Symmetry Groups and Quantum Dynamics of Rigid and Non-Rigid Molecules

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Point Groups

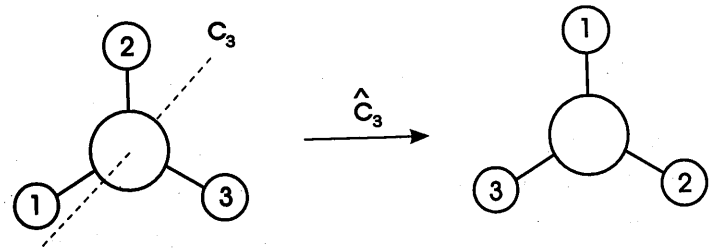
Point Groups

Molecule $\underset{\text{inverse operation}}{\overset{\text{operation}}{\rightleftharpoons}}$ Indistinguishable Molecule

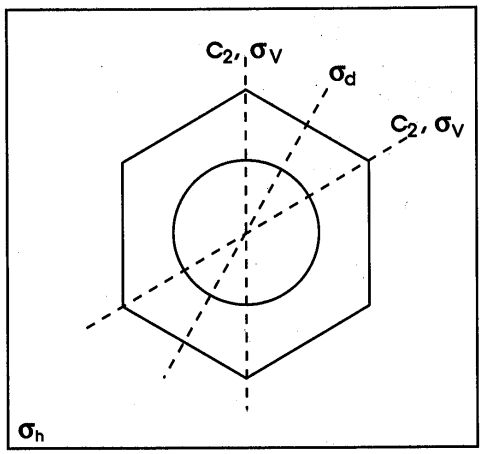
Operator	Symmetry Element
Identity, $\hat{E}$	–
Rotation by $2\pi/n$, $\hat{C}_n$	n-fold symmetry axis
Reflection, $\hat{\sigma}$	plane of symmetry
	σ_v vertical plane
	σ_h horizontal plane
	σ_d diagonal plane
Rotation-reflection or improper rotation, $\hat{S}_n$ $\hat{S}_n = \hat{C}_n\hat{\sigma}_h = \hat{\sigma}_h\hat{C}_n$	n-fold improper symmetry axis
Inversion, $\hat{i}$	centre of inversion

Point Groups

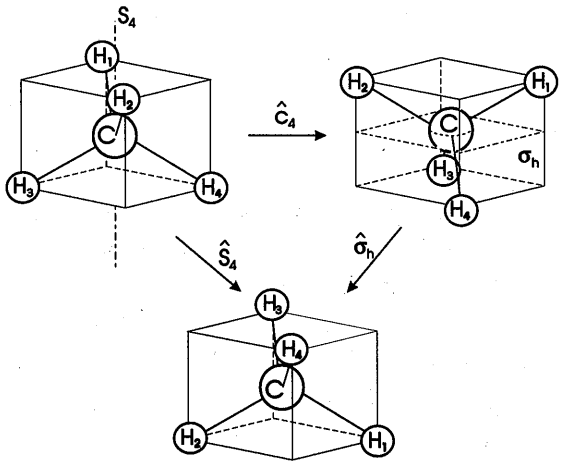
Rotation (BF_3)



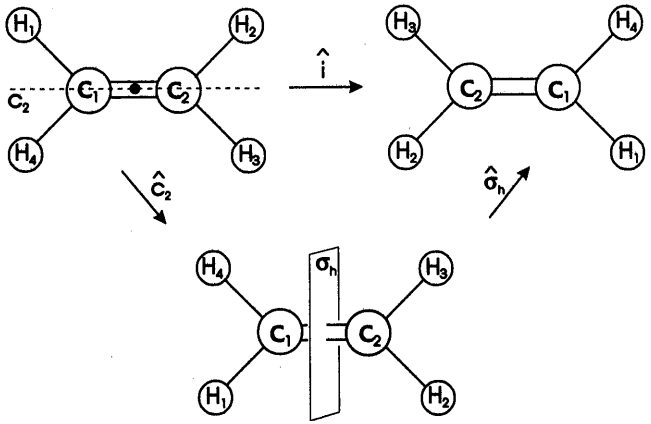
Reflection (C_6H_6, benzene)



Improper Rotation (CH_4, methane)

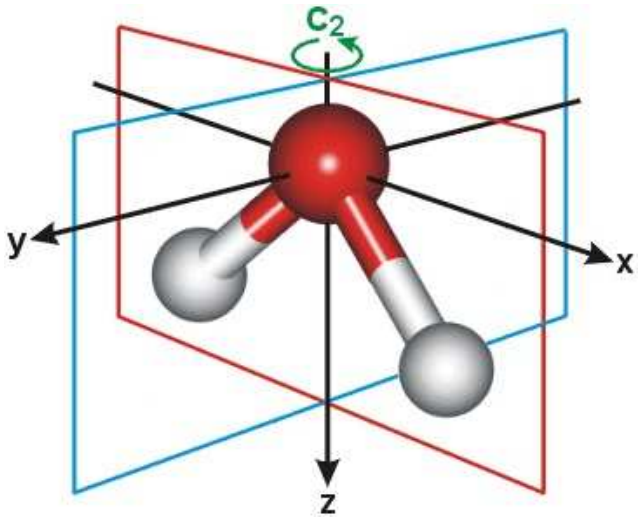


Inversion (C_2H_2, ethene)



Point Groups

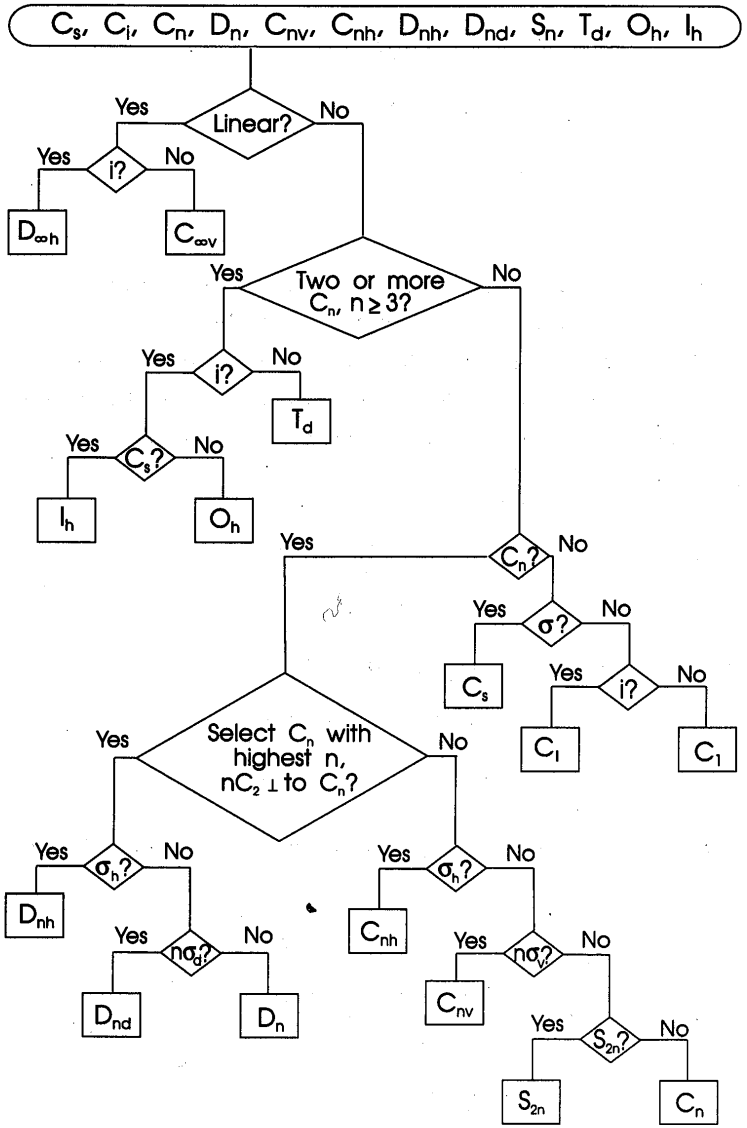
Symmetry elements of water: point group C_{2v}



Multiplication table: $\hat{C}_2 \equiv \hat{C}_2(z)$, $\hat{\sigma}_v \equiv \hat{\sigma}_v(yz)$, $\hat{\sigma}'_v \equiv \hat{\sigma}_v(xz)$

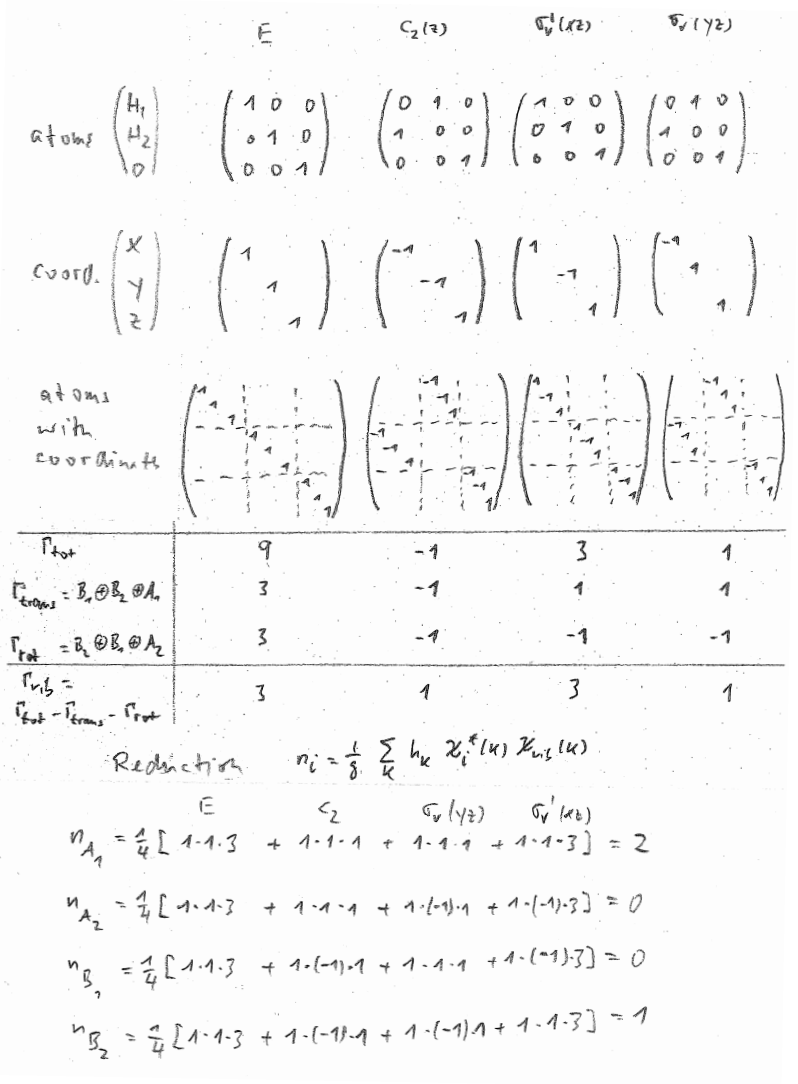
C_{2v}	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v$	$\hat{\sigma}'_v$
$\hat{E}$	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v$	$\hat{\sigma}'_v$
$\hat{C}_2$	$\hat{C}_2$	$\hat{E}$	$\hat{\sigma}'_v$	$\hat{\sigma}_v$
$\hat{\sigma}_v$	$\hat{\sigma}_v$	$\hat{\sigma}'_v$	$\hat{E}$	$\hat{C}_2$
$\hat{\sigma}'_v$	$\hat{\sigma}'_v$	$\hat{\sigma}_v$	$\hat{C}_2$	$\hat{E}$

Point Groups: Algorithm



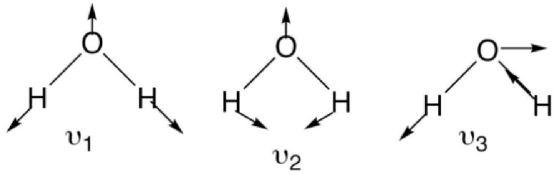
Point Groups: Representations

Example: Water in the yz plane. If in xz plane, B_1 and B_2 are interchanged

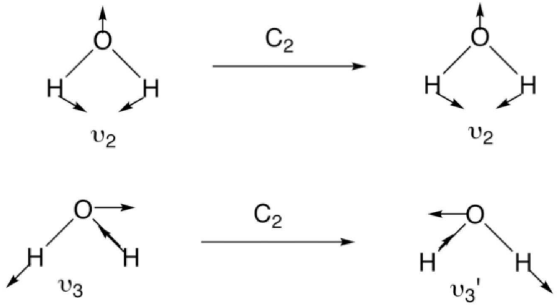


Point Groups: Normal Modes

- Normalmodes



- Interpretation within the point group:



- character table

C_{2v}	$\hat{E}$	$\hat{C}_2(z)$	$\hat{\sigma}_v(yz)$	$\hat{\sigma}'_v(xz)$	
A_1	1	1	1	1	
A_2	1	1	-1	-1	
B_1	1	-1	1	-1	
B_2	1	-1	-1	1	
$\Gamma(v_1)$, $\Gamma(v_2)$	1	1	1	1	A_1
$\Gamma(v_3)$	1	-1	-1	1	B_2

Point Groups: Limitations

Non-rigid molecules

- large amplitude vibrations, for example H_3^+
- more than one stable structure, for example NH_3

Let us look at

- the theoretical basis that leads to point group classification
- the true symmetry of the molecular Hamiltonian

Schrödinger Equation

1. time-dependent

$$\left[i\hbar \frac{\partial}{\partial t} - H(\mathbf{Q}, \mathbf{q}, t) \right] \Psi(\mathbf{Q}, \mathbf{q}, t) = 0$$

$$H(\mathbf{Q}, \mathbf{q}) = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + V(\mathbf{Q}, \mathbf{q}, t)$$

2. time-independent if potential does not depend on t

$$\left[H(\mathbf{Q}, \mathbf{q}) - E_\alpha \right] \psi_\alpha(\mathbf{Q}, \mathbf{q}) = 0$$

- translational motion separable from internal motion in absence of magnetic fields

$$\left[H(\mathbf{R}, \mathbf{r}) - E_\alpha \right] \psi_\alpha(\mathbf{R}, \mathbf{r}) = 0$$

  $\mathbf{Q}, \mathbf{q}$: coordinates in laboratory system; $\mathbf{R}, \mathbf{r}$: coordinates in molecule-fixed system with axes parallel to laboratory system
- internal Schrödinger equation not separable
- sequence of approximations to solve it

Separation of degrees of liberty

1. of nuclei and electrons: adiabatic approximation ($M_I >> m_e$)

$$\psi_\alpha(\mathbf{R}, \mathbf{r}) = \Phi_n(\mathbf{r}; \mathbf{R})\, \Theta_{n\alpha}(\mathbf{R})$$

   - notion of potential energy surface
   - minimum: concept of molecular structure

2. of electrons: Hartree-Fock

$$\Phi_n(\mathbf{r}; \mathbf{R}) = \hat{A} \prod_i \phi_i(\vec{r}_i; \mathbf{R})$$

   - first approximation:
     doesn't describe dissociaton; ca. 2% of electronic energy missing
   - followed by a correlation method such as CI

Separation of degrees of liberty

3. of rotation and vibration

$$T = T_{vib} + T_{rot} + T_{rot,vib} \; ; \quad T_{rot,vib} = 2\vec{\omega} \sum_{I=1}^{3N} M_I \vec{R}_I \times \dot{\vec{R}}_I$$

- Eckart conditions (reference configuration $\mathbf{R^0}$)

$$\sum_{I=1}^{3N} M_I \vec{R}_I^0 \times \vec{R}_I = 0$$

4. of vibrational modes (reference configuration $\mathbf{R^0}$)

$$H_{vib} \approx T_{vib} + V_0 + \frac{1}{2} \frac{\partial^2 V}{\partial R_i R_j}\bigg|_{R^0} \Delta R_i \Delta R_j + \cdots$$

- diagonalization of Hesse matrix
- normal modes: approximate quantum numbers
- selection rules

Symmetry of the Hamiltonian

Molecular Hamiltonian

$$H(\mathbf{R},\mathbf{r}) = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + V(\mathbf{R},\mathbf{r})$$

with the Coulomb interaction potential

$$V(\mathbf{R},\mathbf{r}) = \sum_{I\neq J}\frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} + \sum_{i\neq j}\frac{1}{|\vec{r}_i - \vec{r}_j|} - \sum_{Ii}\frac{Z_I}{|\vec{R}_I - \vec{r}_i|}$$

Invariances

1. rotation,operator J^2
   $[H, J^2] = 0$
2. permutation of any two identical particles, operator (12)
   $[H, (12)] = 0$
3. inversion of the coordinate system, operator E^*
   $[H, E^*] = 0$

Complete Nuclear Permutation and Inversion (CNPI) Groups

CNPI group of water

Water: 2 identical H atoms, operators (12) and E^*

- Multiplication table of $S_2 \times I$ permutation-inversion group:

$S_2 \times I$	E	(12)	E^*	$(12)^*$
E	E	(12)	E^*	$(12)^*$
(12)	(12)	E	$(12)^*$	E^*
E^*	E^*	$(12)^*$	E	(12)
$(12)^*$	$(12)^*$	E^*	(12)	E

- Multiplication table of C_{2v} point group:

C_{2v}	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v$	$\hat{\sigma}'_v$
$\hat{E}$	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v$	$\hat{\sigma}'_v$
$\hat{C}_2$	$\hat{C}_2$	$\hat{E}$	$\hat{\sigma}'_v$	$\hat{\sigma}_v$
$\hat{\sigma}_v$	$\hat{\sigma}_v$	$\hat{\sigma}'_v$	$\hat{E}$	$\hat{C}_2$
$\hat{\sigma}'_v$	$\hat{\sigma}'_v$	$\hat{\sigma}_v$	$\hat{C}_2$	$\hat{E}$

- The two groups are isomorphic.
- Molecular symmetry group is called $C_{2v}(M)$.

Permutation group of three identical particles

- generated by operators $(12) \equiv (21)$, $(23) \equiv (32)$, $(13) \equiv (31)$
  $(12)[123] = [213]$; $(23)[123] = [132]$; $(13)[123] = [312]$
- combinations yield cyclic permutations:

  $(12)(23)[123] = (12)[132] = [231] \Rightarrow (123)[123]$
  1 replaced by 2, 2 replaced by 3, 3 replaced by 1

  $(23)(12)[123] = (23)[213] = [312] \Rightarrow (132)[123]$
  1 replaced by 3, 3 replaced by 2, 2 replaced by 1

- Multiplication table:

S_3	E	(12)	(23)	(13)	(123)	(132)
E	E	(12)	(23)	(13)	(123)	(132)
(12)	(12)	E	(123)	(132)	(23)	(13)
(23)	(23)	(132)	E	(123)	(13)	(12)
(13)	(13)	(123)	(132)	E	(12)	(23)
(123)	(123)	(13)	(12)	(23)	(132)	E
(132)	(132)	(23)	(13)	(12)	E	(123)

- classes: E; {(12), (23), (13)}; {(123), (132)}
  S_3 isomorphic with C_{3v}: (E, $\{3\sigma_v\}$, $\{2C_3\}$)

CNPI group of three identical particles

CNPI group is $S_3 \times I$

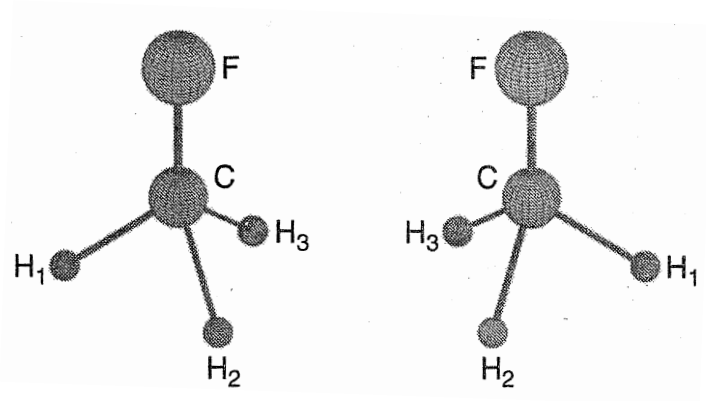
- operators: E, {(12), (23), (13)}, {(123), (132)} and E^*, {$(12)^*$, $(23)^*$, $(13)^*$}, {$(123)^*$, $(132)^*$}
- $S_3 \times I$ isomorphic with D_{3h}
- character table

$S_3 \times I$	E	{(123), (132)}	{(12), (23), (13)}	E^*	{$(123)^*$, $(132)^*$}	{$(12)^*$, $(23)^*$, $(13)^*$}
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
A_2'	1	1	-1	1	1	-1
E'	2	-1	0	2	-1	0
A_1''	1	1	1	-1	-1	-1
A_2''	1	1	-1	-1	-1	1
E''	2	-1	0	-2	1	0

- $D_{3h}(M)$ is the molecular symmetry group of H_3^+, BF_3, $\cdots$

Longuet-Higgins: Not all operations are feasible

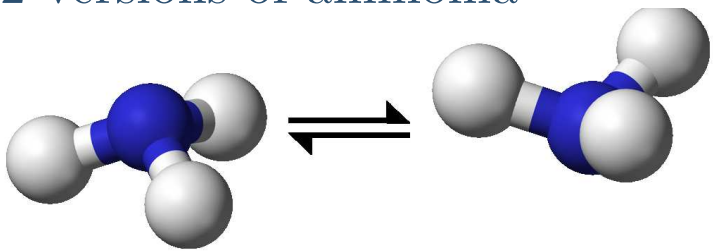
- Two "versions" of CH_3F. They differ from ordering (clockwise, anti-clockwise) of H atoms looking along $F \Rightarrow C$



- passing between the two structures only via high-energy planar transition state: not feasible
- hence (12), (23) and (13) are not feasible operations
- E^* not feasible either
- however $(12)^*$ etc. are feasible
- Molecular symmetry group $C_{3v}(M)$ by E, {(123), (132)}, $\{(12)^*$, $(23)^*$, $(13)^*\}$
- $C_{3v}(M)$ is a sub group of $D_{3h}(M)$, see previous slide

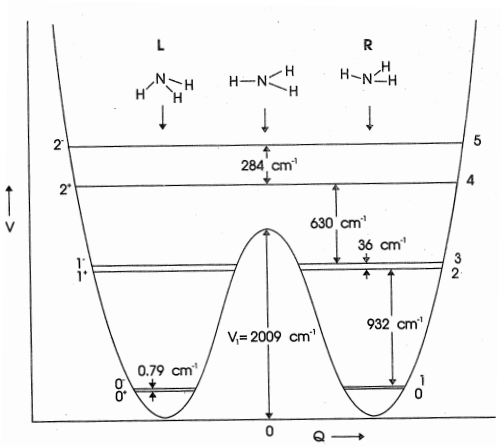
Ammonia NH_3

- CNPI group has order $n = 1! \times 3! \times 2 = 12$
- 2 versions of ammonia



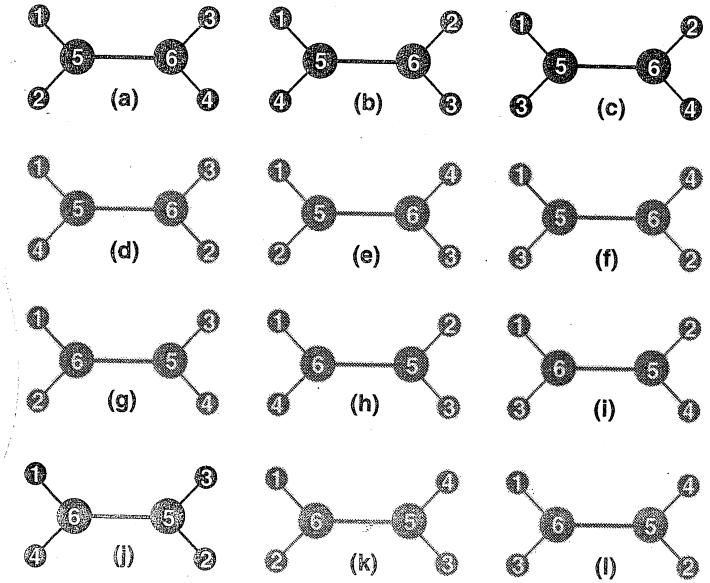
- low inversion barrier: all operations feasible
- Molecular symmetry group is $D_{3h}(M) = C_{3v}(M) \times (E, E^*)$, order $n = 12$
- "doubling" of rovibrational states (symmetric and anti-symmetric with respect to (12) etc.), observable splitting

$C_{3v}(M)$	$D_{3h}(M)$
A_1	$A_1' + A_2''$
A_2	$A_2' + A_1''$
E	$E' + E''$



Ethene $H_2C = CH_2$

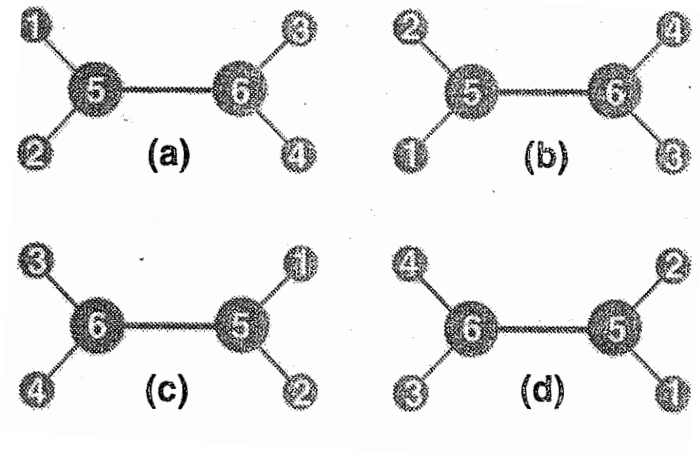
- CNPI group has order $n = 2! \times 4! \times 2 = 96$
- 12 versions of ethene



- unfeasible operations would rupture bonds, (12), (56) etc.
- feasible operations are E, (12)(34), (13)(24)(56), (14)(23)(56) and E^*, (12)(34)*, (13)(24)(56)*, (14)(23)(56)*

Ethene $H_2C = CH_2$: continued

- feasible operations are E, $(12)(34)$, $(13)(24)(56)$, $(14)(23)(56)$ and E^*, $(12)(34)^*$, $(13)(24)(56)^*$, $(14)(23)(56)^*$
- 4 views of version (a): original plus result of three rotations (x, y, z)



- Molecular symmetry group is $D_{2h}(M)$, order $n = 8 = 96/\textit{number of versions}$, i.e. a subgroup of the CNPI group

Rigid linear molecules

- OCS: E, E^*; $(C_{\infty v}(M))$

	E	E^*
Σ^+	1	1
Σ^-	1	-1

- H_2: E, (12), E^*, $(12)^*$; $(D_{\infty h}(M))$

	E	(12)	E^*	$(12)^*$
Σ_g^+	1	1	1	1
Σ_u^+	1	-1	1	-1
Σ_g^-	1	-1	-1	1
Σ_u^-	1	1	-1	-1

  note that the point group operation i corresponds to $(12)^*$

- ethyne (acetylene), $H_{(1)} - C_{(3)} \equiv C_{(4)} - H_{(2)}$: as H_2 but E, $(12)(34)$, E^*, $(12)(34)^*$
- extended molecular symmetry group (EMS) needed to classify vibration (degenerate mode)

Rotational motion

Rotational motion

- Comparison of linear and angular motions

Linear Motion	Angular Motion
Position	
Distance, x	Angle, θ
Velocity	
Velocity, $v = \dot{x} = dx/dt$	Angular velocity, $\omega = \dot{\theta} = d\theta/dt$
Acceleration	
Acceleration, $a = \ddot{x} = d^2x/dt^2$	Angular acceleration, $\alpha = \ddot{\theta} = d^2\theta/dt^2$
Mass	
Mass, m	Moment of inertia, $I = mr^2$
Momentum	
Linear momentum, $p = mv$	Angular momentum, $L = I\omega$
Kinetic energy	
$E_k = \frac{1}{2}mv^2 = p^2/2m$	$E_k = \frac{1}{2}I\omega^2 = L^2/2I$
Force	
Force, F	Torque, T
Newton's second law	
$F = ma = dp/dt$	$T = I\alpha = dL/dt$

- Angular momentum in molecule-fixed axis system (x', y', z'):

$$\begin{pmatrix} L'_x \\ L'_y \\ L'_z \end{pmatrix} = \begin{pmatrix} \sum m_a(y_a'^2 + z_a'^2) & -\sum x'_a y'_a & -\sum x'_a z'_a \\ -\sum y'_a x'_a & \sum m_a(x_a'^2 + z_a'^2) & -\sum y'_a z'_a \\ -\sum z'_a x'_a & -\sum z'_a y'_a & \sum m_a(y_a'^2 + z_a'^2) \end{pmatrix} \begin{pmatrix} \omega'_x \\ \omega'_y \\ \omega'_z \end{pmatrix}$$

- Principal axes by diagonalisation of tensor of inertia

$$\begin{aligned} \mathbf{L}' &= \mathbf{I}'\boldsymbol{\omega}' = \mathbf{X}\mathbf{X}^{-1}\mathbf{I}'\mathbf{X}\mathbf{X}^{-1}\boldsymbol{\omega}' = \mathbf{X}\mathbf{I}\mathbf{X}^{-1}\boldsymbol{\omega}' \\ \mathbf{X}^{-1}\mathbf{L}' &= \mathbf{I}\mathbf{X}^{-1}\boldsymbol{\omega}' \\ \mathbf{L} &= \mathbf{I}\boldsymbol{\omega} \end{aligned}$$

Rotational motion: continued

- Angular momentum in principal axis system (x, y, z):

$$\begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} = \begin{pmatrix} \sum m_a({y_a}^2 + {z_a}^2) & 0 & 0 \\ 0 & \sum m_a({x_a}^2 + {z_a}^2) & 0 \\ 0 & 0 & \sum m_a({y_a}^2 + {z_a}^2) \end{pmatrix} \begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \end{pmatrix}$$

- Rotational energy

$$\begin{aligned} E_{rot} &= \frac{1}{2}\boldsymbol{\omega}^T \mathbf{I}\boldsymbol{\omega} = \frac{1}{2}I_{xx}\omega_x^2 + \frac{1}{2}I_{yy}\omega_y^2 + \frac{1}{2}I_{zz}\omega_z^2 \\ &= \frac{L_x^2}{2I_{xx}} + \frac{L_y^2}{2I_{yy}} + \frac{L_z^2}{2I_{zz}} \\ &= \frac{L_a^2}{2I_A} + \frac{L_b^2}{2I_B} + \frac{L_c^2}{2I_C} \\ &= AL_a^2 + BL_b^2 + CL_c^2 \end{aligned}$$

- Spectroscopic convention for moments of inertia: $I_A \leq I_B \leq I_C$ for rotational constants: $A \geq B \geq C$

Rotational motion: continued

1. Linear polyatomic molecule: $A = 0, B = C$

$$\begin{aligned} T_{rot} &= A\hat{J}_a^2 + B(\hat{J}_b^2 + \hat{J}_c^2) = B(\hat{J}^2 - \hat{J}_a^2) \\ E_{rot} &= BJ(J+1) - Bk_a^2 \end{aligned}$$

2. Spherical top: $A = B = C$, example CH_4

$$\begin{aligned} T_{rot} &= B(\hat{J}_a^2 + \hat{J}_b^2 + \hat{J}_c^2) = B\hat{J}^2 \\ E_{rot} &= BJ(J+1) \end{aligned}$$

3. Symmetric top: two rotational constants are equal

- prolate top: $A > B = C$, example CH_3F

$$\begin{aligned} T_{rot} &= A\hat{J}_a^2 + B(\hat{J}_b^2 + \hat{J}_c^2) = B(\hat{J}^2 - \hat{J}_a^2) + A\hat{J}_a^2 = B\hat{J}^2 + (A-B)\hat{J}_a^2 \\ E_{rot} &= BJ(J+1) + \underbrace{(A-B)k_a^2}_{>0} \end{aligned}$$

  E_{rot} increases with $K_a = |k_a|$ for given J

- oblate top: $A = B > C$, examples NH_3, BF_3, H_3^+

$$\begin{aligned} T_{rot} &= B(\hat{J}_a^2 + \hat{J}_b^2) + C\hat{J}_c^2 = B(\hat{J}^2 - \hat{J}_c^2) + C\hat{J}_c^2 = B\hat{J}^2 + (C-B)\hat{J}_c^2 \\ E_{rot} &= BJ(J+1) + \underbrace{(C-B)k_c^2}_{<0} \end{aligned}$$

  E_{rot} decreases with $K_c = |k_c|$ for given J

Rotational motion: continued

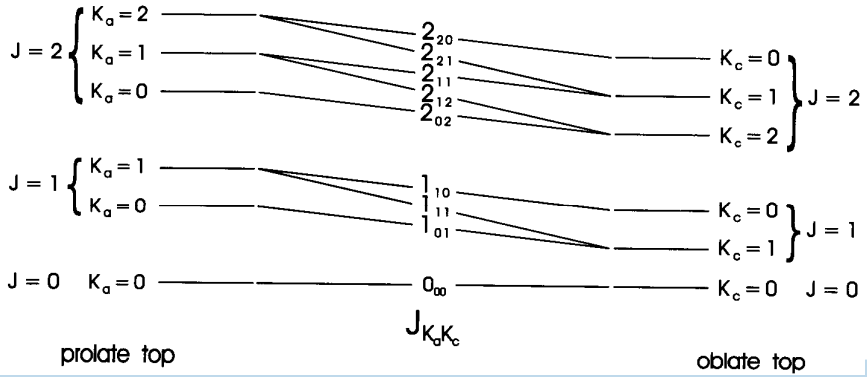
4. Asymmetric top: $A > B > C$, example H_2O

$$\begin{aligned} T_{rot} &= A\hat{J}_a^2 + B(\hat{J}_b^2 + \hat{J}_c^2) \\ &= A\hat{J}_a^2 + \frac{1}{2}(B+C)(\hat{J}_b^2 + \hat{J}_c^2) + \frac{1}{2}(B-C)(\hat{J}_b^2 - \hat{J}_c^2) \\ &= A\hat{J}_a^2 + \frac{1}{2}(B+C)(\hat{J}^2 - \hat{J}_a^2) + \frac{1}{2}(B-C)(\hat{J}^{+2} + \hat{J}^{-2}) \end{aligned}$$

with $\hat{J}^{\pm} = \hat{J}_b \pm i\hat{J}_c$. Matrix elements in the prolate top $|Jk_a\rangle$ basis:

$$\begin{aligned} \langle Jk_a|T_{rot}|Jk_a'\rangle &= Ak_a^2\delta_{k_ak_a'} + \frac{1}{2}(B+C)\left[J(J+1) - k_a^2\right]\delta_{k_ak_a'} \\ &\quad + \frac{1}{2}\underbrace{\langle Jk_a|\hat{J}^{+2}|Jk_a'\rangle}_{\sim\,\delta_{k_ak_a'+2}} + \frac{1}{2}\underbrace{\langle Jk_a|\hat{J}^{-2}|Jk_a'\rangle}_{\sim\,\delta_{k_ak_a'-2}} \end{aligned}$$

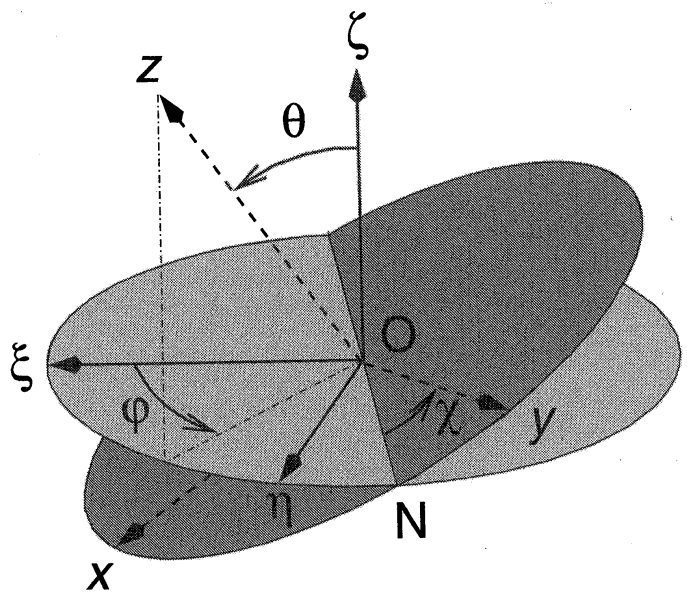
k_a not conserved, but $(-1)^{K_a}$ is (likewise $(-1)^{K_c}$). Correlation with symmetric tops:



Rotational functions: Euler angles

Representation of rotational functions and their symmetry

- $(\theta, \phi, \chi | Jkm\rangle = \sqrt{\frac{2J+1}{8\pi^2}} D^{J*}_{mk}(\phi, \theta, \chi) \sim e^{im\phi} d^J_{mk}(\theta) e^{ik\chi}$
  D^J_{km} are Wigner rotation functions, depending on the Euler angles θ, ϕ, χ
- molecule-fixed axes parallel to laboratory system: (ξ, η, ζ)
  molecule-fixed axes equivalent to principal axes: (x, y, z)
  k and m are internal,z, and exteral, ζ, projections



- x, y, z axes defined with respect to numbered particles
- permutation of particles then reorients (x, y, z) axes, hence the Euler angles change
- transformation of Euler angles in CNPI to be studied casewise: H_2, H_2O

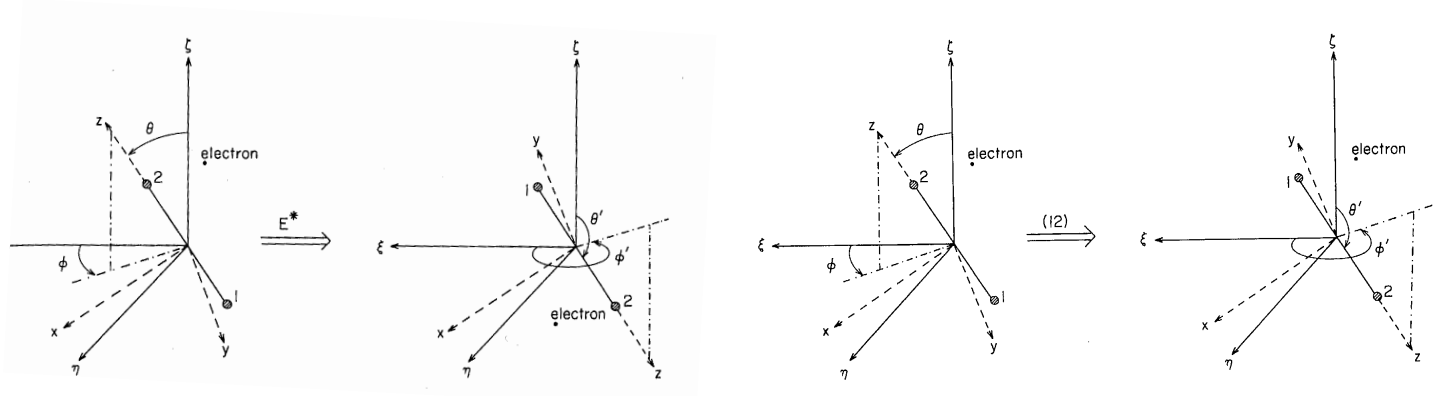
Rotational functions: linear molecule case

- linear polyatomic molecules: $A = 0, B = C$

$$T_{rot} = A\hat{J}_a^2 + B(\hat{J}_b^2 + \hat{J}_c^2) = B(\hat{J}^2 - \hat{J}_a^2) \qquad E_{rot} = BJ(J+1) - Bk_a^2$$

- diatomic: $J_a = k_a = 0$ since $\vec{J} \perp \vec{z}$, χ not defined

$$E_{rot} = BJ(J+1) \qquad (\theta, \phi | Jm\rangle \sim D^{J*}_{m,k=0}(\phi, \theta, \chi) \sim Y_{Jm}(\theta, \phi)$$



$(E^*)(\theta, \phi) = (\pi - \theta, \phi + \pi)$ $(12)(\theta, \phi) = (\pi - \theta, \phi + \pi)$ only for homonuclear

- Effect on rotational function:
$Y_{Jm}(\pi - \theta, \phi + \pi) = (-1)^J Y_{Jm}(\theta, \phi)$

Rigid Molecules

H_2

- Molecular symmetry group $D_{\infty h}(M)$
- Symmetry of vibrational function $|v\rangle$:
  $R = |\vec{R}_1 - \vec{R}_2|$; invariant with respect to all symmetry operations
  $\Gamma(|v\rangle) = \Sigma_g^+$
- Symmetry of rotational function $|Jm\rangle$: (m external projection)

$$(12)(\theta, \phi, R) = (\pi - \theta, \phi + \pi, R)$$
$$(E^*)(\theta, \phi, R) = (\pi - \theta, \phi + \pi, R)$$

- Effect on rotational function:
  $Y_{Jm}(\pi - \theta, \phi + \pi) = (-1)^J Y_{Jm}(\theta, \phi)$
- Character table:

$D_{\infty h}(M)$	$S_2 \times I$	E	(12)	E^*	$(12)^*$	
Σ_g^+	A_1	1	1	1	1	$\Psi(R)$, Y_{Jm} (J even)
Σ_u^+	B_2	1	-1	1	-1	
Σ_g^-	B_1	1	-1	-1	1	Y_{Jm} (J odd)
Σ_u^-	A_2	1	1	-1	-1	

H_2: continued

H_2 isotopologues in the electronic ground state ($X^1\Sigma_g^+$): $\Gamma_{el} = \Sigma_g^+$
$|\Psi\rangle = |el\rangle\,|ns\rangle\,|vib\rangle\,|rot\rangle$
$\Gamma_{tot} = \Gamma_{el} \times \Gamma_{ns} \times \Gamma_{vib} \times \Gamma_{rot}$

- H_2: $i = 1/2$, i.e. fermion. $|\Psi\rangle$ must be anti-symmetric (Σ_u^+ or Σ_g^-)

$$\uparrow + \uparrow = \begin{cases} \textit{triplet} \begin{cases} \uparrow\uparrow \\ \uparrow\downarrow + \downarrow\uparrow \; I = 1, \text{ symmetric } \chi[(12)] = 1, \Gamma = A_1 \; (\Sigma_g^+) \\ \downarrow\downarrow \end{cases} \\ \textit{singlet} \quad \uparrow\downarrow - \downarrow\uparrow \; I = 0, \text{ anti-symmetric } \chi[(12)] = -1, \Gamma = B_2 \; (\Sigma_u^+) \end{cases}$$

- Symmetry

$$I = 1,\ J \text{ even} \ : \Gamma_{tot} = \Sigma_g^+ \times \Sigma_g^+ \times \Sigma_g^+ \times \Sigma_g^+ = \Sigma_g^+ \text{ forbidden}$$
$$I = 1,\ J \text{ odd} \ : \Gamma_{tot} = \Sigma_g^+ \times \Sigma_g^+ \times \Sigma_g^+ \times \Sigma_g^- = \Sigma_g^- \text{ allowed}$$
$$I = 0,\ J \text{ even} \ : \Gamma_{tot} = \Sigma_g^+ \times \Sigma_u^+ \times \Sigma_g^+ \times \Sigma_g^+ = \Sigma_u^+ \text{ allowed}$$
$$I = 0,\ J \text{ odd} \ : \Gamma_{tot} = \Sigma_g^+ \times \Sigma_u^+ \times \Sigma_g^+ \times \Sigma_g^- = \Sigma_u^- \text{ forbidden}$$

- Missing levels (zero statistical weight):
  J even for ortho-hydrogen (triplet), J odd for para-hydrogen (singlet)

H_2: continued

- D_2: $i = 1$, i.e. bosons. $|\Psi\rangle$ must be symmetric (Σ_g^+ or Σ_u^-)
  Nuclear spin functions: $I = 2, 1, 0$, symmetry $\Sigma_g^+, \Sigma_u^+, \Sigma_g^+$

$$\Gamma_{tot} = \Gamma_{el} \times \Gamma_{ns} \times \Gamma_{vib} \times \Gamma_{rot}$$

$$I = 2, 0,\ J \text{ even}: \quad \Gamma_{tot} = \Sigma_g^+ \times \Sigma_g^+ \times \Sigma_g^+ \times \Sigma_g^+ = \Sigma_g^+ \text{ allowed}$$

$$I = 2, 0,\ J \text{ odd}: \quad \Gamma_{tot} = \Sigma_g^+ \times \Sigma_g^+ \times \Sigma_g^+ \times \Sigma_g^- = \Sigma_g^- \text{ forbidden}$$

$$I = 1,\ J \text{ even}: \quad \Gamma_{tot} = \Sigma_g^+ \times \Sigma_u^+ \times \Sigma_g^+ \times \Sigma_g^+ = \Sigma_u^+ \text{ forbidden}$$

$$I = 1,\ J \text{ odd}: \quad \Gamma_{tot} = \Sigma_g^+ \times \Sigma_u^+ \times \Sigma_g^+ \times \Sigma_g^- = \Sigma_u^- \text{ allowed}$$

Missing levels (zero statistical weight):
J even for $I = 1$, J odd for $I = 2, 0$

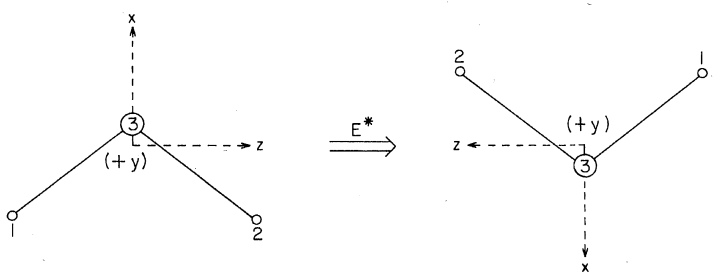
- HD: symmetry group $C_{\infty v}(M)$ (no g/u classification)

$C_{\infty v}(M)$	I	E	E^*	
Σ^+	A_1	1	1	$\Psi(R)$, Y_{Jm} (J even)
Σ^-	A_2	1	-1	Y_{Jm} (J odd)

all states are allowed

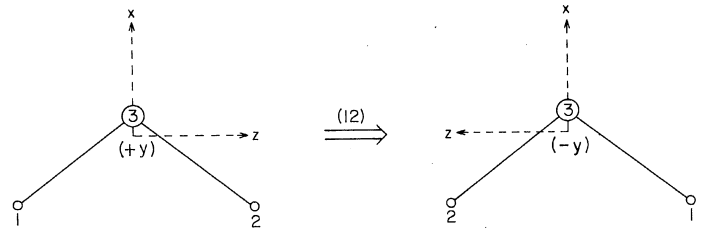
Water

- inversion



$E^*(\theta, \phi, \chi) = (\pi - \theta, \phi + \pi, \pi - \chi)$

- permutation (equivalent x-rotation by π)



$(12)(\theta, \phi, \chi) = (\pi - \theta, \phi + \pi, 2\pi - \chi)$

it follows that $(12)^*(\theta, \phi, \chi) = (\theta, \phi, \chi + \pi)$, i.e. a z-rotation by π

- effect on $|Jkm\rangle$

$$\begin{aligned} (12)|Jkm\rangle &= (-1)^J|J, -k, m\rangle \\ (12)^*|Jkm\rangle &= (-1)^k|J, k\ m\rangle \\ E^*|Jkm\rangle &= (-1)^{J+k}|J, -k, m\rangle \end{aligned}$$

Water: continued

- Wang combinations: $|J, K\pm, m\rangle = \frac{1}{\sqrt{2}}\left(|J, k, m\rangle \pm |J, -k, m\rangle\right)$
- Transformation properties

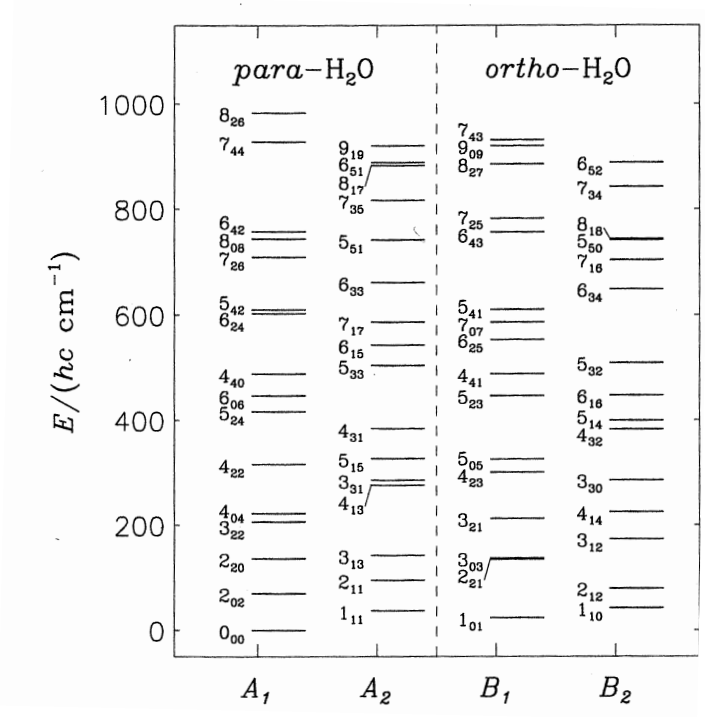
$$
\begin{aligned}
(12)|J, K+, m\rangle &= (-1)^J |J, K+, m\rangle \\
(12)|J, K-, m\rangle &= (-1)^{J+1} |J, K-, m\rangle \\
(12)^*|J, K\pm, m\rangle &= (-1)^K |J, K\pm, m\rangle \\
E^*|J, K+, m\rangle &= (-1)^{J+K} |J, K+, m\rangle \\
E^*|J, K-, m\rangle &= (-1)^{J+K+1} |J, K-, m\rangle
\end{aligned}
$$

- Symmetry (depends on group and axis convention)

$\lvert J, K\pm, m\rangle$	K	$\chi[(12)]$	$\chi[E^*]$	Γ	
				J even	J odd
$\lvert J, K+, m\rangle$	even	$(-1)^J$	$(-1)^J$	A_1	B_1
	odd	$(-1)^J$	$(-1)^{J+1}$	A_2	B_2
$\lvert J, K-, m\rangle$	even	$(-1)^{J+1}$	$(-1)^{J+1}$	B_1	A_1
	odd	$(-1)^{J+1}$	$(-1)^J$	B_2	A_2

Water: rotational symmetry

- The asymmetric top Hamiltonian is diagonalized in the Wang basis
- Degenerate symmetric top states are split into two parity components
- Prolate (K_a) and oblate (K_c) quantum numbers used for labelling
- Symmetry of rotational functions $|JK_aK_c\rangle$:



- symmetric w.r.t. (12):
  A_1, A_2, to be combined with singlet nuclear spin of protons (para)
  anti-symmetric w.r.t. (12):
  B_1, B_2, to be combined with triplet nuclear spin of protons (ortho)
  (just as in H_2)

Water: vibrational symmetry

Symmetry of vibrational functions $|v_1 v_2 v_3\rangle$:

- $\Gamma(\nu_1) = A_1$, $\Gamma(\nu_2) = A_1$, $\Gamma(\nu_3) = B_2$
- Examples:

  $\Gamma(|200\rangle) = A_1 \times A_1 = A_1$,
  $\Gamma(|002\rangle) = B_2 \times B_2 = A_1$,
  $\Gamma(|011\rangle) = A_1 \times B_2 = B_2$,
  $\Gamma(|111\rangle) = A_1 \times A_1 \times B_2 = B_2$, etc.

- Rules for direct products:

  $A \times A = A$, $A \times B = B$, $B \times A = B$, $B \times B = A$,
  “1” $\times$ “1” = “1”, “1” $\times$ “2” = “2”, “2” $\times$ “1” = “2”, “2” $\times$ “2” = “1”

- General expression:

$$\Gamma(|v_1 v_2 v_3\rangle) = A_1^{v_1} \times A_1^{v_2} \times B_2^{v_3} = \begin{cases} A_1 & \text{if } v_3 \text{ even} \\ B_2 & \text{if } v_3 \text{ odd} \end{cases}$$

Water: rovibrational symmetry

- Symmetry: $\Gamma_{rovib} = \Gamma_{rot} \times \Gamma_{vib}$

K_a	K_c	Γ(weight)	
		v_3 even	v_3 odd
e	e	$A_1(1)$	$B_2(3)$
e	o	$B_1(3)$	$A_2(1)$
o	e	$B_2(3)$	$A_1(1)$
o	o	$A_2(1)$	$B_1(3)$

Note: A symmetry states to be combined with singlet nuclear spin B_2, B symmetry states to be combined with triplet nuclear spin A_1

- Dipole transition rules: $\Gamma(\vec{\mu}) = A_2$ (antisymm. w.r.t. E^*)

$\Gamma(\langle\Psi_i|\vec{\mu}|\Psi_f\rangle) = A_1$

Possible transitions: $A_1 \rightleftharpoons A_2$, $B_1 \rightleftharpoons B_2$ with $\Delta J = 0, \pm 1$

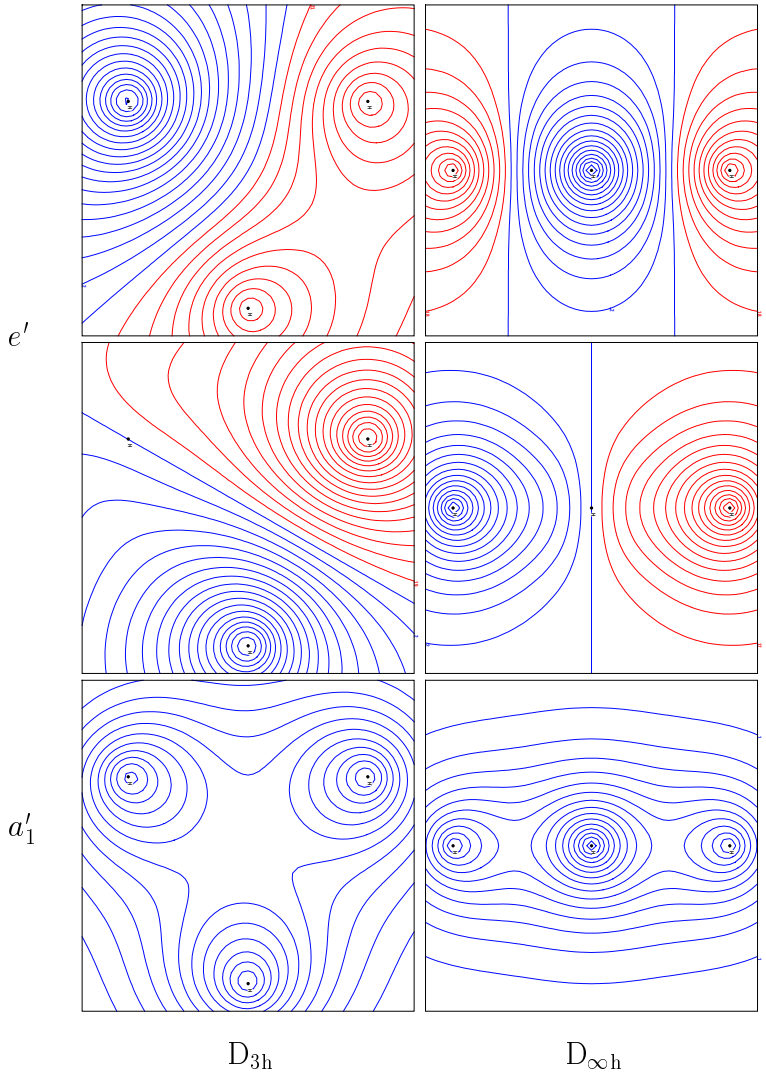
Summary for rigid molecules

Comments:

1. disadvantage of CNPI group: may be very large
2. use subgroup built up by feasible operations: equivalent to point group for rigid molecules
3. exact quantum numbers are J, Γ, n (n is a counting index)
4. spectroscopic (vib, rot) quantum numbers are not exact, but often "good"quantum numbers
5. "spectroscopic" states with same exact symmetry may interact and lead to perturbations in the spectra

Floppy Molecules

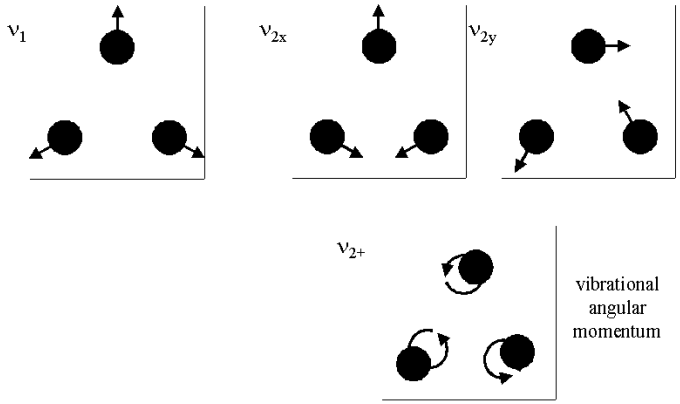
H_3^+: orbitals and electronic states



config.		states	
		D_{3h}	others
σ_g^+	$a_1'^2$	$X\,^1A_1'$	
	$a_1'e'$	$a\,^3E'$	$\rightarrow a\,^3\Sigma_u^+$ & $2\,^3A'$
		$A\,^1E'$	$\rightarrow A\,^1\Sigma^+$ & $3\,^1A'$

H_3^+: vibrational symmetry

- Normal modes: ν_1, $\nu_2^{|\ell|}$, $\ell = -v_2, -v_2+2, \cdots v_2$ (vibrational angular momentum)



- Symmetry classification in $S_3 \times I \equiv D_{3h}(M)$: $\Gamma(\nu_1) = A_1'$, $\Gamma(\nu_2) = E'$
- $v_2 = 1 \rightarrow v_2^{|\ell|} = 1^1\ (E'), \ell = \pm 1$
- Overtones of ν_2: (only symmetric products)

$v_2 = 2$: $\Gamma = E' \times E' = A_1' + [A_2'] + E'$
$A_1' : \frac{1}{2}\{(v_{2x}v_{2y}) + (v_{2y}v_{2x})\} = v_{2x}v_{2y}$
$A_2' : \frac{1}{2}\{(v_{2x}v_{2y}) - (v_{2y}v_{2x})\} = 0$
$E' : \{(v_{2x})^2, (v_{2y})^2\}$

$v_2 = 2 \rightarrow v_2^{|\ell|} = 2^2\ (E'),\ |v_2^{|\ell|} = 2^0\ (A')$
$v_2 = 3 \rightarrow v_2^{|\ell|} = 3^3\ (A_1' + A_2'),\ v_2^{|\ell|} = 3^1\ (E')$

H_3^+: rotational symmetry

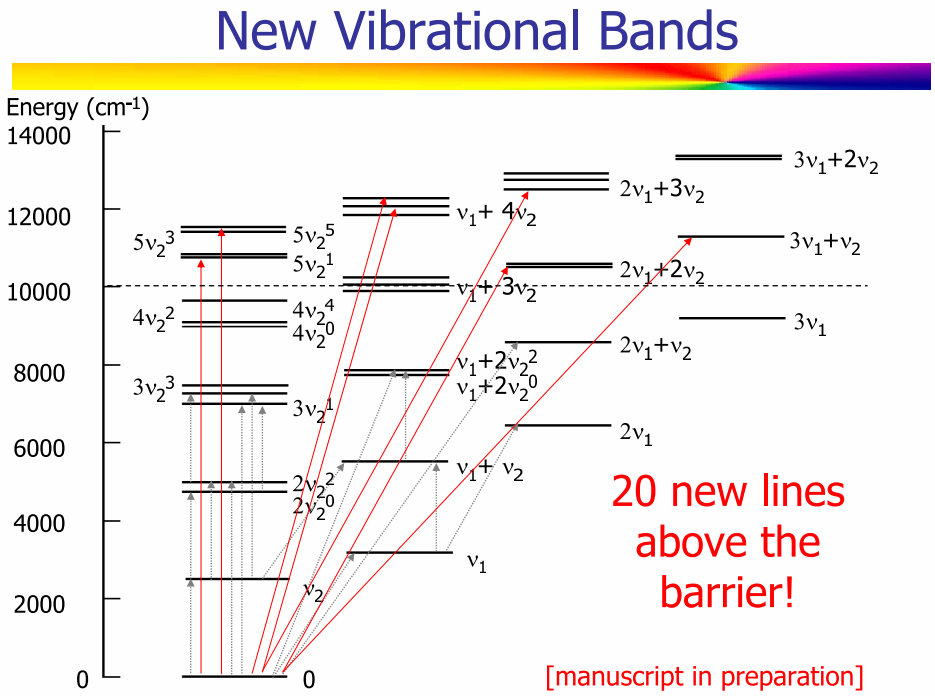
- H_3^+ is an oblate symmetric top
  $|vib, rot\rangle = |v_1, v_2^{|\ell|}\rangle |JK_c\rangle$
- nuclear spin: 3 protons ($i = 1/2$): quartet ($I = 3/2$, A_1'), doublet ($I = 1/2$, E')
- vibrational state $(0, 0^0)$: low J allowed rotational states

J	K_c	Γ_{rovib}	Γ_{tot}	
			$I = 3/2$	$I = 1/2$
0	0	A_1'	-	-
1	1	E''	-	$A_2'' + (A_1'' + E'')$
	0	A_2'	A_2'	-
2	2	E'	-	$A_2' + (\cdots)$
	1	E''	-	$A_2'' + (\cdots)$
	0	A_1'	-	-
3	3	$A_1' + A_2'$	$A_2', -$	-
	2	E'	-	$A_2' + (\cdots)$
	1	E''	-	$A_2'' + (\cdots)$
	0	A_2'	A_2'	-

- vibrational state $(0, 1^1)$: more complicated, ℓ (vibrational angular momentum) to be coupled with molecular rotation
  see, for example, Mol. Phys. **101**, 175 (2003)

floppy H_3^+: large amplitude motion

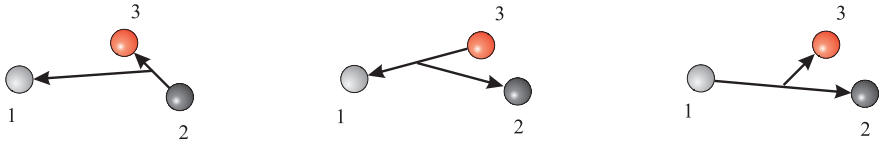
from J. Gottfried, Oka group (Chicago): J. Chem. Phys. **118**, 10890 (2003)



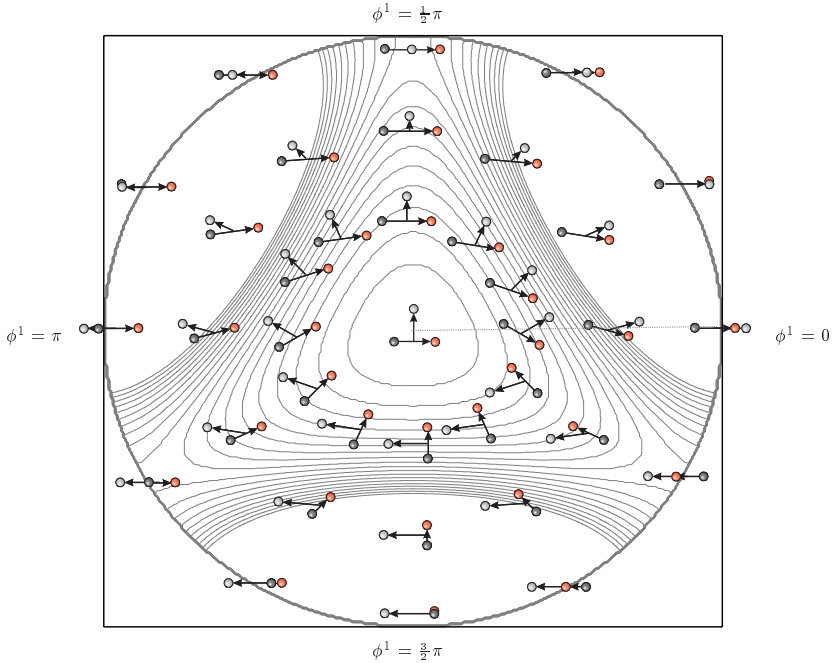
- so far we have classified spectroscopic quantum numbers $(v_1, v_2^{|\ell|})$ in exact symmetry group
- "spectroscopic" states with same symmetry may "perturb" each other
- above "barrier to linearity" spectroscopic quantum numbers begin to fail
- J and exact CNPI quantum numbers hold: J, Γ, n, with n a counting index
- compute rovibrational states using coordinates not derived from potential minimum: hyperspherical coordinates

floppy H_3^+: coordinate systems for triatomics

- Jacobi coordinates: $\mathbf{r}_k, \mathbf{R}_k$



- Hyperspherical coordinates:
  internal coordinates: ρ, θ, ϕ , Euler angles: ϕ^E, θ^E, χ^E



- Hyperpsherical harmonics, $\Psi(\theta, \phi, \phi^E, \theta^E, \chi^E)$ may be symmetrized within $S_3 \times I$ and allow exact computations

Non-rigid Molecules: Single Potential Energy Surface

Non-rigid Ammonia

- $3N-6=6$ vibrational modes: in the C_{3v} point group $\Gamma_{vib} = 2A_1 + 2E$ two versions, tunneling feasible: full CNPI group $S_3 \times I$, molecular symmetry group $D_{3h}(M)$

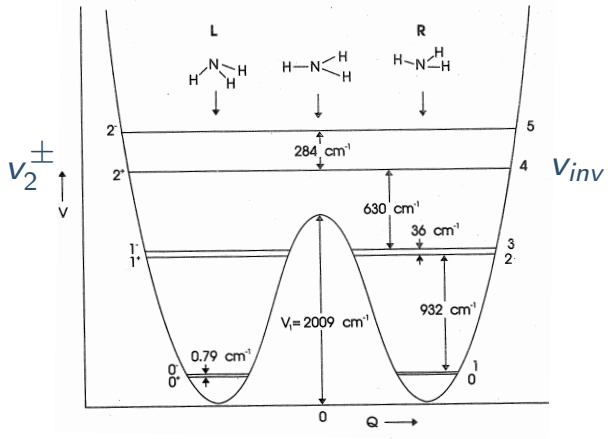
mode	$C_{3v}(M)$ designation	Γ	mode	$D_{3h}(M)$ designation	Γ
ν_1	symmetric stretch	A_1			A_1'
ν_2	bending	A_1	ν_{inv}	inversion	A_2''
ν_3		E			E'
ν_4		E			E'

- character table

$S_3 \times I$		E	{(123), (132)}	{(12), (23), (13)}	E^*	{(123)*, (132)*}	{(12)*, (23)*, (13)*}
$D_{3h}(M)$	$C_{3v}(M)$	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_1'	A_1	1	1	1	1	1	1
A_2'	A_2	1	1	-1	1	1	-1
E'	E	2	-1	0	2	-1	0
A_1''		1	1	1	-1	-1	-1
A_2''		1	1	-1	-1	-1	1
E''		2	-1	0	-2	1	0

Non-rigid Ammonia: continued

- bending levels v_2 split into $v_2^{\pm} \equiv v_{inv}$



- nuclear spin functions as in H_3^+: $I = 3/2$ ($\Gamma = A_1'$), $I = 1/2$ ($\Gamma = E'$)

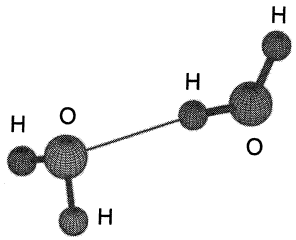
Γ_{ns}	Γ_{rovib}	Γ_{tot}
A_1'	A_2'	$A_1' \times A_2' = A_2'$
	A_2''	$A_1' \times A_2'' = A_2''$
E'	E'	$E' \times E' = A_2'(+A_1' + E')$
	E''	$E' \times E'' = A_2''(+A_1'' + E'')$

- missing levels: v_{inv}^{2n}, $\Gamma = (A_2'' \times A_2'')^n = A_1'$
- also missing: overtones with A_1' symmetry, for example $|v_1, v_2, v_3, v_4\rangle = |0, 0, 2, 0\rangle$
  $\Gamma(|0, 0, 2, 0\rangle) = A_1 \times A_1 \times E^2 \times A_1 = A_1 + E \rightarrow (A_1' + A_2'') + (E' + E'')$
- reverse correlation table with proton statistical weights

$C_{3v}(M)$	$A_1(4)$	$A_2(4)$	$E(4)$
$D_{3h}(M)$	$A_1'(0) + A_2''(4)$	$A_2'(4) + A_1''(0)$	$E'(2) + E''(2)$

Water dimer

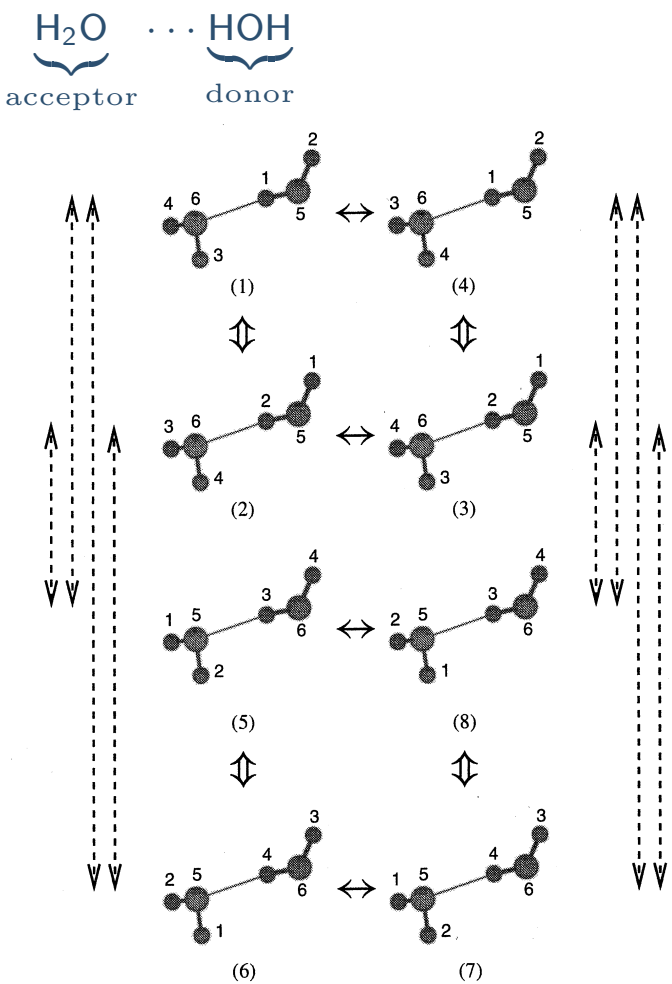
- Order of CNPI group $= 4! \times 2! \times 2 = 96$, order of the C_s point group of rigid dimer $= 2$, hence $96/2 = 48$ versions
- Donor-acceptor complex: $\underbrace{H_2O}_{\text{acceptor}} \cdots \underbrace{HOH}_{\text{donor}}$



- feasible operations:
  1. exchange of acceptor H atoms by rotation, "acceptor switching", $\Delta E \approx 200\text{cm}^{-1}$
  2. exchange of donor H atom that makes hydrogen bond, "bifurcation", $\Delta E \approx 650\text{cm}^{-1}$
  3. exchange of donor and acceptor roles, "donor-acceptor interchange", $\Delta E \approx 300\text{cm}^{-1}$

  hence $2 \times 2 \times 2 = 8$ connected versions
- 6 sets of 8 versions, passing between sets involves bond breaking. Not feasible

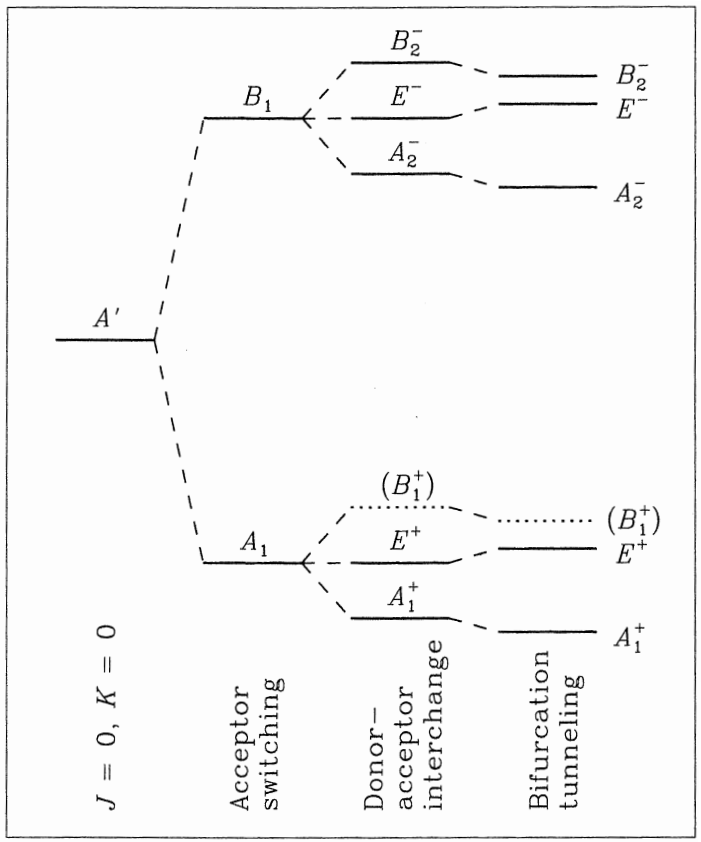
Water dimer: continued



- acceptor switching: for example (1) $\rightleftharpoons$ (4)
- donor-acceptor interchange: for example (1) $\rightleftharpoons$ (5)
- bifurcation (donor tunnelling): for example (1) $\rightleftharpoons$ (2)

Water dimer: continued

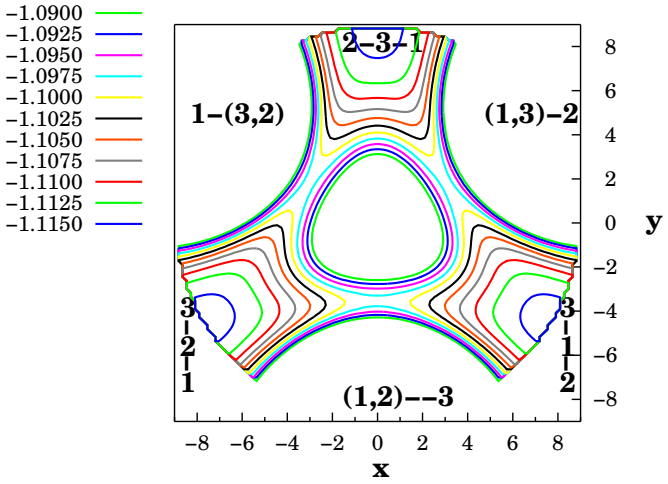
each hypothetical rigid dimer state is split into eight states, observable



1. acceptor switching, $\Delta E \approx 200\text{cm}^{-1}$
2. donor-acceptor interchange, $\Delta E \approx 300\text{cm}^{-1}$
3. bifurcation (donor switching), $\Delta E \approx 650\text{cm}^{-1}$
   can be surpassed by donor-acceptor interchanges (1) $\rightleftharpoons$ (5) $\rightleftharpoons$ (2)

Triplet H_3^+: delocalized ro-vibrational states

H_3^+: Phys. Rev. Lett. **86**, 1183 (2001) ; J. Mol. Spectrosc. **221**, 163 (2003)
H_2D^+: J. Phys. Chem. A **110**, 110 (2006)
D_3^+: J. Chem Phys. **128**, 054301 (2008)



$$|\Psi_A^{\pm}\rangle \sim |\Psi_I^{\pm}\rangle + |\Psi_{II}^{\pm}\rangle + |\Psi_{III}^{\pm}\rangle$$
$$|\Psi_{E,\xi}^{\pm}\rangle \sim |\Psi_I^{\pm}\rangle + \omega\,|\Psi_{II}^{\pm}\rangle + \omega^2|\Psi_{III}^{\pm}\rangle$$
$$|\Psi_{E,\eta}^{\pm}\rangle \sim |\Psi_I^{\pm}\rangle + \omega^2|\Psi_{II}^{\pm}\rangle + \omega\,|\Psi_{III}^{\pm}\rangle \quad ; \quad \omega = e^{\frac{2\pi i}{3}}$$

$$|\Psi^{\pm}\rangle = \frac{1}{\sqrt{2}}|v_1 v_2^{|\ell|} v_3\rangle\ (|N\ell\rangle \pm |N-\ell\rangle)$$

Symmetry of localized ro-vibrational states

- linear molecule, $D_{\infty h}(M)$
- normal modes:
  ν_1 (symmetric stretch), ν_2 (bending), ν_3 (anti-symmetric stretch)
- symmetry classification in $S_3 \times I$ and $D_{\infty h}(M)$:
  $\Gamma(\nu_1) = A_1', (\Sigma_g^+)$, $\Gamma(\nu_2) = E', (\Pi_u)$, (does not exist purely vibrational),
  $\Gamma(\nu_3) = A_2', (\Sigma_u^+)$
  vibrational angular momentum of ν_2: $\ell = -v_2, -v_2+2, \cdots v_2$
- rovibrational states:
  $\Psi^{\pm} = |v_1, v_2^{|\ell|}, v_3\rangle \frac{1}{\sqrt{2}} (|N, \ell, m\rangle \pm |N, -\ell, m\rangle)$
  $\mathbf{N} = \mathbf{J} - \mathbf{S}$, ℓ is its a-axis projection
- electronic symmetry: Σ_u^+
- rovibronic symmetry of rigid triplet H_3^+

mode	Γ_{vib}		Γ_{rovib}		$\Gamma_{rovibr} = \Gamma_{rovib} \times \Gamma_{el}$	
	$S_3 \times I$	$D_{\infty h}$	N even	N odd	N even	N odd
$(1,0,0)$	A_1'	Σ_g^+	Σ_g^+	Σ_g^-	Σ_u^+	Σ_u^-
$(0,1^1,0)+$	E'	"Π_u"	Σ_u^-	Σ_u^+	Σ_g^-	Σ_g^+
$(0,1^1,0)-$			Σ_u^+	Σ_u^-	Σ_g^-	Σ_g^+
$(0,0,1$	A_2'	Σ_u^+	Σ_u^+	Σ_u^-	Σ_g^-	Σ_g^+

Symmetry of delocalized ro-vibrational states

- Tunnelling triplet H_3^+: all CNPI, $S_3 \times I$, operations feasible, molecular symmetry group is $D_{3h}(M)$
- Reverse correlation table

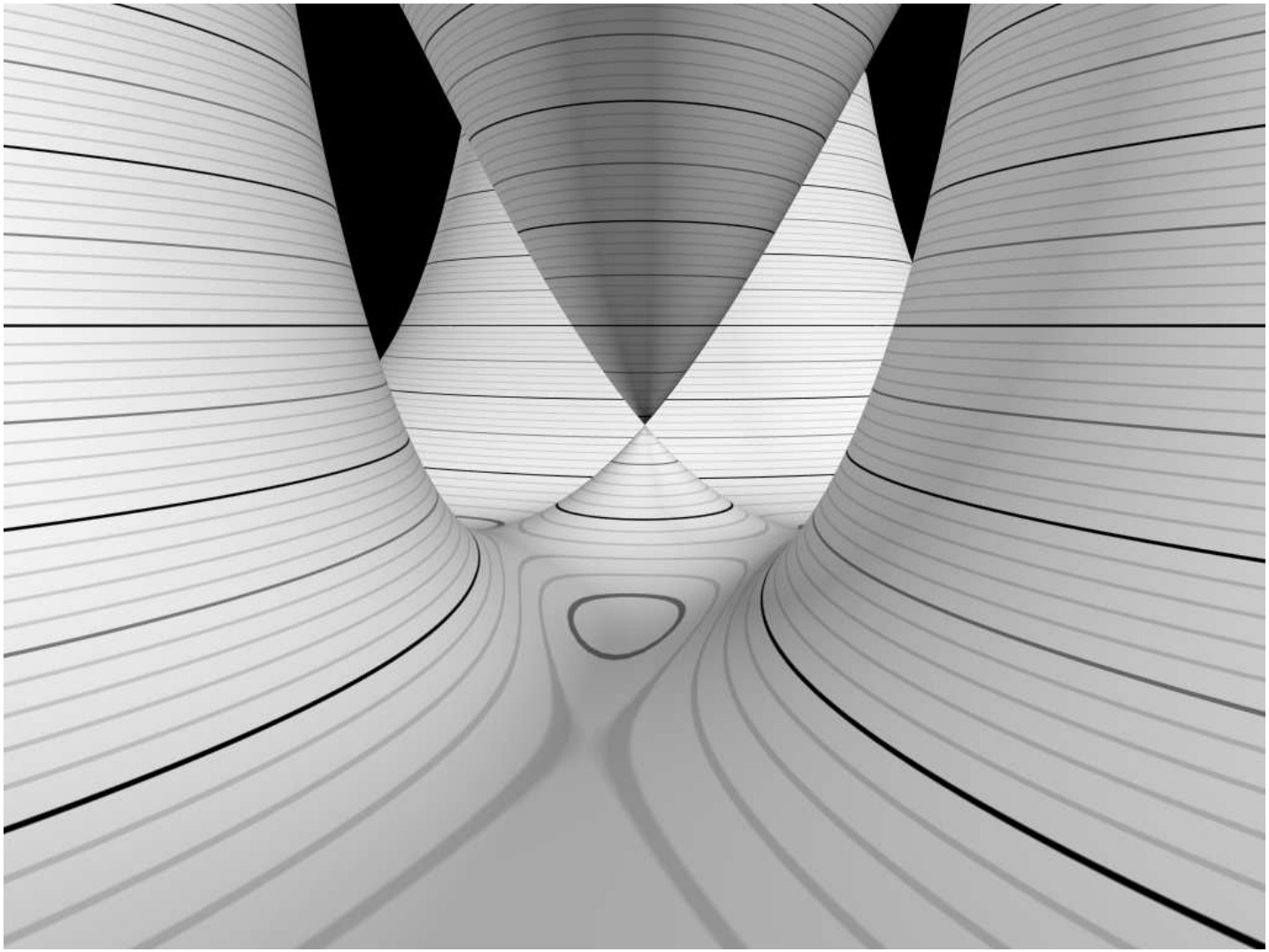
$D_{\infty h}(M)$	$D_{3h}(M)$	$D_{\infty h}(M)$	$D_{3h}(M)$
$\Sigma_g^+(2)$	$A_1'(0) + E'(2)$	$\Sigma_u^+(6)$	$A_2'(4) + E'(2)$
$\Sigma_g^-(6)$	$A_2''(4) + E''(2)$	$\Sigma_u^-(2)$	$A_1''(0) + E''(2)$

- Nuclear spin effect:
  quartet $I = 3/2$, A_1', combines with A_2' and A_2'' rovibronic symmetry
  doublet $I = 1/2$, E', combines with E' and E'' rovibronic symmetry
- Rovibronic symmetry of tunneling triplet H_3^+

state	Γ_{rovib}		$\Gamma_{rovibr} = \Gamma_{rovib} \times A_2'$	
	N even	N odd	N even	N odd
$(1,0,0)$	$A_1' + E'$	$A_2'' + E''$	$A_2' + E'$	$A_1'' + E''$
$(0,1^1,0)+$	$A_1'' + E''$	$A_2' + E'$	$A_2'' + E''$	$A_1' + E'$
$(0,1^1,0)-$	$A_2' + E'$	$A_1'' + E''$	$A_1' + E'$	$A_2'' + E''$
$(0,0,1)$	$A_2' + E'$	$A_1'' + E''$	$A_1' + E'$	$A_2'' + E''$

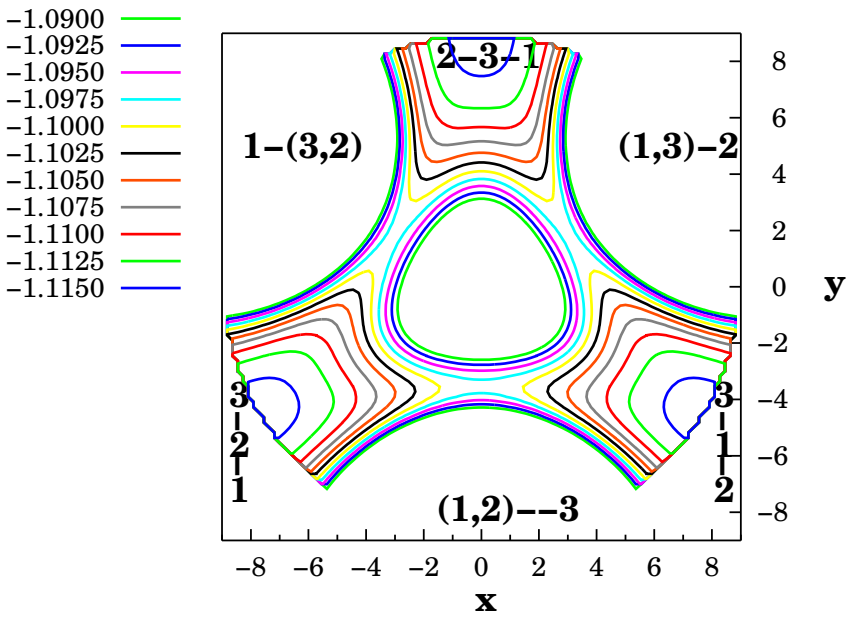
Non-rigid Molecules: Multiple Potential Energy Surfaces

Lowest triplet states of H_3^+: view of surfaces



H_3^+: Characterisation of the $^3E'$ surface

- upper sheet:
  dissociation channel: $2H\,(^2S)\ +\ H^+$, $-1.0000\,E_h$
  energy minimum: (D_{3h}): $-1.034590\,E_h$, $r = 3.610\,a_0$
- lower sheet:
  dissociation channel: $H_2^+\,(^2\Sigma_g^+)\ +\ H\,(^2S)$, $-1.102634\,E_h$
  energy minimum: $(D_{\infty h})$: $-1.116106\,E_h$, $r = 2.454\,a_0$

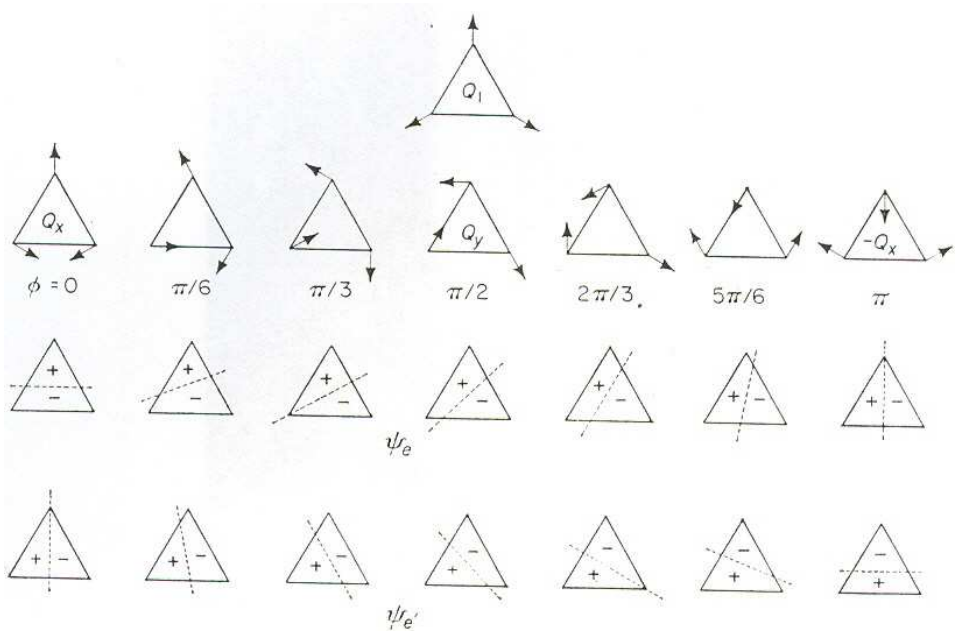


depth: $2947\,cm^{-1}$
barrier height: $2598\,cm^{-1}$

van der Waals complex

Geometrical phase

Longuet-Higgins, *Adv. Spectrosc.* **2**, 429 (1961)



- adiabatic electronic wave functions φ:

$$\oint_0^{2\pi} d\phi\, \varphi(Q_1, Q_2, \phi; \mathbf{r}) = \pi$$

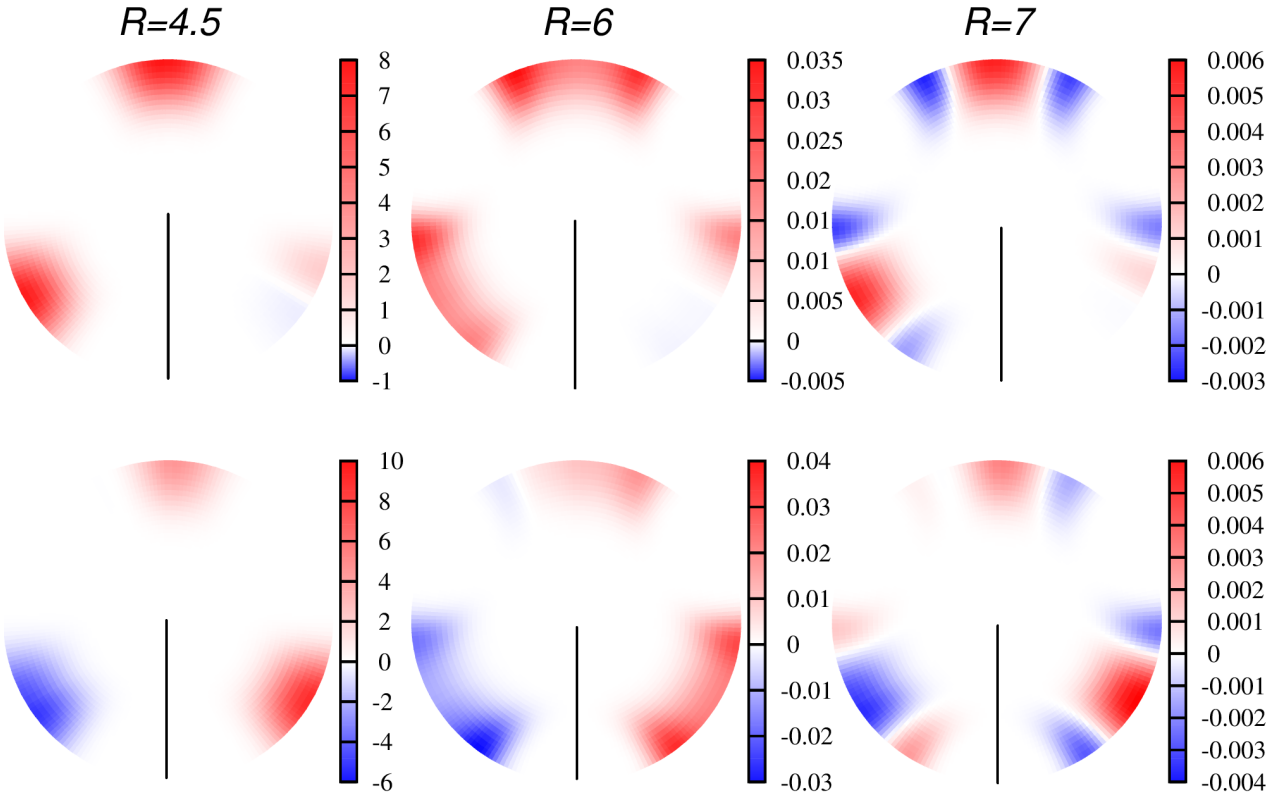
- boundary conditions for rovibrational wave functions Θ:

$$\Psi(Q_1, Q_2, \phi = 0) = -\Psi(Q_1, Q_2, \phi = 2\pi)$$

Triplet H_3^+: Including geometrical phase

A. Alijah, V. Kokoouline, Chem. Phys. **460**, 43 (2015)

Lowest vibrational A_1' state in diabatic representation, upper and lower components
Plot in hyperspherical coordinates



1-state (adiabatic) and 2-state (diabatic) calculations

	1-state calculation						2-state calculation					
(v_1, v_2^ℓ, v_3)	i	A_1'	i	A_2'	i	E'	i	A_1'	i	A_2'	i	E'
$(0, 0^0, 0)$	0	0.00			0	0.00	0	0.00			0	1.04
$(0, 0^0, 1)$			0	738.49	1	738.49			0	738.91	1	738.86
$(1, 0^0, 0)$	1	975.05			2	975.07	1	975.34			2	976.08
$(0, 2^0, 0)$	2	1273.73			3	1273.80	2	1274.13			3	1274.98
$(1, 0^0, 1)$			1	1474.51	4	1474.49			1	1475.24	4	1475.19
$(0, 0^0, 2)$	3	1573.69			5	1573.87	3	1574.17			5	1574.92
$(0, 2^0, 1)$			2	1730.35	6	1728.45			2	1730.77	6	1728.84
$(2, 0^0, 0)$	4	1922.54			7	1923.12	4	1922.94			7	1923.80
$(1, 2^0, 0)$	5	1940.32	3		8	1951.07	5	1940.88	3		8	1951.76
$(0, 0^0, 3)$			4	1972.74	9	1970.85			4	1974.17	9	1972.24
$(1, 0^0, 2)$	6	2158.70			10	2137.06	6	2159.79			10	2137.86
$(0, 4^0, 0)$	7	2188.46			11	2166.46	7	2189.69			11	2167.77
$(2, 0^0, 1)$			5	2204.86	12	2251.08			5	2205.80	12	2253.44
$(1, 2^0, 1)$			6	2271.04	13	2259.41			6	2273.62	13	2261.07
$(0, 2^0, 2)$	8	2308.68			14	2308.76	8	2311.55			14	2338.04
$(3, 0^0, 0)$	9	2340.10			15	2335.12	9	2341.46			15	2358.48
			7	2402.71					7	2407.11	16	2363.82
							10	2374.13	7		16	2363.82
							11	2403.16			17	2396.43
							12	2407.11			18	2413.19
							13	2423.89			19	2417.62
											20	2429.16

Symmetry properties in diabatic and diabatic picture

1. adiabatic (one-state) representation: electronic state $^3\Sigma_u^+$, symmetry A_2' in CNPI symmetry of vibrational states
   - ortho nuclear spin
     $\Gamma_{el} \times \Gamma_{ns} = A_2' \times A_1' = A_2'$, vibrational state must have A_1' symmetry
     $\Gamma_{tot} = \Gamma_{el} \times \Gamma_{ns} \times \Gamma_{vib} = A_2' \times A_1' \times A_1' = A_2'$
   - para nuclear spin
     $\Gamma_{el} \times \Gamma_{ns} = A_2' \times E' = E'$, vibrational state must have E' symmetry
     $\Gamma_{tot} = \Gamma_{el} \times \Gamma_{ns} \times \Gamma_{vib} = A_2' \times E' \times E' = A_2'(+A_1' + E')$
2. diabatic (two-state) representation: electronic state $^3E'$, symmetry E' in CNPI symmetry of vibrational states
   - ortho nuclear spin
     $\Gamma_{el} \times \Gamma_{ns} = E' \times A_1' = E'$, vibrational state must have E' symmetry
     $\Gamma_{tot} = \Gamma_{el} \times \Gamma_{ns} \times \Gamma_{vib} = E' \times A_1' \times E' = A_2'(+A_1' + E')$
   - para nuclear spin
     $\Gamma_{el} \times \Gamma_{ns} = E' \times E' = A_1' + A_2' + E'$, vibrational state may have any symmetry

$$\Gamma_{tot} = \Gamma_{el} \times \Gamma_{ns} \times \Gamma_{vib} = \begin{cases} E' \times E' \times A_1' & = & A_2'\left(+A_1' + E'\right) \\ E' \times E' \times A_2' & = & A_2'\left(+A_1' + E'\right) \\ E' \times E' \times E' & = & A_2'\left(+A_1' + 3E'\right) \end{cases}$$

3. statistical weights of vibrational states

Γ_{vib}	$W(1\,st.)$	$W(2\,st.)$	
A_1'	4	2	
A_2'	0	2	may be helpful to detect geometrical phase
E'	2	6	

Summary and Literature

Summary

- Point group symmetry is approximate and can only be used for rigid molecules
- The CNPI, complete nuclear permutation inversion group, introduced by Longuet-Higgins, gives the exact symmetry
- CNPI may be very large, unfeasible operations are removed to obtain the molecular symmetry (MS) group.
  Example: ethene, order of CNPI group $= 2! \times 4! \times 2 = 96$. The MS group ($D_{2h}(M)$ has order 8.
- CNPI describes rigid molecules, in this case the CNPI group is isomorphic with the point group.
  Example: water, order of CNPI group $= 2! \times 1 \times 2 = 4$, order of point group C_{2v} is 4. The MS group is $C_{2v}(M)$.
- CNPI describes floppy molecules that strongly depart from equilibrum configuration.
  Example: singlet H_3^+, triangle at equilibrium, but linear configurations accessible at high energy. Breakdown of point group classification of vibrational states.
- CNPI describes non-rigid molecules that have more than one minimum on the potential energy surface.
  Example: ammonia, weakly bound complexes such as the water dimer
- CNPI describes non-rigid molecules that cannot be treated within the adiabatic approximation of a single electronic state. The participating electronic states may have different symmetry.
  Example: triplet H_3^+ which shows a Jahn-Teller effect

Literature

1. H. C. Longuet-Higgins, The Symmetry Groups of Non-rigid Molecules, Mol. Phys. **6**, 445-460 (1963)
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5. P. R. Bunker & P. Jensen, Molecular Symmetry and Spectroscopy, NRC Research Press, Ottawa (2006) printed on demand
6. P. R. Bunker & P. Jensen, Fundamentals of Molecular Symmetry, Institue of Physics, Bristol (2005) (kind of concise version of the above)
7. P. Bernath, Spectra of Atoms and Molecules, Oxford University Press (2016), third edition (excellent general reference on high resolution spectroscopy, but not CNPI)

Illustrations used in this presentation are taken from the above references