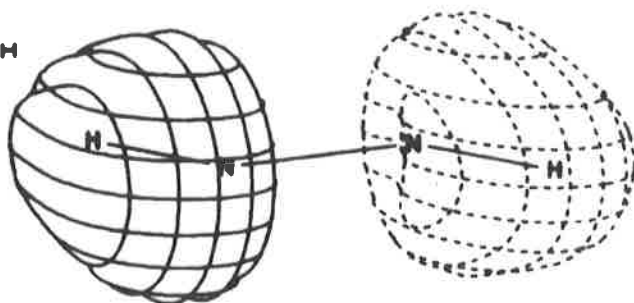
$4A_g \quad E=-0.4027 \quad \sigma$



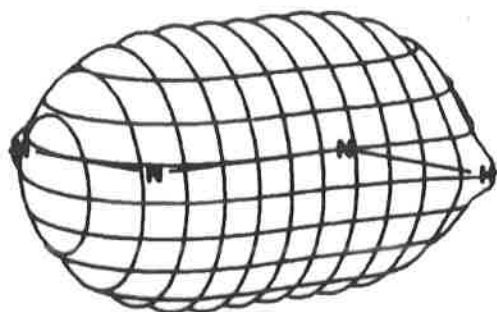
$3A_u \quad E=-0.6463 \quad \sigma$



$3A_g \quad E=-0.6809 \quad \sigma_{NN}, \sigma_{NH}$



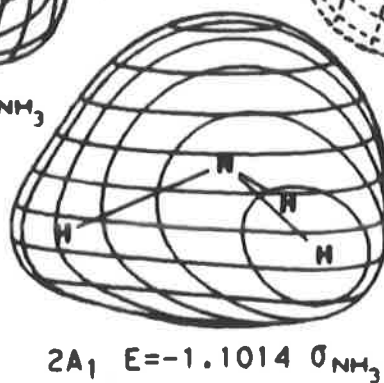
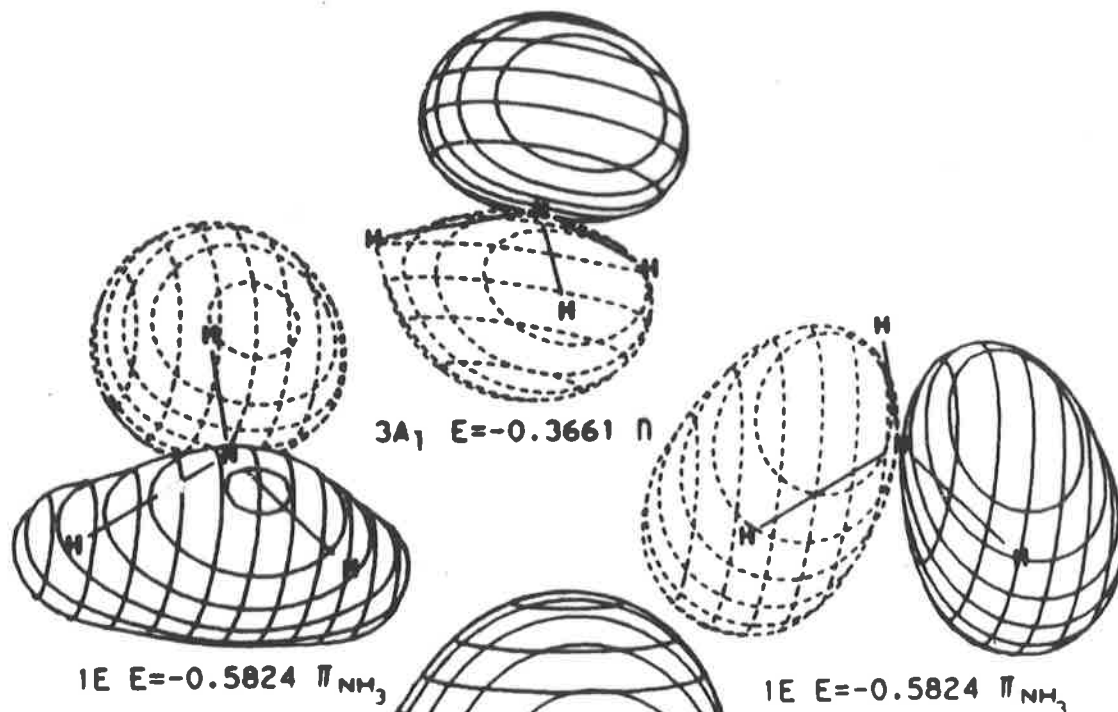
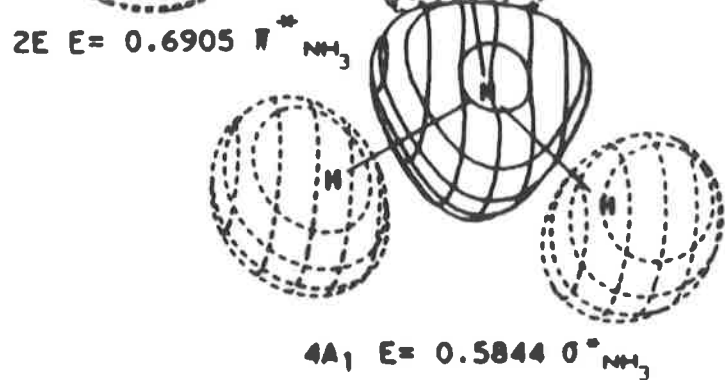
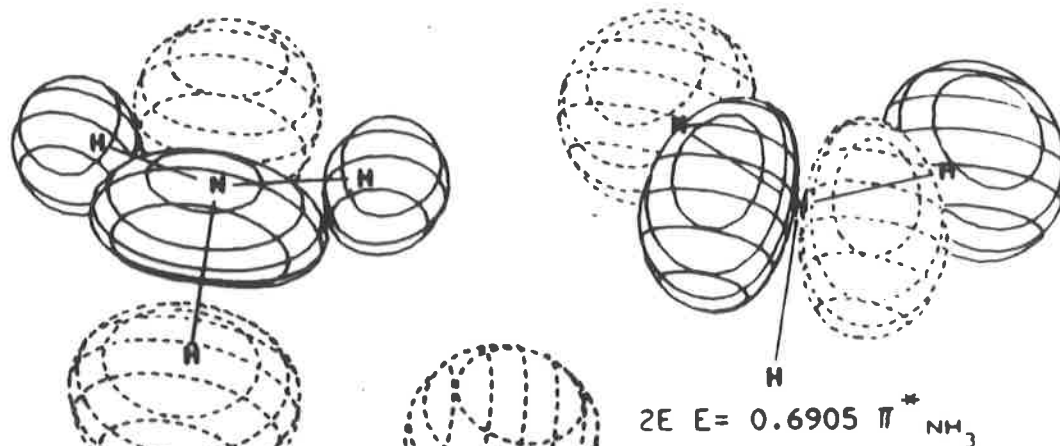
$2A_u \quad E=-0.9568 \quad \sigma_{NH}$



$2A_g \quad E=-1.3945 \quad \sigma_{NN}, \sigma_{NH}$

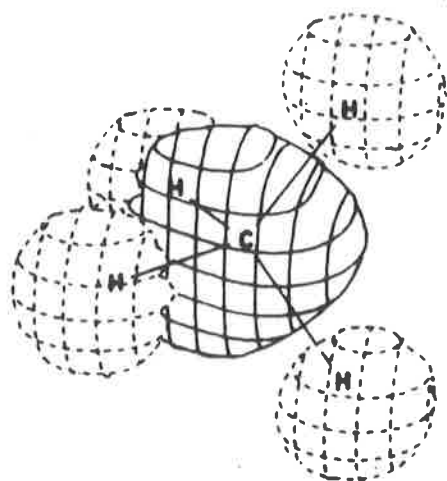
8. Ammonia

Symmetry: C_{3v}

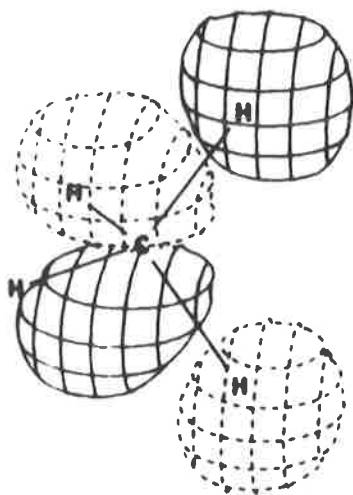


7. Methane

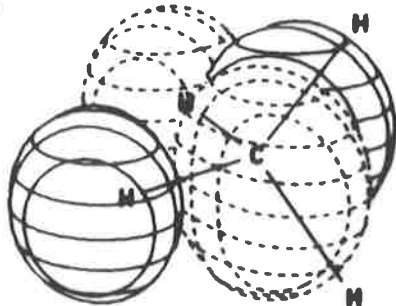
Symmetry: T_d



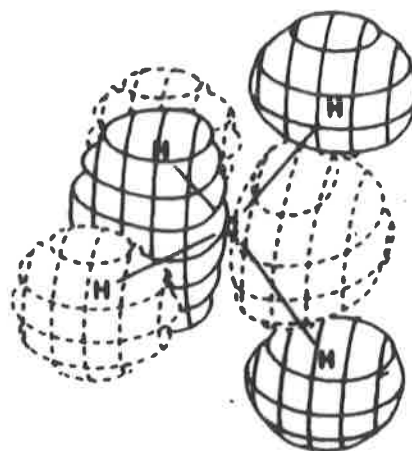
$3A_1$ $E = 0.6887$



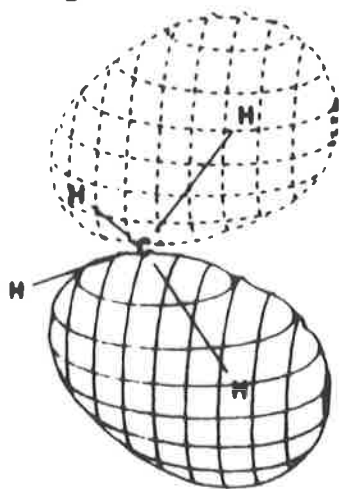
$2T_2$ $E = 0.6441$



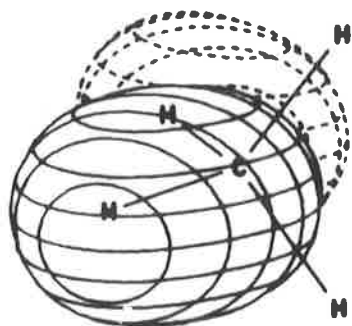
$2T_2$ $E = 0.6441$



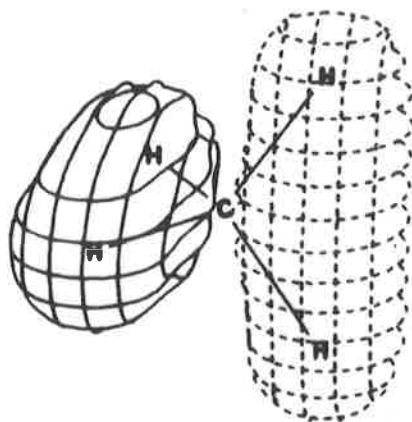
$2T_2$ $E = 0.6441$



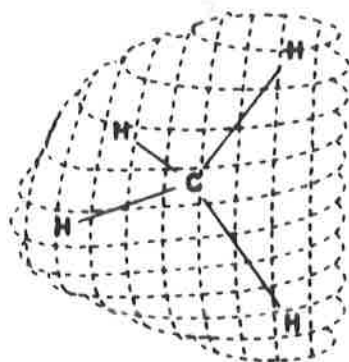
$1T_2$ $E = -0.5418$



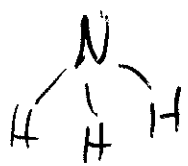
$1T_2$ $E = -0.5418$



$1T_2$ $E = -0.5418$



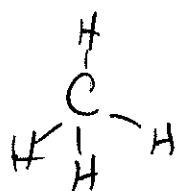
$2A_1$ $E = -0.9320$



belongs to point group C_{3v}

Every electronic wavefunction of NH_3 belongs to

A_1 , or A_2 or E



belongs to point group T_d

Every electronic wavefunction of CH_4 belongs to

A_1 , A_2 , E , T_1 , or T_2

$\mathcal{H}\Psi_i = E_i\Psi_i$ Schrödinger eqn

R_{op} is a symmetry operation: $R_{op}\mathcal{H} = \mathcal{H}R_{op}$

leads to:

$$\mathcal{H}R_{op}\Psi_i = E_i R_{op}\Psi_i$$

from which we see that $R_{op}\Psi_i$ is also an eigenfunction

a) if non-degenerate, then only one Ψ_i for a given E_i which means that

$$R_{op}\Psi_i = (\pm 1)\Psi_i$$

b) if degenerate

$$R_{op}\Psi_{il} = \sum_{j=1}^k r_{ij}\Psi_{ij}$$

E_i has more than one eigenfunction

same for any other symmetry operation

$$S_{op}\Psi_{ij} = \sum_{m=1}^k s_{mj}\Psi_{im}$$

$$T_{op} = S_{op}R_{op} \quad \sum_{m=1}^k t_{ml}\Psi_{im}$$

$$T_{op}\Psi_{il} =$$

$$\text{Sym Rep } \Psi_{il} = \text{Sym} \sum_{j=1}^k r_{jl} \Psi_{ij} = \sum_{j=1}^k \sum_{m=1}^k S_{mj} r_{jl} \Psi_{im}$$

$\therefore t_{ml} = \sum_{j=1}^k S_{mj} r_{jl}$ the relation that defines representations as well as group operations.

Every electronic wavefunction belongs to (or "transforms as" or "has the same symmetry as") one of the IRREDUCIBLE REPRESENTATIONS of the POINT GROUP to which the nuclear configuration (i.e., the spatial arrangements of the atoms) of the molecule belongs.

VIBRATIONAL:
The same holds for the vibrational wavefunctions of the molecule

$$Q_{\text{vibr}} = \prod_i \left(\frac{e^{-h\nu_i/2kT}}{1 - e^{-h\nu_i/kT}} \right) \text{ if using } D_e$$

$$\text{or} = \prod_i \left(\frac{1}{1 - e^{-h\nu_i/kT}} \right) \text{ if using } D_0$$

There are $3n-5$ modes of vibration for a linear molecule

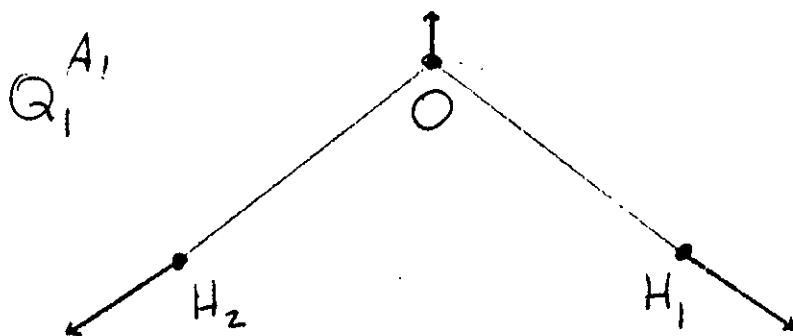
$3n-6$ modes of vibration for a non-linear molecule

vibrational energy levels:

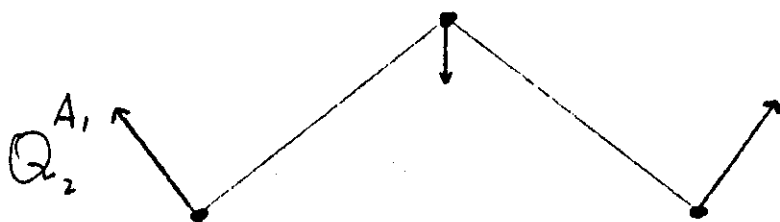
$$E_{\nu_1, \nu_2, \nu_3, \dots} = g_1 \left(\nu_1 + \frac{1}{2} \right) h\nu_1 + g_2 \left(\nu_2 + \frac{1}{2} \right) h\nu_2 + \dots$$

$M^{-1/2} \underline{l} =$

	Q_1	Q_2	Q_3
$\xi_1 = \Delta y_o$	0	0	-.06748
$\xi_2 = \Delta z_o$.04904	-.06772	0
$\xi_3 = \Delta y_{H_1}$.57069	.41297	.53634
$\xi_4 = \Delta z_{H_1}$	-.38917	.53781	-.41510
$\xi_5 = \Delta y_{H_2}$	-.57069	-.41297	.53634
$\xi_6 = \Delta z_{H_2}$	-.38917	.53781	.41510

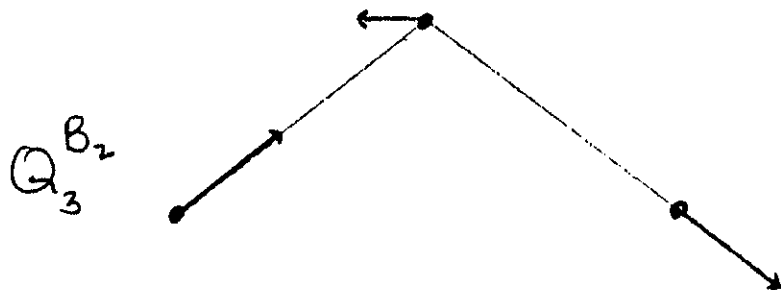


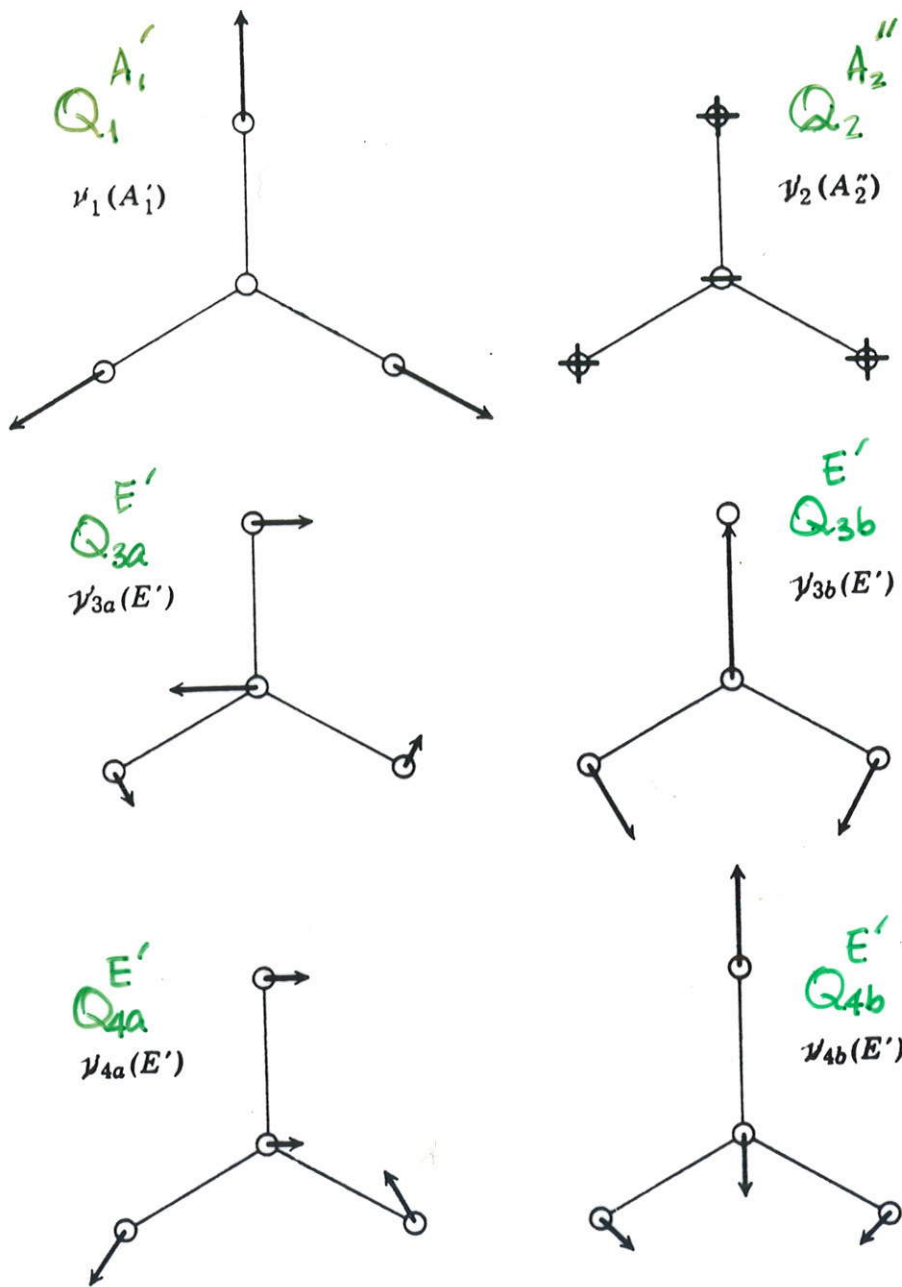
Q_1 is mostly ^{symmetric} bond stretch



Note: There are no out-of-plane vibrations

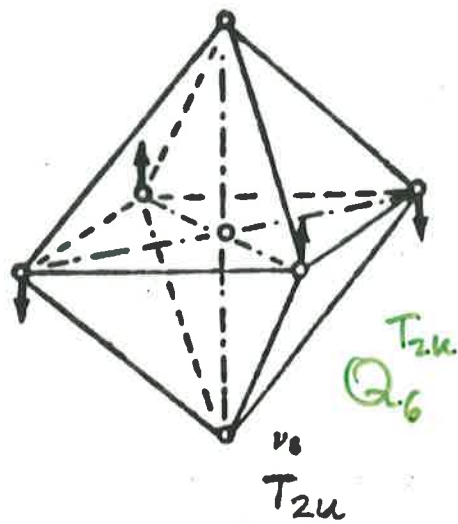
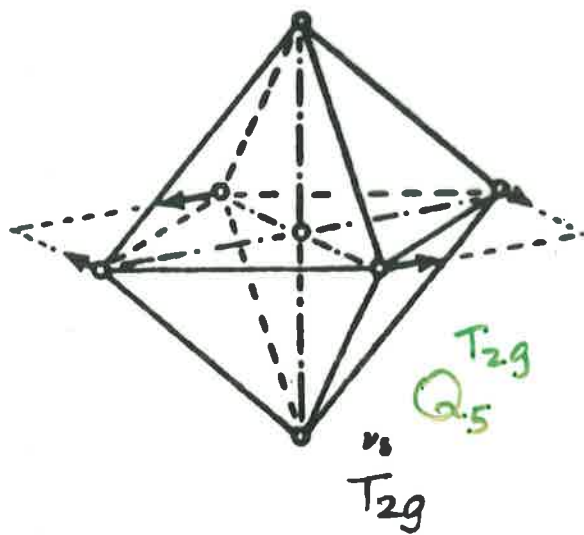
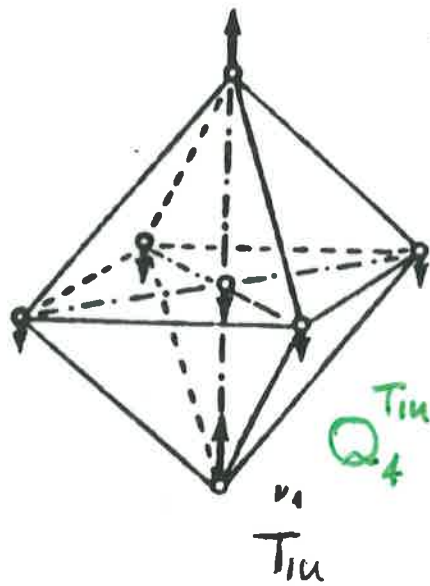
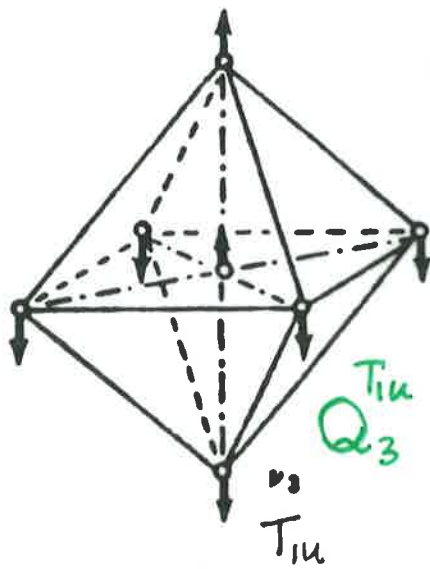
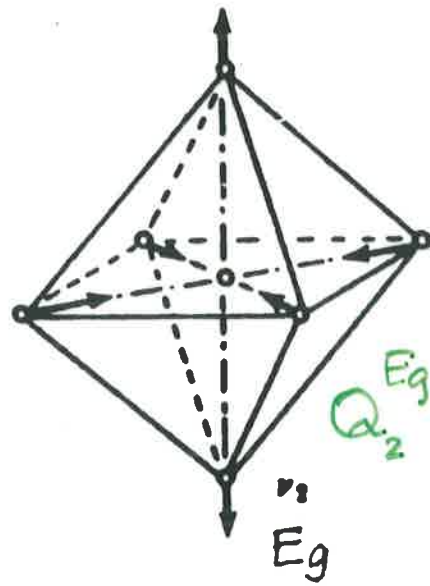
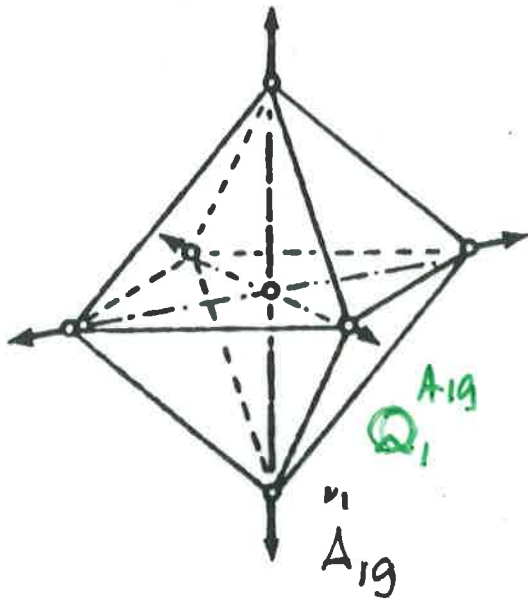
Q_2 is mostly bond angle deformation





The six normal modes of vibration of the carbonate ion.

Each of the normal modes forms a basis for or "belongs to" an irreducible representation of the molecule.



Vibrational wavefunction (harmonic) ^{if}
is still a harmonic oscillator function
just like for a diatomic molecule
EXCEPT that the coordinate is not
the simple one ($R - R_e$) but a coordinate
(called a "normal coordinate") which includes
several nuclear displacements at once.

$$\Psi_{\text{vibr}} = \underbrace{\psi_{v_1}(Q_1)} \cdot \psi_{v_2}(Q_2) \cdot \psi_{v_3}(Q_3) \quad \text{for H}_2\text{O}$$

a harmonic
oscillator function
in terms of coordinate
 Q_1

vibrational quantum
number v_1

such that contribution
to energy is $(v_1 + \frac{1}{2})h\nu_1$

ROTATION and NUCLEAR SPIN:

spherical top - 3 identical moments of inertia
 SF_6, CH_4, C_{60}

$$E_{rot, JKM} = \frac{\hbar^2}{2I} J(J+1)$$

quantum numbers J, K, M

$$K = -J \text{ to } +J$$

$$M = -J \text{ to } +J$$

$$\therefore \text{degeneracy} = (2J+1)^2$$

$$q_{rot} = \sum_{J=0}^{\infty} (2J+1)^2 e^{-\frac{\hbar^2}{2I} \frac{J(J+1)}{kT}}$$

Approximation: high temperature limit, replace sum with integral

$$q_{rot} \approx \int_0^{\infty} (2J)^2 e^{-\frac{\hbar^2}{2IkT} J^2} dJ \quad (\text{neglect } 1)$$

$$\int_0^{\infty} x^2 e^{-a x^2} dx = \frac{1}{4a} \sqrt{\frac{\pi}{a}}$$

$$= \frac{\sqrt{\pi}}{a^{3/2}} \text{ where } a = \left(\frac{\hbar^2}{2IkT} \right)$$

$$q_{rot} = \pi^{1/2} \left(\frac{2IkT}{\hbar^2} \right)^{3/2}$$

Nuclear spins have to be taken into account too, as we shall see.

General rotor

$$q_{rot} = \pi^{1/2} \left(\frac{2I_A kT}{\hbar^2} \right)^{1/2} \left(\frac{2I_B kT}{\hbar^2} \right)^{1/2} \left(\frac{2I_C kT}{\hbar^2} \right)^{1/2}$$

symmetric top: 2 identical moments of inertia 3rd one is unique

$$E_{rot, JKM} = \frac{\hbar^2}{2I_{xx}} J(J+1) + \frac{\hbar^2}{2} K^2 \left(\frac{1}{I_{zz}} - \frac{1}{I_{xx}} \right)$$

How do the nuclear spins come in?

Just as in diatomics, if molecule has equivalent atoms that can be permuted then only some nuclear spin states pair up with rotational states.

Example:

Consider CH_3X 3 protons $I_H = \frac{1}{2}$

The nuclear spin functions for each H are α, β

Therefore there are 8 spin states possible

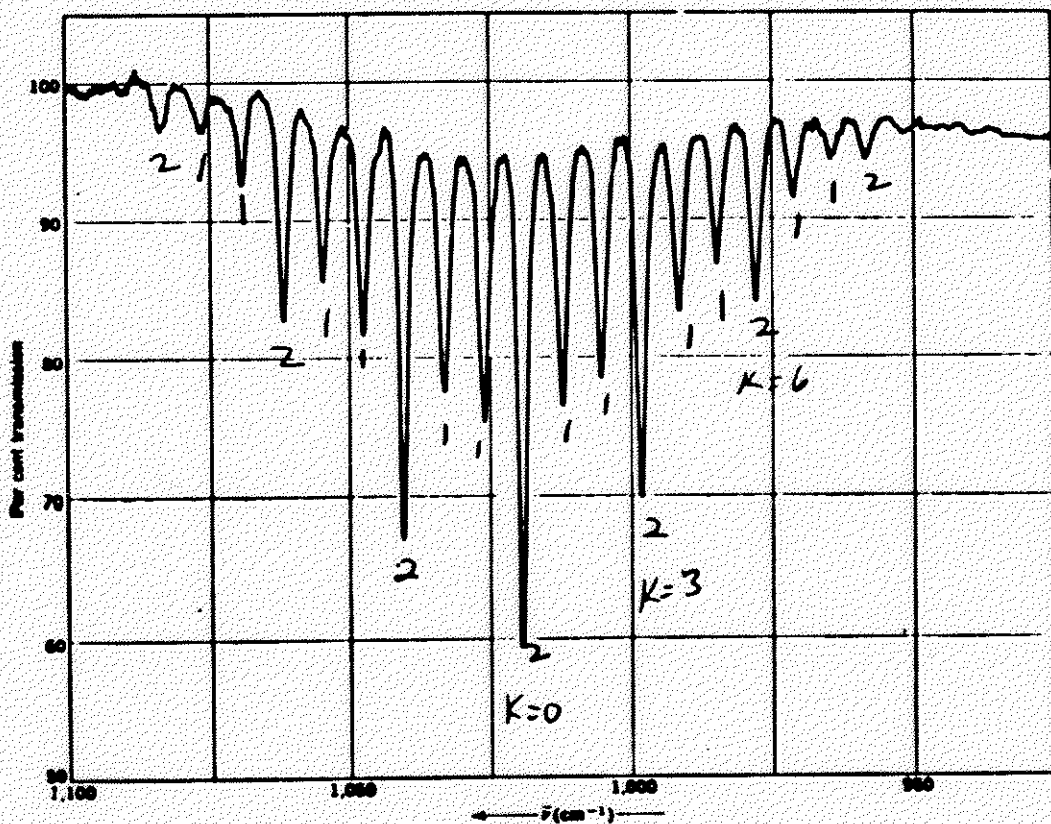
	1	2	3	
a	α	α	α	symmetric with respect to $C_3 = P_{12}P_{23}$ and $C_3^2 = P_{13}P_{23}$
b	β	α	α	
c	α	β	α	
d	α	α	β	
e	α	β	β	need to form a linear combination of these
f	β	α	β	
g	β	β	α	
h	β	β	β	symmetric with respect to C_3 and C_3^2

After the correct combinations are formed, it will be found that we get $T_1 + E$ from the set of spin functions b, c, d and also $A_1 + E$ from the set c, f, g. It can be easily shown that a is A_1 and h is also A_1 .

The rotational functions on the other hand have different symmetries depending on whether they have $K=0$ or $|K|=3p$ or $|K|=3p \pm 1$ where $p = \text{integer}$.

	rotational function belongs to
$K=0$	A_1
$ K =3p$	$2A_1$ (plus and minus values of K)
$ K =3p \pm 1$	E

CH_3Cl prolate symmetric top sharp perpendicular band. Note the P branches superimposed on a very broad background of P and R branches.



K value in $v=0$ state is shown for some peaks

FIG. 7-15 A perpendicular band of the symmetry-top molecule CH_3Cl .

Note alternation of intensities. There is a factor $2:1:1:2:1:1$ etc... superimposed on the Boltzmann factor which determines relative intensities (Populations of diff K levels of the ground state) due to different numbers of nuclear spin states associated with different K values.

The product function $\Psi_{rot}(J, K, M) \cdot \Psi_{nuclear\ spin}$ is such that A_1 only goes with A_1 , E goes with E . So, of the 8 spin states

A_1 only 4 go with $K=0$ states
 A_1 only 4 go with $|K|=3p$ states
 E only 4 go with $|K|=3p \pm 1$ states

provided the electronic and vibrational functions are symmetric

For the A_1 vibrations the K states are populated by $4A_1, (4A_1), (2E)$ nuclear spin states

For the E vibrations these K states are paired with E, E , and both.

Thus, having the 3 classes of rotational states leads to a symmetry number of 3

in the same way that having the 2 classes of rotational states (odd J , even J) for diatomic molecules led to a symmetry number of 2.

The relative weights are different for CD_3X because the total number of nuclear spin states are different (27 instead of only 8);

nevertheless the rotational states are classified into the 3 classes of states:

$K=0, |K|=3p$ and $|K|=3p \pm 1$ states.

$$g_{rot} = \sum_{J, M, K=0} (4) \dots$$

$$+ \sum_{J, M, |K|=3p} (8) \dots$$

$$+ \sum_{J, M, |K|=3p \pm 1} (4) \dots$$

Summary

Mole cule type	number of types of rotl states; rotl subgrp	any given nuclear a spin state can only go with	symmetry number
linear $D_{\infty h}$	2	J_{odd} <i>or</i> J_{even}	2
CH_3X C_{3v}	3 C_3	$K = 0$ <i>or</i> $ K = 3p$ <i>or</i> $ K = 3p \pm 1$	3
BF_3 D_{3h}	6 D_3		6
CH_4 T_d	12 T		12
C_6H_6 D_{6h}	12 D_6		12
SF_6 O_h	24 O		24
any point group	rotl subgrp order n	generates n different types of rotational states	n