

A talk on the relation between Point Groups and Permutation-Inversion Groups By P. R. Bunker

References:

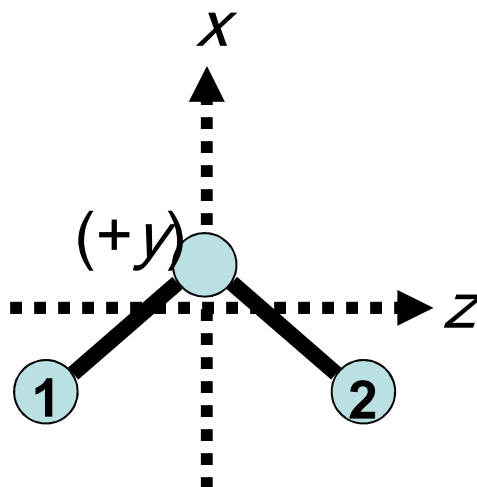
J. T. Hougen, J. Chem. Phys., 37, 1433 (1962); 39, 358 (1963).

H. C. Longuet-Higgins, Mol. Phys., 6, 445 (1963).

**P. R. Bunker and Per Jensen, "Fundamentals of Molecular Symmetry,"
CRC Press, Taylor and Francis (2004), p 164-176. We call this book BJ1.**

**P. R. Bunker and Per Jensen, "Molecular Symmetry and Spectroscopy,"
NRC Research Press, Ottawa (2006), p 58-64. We call this book BJ2.**

The C_{2v} Point Group of H_2O



The Point Group of H_2O consists of the four Point Group symmetry operations

E , C_{2x} , σ_{xz} and σ_{xy}

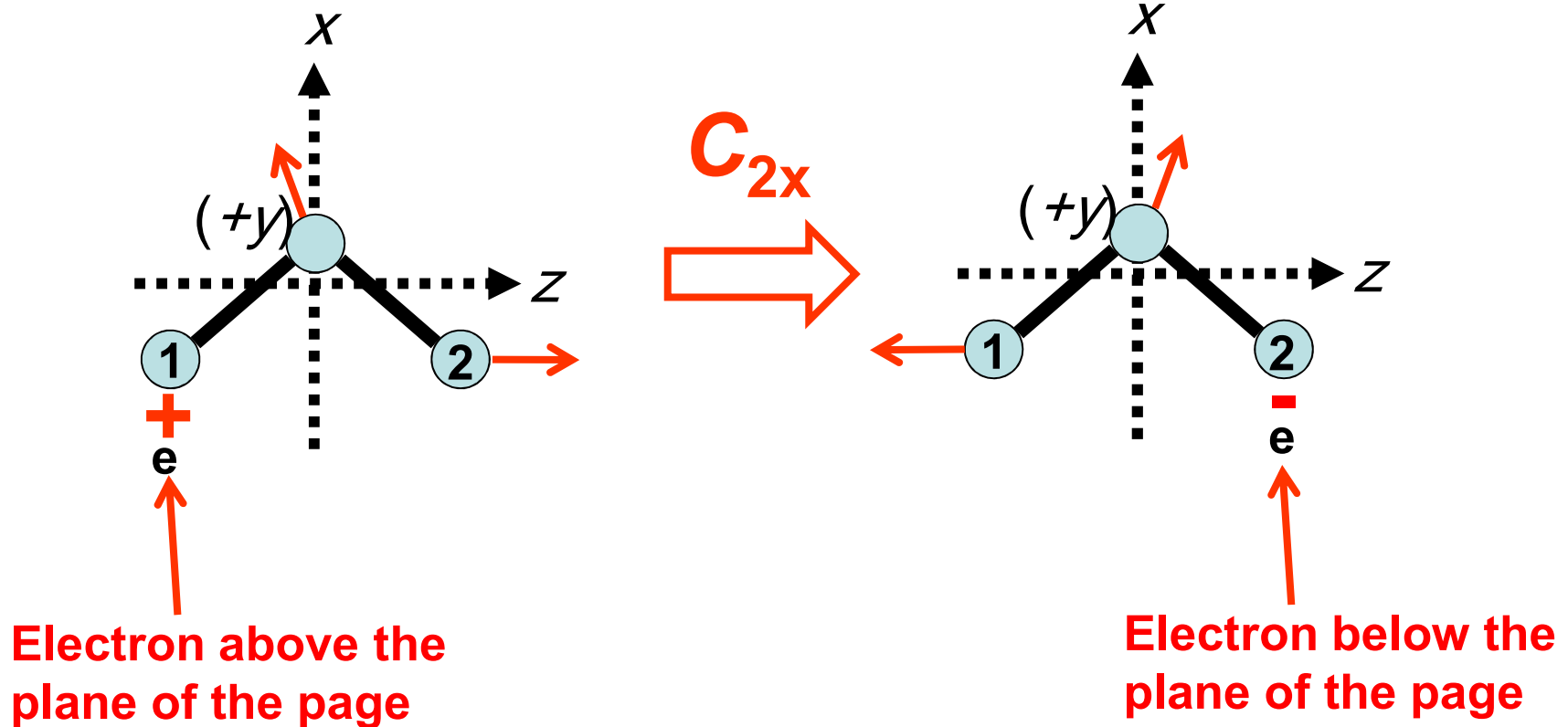
Identity operation

C_2 rotation about x axis

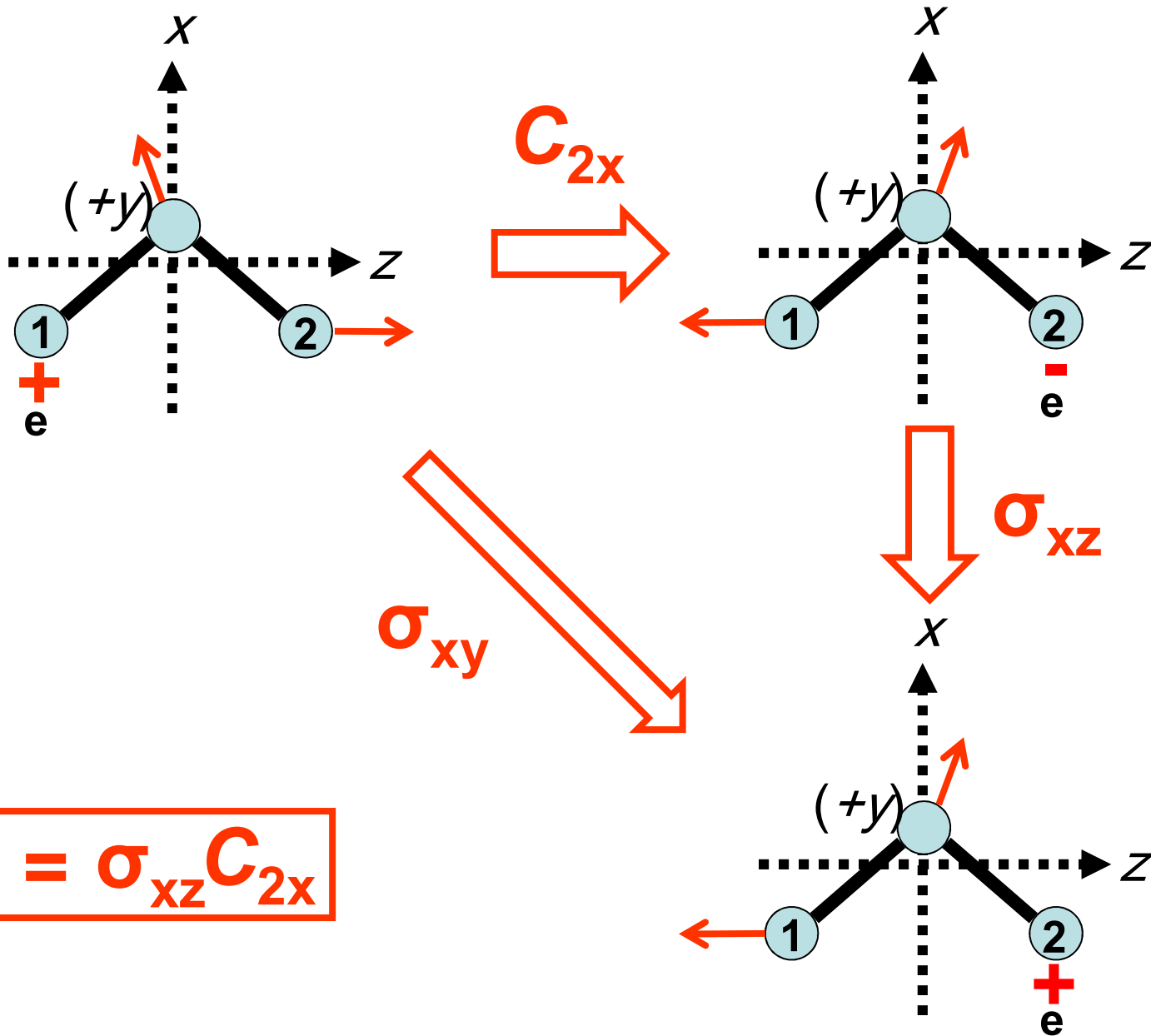
Reflection in xz plane

Reflection in xy plane

Point Group operations act on vibrational displacements and electronic coordinates



Successive application of PG operations



$$\sigma_{xy} = \sigma_{xz} C_{2x}$$

$$\sigma_{xy} = \sigma_{xz} C_{2x}$$

$$\sigma_{xz} = \sigma_{xy} C_{2x}$$

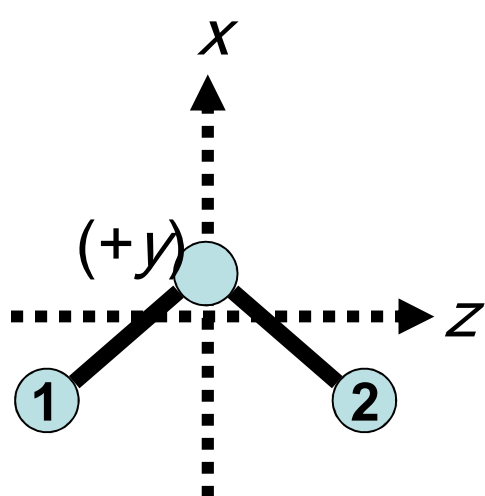
$$C_{2x} = \sigma_{xy} \sigma_{xz}$$

$$\sigma_{xy} = C_{2x} \sigma_{xz}$$

$$\sigma_{xz} = C_{2x} \sigma_{xy}$$

$$C_{2x} = \sigma_{xz} \sigma_{xy}$$

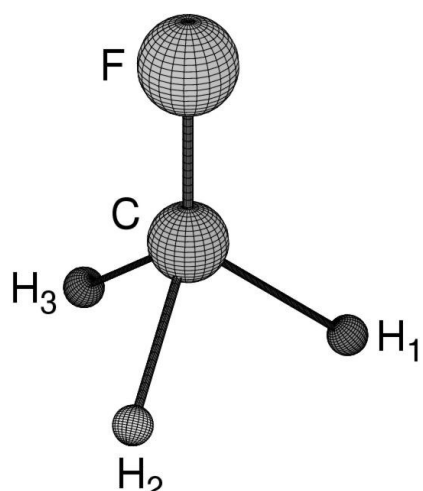
Character Table for the Point Group C_{2v}



	E	C_{2x}	σ_{xz}	σ_{xy}
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	-1	1
B_2	1	-1	1	-1

4 irreducible representations

Character table for the Point Group C_{3v}



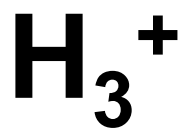
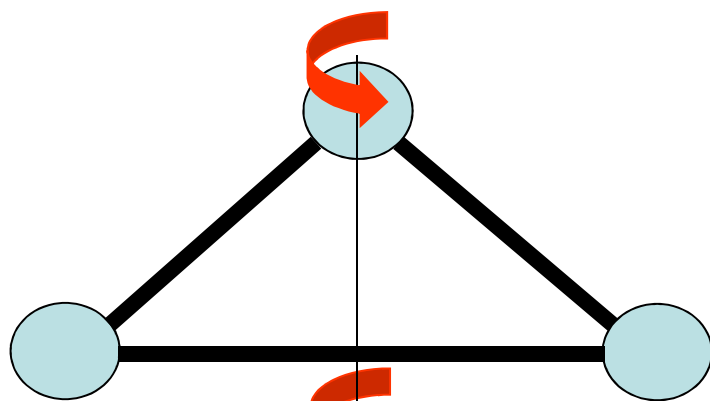
	E	C_3 C_3^2	σ_1 σ_2 σ_3
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

Reflection in FCH₁ plane

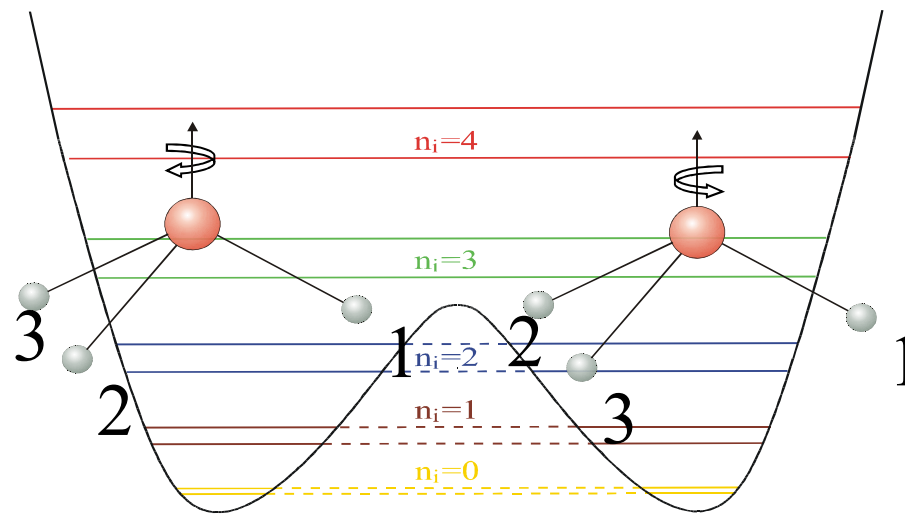
3 irreducible representations

Point Group Symmetry is based on the geometry of the equilibrium molecular structure in a single electronic state.

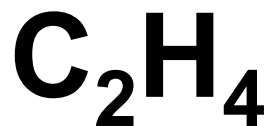
It has limitations when one needs to consider the effects of molecular rotation, tunneling, or electronic states of a molecule having different Point Group symmetries



Rotational distortion



Tunneling



Excited state geometry \neq Ground state geometry



**A more general symmetry is
“Energy Invariance” symmetry**

**In the language of Quantum
Mechanics this means that
symmetry operations R are
such that they commute with
the molecular Hamiltonian H .**

$$RH = HR$$

Symmetry Operations

[commute with the full Hamiltonian]



- Uniform Space-----Any translation in space
- Isotropic Space-----Any rotation in space
- Identical Electrons-----Permute electrons
- Identical Nuclei-----Permute identical nuclei
- Parity Conservation-----Invert coordinates and momenta
- Time Reversal-----Reverse momenta and spins
- Charge Conjugation-----Interchange particles and antiparticles

Point Group operations do not commute with the full (rotation-vibration-electronic-nuclear spin) Hamiltonian. They do commute with the vibronic (vibrational-electronic) Hamiltonian.

Symmetry Operations

[commute with the full Hamiltonian]



- Uniform Space-----Any translation in space
- Isotropic Space-----Any rotation in space
- Identical Electrons-----Permute electrons
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The Complete Nuclear Permutation Inversion Group

We just consider the group of these two types of symmetry operation

The Complete Nuclear Permutation Inversion (CNPI) Group

Contains all possible permutations of identical nuclei including E. It also contains the inversion operation E^ and all possible products of E^* with the identical nuclear permutations.*

$$G_{\text{CNPI}} = G_{\text{CNP}} \times \{E, E^*\}$$

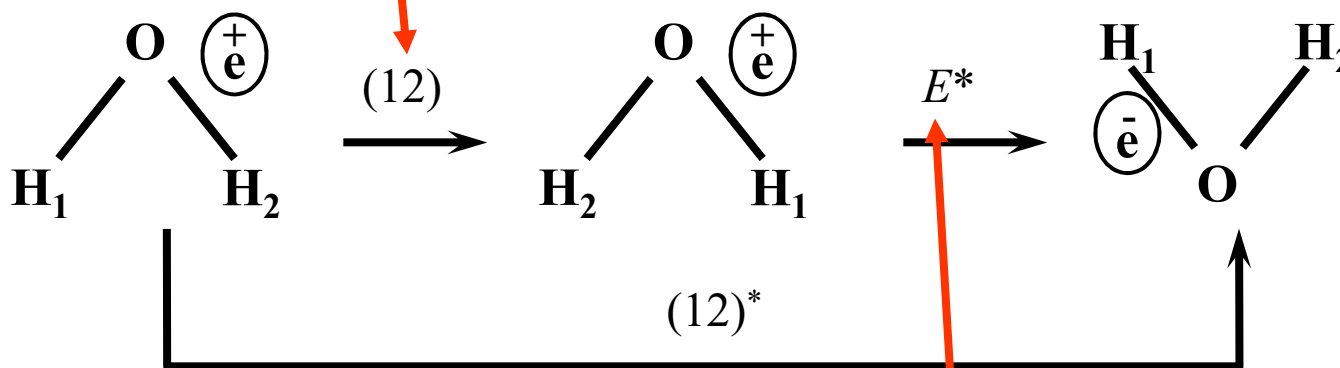
$$\begin{aligned} \text{For H}_2\text{O} \quad G_{\text{CNPI}} &= \{E, (12)\} \times \{E, E^*\} \\ &= \{E, (12), E^*, (12)^*\} \end{aligned}$$

The CNPI Group for the Water Molecule

*Nuclear permutations permute nuclei (coordinates and spins).
Do not change electron coordinates in space*

The Complete Nuclear Permutation Inversion (CNPI) group

for the water molecule is $\{E, (12)\} \times \{E, E^*\} = \{E, (12), E^*, (12)^*\}$



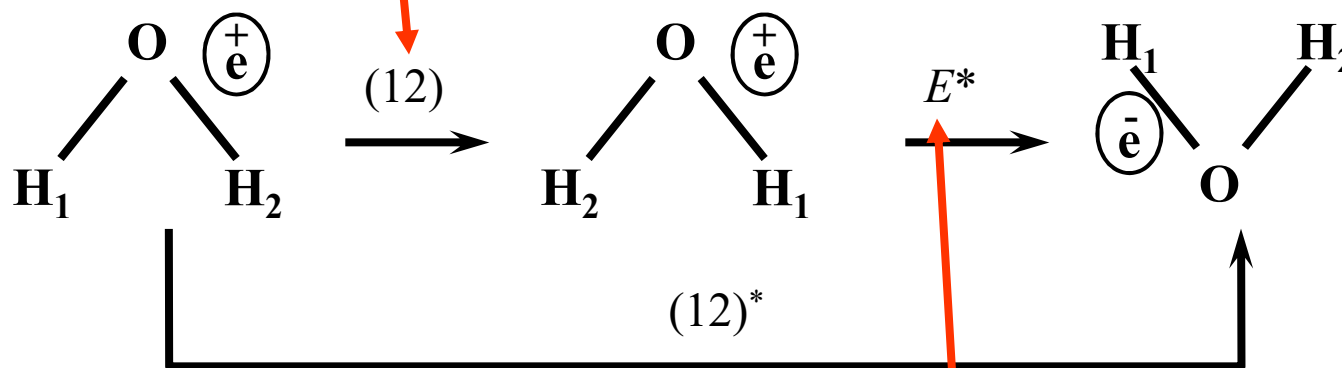
E^{} inverts coordinates of nuclei and electrons
at the centre of mass; it does not change spins.*

The CNPI Group for the Water Molecule

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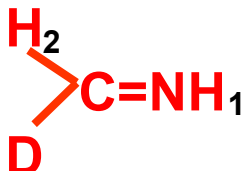
The Complete Nuclear Permutation Inversion (CNPI) group

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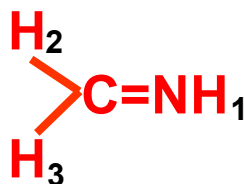
E^ Inverts coordinates of nuclei and electrons
at the centre of mass; it does not change spins.*

CNPI group of $\begin{array}{c} \text{H}_2 \\ \diagup \\ \text{C}=\text{NH}_1 \\ \diagdown \\ \text{D} \end{array}$ is the same as that of H_2O

CNPI group of  is the same as that of H₂O

$$G_{\text{CNPI}} = \{E, (12)\} \times \{E, E^*\} = \{E, (12), E^*, (12)^*\}$$

In this group, the number of operations (called the “order” h) = $2! \times 2 = 4$



CNPI group = $\{E, (123), (132), (12), (23), (31)\} \times \{E, E^*\}$,
 where (123) means 1 is replaced by 2, 2 is replaced by 3, and 3 is replaced by 1.

For this CNPI group, the order $h = 3! \times 2 = 12$.

**The benzene molecule C_6H_6 has six carbon nuclei and six protons.
Its CNPI group has order $6! \times 6! \times 2$**

**The toluene molecule $C_6H_5CH_3$ has seven carbon nuclei and eight protons.
Its CNPI group has order $7! \times 8! \times 2$**

The order of the CNPI group, and the operations in the CNPI group, depend only on the chemical formula

The order of various CNPI groups:

H_2	$2! \times 2 = 4,$	C_2H_6	$2! \times 6! \times 2 = 2880,$
H_2O	$2! \times 2 = 4,$	$\text{C}_2\text{H}_5\text{OH}$	$2! \times 6! \times 2 = 2880,$
BF_3	$3! \times 2 = 12,$	C_6H_6	$6! \times 6! \times 2 = 1036800,$
CH_3F	$3! \times 2 = 12,$	$\text{CH}_3\text{COCH}_2\text{CH}_2\text{OH}$	$4! \times 8! \times 2! \times 2 = 3870720,$
CH_4	$4! \times 2 = 48,$	$\text{C}_6\text{H}_5\text{CH}_3$	$7! \times 8! \times 2 \approx 4 \times 10^8.$
C_2H_4	$2! \times 4! \times 2 = 96,$	$(\text{C}_6\text{H}_6)(\text{H}_2\text{O})_2$	$6! \times 10! \times 2! \times 2 \approx 10^{10}.$
SF_6	$6! \times 2 = 1440,$	C_{60}	$60! \times 2 \approx 10^{82}.$

The character table of the CNPI group of the water molecule. This group is called $C_{2v}(M)$ and it is isomorphic with the Point Group C_{2v}

	E	(12)	E*	(12)*
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	-1	1
B_2	1	-1	1	-1

We use the irreducible representations (irreps) to label molecular energy levels. They are often called “symmetry labels.” To be able to do this it is necessary that the operations in the group commute with the Hamiltonian, as we now show.

If one wants to label energy levels using the irreps of the group of operations R , we must have $RH=HR$ for all R . The effect of R is to change the coordinates.

For the water molecule (Ψ nondegenerate) :

$$H\Psi = E\Psi$$

Act with the symmetry operation R on each side

$$RH\Psi = RE\Psi$$

$RH = HR$, and E is a number that must commute with R , so we have:

$$H(R\Psi) = E(R\Psi)$$

Thus $R\Psi$ has the same eigenvalue as Ψ . Since Ψ is nondegenerate we can only have $R\Psi = c\Psi$ where c is a constant.

↑
For nondegenerate states this is the effect of a symmetry operation on an eigenfunction:

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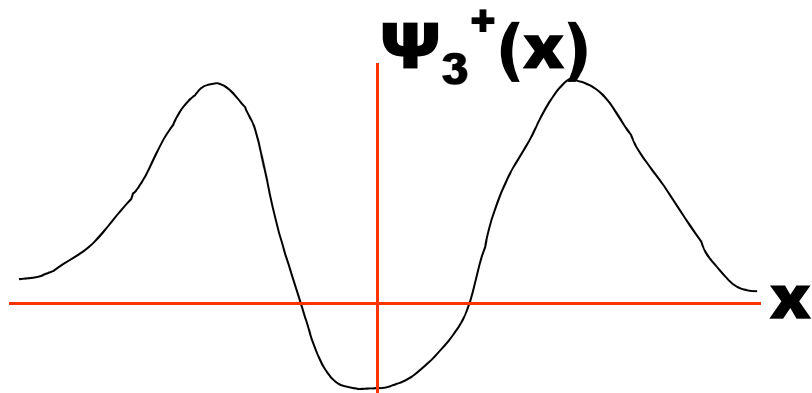
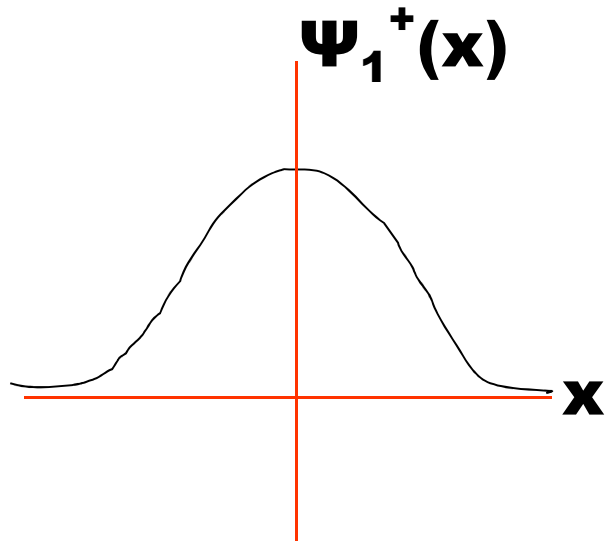
Thus $R\Psi = c\Psi$ since E is nondegenerate.

For water we have $R^2 = E$, so $c^2 = 1$ and thus $c = \pm 1$

$$E\psi = \psi, \quad (12)\psi = \pm\psi, \quad E^*\psi = \pm\psi, \quad (12)^*\psi = \pm\psi$$

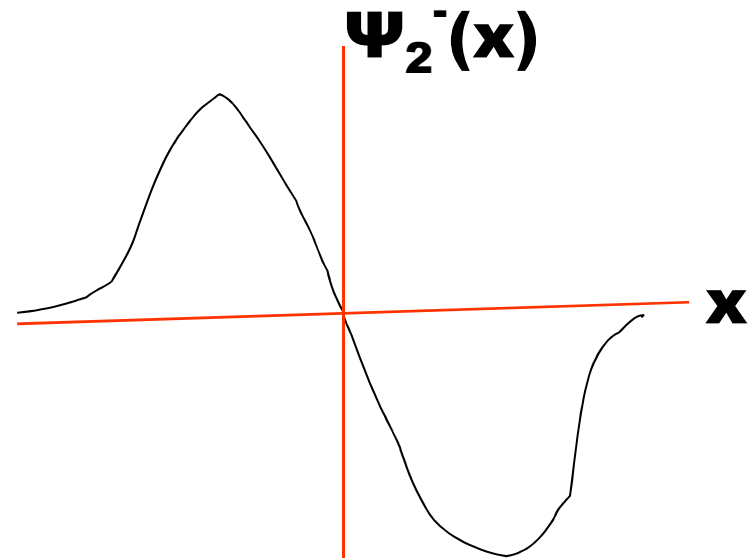
Wavefunctions have symmetry. Effect of E^* gives the “parity.”

+ Parity



$$\Psi^+(-x) = \Psi^+(x)$$

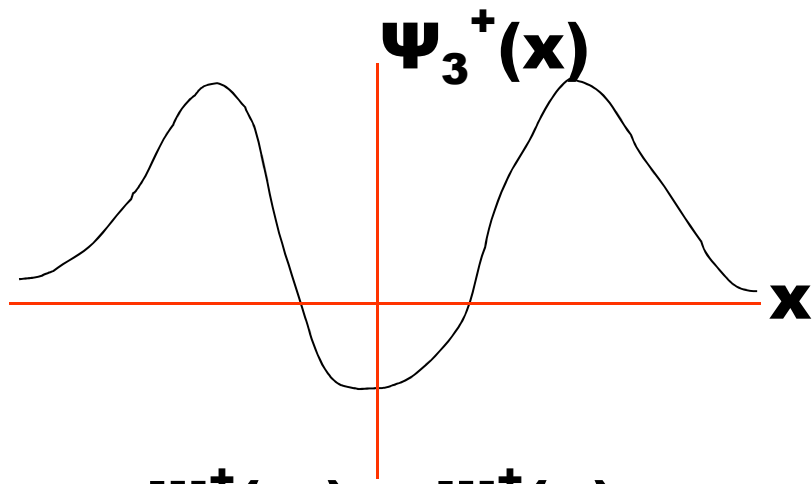
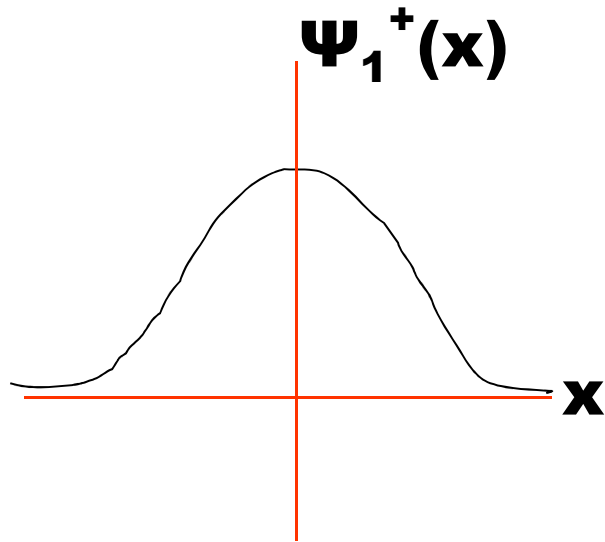
- Parity



$$\Psi^-(-x) = -\Psi^-(x)$$

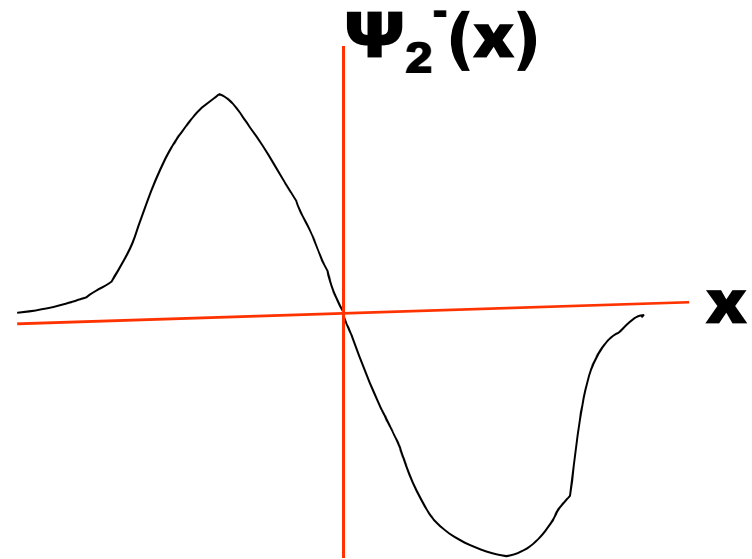
Eigenfunctions of H
must satisfy
 $E^*\Psi = \pm\Psi$

+ Parity



$$\Psi^+(-x) = \Psi^+(x)$$

- Parity



$$\Psi^-(-x) = -\Psi^-(x)$$

Eigenfunctions of H
must satisfy

$$E^*\Psi = \pm\Psi \text{ and}$$

$$(12)\Psi = \pm\Psi$$

Four symmetry types of wavefunction for H_2O depending on whether the wavefunction is multiplied by +1 or -1 by (12) or E^*

(12)	E^*
1	1
1	-1
-1	-1
-1	1

The effect of $(12)^*$ is the product of the effects of (12) and E^*

(12)	E^*	$(12)^*$
1	1	1
1	-1	-1
-1	-1	1
-1	1	-1

The effect of the identity operation has to be +1

E	(12)	E*	(12)*
1	1	1	1
1	1	-1	-1
1	-1	-1	1
1	-1	1	-1

Thus we can use the irreps (or symmetry labels) of the CNPI group to label the molecular energy levels of the water molecule.

	E	(12)	E*	(12)*
A ₁	1	1	1	1
A ₂	1	1	-1	-1
B ₁	1	-1	-1	1
B ₂	1	-1	1	-1

It can be shown that for any molecule, its energy levels can be labeled using the irreps of its CNPI group.

These labels are used to determine if certain integrals vanish without the need of numerically calculating the integrals. To do this we make use of the “Vanishing Integral Theorem.” This is one of the major uses of symmetry in the understanding of molecules.

[See Chapter 6 of BJ2]

The Vanishing Integral Theorem involves the integral of an operator “Op” between two states n and m and it states for the water molecule that:

$$\int \phi_n^* \text{Op} \phi_m d\mathbf{q} = 0 \text{ if } \phi_n^* \text{Op} \phi_m \text{ is not of symmetry } A_1$$

We can use the symmetry labels to determine whether an off-diagonal matrix element of the Hamiltonian H is zero, i.e., whether two energy levels can perturb each other. They can also be used to determine whether an off-diagonal matrix element of the dipole moment operator μ_A is zero (where A is a space fixed direction), i.e., whether a spectroscopic transition is forbidden.

The dipole moment operator μ_A

The dipole moment of a molecule in the space fixed direction A is given by

$$\mu_A = \sum_i A_i e_i$$

where i runs over all the nuclei and all the electrons in the molecule, A_i is the A-coordinate of particle i and e_i is its charge (-e for each electron).

μ_A is unaffected by any permutation of identical nuclei since such nuclei have the same charge, and it is reversed in sign by the inversion E^* since all the A_i are changed in sign by E^* . Thus, μ_A has CNPI symmetry A_2 for the water molecule.

If $\int \varphi_n^* \mu_A \varphi_m dq = 0$ (integration over all coords q) then the transition $\varphi_n \rightarrow \varphi_m$ is forbidden.

The Symmetry Labels of the CNPI Group of H₂O

	E	(12)	E*	(12)*	
A ₁	1	1	1	1	Symmetry of H
A ₂	1	1	-1	-1	
B ₁	1	-1	-1	1	Symmetry of μ_A
B ₂	1	-1	1	-1	

Using symmetry labels and the vanishing integral theorem we deduce that:

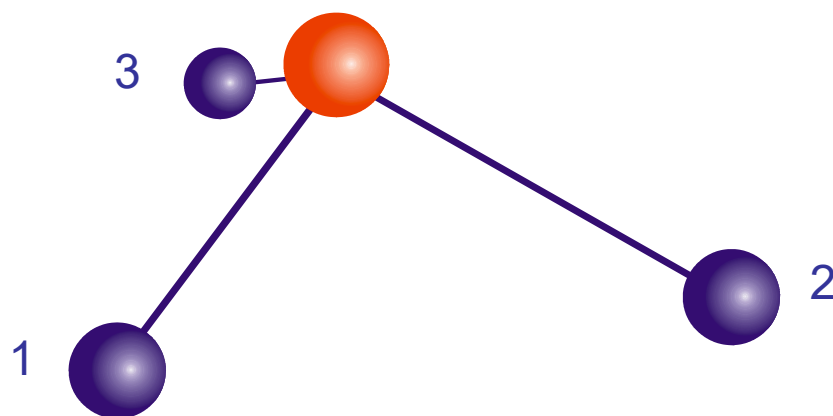
$\int \Psi_a^* H \Psi_b d\tau = 0$ if symmetry of $\Psi_a^* H \Psi_b$ is not A₁,
that is, if the symmetry of Ψ_a is not the same as Ψ_b

$\int \Psi_a^* \mu_A \Psi_b d\tau = 0$ if symmetry of $\Psi_a^* \mu_A \Psi_b$ is not A₁,
that is, if the symmetry of the product $\Psi_a \Psi_b$ is not A₂

For any molecule its full Hamiltonian commutes with the operations in its CNPI group. The irreps of the CNPI group can thus be used to label the molecular energy levels and to determine which integrals of the Hamiltonian vanish and which electric dipole transitions are forbidden.

BUT the CNPI group has a shortcoming

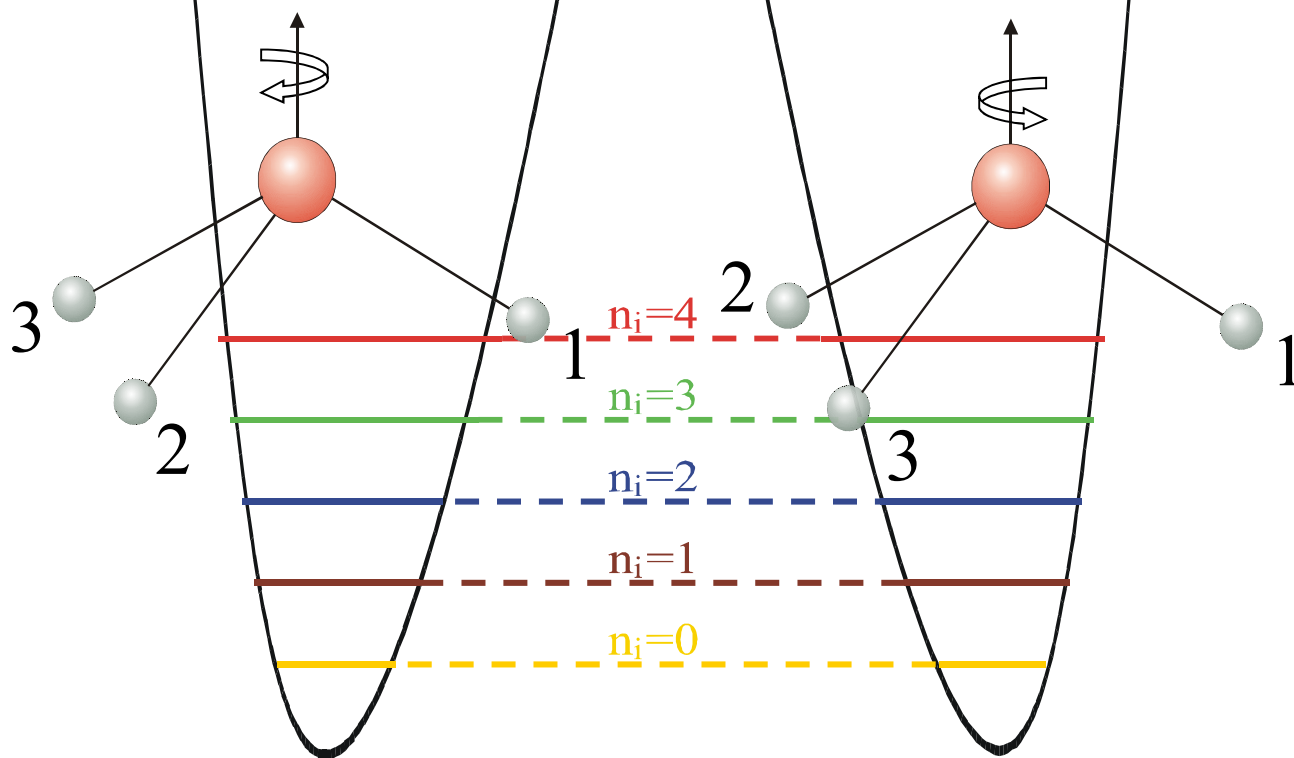
It often gives superfluous symmetry labels when a molecule has more than one “Version.”



There are two ***VERSIONS***
of the equilibrium structure

PH₃

**TWO VERSIONS: Distinguished
by numbering the identical nuclei**



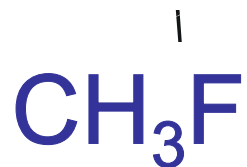
Very
high
potential
barrier

~12000 cm⁻¹

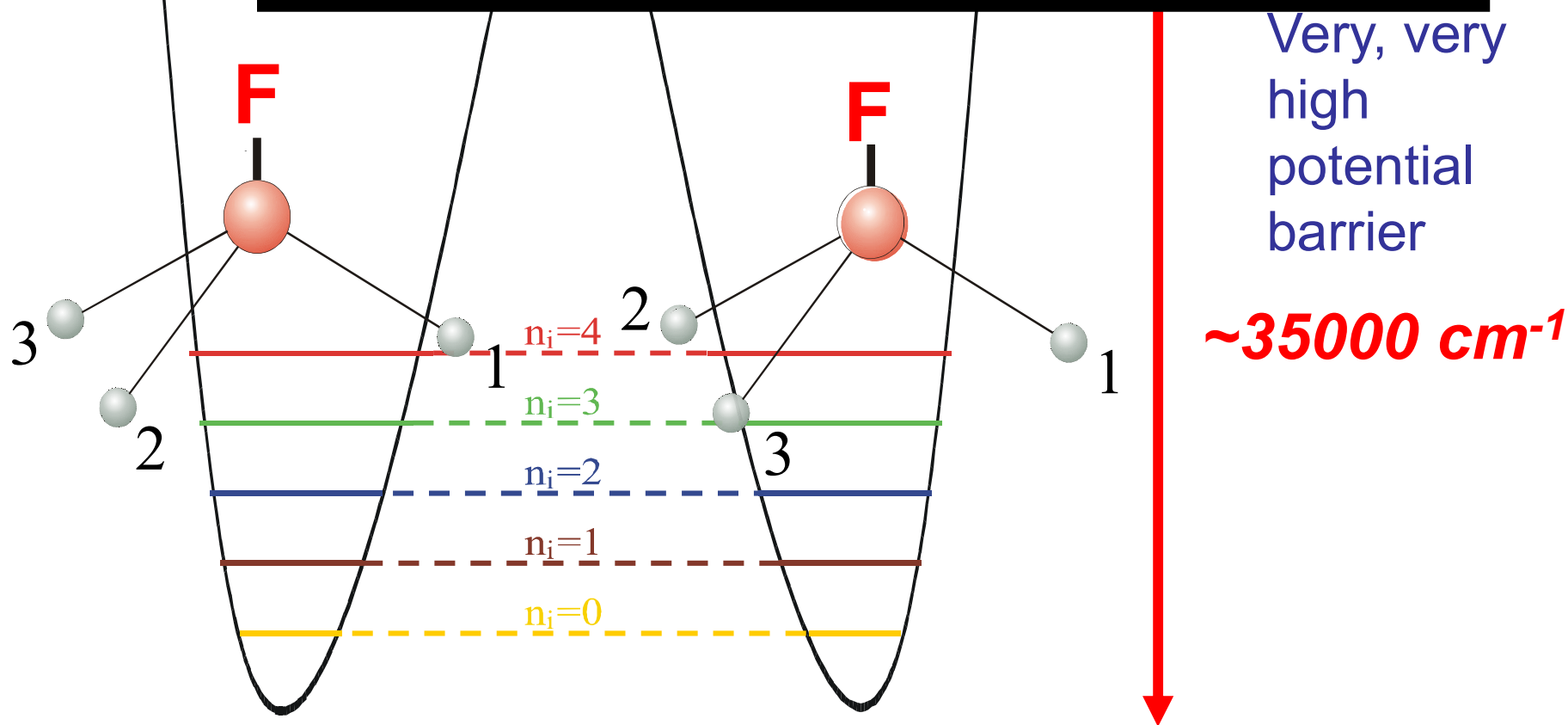
Tunneling splitting negligible

It is rather obvious that PH_3 , like NH_3 , has two versions. It is perhaps less obvious that CH_3F has two versions.

This becomes clear when one numbers the identical nuclei. The two versions are shown in the next image and they can be interconverted through the planar configuration obtained by rotating one CH_2 moiety about its C_2 axis relative to the remaining HFC moiety.



**TWO VERSIONS: Distinguished
by numbering the identical nuclei**

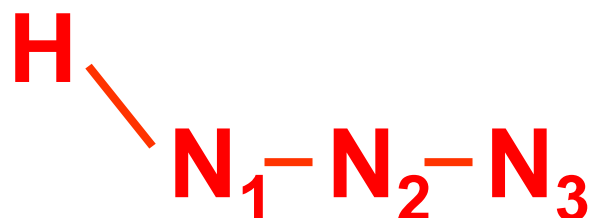


Tunneling splitting even more negligible

The number of versions of the minimum is given by:
(order of CNPI group)/(order of point group).

[See Bone et al., Mol. Phys., 72, 33 (1991)]

HN₃ has 12/2 = 6 versions of its equilibrium structure



1-3-2

2-1-3

2-3-1

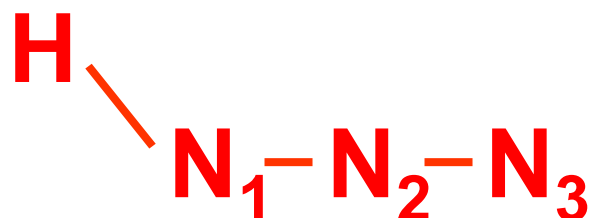
3-1-2

3-2-1

The number of versions of the minimum is given by:
(order of CNPI group)/(order of point group).

[See Bone et al., Mol. Phys., 72, 33 (1991)]

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1—3—2

2—1—3

2—3—1

3—1—2

3—2—1

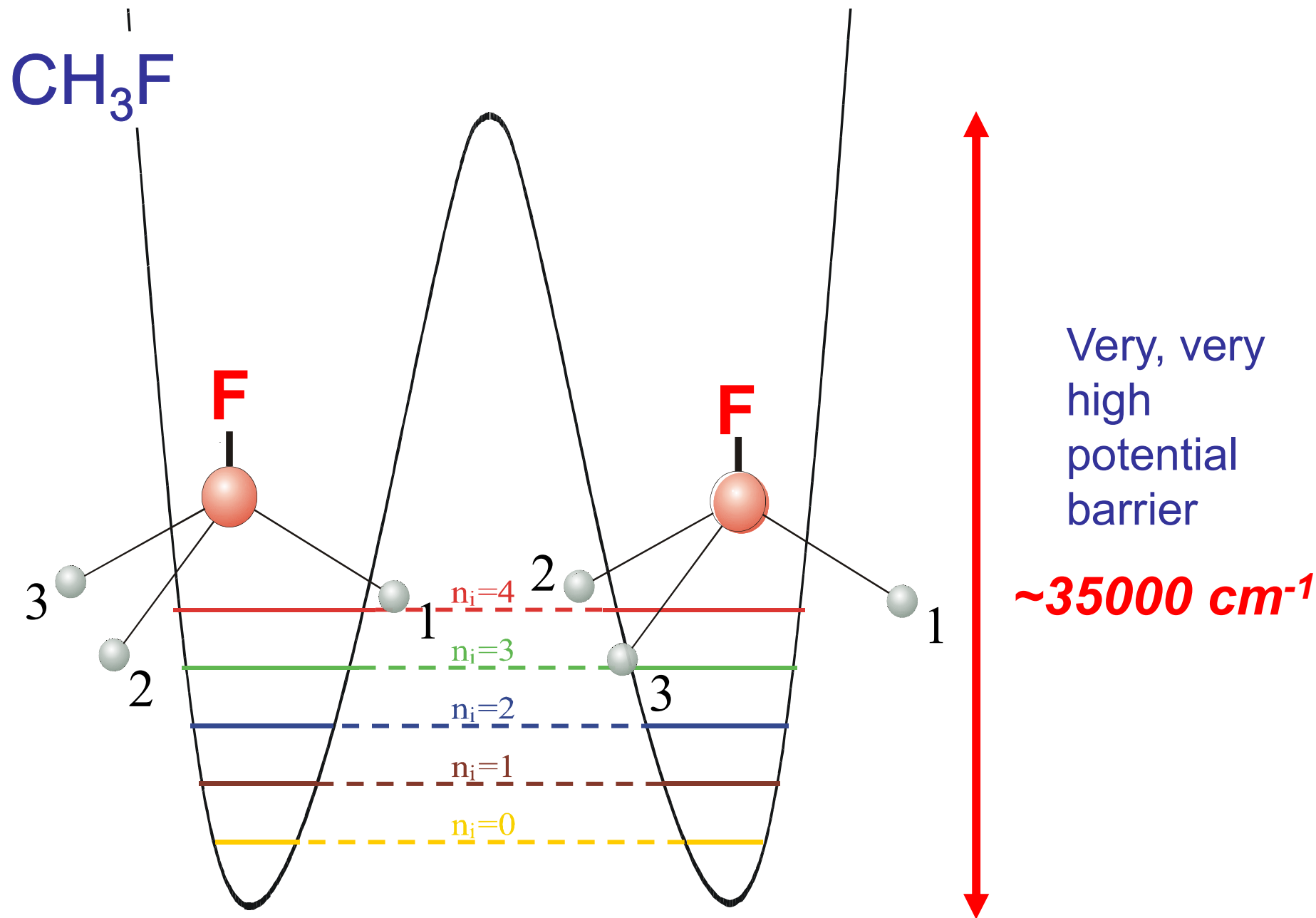
**Benzene, C₆H₆ has
(6!x6!x2)/24**

= 1036800/24

= 43200 versions

What happens when we use the CNPI group to symmetry label the energy levels of a molecule that has more than one version and no observed tunneling?

Let us consider the rotation-vibration energy levels of the CH₃F molecule in its ground electronic state as an example.



The tunneling splittings are exceedingly miniscule and have not been seen experimentally.

Character Table of CNPI group of CH₃F

$$G_{\text{CNPI}} = \{E, (12), (13), (23), (123), (132), E^*, (12)^*, (13)^*, (23)^*, (123)^*, (132)^*\}$$

$D_{3h}(\mathbf{M})$

**E (123) (12) E^* $(123)^*$ $(12)^*$
 (132) (31) $(132)^*$ $(31)^*$
 (23) $(23)^*$**

6 irred. reps

A_1' :	1	1	1	1	1	1
A_1'' :	1	1	1	-1	-1	-1
A_2' :	1	1	-1	1	1	-1
A_2'' :	1	1	-1	-1	-1	1
E' :	2	-1	0	2	-1	0
E'' :	2	-1	0	-2	1	0

The CNPI group for CH₃F has six irreps and therefore there can be six different CNPI group symmetries for the rotation-vibration eigenfunctions of ground state CH₃F.

HOWEVER, if one did a numerical calculation of the rotation-vibration eigenfunctions and eigenvalues of CH₃F using a very high quality ab initio potential energy surface encompassing the entire nuclear coordinate space (i.e., including both minima) and then determined the CNPI group symmetries of the eigenfunctions, one would find that the energy levels “paired” up into three possibilities:

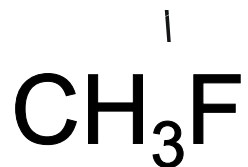
$$\underline{A_1' + A_2''} \quad \underline{A_1'' + A_2'} \quad \text{or} \quad \underline{E' + E''}$$

Tunneling between the minima would split each of these degeneracies, but experimentally such splittings are not resolved. Each energy level is labelled with the sum of two irreps of the CNPI group because there are two versions and no observed tunneling splittings.

**For C_6H_6 :Number of versions = $6! \times 6! \times 2 = 43200$,
and using the CNPI group each energy level would
get as symmetry label the sum of 43200 irreps.**

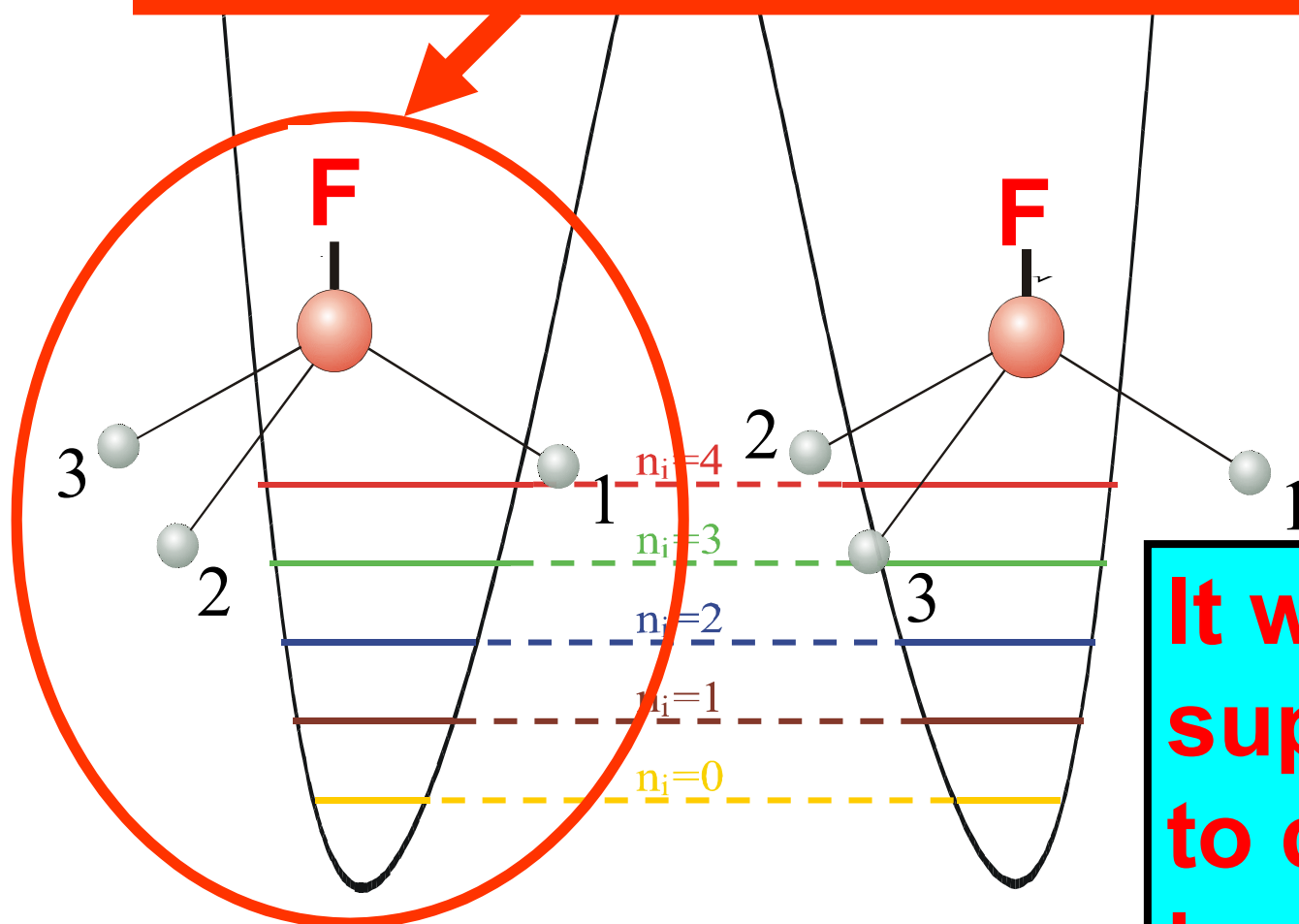
**For understanding the spectrum
when there is no observed tunneling
this is a “superfluous” degeneracy**

It is possible to set up a sub-group of the CNPI Group, called the Molecular Symmetry Group, with symmetry labels that do not give rise to superfluous degeneracies.



Ab initio calc with neglect of tunneling

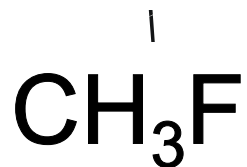
Useful ab initio calculation in here



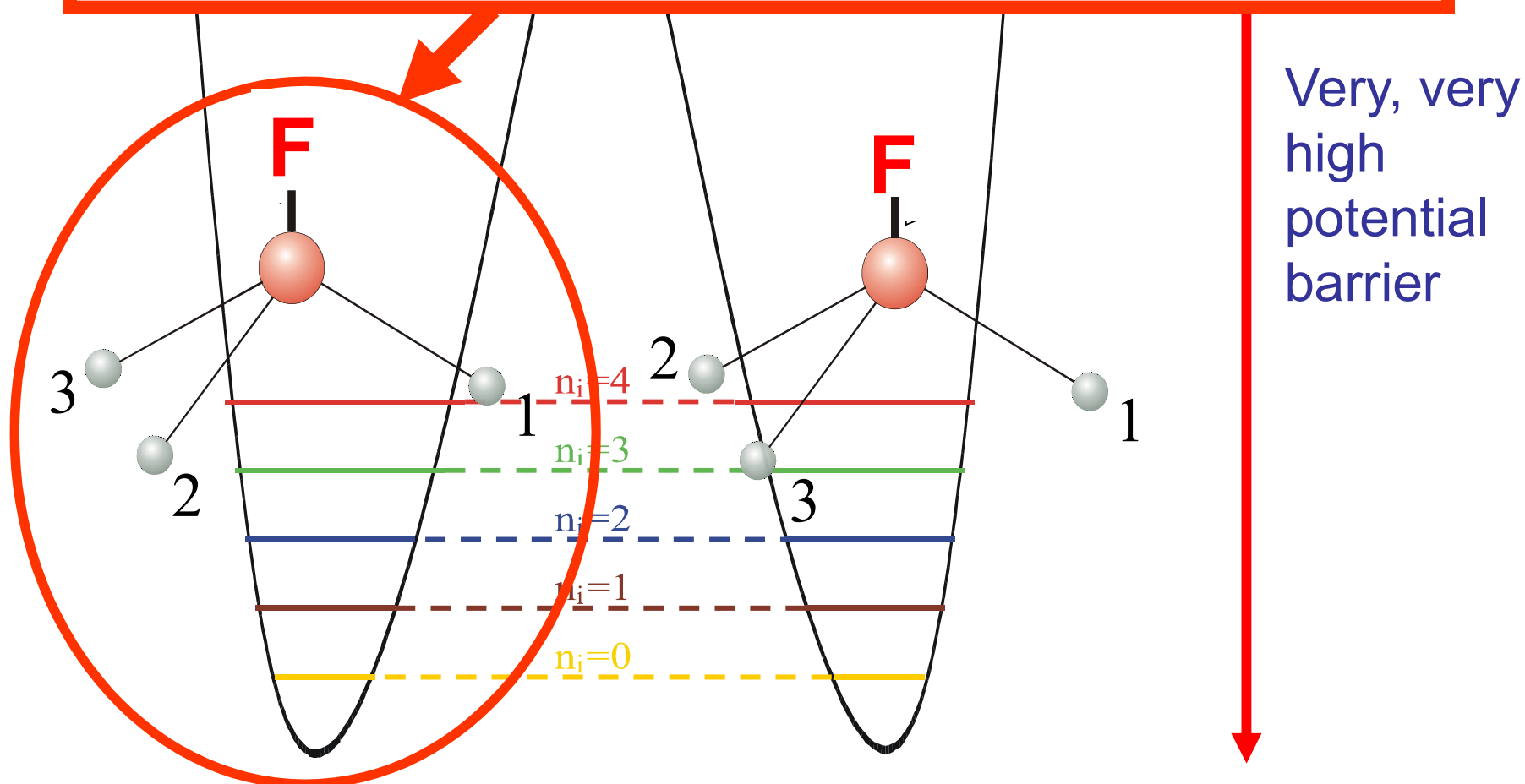
Very, very
high
potential
barrier

It would be
superfluous
to calc points
in other min

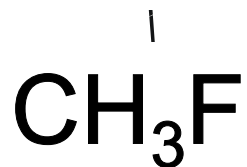
No observed tunneling through barrier



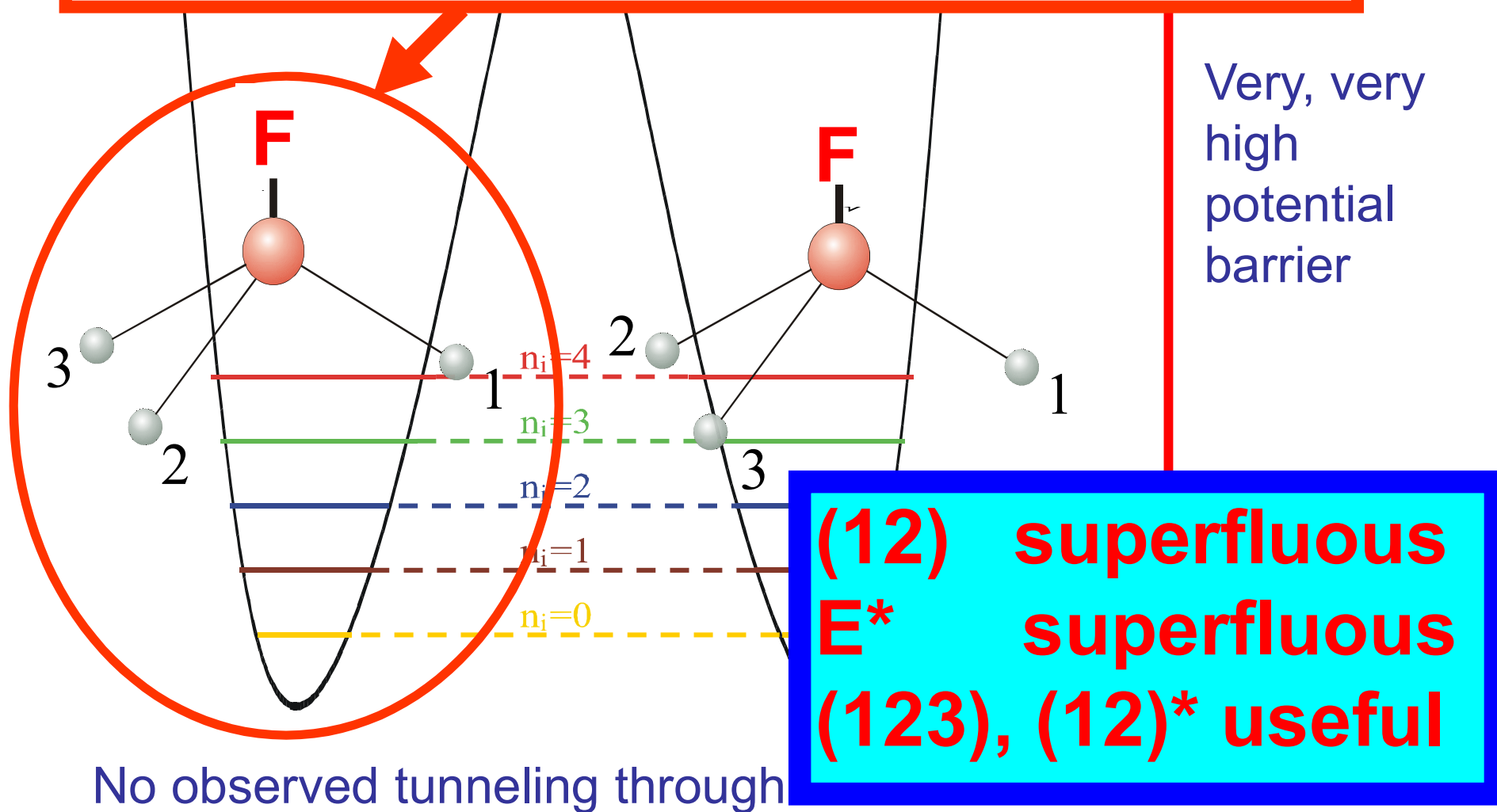
Only P and P* operations from in here are useful



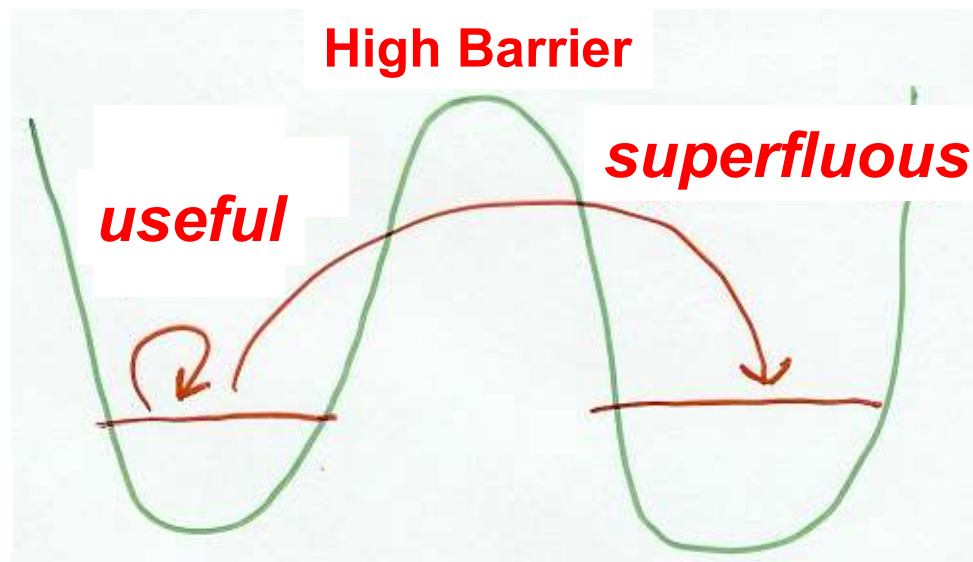
No observed tunneling through barrier



Only P and P* operations from in here are useful



If no tunneling
splittings are
resolved.



superfluous.

For CH_3F :

$$G_{\text{CNPI}} = \{E, (12), (13), (23), (123), (132), E^*, (12)^*, (13)^*, (23)^*, (123)^*, (132)^*\}$$

The **useful** operations constitute the Molecular Symmetry Group

$$G_{\text{MS}} = \{E, (123), (132), (12)^*, (13)^*, (23)^*\}$$

The superfluous operations in the CNPI group are those operations that connect versions of the molecule between which there is an insuperable potential energy barrier and hence no observable tunneling splitting.

It is important to realize that the determination that an operation is superfluous depends on the size of the tunneling splitting relative to the resolving power of ones apparatus

Superfluous operations of the CNPI group are called “unfeasible” and the useful operations are called “feasible.”

Character Table of CNPI group of CH₃F

$$G_{\text{CNPI}} = \{E, (12), (13), (23), (123), (132), E^*, (12)^*, (13)^*, (23)^*, (123)^*, (132)^*\}$$

$D_{3h}(\mathbf{M})$	E	(123) (132)	(12) (31) (23)	E^*	$(123)^*$ $(132)^*$	$(12)^*$ $(31)^*$ $(23)^*$
A_1' :	1	1	1	1	1	1
A_1'' :	1	1	1	-1	-1	-1
A_2' :	1	1	-1	1	1	-1
A_2'' :	1	1	-1	-1	-1	1
E' :	2	-1	0	2	-1	0
E'' :	2	-1	0	-2	1	0

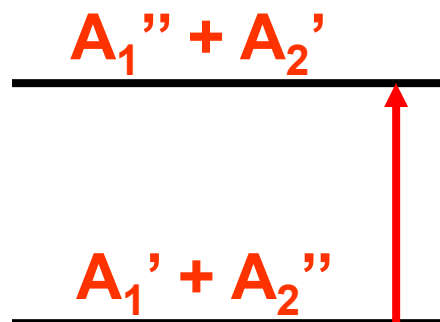
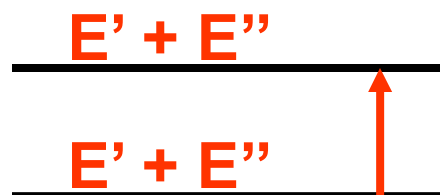
H
 A_1'

$\mu_{A_1''}$
 A_1''

Character table of the MS group of CH₃F

$C_{3v}(M)$	E	(123)	$(12)^*$	
		(132)	$(13)^*$	
			$(23)^*$	
A_1	1	1	1	$\swarrow H \quad A_1$
A_2	1	1	-1	$\leftarrow \mu_A \quad A_2$
E	2	-1	0	

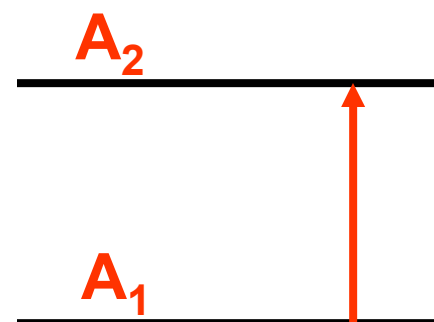
CH₃F: CNPIG



$D_{3h}(M)$

μ_A is A_1''

MSG



$C_{3v}(M)$

μ_A is A_2

Can use either to determine if an integral vanishes.
but clearly it is easier to use the **MSG**. This would
particularly be the case for benzene with 43200 versions

superfluous

Unfeasible elements of the CNPI group
interconvert versions that are separated
by an insuperable energy barrier

useful

The subgroup of **feasible** elements forms a group called

**THE MOLECULAR SYMMETRY GROUP
(MS GROUP)**

Note that for the NH_3 molecule, which has two versions like CH_3F but for which the tunneling splittings are resolved rather easily, all elements of the CNPI group are feasible and for NH_3 the Molecular Symmetry Group is the CNPI group $D_{3h}(\text{M})$.

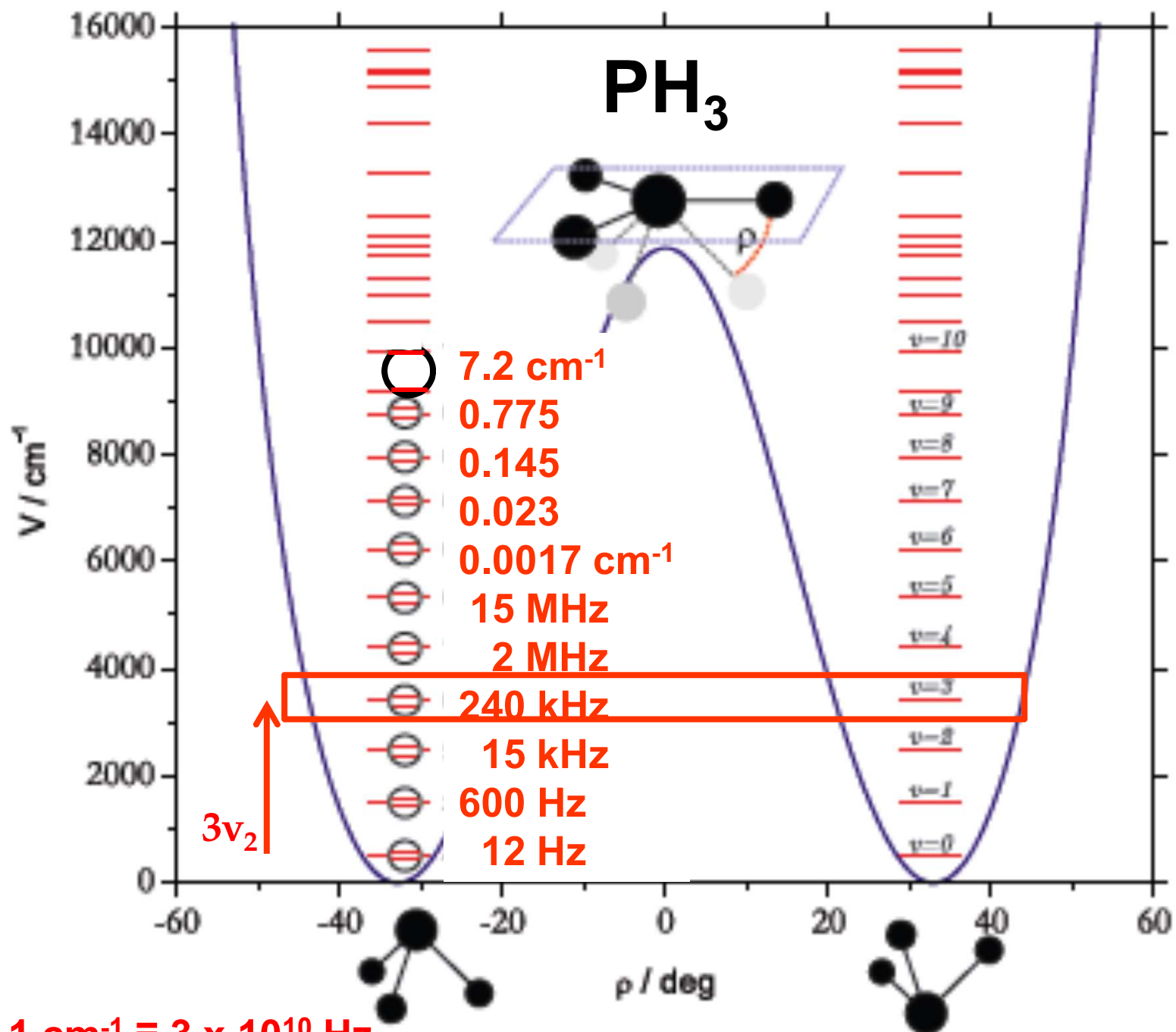
The PH_3 molecule is an interesting intermediate example for which a careful ab initio calculation of the rotation-vibration energy levels has been made.

THE PH₃ MOLECULE

Barrier height = 12300 cm⁻¹

**Schwerdtfeger, Laakkonen and Pekka Pyykkö,
J. Chem. Phys., 96, 6807 (1992)**

**Recent theoretical calculations
using the full 6-d PE surface:
Sousa-Silva, Tennyson and Yurchenko
JCP 145, 091102 (2016)
Yield theoretical tunneling splittings**



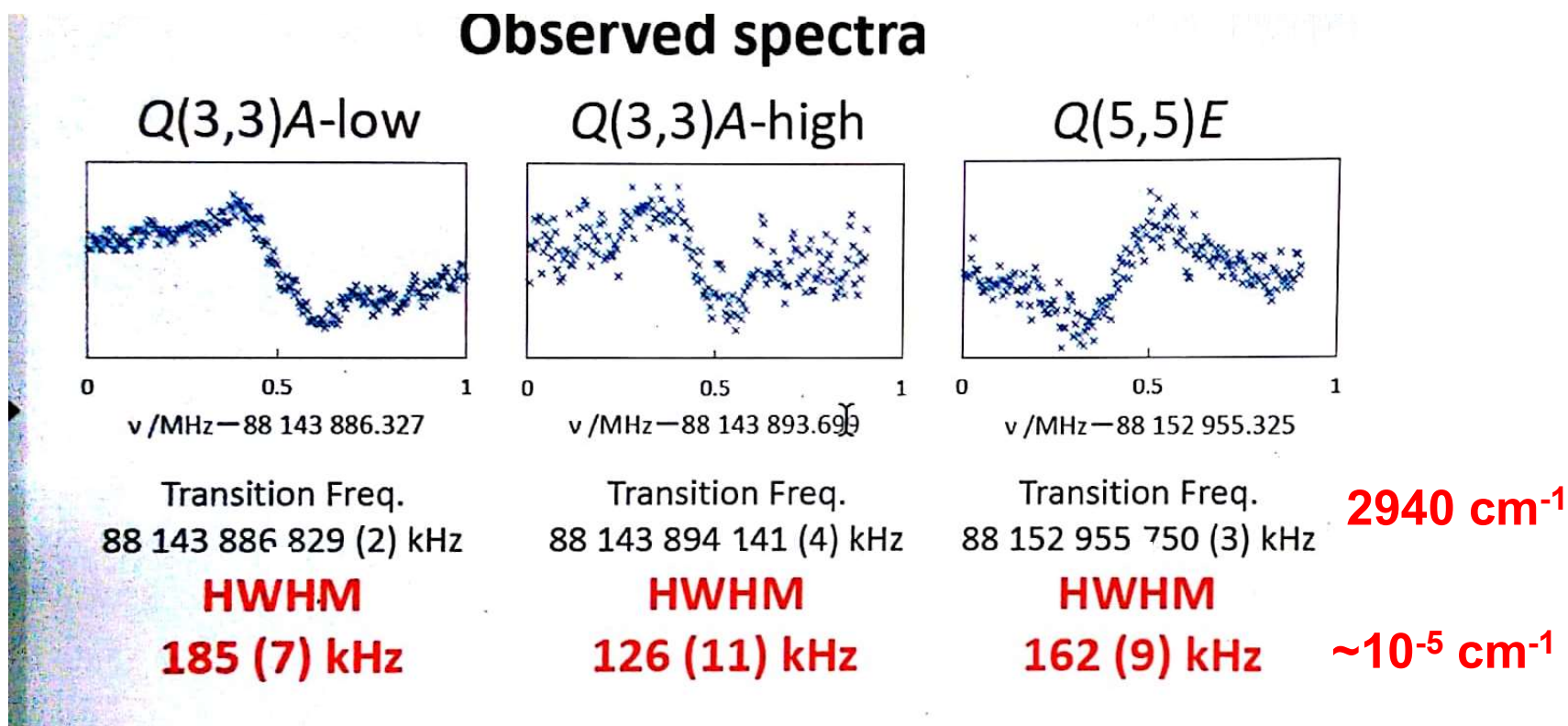
Comb-referenced sub-Doppler resolution spectroscopy of the $3\nu_2$ band of PH_3

Shoko Okuda and Hiroyuki Sasada

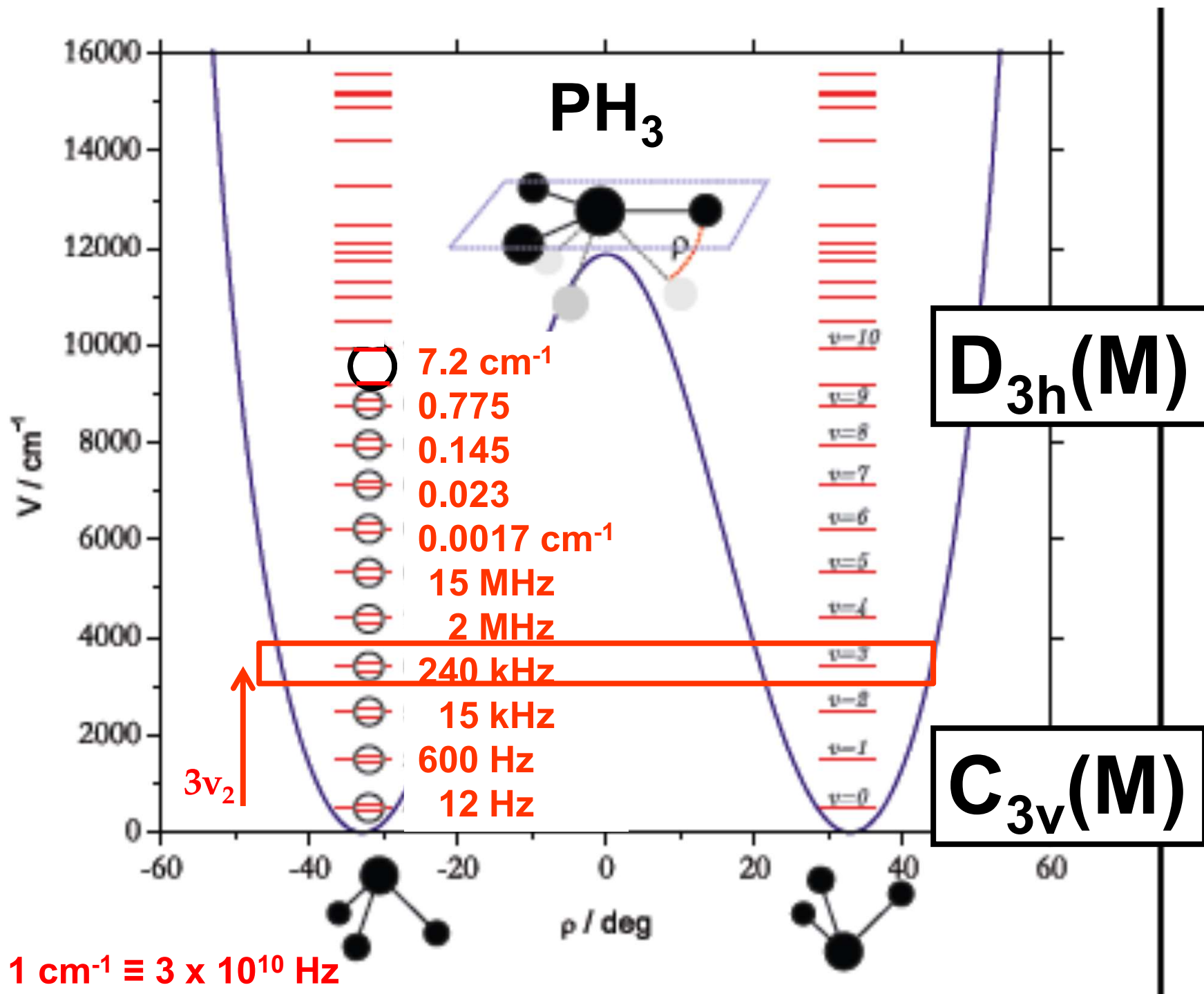
Keio University, Yokohama, Japan

(HRMS meeting Helsinki, August 2017).

No tunneling splittings resolved



Thus for symmetry labelling the energy levels up to the $3v_2$ level, one should use the $C_{3v}(M)$ group as the MSG but above that (i.e., for hot PH_3) one should use the $D_{3h}(M)$ group as the MSG. Also, if the resolution for the $3v_2$ band were improved, and the tunneling splitting resolved, it would be necessary to use the $D_{3h}(M)$ group to label the energy levels there.



WE NOW RELATE THE MSG AND THE POINT GROUP

Use equi.
molecular
geometry

→ **Point Group**

Use all P and
P* operations



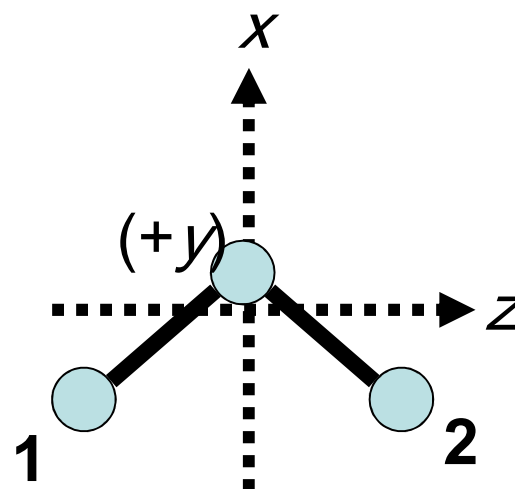
MS Group

← **CNPI Group**
*Delete superfluous
symmetry operations*

The groups have been derived by two quite different routes

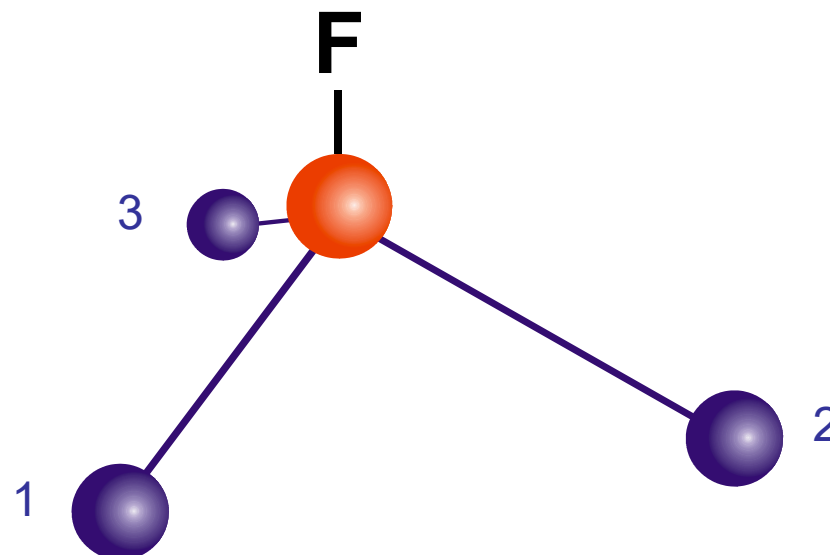
Point Group and MSG of H₂O

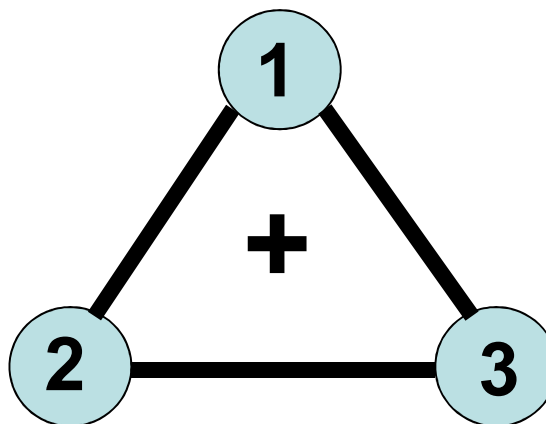
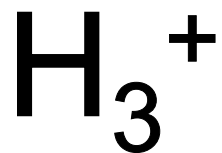
C_{2v}	E	C_{2x}	σ_{xz}	σ_{xy}
$C_{2v}(M)$	E	(12)	E^*	$(12)^*$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	-1	1
B_2	1	-1	1	-1



Point Group and MSG of CH₃F

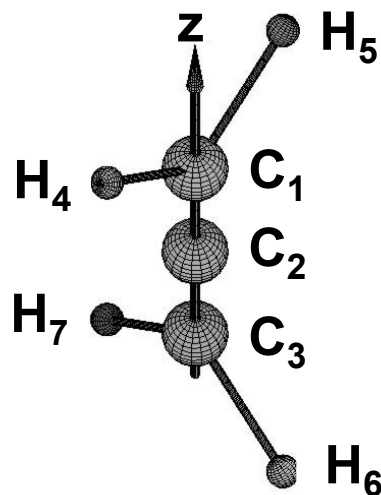
C_{3v}	E	C_3 C_3^2	σ_1 σ_2 σ_3
$C_{3v}(M)$	E	(123) (132)	$(12)^*$ $(13)^*$ $(23)^*$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0





Point Group D_{3h}	E	$2C_3$	$3C_2'$	σ_h	$3S_3$	$3\sigma_v$
Molecular Symmetry Group $D_{3h}(\text{M})$	E	(123) (132)	(12) (31) (23)	E^*	$(123)^*$ $(132)^*$	$(12)^*$ $(31)^*$ $(23)^*$
A_1' :	1	1	1	1	1	1
A_1'' :	1	1	1	-1	-1	-1
A_2' :	1	1	-1	1	1	-1
A_2'' :	1	1	-1	-1	-1	1
E' :	2	-1	0	2	-1	0
E'' :	2	-1	0	-2	1	0

The allene molecule C_3H_4



$$h(\text{CNPI}) = 3! \times 4! \times 2 = 288$$

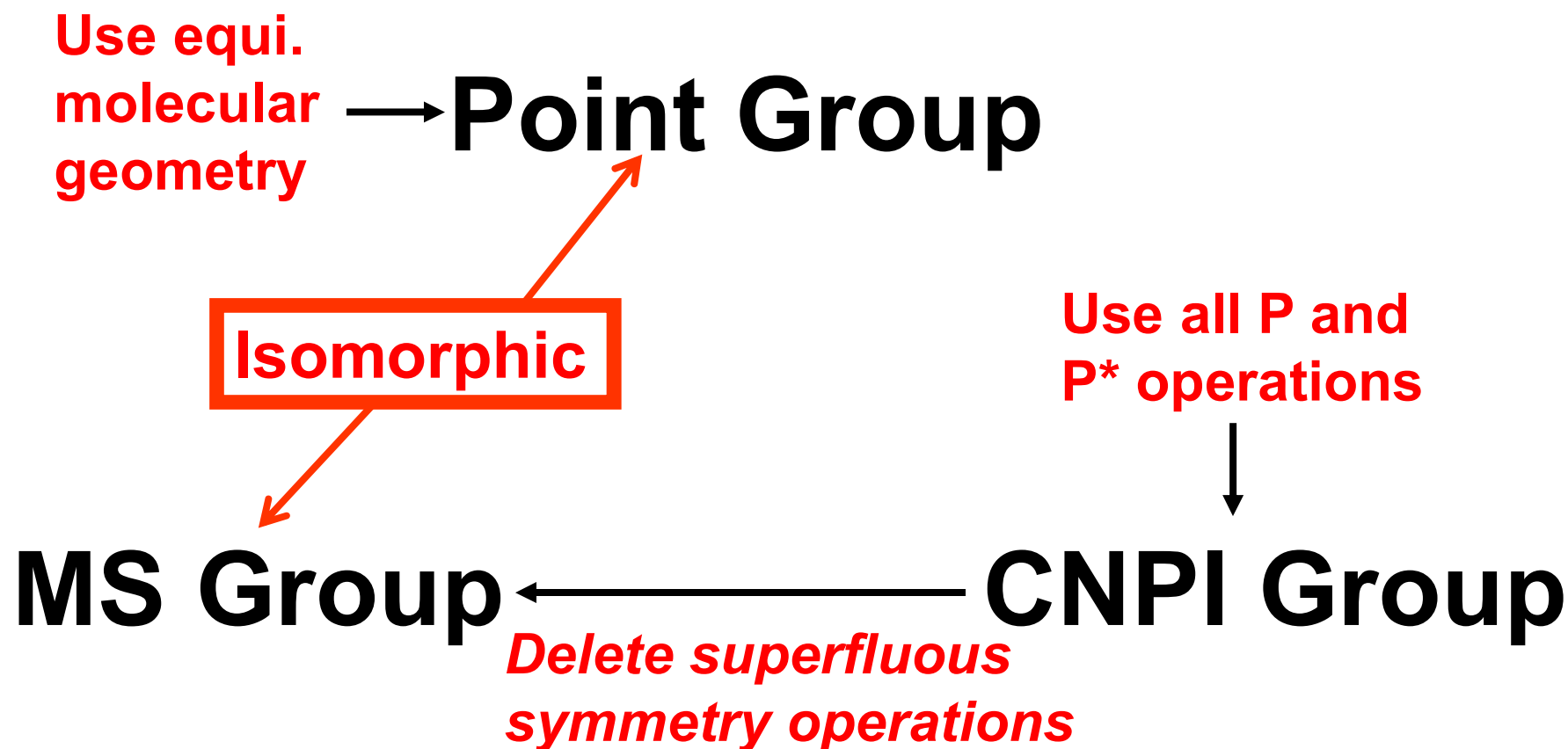
Point Group is D_{2d} which has 8 operations as does the **MSG**.

Isomorphism of the **MSG** and Point Group:

$$\begin{array}{cccccc}
 E & C_2(z) & C_2' & C_2' & \sigma_d & \sigma_d \\
 \{E, (45)(67), (13)(46)(57), (13)(47)(56), (45)^*, (67)^*, \\
 S_4 & S_4 \\
 (4657)(13)^*, (4756)(13)^*\}
 \end{array}$$

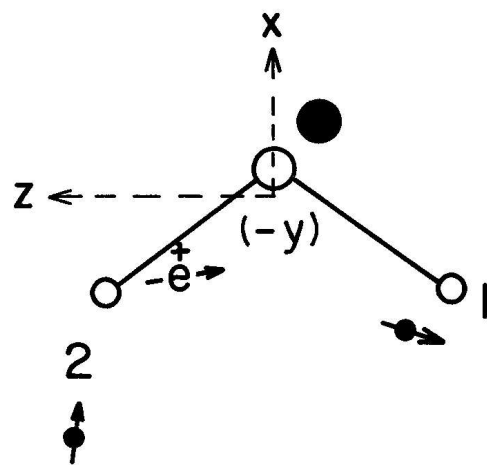
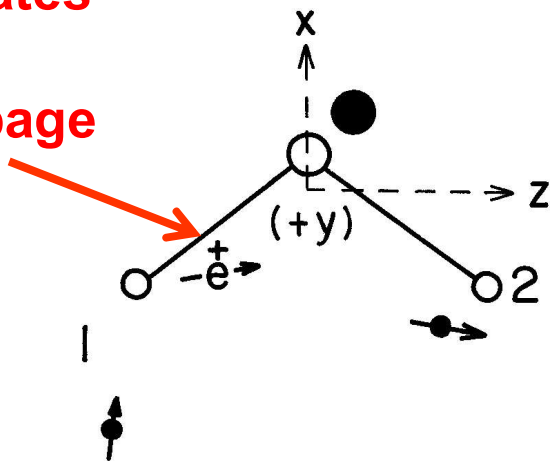
They are isomorphic and have the same character tables

For non-tunneling non-linear mols



This isomorphism is no accident as we show using the water molecule

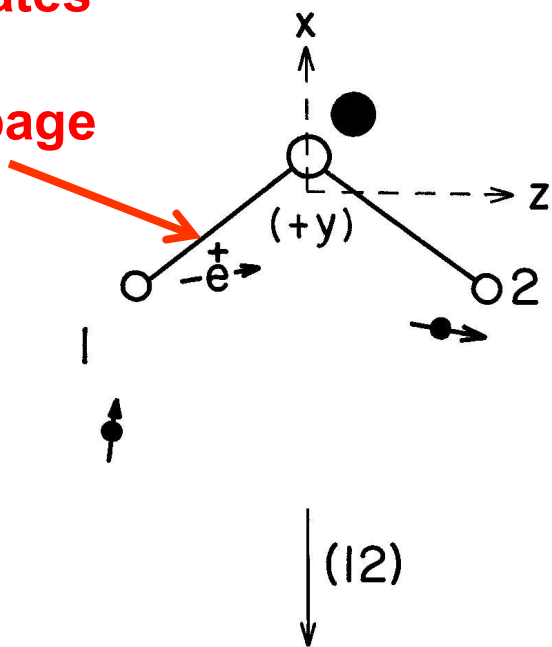
**'+' indicates
electron
above page**



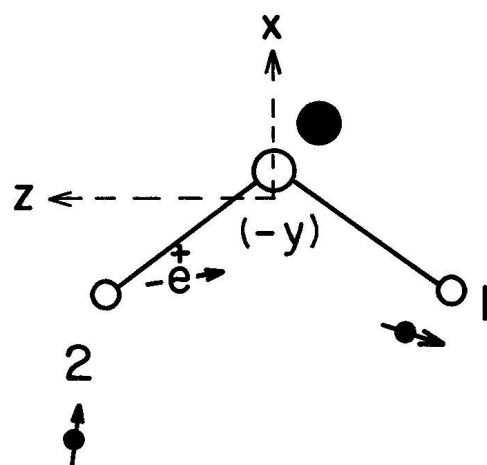
**Black are instantaneous
positions in space. White
are equilibrium positions.
N.B. $+z$ is $1 \rightarrow 2$. Arrows on
particles indicate spin**

**Then do (12).
Note that axes have moved.
rotational coordinates and
xyz electronic coordinates are
transformed by MS group.**

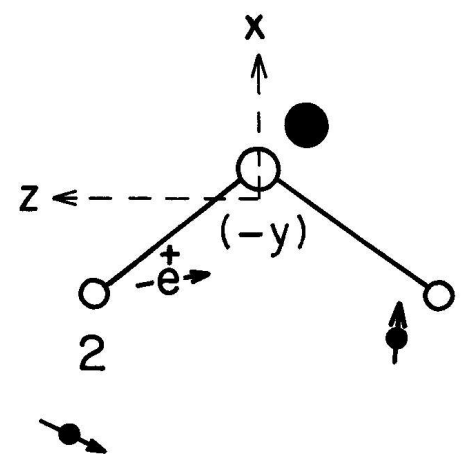
**'+' indicates
electron
above page**



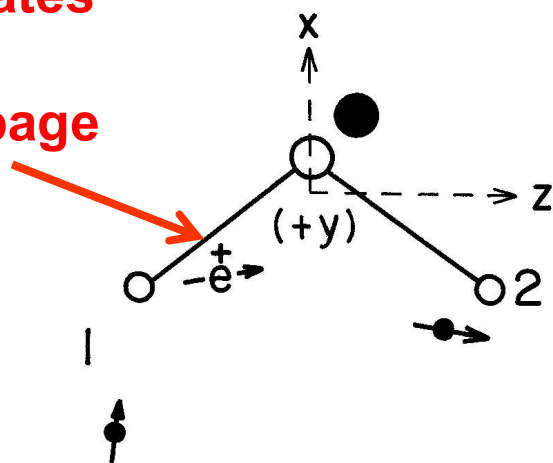
**Undo the permutation
of the nuclear spins**



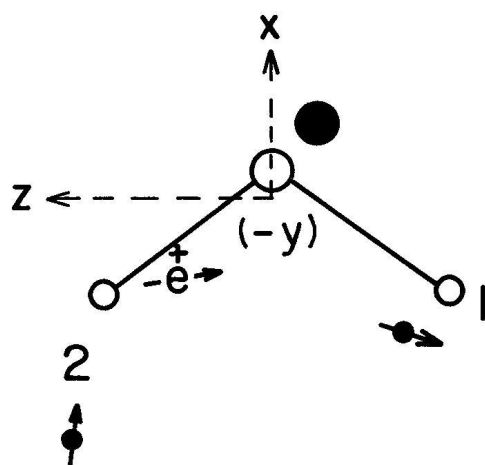
p_{12}



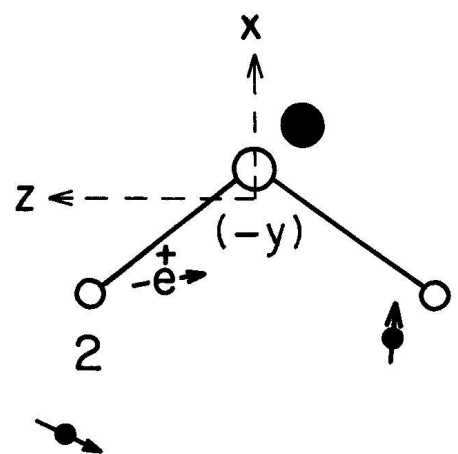
'+' indicates
electron
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(12)



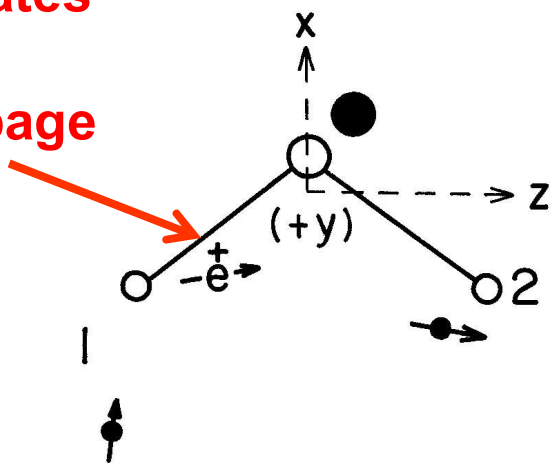
p_{12}



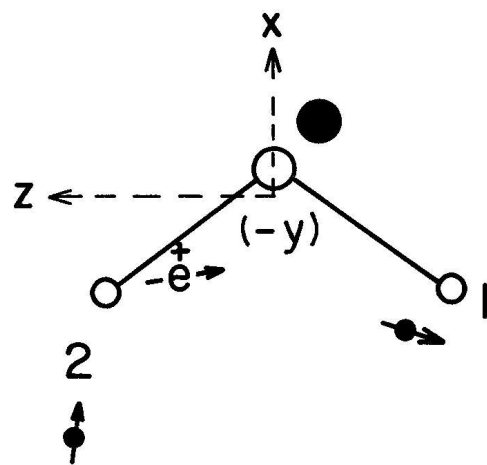
Undo the permutation
of the nuclear spins

We next undo the
rotation of the axes
by a bodily rotation
of the molecule
about x-axis thru π

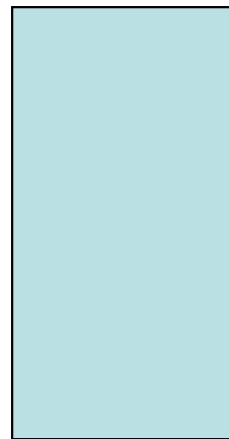
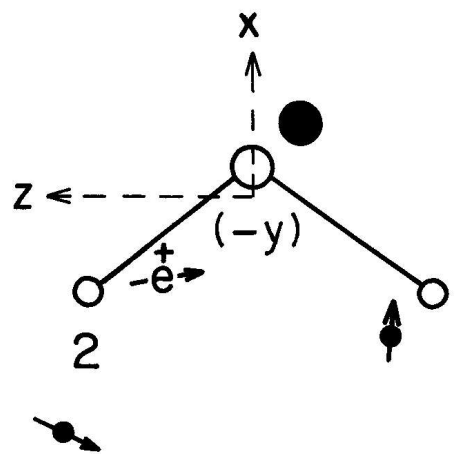
**'+' indicates
electron
above page**



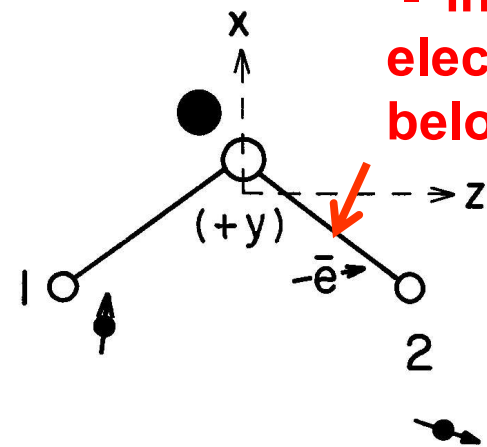
(12)



p_{12}

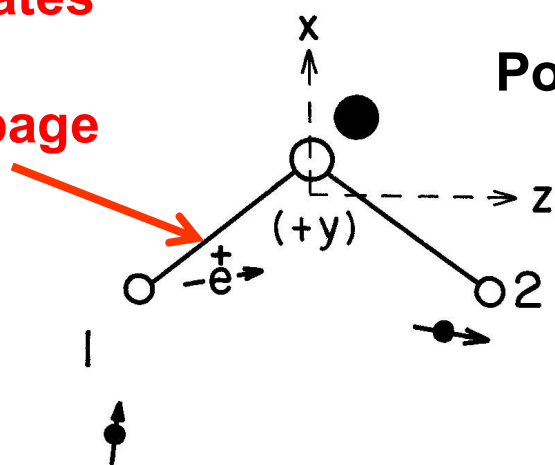


**'-' indicates
electron
below page**



R_x^{π}

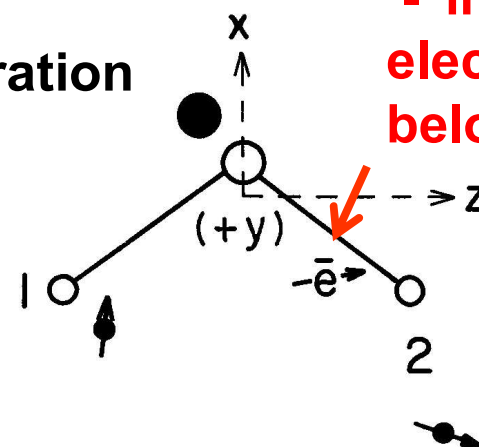
**'+' indicates
electron
above page**



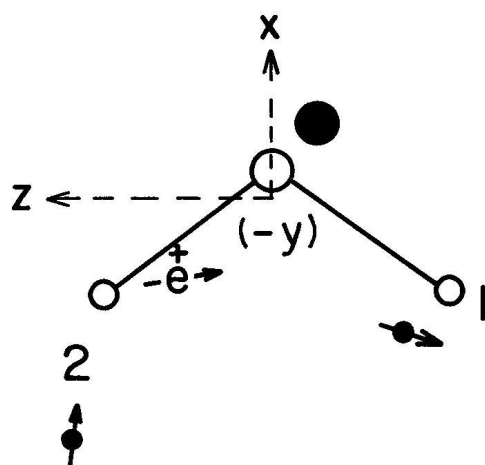
Point Group operation

C_{2x}
only transforms
electronic and
vibrational
coordinates

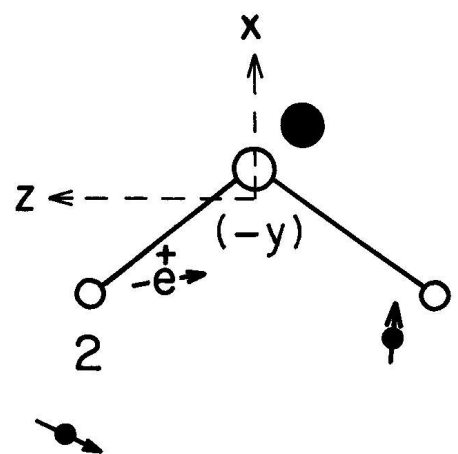
**'-' indicates
electron
below page**



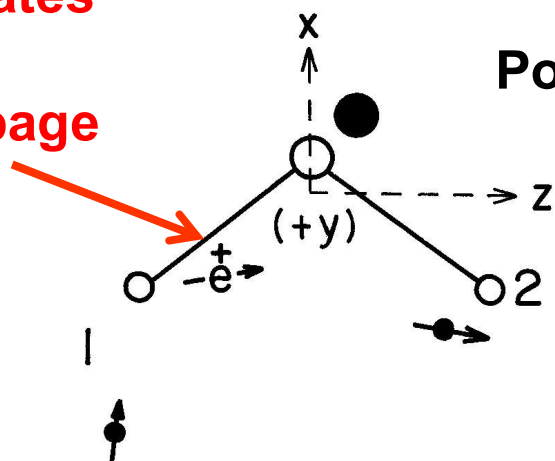
(12)



p_{12}



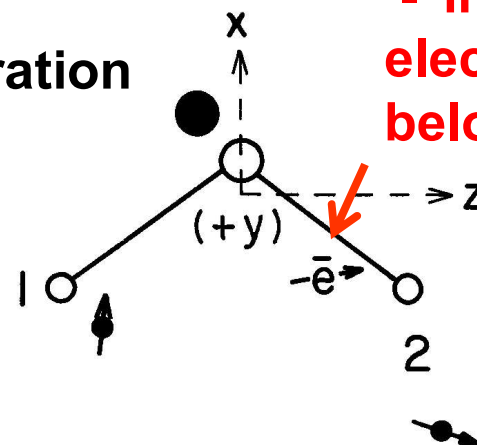
**'+' indicates
electron
above page**



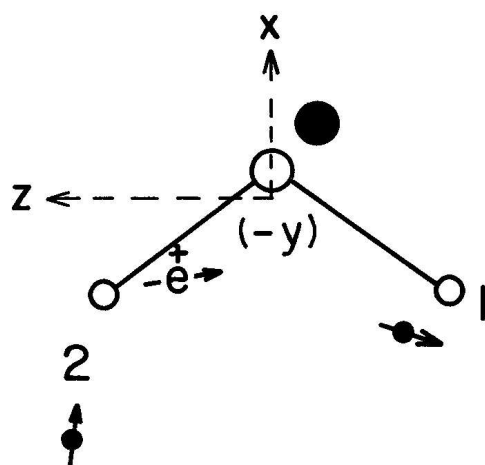
Point Group operation

C_{2x}
only transforms
electronic and
vibrational
coordinates

**'-' indicates
electron
below page**

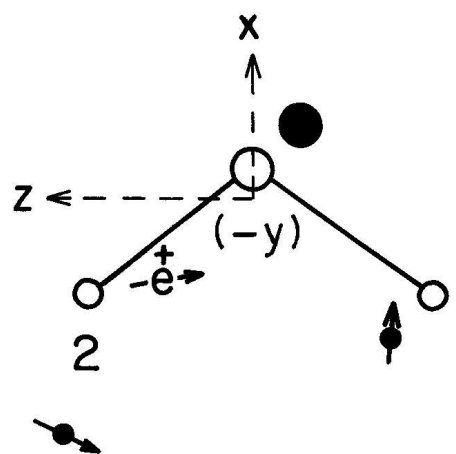


(12)



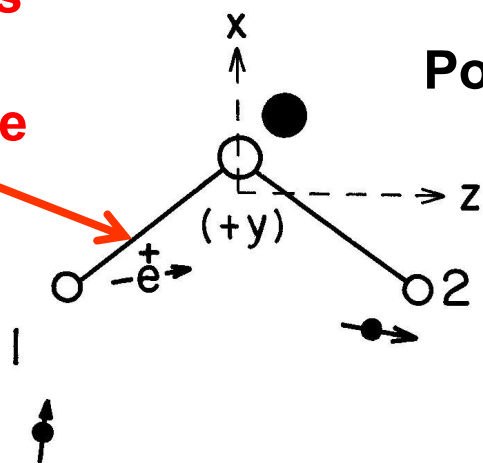
**We now
reverse these**

p_{12}



R_x^{π}

**'+' indicates
electron
above page**

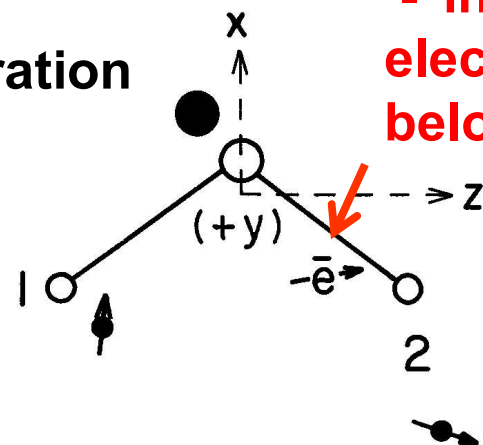


Point Group operation

C_{2x}

only transforms
electronic and
vibrational
coordinates

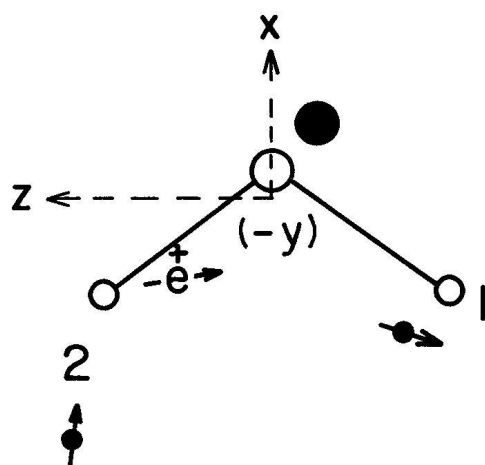
**'-' indicates
electron
below page**



(12)

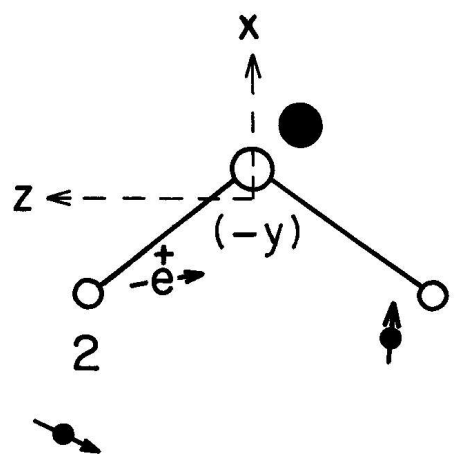
R_x^{π}

only transforms
rotational
coordinates

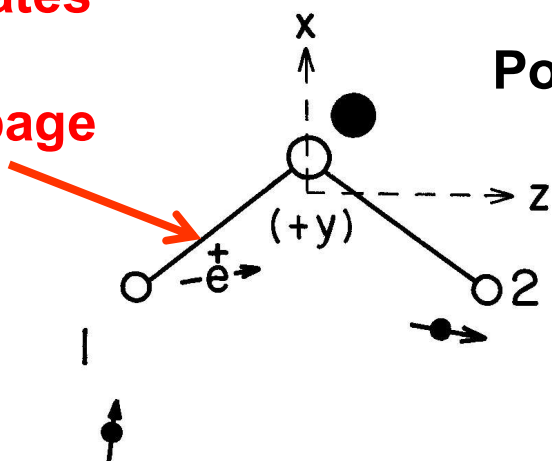


p_{12}

only transforms
nuclear spin
coordinates



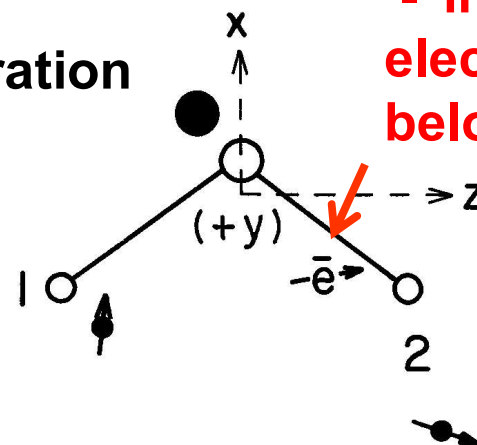
'+' indicates
electron
above page



Point Group operation

C_{2x}
only transforms
electronic and
vibrational
coordinates

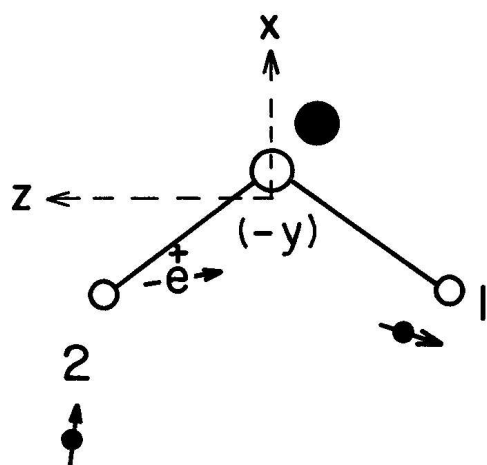
'-' indicates
electron
below page



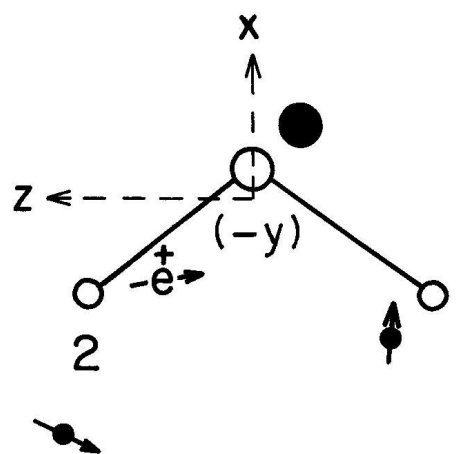
(12)

This shows that
 $(12) = p_{12} R_x^\pi C_{2x}$

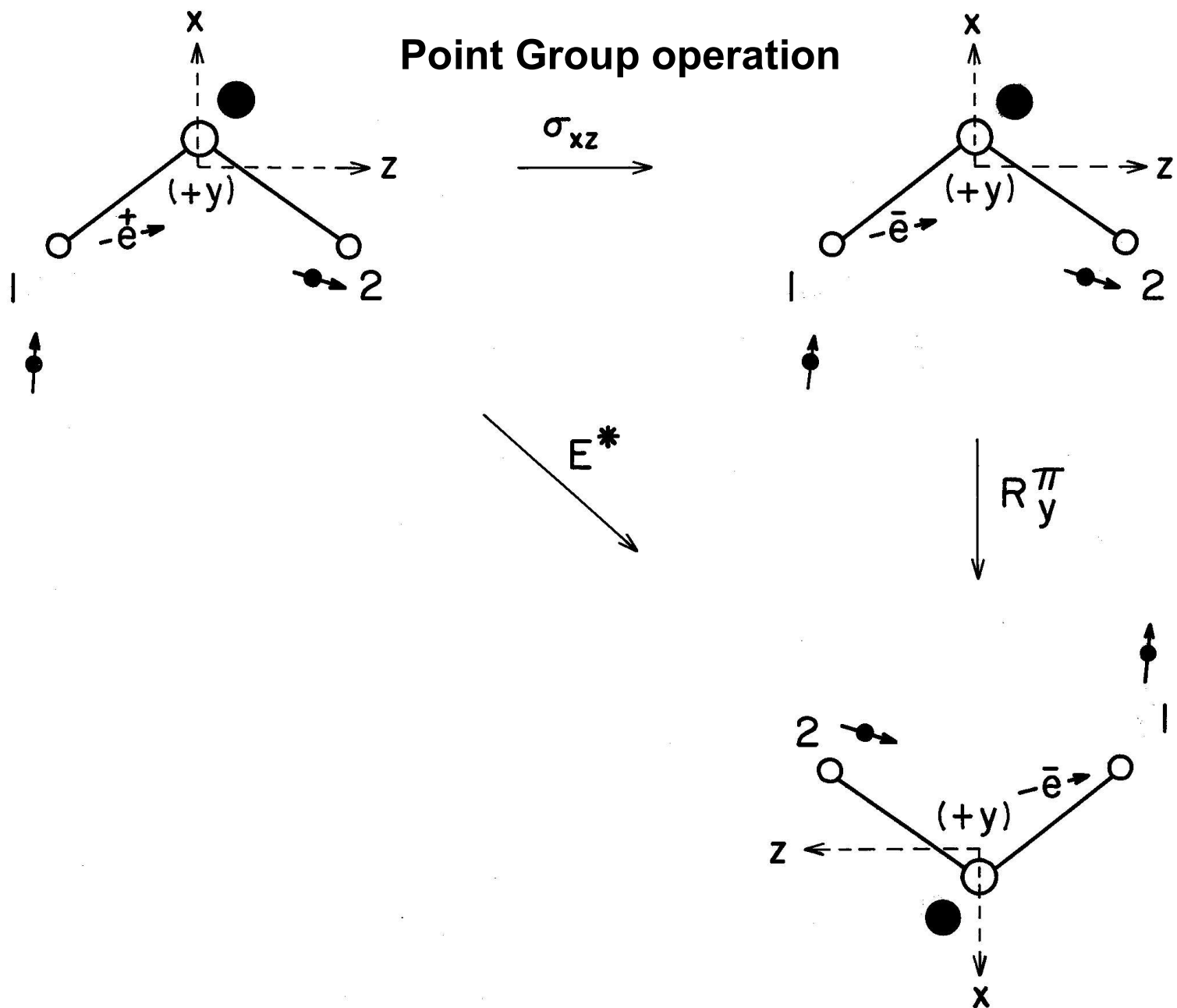
R_x^π only transforms
rotational
coordinates



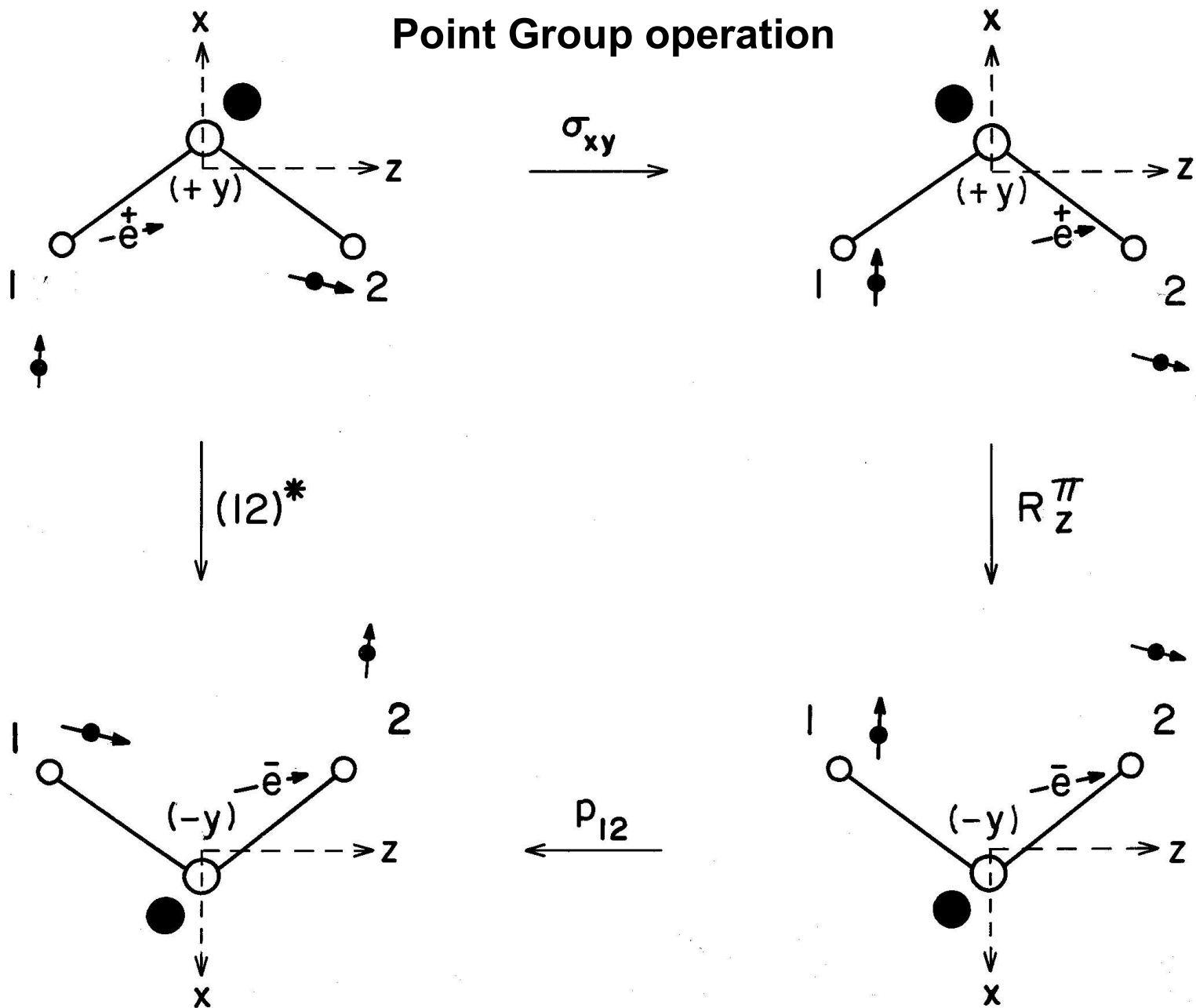
p_{12}
only transforms
nuclear spin
coordinates



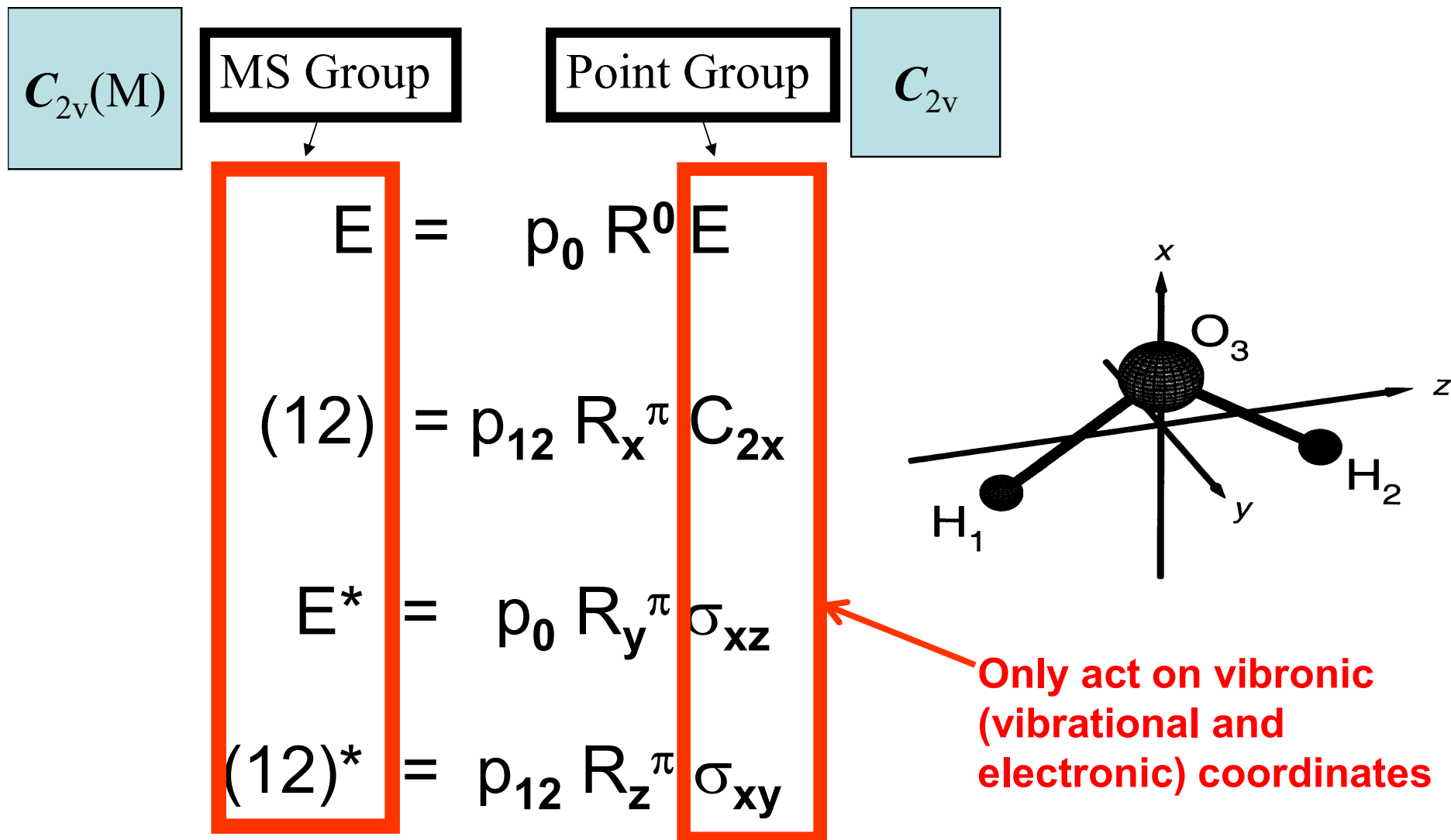
Point Group operation



Point Group operation



MS Group and Point Group of H_2O



The operations in a Point Group commute with the vibronic Hamiltonian and they do not transform the rotation or nuclear spin coordinates. We can symmetry label the vibronic states using the Point Group. Using the same names for the irreps of the MS group as for the isomorphic Point Group means that the same symmetry labels are obtained for vibronic states using the MS group.

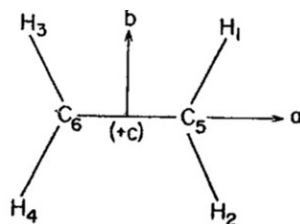
The names and character tables of PI groups for non-tunneling (“rigid”) molecules

For nonlinear rigid molecules the MS Group and the Point Group are isomorphic and we can use the same character table for each. We add “(M)” to the point group name to designate the MS Group. As examples, the MS groups of CH_3F and C_6H_6 are $C_{3v}(\text{M})$ and $D_{6h}(\text{M})$, respectively.

Linear rigid molecules are discussed in Section 8.3.4 on page 172 of BJ1 and in Chapter 17 of BJ2. For such molecules the Extended MS group is isomorphic to the Point Group and we add “(EM)” to the Point Group name so that we have $D_{\infty h}(\text{EM})$ and $C_{\infty v}(\text{EM})$ groups.

The group elements and character tables for these PI groups are given in the appendices of BJ1 and BJ2. In the final section of the talk we use the MS group $D_{2h}(\text{M})$ as an example to show the special place of the Point Group inversion operation i .

The Molecular Symmetry Group $D_{2h}(M)$ of the non-tunneling ethylene molecule



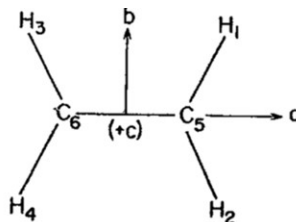
$D_{2h}(M):$	E	$(12)(34)$	$(13)(24)(56)$	$(14)(23)(56)$	E^*	$(12)(34)^*$	$(13)(24)(56)^*$	$(14)(23)(56)^*$	
$D_{2h}:$	E	C_{2a}	C_{2b}	C_{2c}	σ_{ab}	σ_{ac}	σ_{bc}	i	
Equiv. rot.:	R^0	R_a^π	R_b^π	R_c^π	R_c^π	R_b^π	R_a^π	R^0	
$A_g:$	1	1	1	1	1	1	1	1	: $\alpha_{aa}, \alpha_{bb}, \alpha_{cc}$
$A_u:$	1	1	1	1	-1	-1	-1	-1	: Γ^*
$B_{1g}:$	1	1	-1	-1	-1	-1	1	1	: \hat{J}_a, α_{bc}
$B_{1u}:$	1	1	-1	-1	1	1	-1	-1	: T_a
$B_{2g}:$	1	-1	1	-1	-1	1	-1	1	: \hat{J}_b, α_{ac}
$B_{2u}:$	1	-1	1	-1	1	-1	1	-1	: T_b
$B_{3g}:$	1	-1	-1	1	1	-1	-1	1	: \hat{J}_c, α_{ab}
$B_{3u}:$	1	-1	-1	1	-1	1	1	-1	: T_c

Under each PI group operation is given the Point Group operation onto which it is mapped. Each PI operation is the product of the Point Group operation and equivalent rotation written under it times the appropriate nuclear spin permutation. Such products are written in image 74 for $C_{2v}(M)$

The Point Group inversion operation i

Centro-symmetric molecules like ethylene have the inversion operation i in their Point Group. This operation inverts vibrational displacements and electronic coordinates in the molecule mid-point. It should be distinguished from the space inversion (parity) operation E^* involved in PI groups. We explain this using the ethylene molecule, and its MS group $D_{2h}(M)$, as an example.

The Molecular Symmetry Group $D_{2h}(M)$ of the non-tunneling ethylene molecule



$D_{2h}(M):$	E	$(12)(34)$	$(13)(24)(56)$	$(14)(23)(56)$	E^*	$(12)(34)^*$	$(13)(24)(56)^*$	$(14)(23)(56)^*$	
$D_{2h}:$	E	C_{2a}	C_{2b}	C_{2c}	σ_{ab}	σ_{ac}	σ_{bc}	i	
Equiv. rot.:	R^0	R_a^π	R_b^π	R_c^π	R_c^π	R_b^π	R_a^π	R^0	
<hr/>									
$A_g:$	1	1	1	1	1	1	1	1	: $\alpha_{aa}, \alpha_{bb}, \alpha_{cc}$
$A_u:$	1	1	1	1	-1	-1	-1	-1	: Γ^*
$B_{1g}:$	1	1	-1	-1	-1	-1	1	1	: \hat{J}_a, α_{bc}
$B_{1u}:$	1	1	-1	-1	1	1	-1	-1	: T_a
$B_{2g}:$	1	-1	1	-1	-1	1	-1	1	: \hat{J}_b, α_{ac}
$B_{2u}:$	1	-1	1	-1	1	-1	1	-1	: T_b
$B_{3g}:$	1	-1	-1	1	1	-1	-1	1	: \hat{J}_c, α_{ab}
$B_{3u}:$	1	-1	-1	1	-1	1	1	-1	: T_c

We have $(14)(23)(56)^* = p_{(14)(23)(56)} R^0 i$

where $p_{(14)(23)(56)}$ is the permutation of the nuclear spins

and R^0 is the identity rotation.

All rigid centrosymmetric molecules have a special PI group operation that we shall call I^* in their MS (or EMS) symmetry group. For ethylene this is the operation $(14)(23)(56)^*$. The operation I^* is the product of the permutation operation I and E^* , where I exchanges pairs of nuclei symmetrically located about the molecular mid-point. For ethylene $I = (14)(23)(56)$.

The operation $I^* = p_i R^0 i$

where p_i is the exchange of the nuclear spin coordinates of nuclei symmetrically located about the molecular mid-point. Since $(p_i)^2 = E$ and R^0 is the identity rotation we have

$$i = p_i I^*$$

Since I^* commutes with the full rovibronic-nuclear spin Hamiltonian then i commutes with the rovibronic Hamiltonian.

Vibronic states are either symmetric (*gerade* or *g*) or unsymmetric (*ungerade* or *u*) under the effect of the Point Group operation *i*. Because the point group operation *i* commutes with the rovibronic Hamiltonian, the rotational levels of *g* and *u* vibronic states can only be coupled by the nuclear spin hyperfine Hamiltonian.

See Critchley et al, Phys. Rev. Letters, 86, 1725 (2001) for an example of *g-u* mixing in the centro-symmetric molecule H₂⁺.

The *g/u* label is NOT the parity label +/- . The parity label is the effect of the spatial inversion operation *E*^{*} on an overall rovibronic nuclear spin state.

SUMMARY

RH=HR defines a “Symmetry Operation” R

CNPI Groups **Group of all P and P* operations**

With RH=HR **Label energy levels using irreps**

Irrep Labels **Determine which $\int \phi_n^* O \phi_m dq = 0$**

Using CNPI Groups **Superfluous symmetry labels
because of VERSIONS**

Mol Symm Groups **Unfeasible operations omitted**

Non-tunneling molecules **$R_{PG} H_{ve} = H_{ve} R_{PG}$**

**Can use Point Group to label vibronic states of non-tunneling molecules
since Point Group elements R_{PG} commute with vibronic Hamiltonian H_{ve}**