Part III Symmetry and Bonding

Chapter 7 Normal Modes (简正模)

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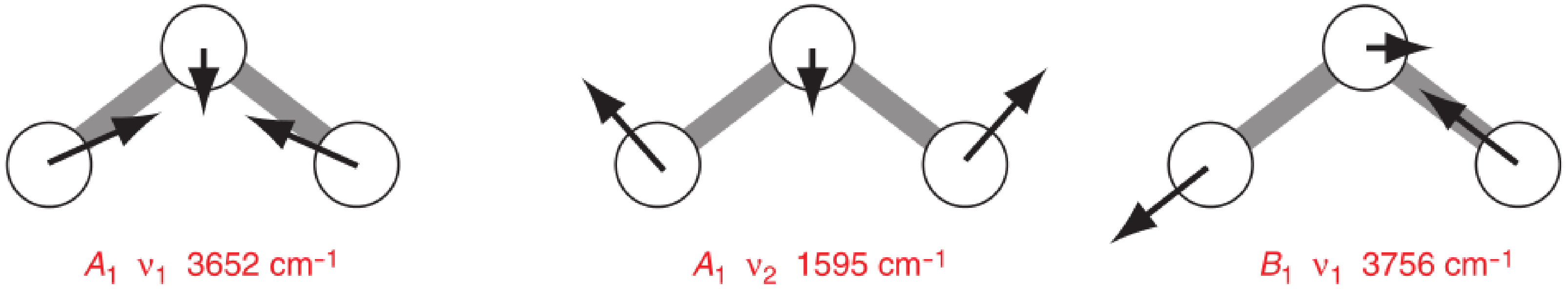
7. Normal modes

- This section is devoted to *using symmetry considerations to help understand the vibrations of molecules* and *spectra that arise due to transitions between the associated energy levels*.

- The vibrations of a molecule: *a finite number of special vibrations called* ***normal modes***.

  e.g., three normal modes of **H_2O** and their fundamental transitions



- *Each normal mode has a set of energy levels*, and the transitions between these levels give rise to infra-red spectra of the type.

7. Normal modes

Here we will show ideas about

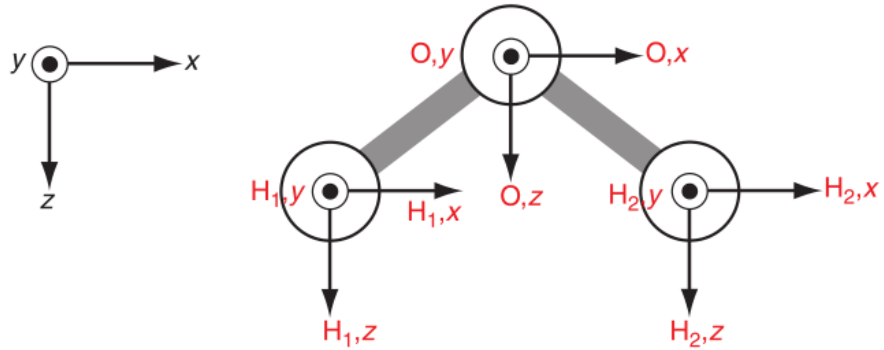
i) how to classify normal modes according to symmetry,

ii) how to predict which modes give rise to ***infra-red spectra*** and ***vibrational Raman scattering***.

- We will use the symmetry arguments to explain the occurrence of *more complex features* of infra-red spectra, such as ***overtones*** and ***combination bands***.

7.1 Normal mode analysis

- **Vibrations involve the physical displacement of atoms from their equilibrium positions**.
- ***Example***, H_2O (C_{2v}), basis (x, y and z displacement vectors on each atom).



Basis (*9* vectors) → a 9-D rep.!

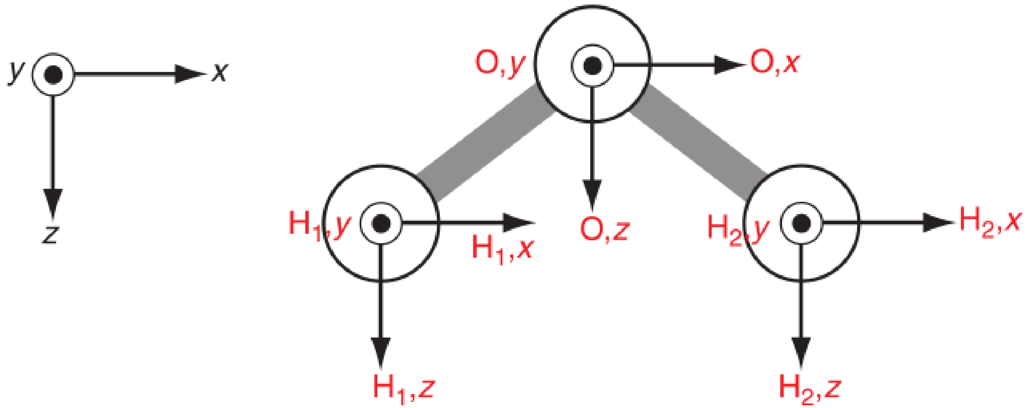
C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
A_1	1	1	1	1	z		$x^2; y^2; z^2$
A_2	1	1	−1	−1		R_z	xy
B_1	1	−1	1	−1	x	R_y	xz
B_2	1	−1	−1	1	y	R_x	yz

- To simplify the problem, we first separate the displacement vectors into groups which are *mapped onto one another* by the operations of the point group.

与之前对原子轨道进行对称性分类相似！

- O,x ~ ***?*** , O,y ~ ***?*** , O,z ~ ***?***
- Other groups of vectors: (H_1,x, H_2,x); (H_1,z, H_2,z); (H_1,y, H_2,y)

7.1 Normal mode analysis



C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
A_1	1	1	1	1	z		$x^2; y^2; z^2$
A_2	1	1	−1	−1		R_z	xy
B_1	1	−1	1	−1	x	R_y	xz
B_2	1	−1	−1	1	y	R_x	yz
$(H_1,x,\ H_2,x)$ Γ_1	2	0	2	0	$= A_1 \oplus B_1$		
$(H_1,y,\ H_2,y)$ Γ_2	2	0	-2	0	$= A_2 \oplus B_2$		

Vector(s)	*IR*
O,x	B_1 (from the table)
O,y	B_2
O,z	A_1
$(H_1,x,\ H_2,x)$	$A_1 \oplus B_1$
$(H_1,z,\ H_2,z)$	$A_1 \oplus B_1$
$(H_1,y,\ H_2,y)$	$A_2 \oplus B_2$
Total	$3A_1 \oplus 3B_1 \oplus A_2 \oplus 2B_2$

SALC

Full set (3N)	$3A_1 \oplus 3B_1 \oplus A_2 \oplus 2B_2$
Translations (x,y,z)	B_1, B_2, A_1 (from the table)
Rotations (R_x,R_y,R_z)	B_2, B_1, A_2 (from the table)
Vibrations (3N-6)	$2A_1 \oplus B_1$

- *3N-6* normal modes for non-linear molecules.

7.1.1 Form of the normal modes

Ex.32

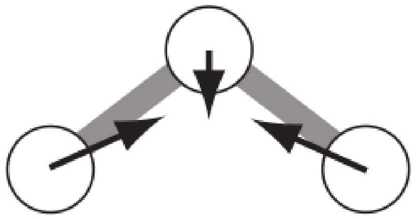
- ***In a normal mode, the centre of mass has to remain fixed***. Accordingly, the atoms have to move in ways which balance one another out and in addition the amount by which each atom moves will be affected by its mass. (lower mass → larger displacement)
- However, it is rather ***tedious*** to *derive the form of the normal modes* in a basis of ***(x,y,z)*** displacements even for simple molecules!
- Alternatively, use ***internal displacements*** to derive the forms of normal modes—***two rules***

  (i) there is 1 stretching vibration per bond

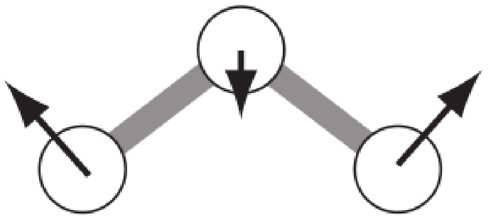
  (ii) we must treat symmetry-related atoms together

***Internal coordinates*(内坐标)**:
bond lengths, bond angles,
dihedral angles

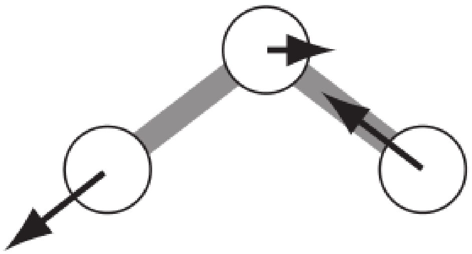
- H_2O has **two** *stretching* modes and **one** *angle bending* mode.



A_1 ν_1 3652 cm^{-1}



A_1 ν_2 1595 cm^{-1}



B_1 ν_3 3756 cm^{-1}

7.1.1 Form of the normal modes

Using internal displacements (coordinates)!

Example: H_2O

- First use the two O-H bond stretches as a basis:

The ***A_1*** stretching (*z*-like): $(\vec{r}_1 + \vec{r}_2)$

~Symmetric (in-phase) stretching

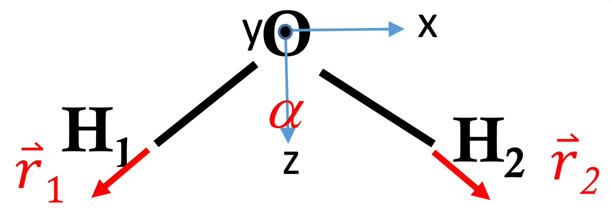
The ***B_1*** stretching (*x*-like): $(-\vec{r}_1 + \vec{r}_2)$

~anti-symmetric (out-of-phase) stretching

- use the H-O-H angle ***α*** bending as a basis.

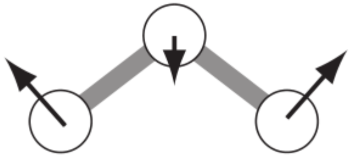
The angle bending transforms as ***A_1*** *IR*.

The ***A_1*** bending & symmetric stretching mix!

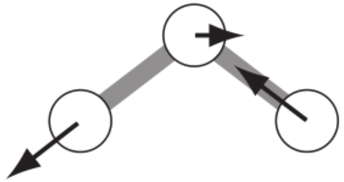


C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
A_1	1	1	1	1	z		$x^2; y^2; z^2$
A_2	1	1	−1	−1		R_z	xy
B_1	1	−1	1	−1	x	R_y	xz
B_2	1	−1	−1	1	y	R_x	yz
$\Gamma^{(2r)}$	2	0	2	0	$= A_1 \oplus B_1$		
$\Gamma^{(\alpha)}$	1	1	1	1	$= A_1$		

A_1 ν_1 3652 cm^{-1}



A_1 ν_2 1595 cm^{-1}



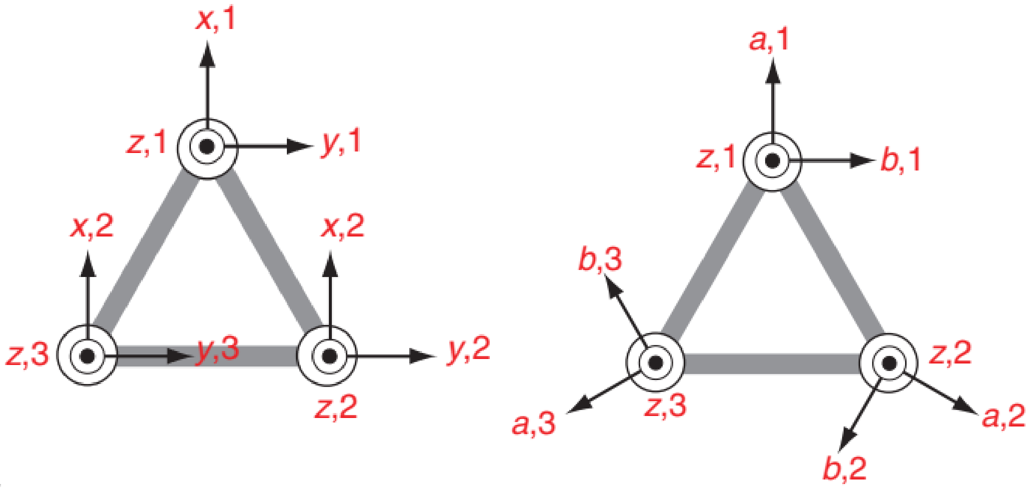
B_1 ν_1 3756 cm^{-1}

Neither purely bending nor stretching.

7.1.2 Normal modes of H_3^+

- Example: *intersteller molecule* H_3^+ (point group D_{3h}).

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$			
A_1'	1	1	1	1	1	1			$x^2+y^2; z^2$
A_2'	1	1	−1	1	1	−1		R_z	
E'	2	−1	0	2	−1	0	(x, y)		$(x^2-y^2, 2xy)$
A_1''	1	1	1	−1	−1	−1			
A_2''	1	1	−1	−1	−1	1	z		
E''	2	−1	0	−2	1	0		(R_x, R_y)	(xz, yz)



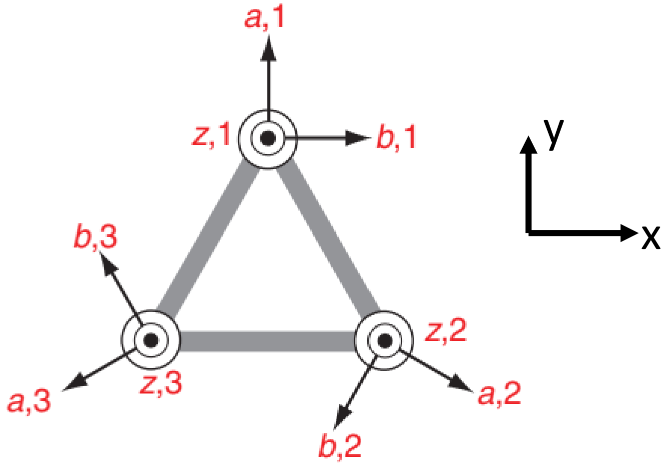
- In ***a general axis system***: *(z,1 z,2 z,3), (x,1 x,2 x,3, y,1 y,2 y,3)* → ***a 6-D rep.!***

- In ***a local axis system:*** *(z,1 z,2 z,3)*, *(a,1 a,2 a,3)*, and *(b,1 b,2 b,3)* → ***all 3-D reps.!***

Radial displacements

Tangential displacements

7.1.2 Normal modes of H_3^+



D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$			
A_1'	1	1	1	1	1	1			$x^2+y^2; z^2$
A_2'	1	1	−1	1	1	−1		R_z	
E'	2	−1	0	2	−1	0	(x, y)		$(x^2-y^2, 2xy)$
A_1''	1	1	1	−1	−1	−1			
A_2''	1	1	−1	−1	−1	1	z		
E''	2	−1	0	−2	1	0		(R_x, R_y)	(xz, yz)

(z,1 z,2 z,3)	(3	0	-1	-3	0	1)	$A_2''\oplus E''$
(a,1 a,2 a,3)	(3	0	1	3	0	1)	$A_1'\oplus E'$
(b,1 b,2 b,3)	(3	0	-1	3	0	-1)	$A_2'\oplus E'$
Total							$A_1'\oplus A_2'\oplus 2E'\oplus A_2''\oplus E''$
–translations (x,y,z)							$E'\oplus A_2''$
–rotations (R_x,R_y,R_z)							$E''\oplus A_2'$
Vibrations							$A_1'\oplus E'$

E'_y $2b_1-b_2-b_3$

E'_x b_2-b_3

Q: How does its three normal modes look like?

1st approx.:

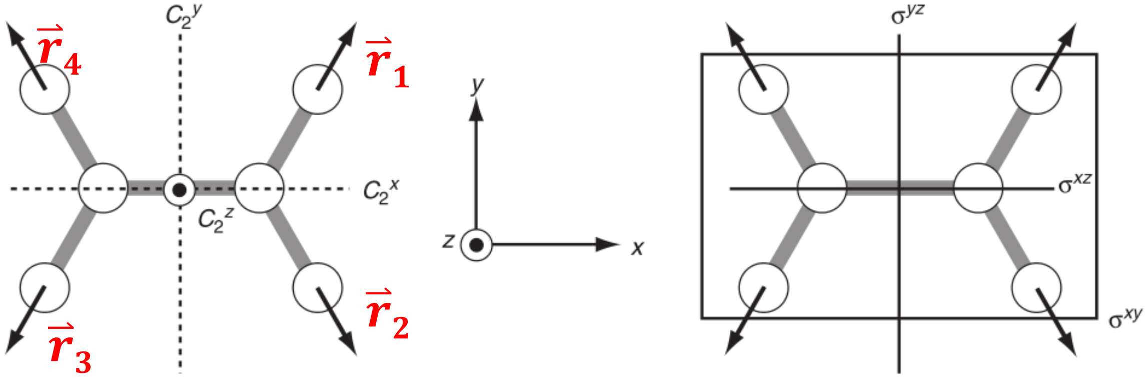
A_1': $a_1+a_2+a_3$

E'_y $2a_1-a_2-a_3$

E'_x a_2-a_3

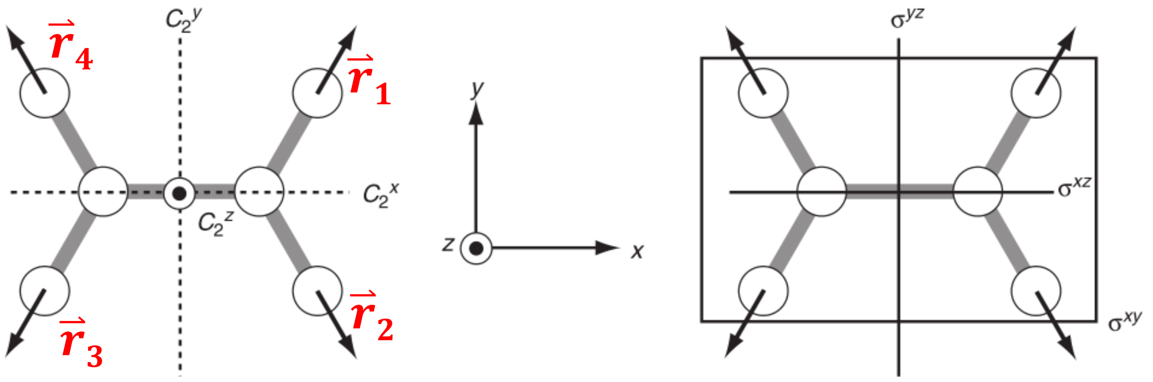
7.1.3 X–H stretching analysis

- On account of the low mass of the hydrogen atom, it is often the case that particular normal modes are ***dominated*** by ***X–H stretching motions***.
- Therefore it is practically useful to make a symmetry analysis ***using a basis consisting of only X–H stretches***, but not a general set of *(x,y,z)* displacements on each atom.
- Of course, such an approach will only reveal the ***symmetries of those normal modes involving the X–H stretches.***
- Example: the *C–H stretches of ethene* (point group D_{2h}).

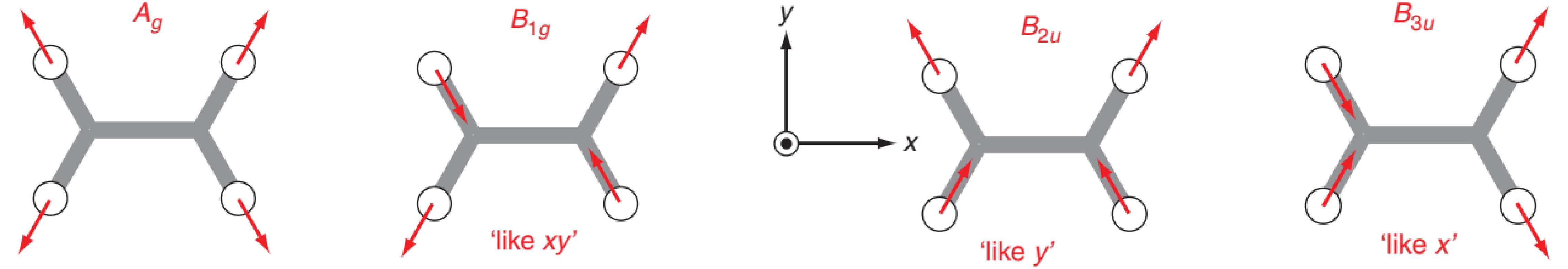


7.1.3 X–H stretching analysis

D_{2h}	E	C_2^z	C_2^y	C_2^x	i	σ^{xy}	σ^{xz}	σ^{yz}		
A_g	1	1	1	1	1	1	1	1		$x^2; y^2; z^2$
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	
Γ	4	0	0	0	0	4	0	0		



$\rightarrow \Gamma = A_g \oplus B_{1g} \oplus B_{2u} \oplus B_{3u}$



A_g, Totally symmetric

$(\vec{r}_1+\vec{r}_2+\vec{r}_3+\vec{r}_4)$

B_{1g}, like xy

$(\vec{r}_1-\vec{r}_2+\vec{r}_3-\vec{r}_4)$

B_{2u}, like y

$(\vec{r}_1-\vec{r}_2-\vec{r}_3+\vec{r}_4)$

B_{3u}, like x

$(\vec{r}_1+\vec{r}_2-\vec{r}_3-\vec{r}_4)$

- These pictures arising from combination of internal displacements are ***only approximations*** to the real normal modes. (In reality, the carbon atoms would also need to move by small amounts in order to ensure that the centre of mass remain fixed.)
- In the next two sections, we will see how ***a symmetry analysis*** helps us to determine whether or not a particular normal mode will give rise to absorptions in the infra-red or vibrational Raman scattering (i.e. whether or not a mode is '*infra-red* or *Raman active*').
- We will start out by looking at ***the symmetry of the harmonic oscillator wavefunctions***, which are a first approximation to the vibrational wavefunctions of the molecule, and then move on to discuss the selection rules for transitions between them.

前一节回顾：简正(振动)模的对称性分析及其形式

◆ 多原子分子的振动指的是分子中原子间周期性运动（不包括分子整体的平动和转动），振动过程中存在原子偏离平衡位置的物理位移。通常由一定数量的简正振动(模)来描述，直线形分子有***3N-5***个，非直线形分子有***3N-6***个。

◆每个简正振动均有一系列能级，对称性许可时，其振动能级的跃迁可在红外光谱(或振动拉曼散射光谱）中产生特征峰(信号);

◆简正(振动)模的对称性分析----基于所使用的基，有两类方法：

i）基于每个原子偏离平衡位置的位移矢量，可以是直角坐标系下的(x,y,z)，也可以是便于对称性分类处理而设置的局域坐标系下的(a,b,c); （缺点：不便于想象振动模式）

ii）基于分子的内(坐标)位移，甚至是部分内坐标如X-H键伸缩位移。（缺点：近似图像）

◆简正振动(模)对称性分析时须注意两个一致性：1）自由度数量一致性；2）对称性一致性

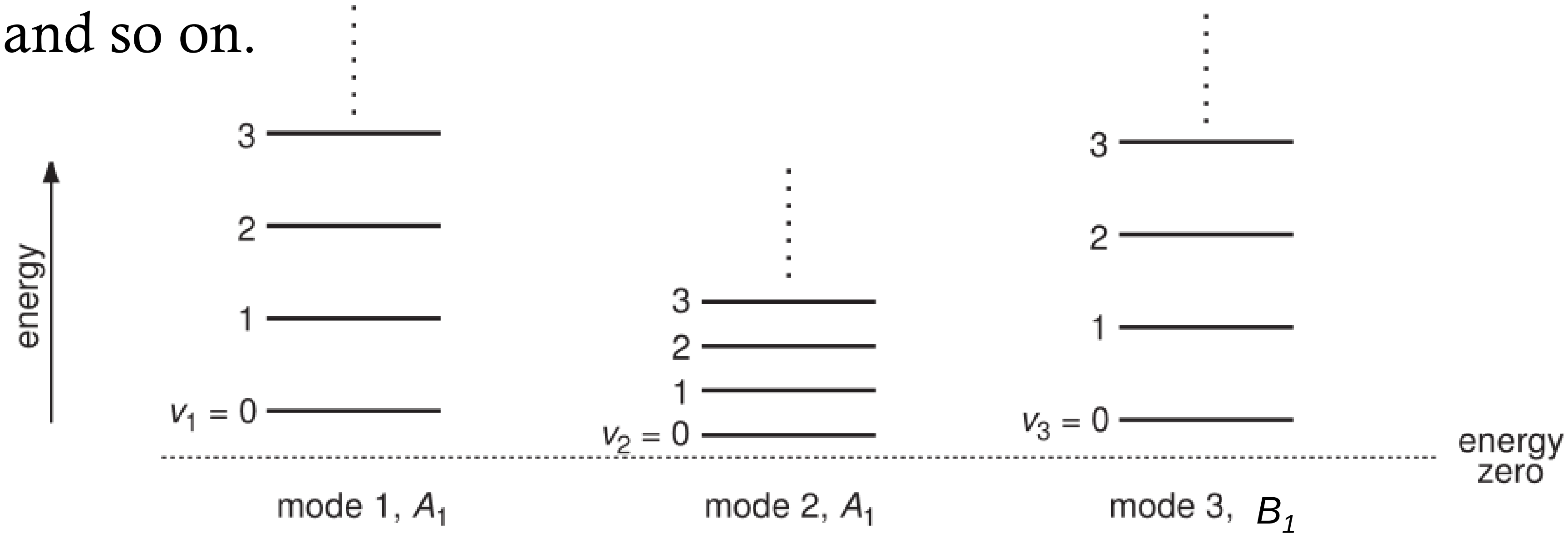
7.2 Symmetry of the vibrational wavefunctions

- If we assume that the vibrations are harmonic, each normal mode has associated with a set of energy levels: (ω_i is the *vibrational frequency* of the *i*th normal mode).

$$E_{v_i} = \left(v_i + \frac{1}{2}\right)\hbar\omega_i \qquad v_i = 0, 1, 2 \ldots$$

- The normal modes can be excited independently of one another so, for example, we can have the first normal mode in the $v_1 = 1$ level, the second in the ground state ($v_2 = 0$), the third in the $v_3 = 3$ level and so on.

The set of energy levels available for H_2O.



7.2 Symmetry of the vibrational wavefunctions

- For a diatomic, the harmonic oscillator wavefunctions depend only on the ***displacement x***, where **$x=(r-r_e)$**.

In terms of the *scaled coordinate* $\boldsymbol{q = x\,(km/\hbar^2)^{1/4}}$, the form of the first few wavefunctions and their energies are:

Hermite polynomials

ν	$\psi_\nu = \boldsymbol{H_\nu(q)}\exp(-q^2/2)$	E_ν
0	$\exp(-\frac{1}{2}q^2)$	$\frac{1}{2}$
1	$2q\exp(-\frac{1}{2}q^2)$	$\frac{3}{2}$
2	$(4q^2-2)\exp(-\frac{1}{2}q^2)$	$\frac{5}{2}$
3	$(8q^3-12q)\exp(-\frac{1}{2}q^2)$	$\frac{7}{2}$

Normal coordinate $\boldsymbol{Q_i}$ in the place of $\boldsymbol{q}$ for complex molecules!

- In more complex molecules, *a normal mode involves several atoms changing their positions*, but we can define a single normal coordinate $\boldsymbol{Q_i}$ to describe the motion (of *i*th normal mode).

- ***Key point:*** $\Gamma^{(\boldsymbol{Q_i})} = \Gamma^{(\boldsymbol{i})}$

7.2.1 Symmetry of the ground state vibrational wavefunction

- For ***a non-degenerate normal mode***, its ***ground-state wavefunction*** is $\psi_0 = \exp(-\frac{1}{2}Q_i^2)$.

  $\hat{R}Q_i = +/-Q_i$ (effect of symmetry operation on Q_i)

→ $\hat{R}Q_i^2 = (+1)\,Q_i^2$

i.e. Q_i^2 transforms as ***the totally symmetric IR***, so does $\psi_0 = \exp(-\frac{1}{2}Q_i^2)$.

→ ***The ground state wavefunction always transforms as the totally symmetric IR***.

- For degenerate normal modes, ***the conclusion remains the same*** and the statement above therefore applies to all normal modes.

7.2.2 Symmetry of excited states: non-degenerate normal modes

State	Wavefunction	Symmetry
$v_i = 0$	$\psi_0 = exp\,(-\frac{1}{2}Q_i^2)$	$\Gamma^{tot.\ sym.}$
$v_i = 1$	$\psi_1 = Q_i\, exp\,(-\frac{1}{2}Q_i^2)$	$\Gamma^{(i)} \otimes \Gamma^{tot.\ sym.} = \Gamma^{(i)}$
$v_i = 2$	$\psi_2 = (4Q_i^2-2)\, exp\,(-\frac{1}{2}Q_i^2)$	$\Gamma^{tot.\ sym.} \otimes \Gamma^{tot.\ sym.} = \Gamma^{tot.\ sym.}$
$v_i = 3$	$\psi_3 = (8Q_i^3-12Q_i)\, exp\,(-\frac{1}{2}Q_i^2)$	$\Gamma^{(i)} \otimes \Gamma^{tot.\ sym.} = \Gamma^{(i)}$

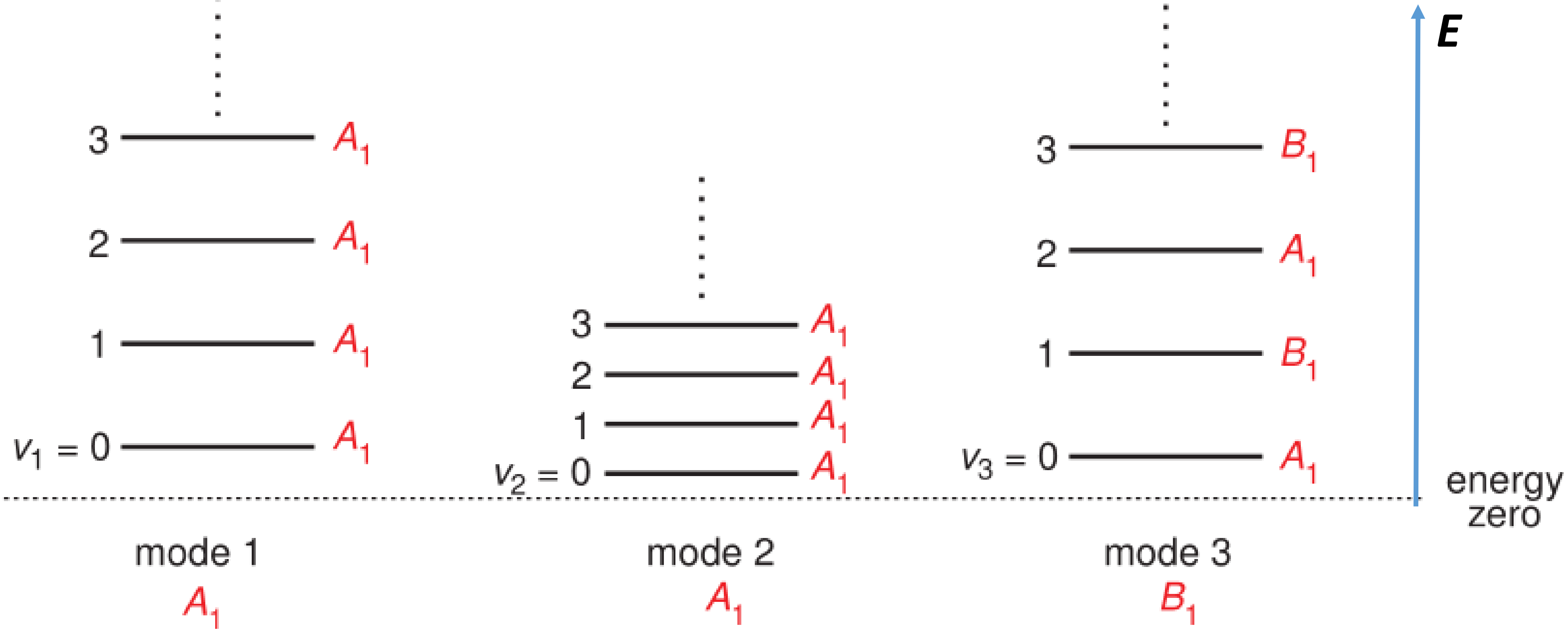
The first excited state transforms as the same ***IR*** *as the normal mode.*

Key point: $\Gamma^{(Q_i)} = \Gamma^{(i)}$

For ***non-degenerate normal modes***, vibrational wavefunctions with $v = 0, 2, 4, \ldots$ (even v) transform as *the totally symmetric IR*, and those with ***odd v have the same IR*** as does the normal mode.

7.2.2 Symmetry of excited states: non-degenerate normal modes

For **non-degenerate normal modes**, vibrational wavefunctions with $\boldsymbol{v} = 0, 2, 4, \ldots$ (even $\boldsymbol{v}$) transform as *the totally symmetric IR*, and those with ***odd v have the same IR*** as does the normal mode.



Normal Modes of H_2O

Symmetry of excited states: ***degenerate normal modes***

For ***degenerate normal modes***,

- As for non-degenerate modes, the ground state (***ν = 0***) transforms as *the totally symmetric IR*, and the first excited state (***ν =1***) transforms as the same IR as the normal mode.
- The symmetry properties of higher excited states follow a more complex pattern which is beyond the scope of this course but is considered in detail ***in Perturbation Theory***.

7.2.3 Overall symmetry of the vibrational wavefunction

- The symmetry of ***the overall vibrational wavefunction*** for a molecule is given by the product

$$\Gamma_{tot} = \Gamma_{v_1}^{(1)} \otimes \Gamma_{v_2}^{(2)} \otimes \cdots$$

$\Gamma_{v_1}^{(1)}$ ~ the ***IR*** of the wavefunction for the *1*st normal mode with quantum number v_1;

$\Gamma_{v_2}^{(2)}$ ~ the ***IR*** of the wavefunction for the *2*nd normal mode with quantum number v_2

…

- In H_2O, suppose that for the three normal modes $v_1=0$, $v_2=1$ and $v_3=1$, the ***IR***s for each of these wavefunctions are A_1 , A_1 and B_1 , respectively.

→ The *IR* of the overall vibrational wavefunction is therefore $A_1 \otimes A_1 \otimes B_1 = B_1$.

7.2.3 Overall symmetry of the vibrational wavefunction

- For a molecule in which none of the vibrational modes are excited (all the $\boldsymbol{v}_i$ are zero), the overall vibrational wavefunction transforms as ***the totally symmetric IR***.
- Also, if just one normal mode is excited to the ***v = 1*** state, and all of the other normal modes have ***v = 0***, the overall vibrational wavefunction has *the same* ***IR*** as the normal mode which is excited.

7.3 Using symmetry to determine which transitions are allowed

- **The wavefunctions** for a normal mode are the same as those for **a harmonic oscillator** (but replacing the displacement x by the normal coordinate Q_i). The usual selection rules apply. That is, for a transition to be allowed

  (1) The dipole must change as the normal coordinate changes about equilibrium.

  (2) $\Delta v_i = \pm 1$.

- The (2) implies that ***the quantum number of only one mode is allowed to change by ±1***.
- Due to **anharmonicity**, transitions with ***higher values of*** Δv are weakly allowed (**overtones**), as are transitions in which more than one mode changes quantum number (**combination lines**).
- A symmetry analysis gives us a systematic way of determining which particular transitions associated with particular normal modes are going to give rise to absorptions in the infra-red or vibrational Raman scattering.

7.3.1 Transitions between the energy levels of a single normal mode

- Since all of the ground states transform as *the totally symmetric IR*, the symmetry of the overall vibrational wavefunction is just determined by ***that of the one normal mode which is being excited***.
- The intensity $\boldsymbol{I}$ of a transition between two vibrational levels, $\boldsymbol{v_i} \rightarrow \boldsymbol{v_i'}$, is proportional to the square of *the transition moment* $\boldsymbol{R_{v_i v_i'}}$ between those levels, i.e., $\boldsymbol{I_{v_i v_i'}} \propto \boldsymbol{R^2_{v_i v_i'}}$
- *This transition moment* between states $\boldsymbol{v_i}$ and $\boldsymbol{v_i'}$ of the ith normal mode is given by

$$\boldsymbol{R_{v_i v_i'}} = \int_{-\infty}^{+\infty} \boldsymbol{\psi_{v_i'} \hat{\mu} \psi_{v_i}\, dQ_i}$$

$\hat{\boldsymbol{\mu}}$ is the ***dipole moment operator*** which just depends on the coordinates x, y and z, since it simply describes the distribution of charge in space.

7.3.1 Transitions between the energy levels of a single normal mode

- The ***IR*** of the integrand can be found by first determining the ***IR***s of $\psi_{v_i'}$, $\hat{\mu}$ and ψ_{v_i} and then taking the direct product,

function/operator	$\psi_{v_i'}$	$\hat{\mu}$	ψ_{v_i}
irreducible representation	$\Gamma_{v_i'}^{(i)}$	Γ_μ	$\Gamma_{v_i}^{(i)}$

$$\Gamma_{v_i'}^{(i)} \otimes \Gamma_\mu \otimes \Gamma_{v_i}^{(i)} =$$

$$\left\{ \begin{array}{lll} \subseteq \Gamma^{tot.sym.} & \rightarrow R_{v_i v_i'} \neq 0 & \text{Transition allowed, } \textit{infra-red active} \\ \not\subset \Gamma^{tot.sym.} & \rightarrow R_{v_i v_i'} = 0 & \text{Transition forbidden, } \textit{infra-red inactive} \end{array} \right.$$

- ***The dipole moment operator*** $\hat{\mu}$ ~ a function of x, y and z,

→ Γ_μ: either the ***IR*** of x, or of y, or of z, all three possibilities should be considered.

The fundamental transition

- *The fundamental transition (v=0→v′=1)* of *i*th normal mode.

$\nu = 0$ state $(\Gamma^{(i)}_{v=0} = \Gamma^{tot.sym.})$ → $\nu = 1$ state $(\Gamma^{(i)}_{v'=1} = \Gamma^{(i)}_{nm})$

The *IR* of the *i*th normal mode.

The triple direct product for ***the transition moment*** is :

$$\Gamma^{(i)}_{v'=1} \otimes \Gamma_{\mu} \otimes \Gamma^{(i)}_{v=0} = \Gamma^{(i)}_{nm} \otimes \Gamma_{\mu} \otimes \Gamma^{tot.sym.}$$

$$= \Gamma^{(i)}_{nm} \otimes \Gamma_{\mu}$$

The fundamental transition is allowed in the infra-red when the ***IR*** of the normal mode ***is the same as that of x, y or z.***

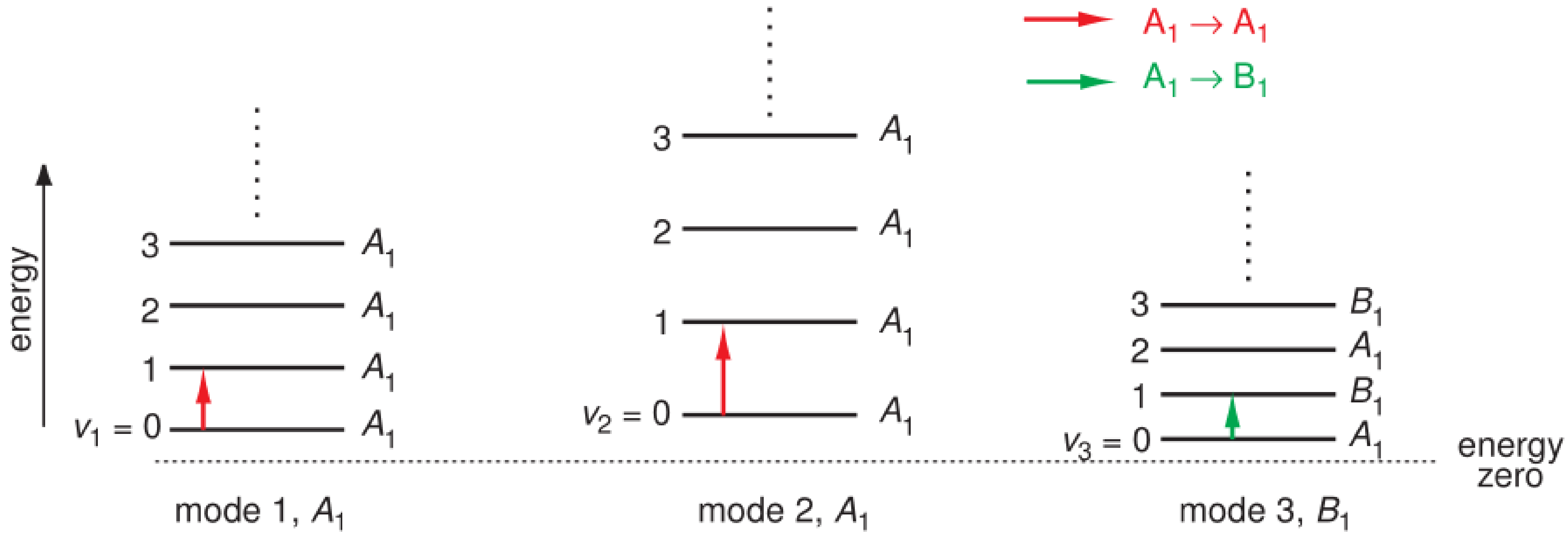
- A normal mode whose fundamental transition is allowed in the infra-red is said to be ***infra-red active***.

The fundamental transition

Example: **H_2O**

C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
A_1	1	1	1	1	z		$x^2; y^2; z^2$
A_2	1	1	−1	−1		R_z	xy
B_1	1	−1	1	−1	x	R_y	xz
B_2	1	−1	−1	1	y	R_x	yz

- The fundamentals of the A_1 normal modes *are allowed* since z transforms like A_1;
- The fundamental of the B_1 normal mode *is allowed* since x transforms like B_1.



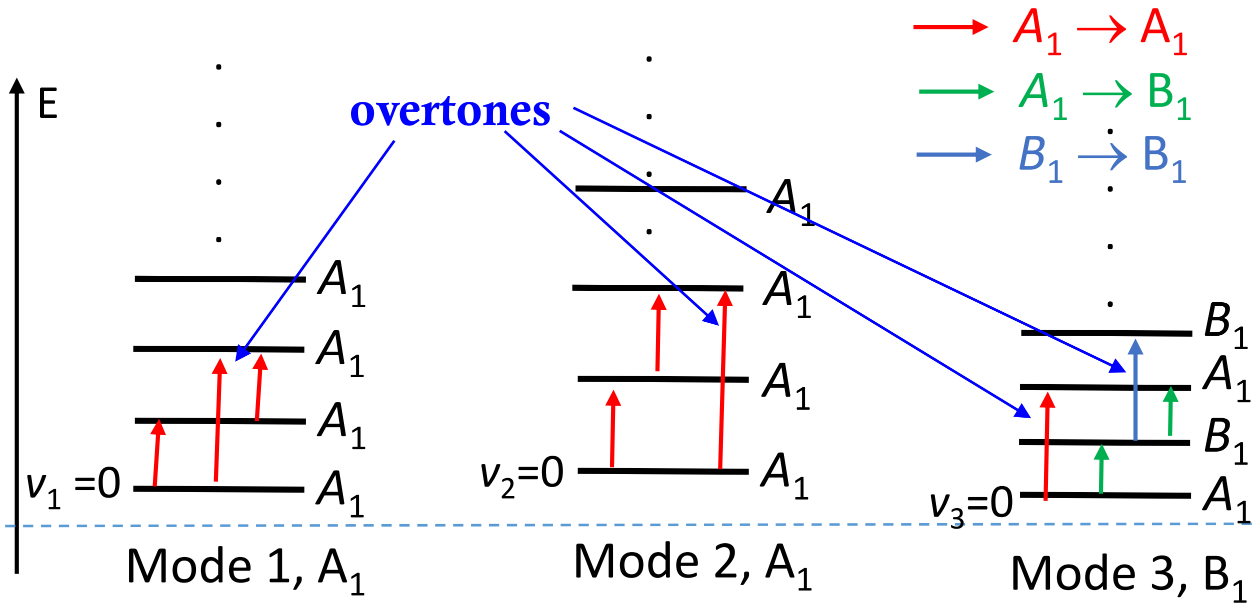
Other symmetry allowed transitions within the same normal mode

- For ***transitions other than the fundamental***, we would, in principle, need to work out the triple direct product in each case.

  Example: H_2O,

i) A_1 modes: all transitions are due to $A_1 \rightarrow A_1$ and ***symmetry-allowed.***

ii) B_1 mode: ***allowed*** transitions are $A_1 \rightarrow A_1$, $A_1 \rightarrow B_1$, $B_1 \rightarrow A_1$, and $B_1 \rightarrow B_1$.



For a $B_1 \rightarrow B_1$ transition, the triple product is

$$B_1 \otimes \Gamma_\mu \otimes B_1 = A_1$$

Thus it is ***IR-active***.

A note of caution

- ***The symmetry argument*** is powerful:

I. All it does is to ***predict whether or not a transition is allowed.***

II. ***It does not predict how strong a transition will be in the spectrum.***

III. In ***harmonic oscillator*** model, the selection rule is $\Delta v = \pm 1$.

➢For a polyatomic molecule, the only allowed transitions are those in which **the quantum number for a particular normal mode changes by one**.

➢Furthermore, *a transition will only have significant intensity if the lower level is appreciably occupied*. In practice, for small molecules, *easily observable transitions will come from the ground vibration states*, i.e., **the symmetry allowed fundamental transitions are visible**!

➢**H_2O**: The fundamentals of the A_1 , B_1 normal modes are observable.

A note of caution: anharmonicity & overtones

- However, the vibrations of real molecules are ***not harmonic*** and so the $\Delta v = \pm 1$ rule does not always apply strictly.

- ***Anharmonicity***-induced visible transitions with $|\Delta v| > 1$:

  i) ***symmetry allowed*** !

  ii) transition from ***a significantly populated lower level***.

- For example, in H_2O the **0 → 2** transitions in each normal mode satisfy these criteria (they are all $A_1 \rightarrow A_1$), and these ***first overtone bands*** are often seen.

7.3.2 Raman scattering

- For ***Raman scattering***, the ***transition moment*** depends on the polarizability operator $\hat{\alpha}$

$$R_{v_i v_i'} = \int_{-\infty}^{+\infty} \psi_{v_i'} \hat{\alpha} \psi_{v_i}\, dQ_i$$

with $\hat{\alpha} \propto pq\ (p, q \sim x, y, z)$

function/operator	$\psi_{v_i'}$	$\hat{\alpha}$	ψ_{v_i}
irreducible representation	$\Gamma^{(i)}_{v_i'}$	Γ_α	$\Gamma^{(i)}_{v_i}$

The ***IR*** of the integrand is thus given by the triple product, $\Gamma^{(i)}_{v_i'} \otimes \Gamma_\alpha \otimes \Gamma^{(i)}_{v_i}$

→ Vibrational Raman scattering occurs when this direct product contains the totally symmetric ***IR***.

- For the ***fundamental transition*** of *i*th normal mode, the triple product is

$$\Gamma^{(i)}_{nm} \otimes \Gamma_\alpha \otimes \Gamma^{Tot.sym} = \Gamma^{Tot.sym} \ \textbf{if}\ \Gamma^{(i)}_{nm} = \Gamma_\alpha \quad (\because \Gamma^{(i)}_{v=1} = \Gamma^{(i)}_{nm}\ \&\ \Gamma^{(i)}_{v=0} = \Gamma^{Tot.sym})$$

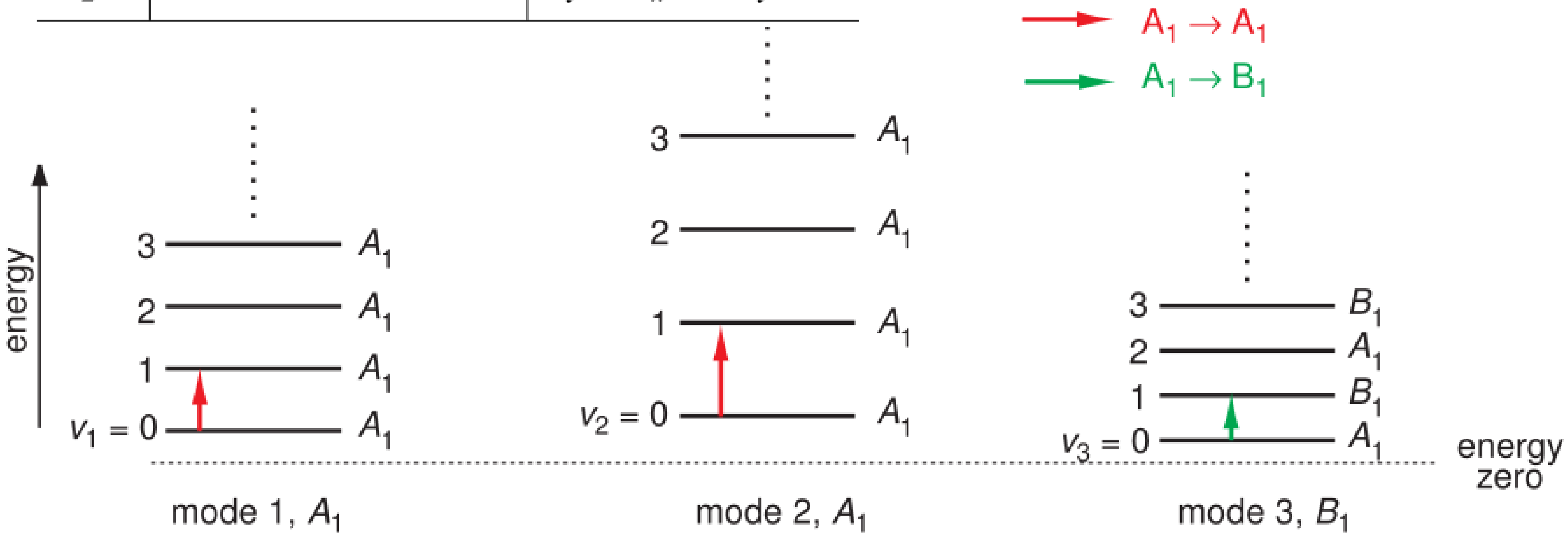
The fundamental transition will be Raman allowed when the symmetry of the normal mode matches that of ***pq***. (p, $q \sim x$, y or z)

7.3.2 Raman Scattering

Example： $H_2O(C_{2v})$, three normal modes.

C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
A_1	1	1	1	1	z		$x^2; y^2; z^2$
A_2	1	1	−1	−1		R_z	xy
B_1	1	−1	1	−1	x	R_y	xz
B_2	1	−1	−1	1	y	R_x	yz

- Normal modes 1&2: **A_1** *IR*, z^2
- Normal mode 3: **B_1** *IR*, xz
- All three modes Raman active!



7.3.3 Features and coincidences

- If we concentrate on just the fundamental transitions (which are likely to be the strongest), each normal mode which is ***infra-red active*** will give rise to a band or '***feature***' in the ***infra-red*** spectrum.

- Similarly, each normal mode which is ***Raman active*** will ***give rise to a feature*** in the ***Raman scattering*** spectrum.

e.g, H_2O:

three normal modes are both infra-red and Raman active,

→ *three features* in both IR and Raman scattering spectrum

7.3.3 *Features* (特征峰） *and coincidences*

- Three normal modes of H_3^+

A_1' *Raman active*

E' *IR active* *Raman active*

→ Raman spectrum ~ ***two features***

infra-red spectrum ~ ***one feature***

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$			
A_1'	1	1	1	1	1	1			$x^2+y^2; z^2$
A_2'	1	1	−1	1	1	−1		R_z	
E'	2	−1	0	2	−1	0	(x, y)		$(x^2-y^2, 2xy)$
A_1''	1	1	1	−1	−1	−1			
A_2''	1	1	−1	−1	−1	1	z		
E''	2	−1	0	−2	1	0		(R_x, R_y)	(xz, yz)

- *Coincidence*: The same normal mode is active in both the infra-red and Raman, exhibiting a feature of the same frequency.

H_2O: *Three coincidences*

H_3^+ **:** ***One** coincidence* (from the E' mode).

7.3.4 Combination lines

- A ***combination line*** is a transition in which the quantum numbers associated with two or more normal modes change.

- ***(v_1, v_2, v_3. . .) : a notation*** gathering the vibrational quantum number for each normal mode describes the overall vibrational state of a molecule.

- The symmetry of the overall state can be found by taking the direct product of the ***IR***s of the individual vibrational wavefunctions:

$$\Gamma_{v_1}^{(1)} \otimes \Gamma_{v_2}^{(2)} \otimes \Gamma_{v_3}^{(3)} \otimes \cdots$$

- For a vibrational state ***(1,0,1)*** in H_2O, the overall symmetry is $\mathbf{A_1 \otimes A_1 \otimes B_1 = B_1}$.

Q： Is the double-excitation transition, ***(0,0,0)→(1,0,1) ,*** in H_2O symmetry-allowed?

The overall symmetry of the ground state ***(0,0,0)*** is $\mathbf{A_1 \otimes A_1 \otimes A_1 = A_1}$.

We have shown that ***A_1→B_1*** transition is allowed.

7.3.5 Rule of mutual exclusion

Molecules having ***a centre of symmetry* (*i*)** have two distinct classes of ***IR***s:

***IR**s labelled with a subscript g*

~symmetric with respect to *i*

***IR**s labelled with a subscript u*

~anti-symmetric with respect to *i*

Functions pq (p,q ~x,y,z)

$\hat{i}(pq) = (+1)pq$ → *g-class* ***IR***

Functions x, y, z.

$\hat{i}q = (-1)q$ → *u-class* ***IR***

*Raman scattering active normal modes match functions pq in **IR**.*

*Infra-red active normal modes match the functions x,y,z in **IR**.*

Fundamental transition($v=0 \rightarrow 1$)

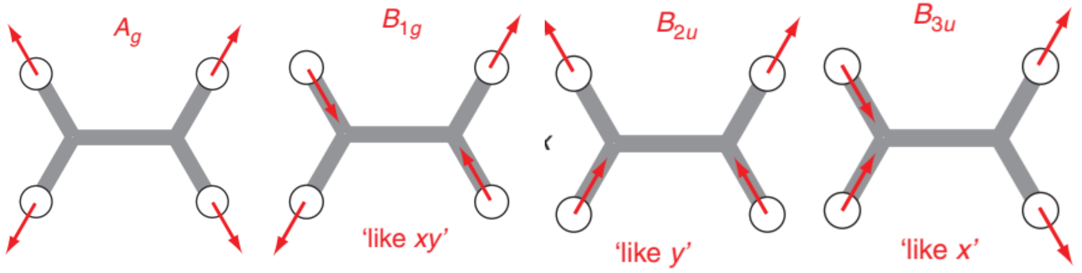
The rule of mutual exclusion: for a molecule with a centre of inversion, the fundamental of a particular normal mode cannot both give rise to an absorption in the *infra-red* and *vibrational Raman scattering*. In other words, if the transition is allowed in the *infra-red* it will not also give rise to *Raman scattering*.

7.3.5 Rule of mutual exclusion

Exs.34-39

- **For a molecule with a centre of inversion, a normal mode which is active in the infra-red will not be active in the Raman.**
- Example: the C–H stretching normal modes for ethane.

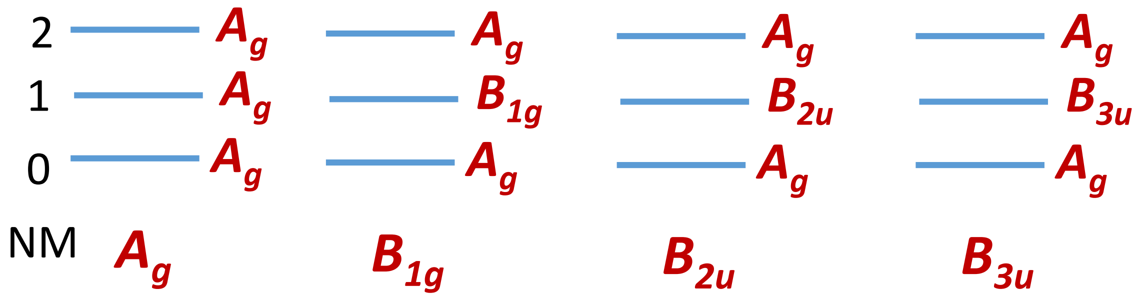
Normal Mode IR	*similar function*	*Infra-red*	*Raman scattering*
A_g	q^2	*inactive*	*active*
B_{1g}	xy	*inactive*	*active*
B_{2u}	y	*active*	*inactive*
B_{3u}	x	*active*	*inactive*



D_{2h}	E	C_2^z	C_2^y	C_2^x	i	σ^{xy}	σ^{xz}	σ^{yz}		
A_g	1	1	1	1	1	1	1	1		$x^2; y^2; z^2$
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

Q: Please work out the symmetry allowed overtones and combination lines in both types of spectra.

Overtones and combination lines of C-H stretches in C_2H_4



D_{2h}	E	C_2^z	C_2^y	C_2^x	i	σ^{xy}	σ^{xz}	σ^{yz}		
A_g	1	1	1	1	1	1	1	1		$x^2; y^2; z^2$
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

- Overtones: (0→2)

NM $\underbrace{A_g \quad B_{1g} \quad B_{2u} \quad B_{3u}}$

v=0→v=2 $A_g \rightarrow A_g$ Raman active

Combining with A_g normal mode does not affect the symmetry of the state.

- Combination lines: (0→1&0→1)

B_{1g} & B_{2u} $A_g \rightarrow B_{1g} \otimes B_{2u} = B_{3u}$ IR active!

B_{1g} & B_{3u} $A_g \rightarrow B_{1g} \otimes B_{3u} = B_{2u}$ IR active!

B_{2u} & B_{3u} $A_g \rightarrow B_{2u} \otimes B_{3u} = B_{1g}$ Raman active!

A_g & B_{2u} $A_g \rightarrow A_g \otimes B_{2u} = B_{2u}$ IR active!

A_g & B_{3u} $A_g \rightarrow A_g \otimes B_{3u} = B_{3u}$ IR active!

A_g & B_{1g} $A_g \rightarrow A_g \otimes B_{1g} = B_{1g}$ Raman active!

7.4 Summary

- Symmetry properties of vibrational wavefunctions:

1. The ground state wavefunction (v = 0) for any normal mode transforms as the totally symmetric IR.

2. The first excited state wavefunction (v = 1) for any normal mode transforms in the same way as does the normal mode i.e. its IR is the same as that of the normal mode.

3. For non-degenerate normal modes the states with even v (0, 2, 4 . . .) transform as the totally symmetric IR, whereas the states with odd v (1, 3, 5 . . .) transform in the same way as the normal mode i.e. their IR is the same as that of the normal mode.

4. The overall symmetry of the vibrational wavefunction is found by taking the direct product of the irreducible representations for the wavefunction associated with each normal mode.

7.4 Summary

- The fundamental of a particular normal mode is allowed in the infra-red if the IR of the normal mode matches that of x, y or z.
- The fundamental of a particular normal mode gives vibrational Raman scattering if the IR of the normal mode matches that of pq, where p and q are any of x, y or z.
- Whether or not a general transition from $\boldsymbol{v_i}$ to $\boldsymbol{v_i'}$ is allowed in the ***infra-red*** can be found by examining the direct product

$$\boldsymbol{\Gamma}^{(i)}_{v_i'} \otimes \boldsymbol{\Gamma}_{\mu} \otimes \boldsymbol{\Gamma}^{(i)}_{v_i}$$

If this product contains the totally symmetric IR the transition is symmetry allowed. ($\boldsymbol{\Gamma}_{\mu}$ itself transforms as x, y or z.)

7.4 Summary

- Whether or not a general transition from $\mathrm{v_i}$ to $\mathrm{v_i'}$ gives rise to Raman scattering can be found by examining the direct product

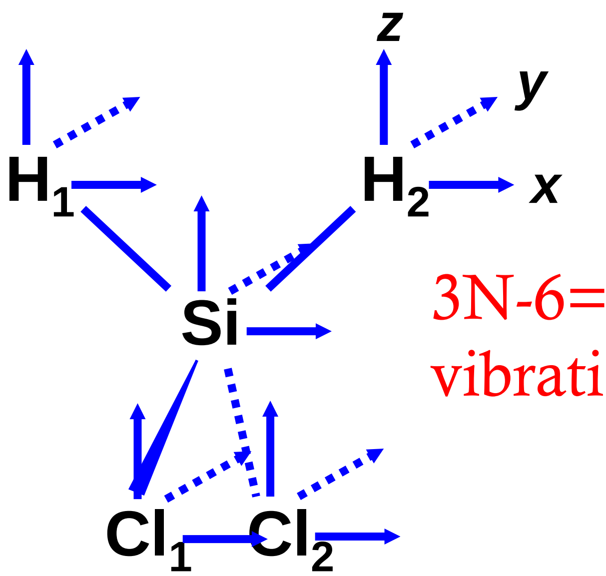
$$\boldsymbol{\Gamma_{v_i'}^{(i)} \otimes \Gamma_{\alpha} \otimes \Gamma_{v_i}^{(i)}}$$

If this product contains the totally symmetric IR the transition is symmetry allowed. ($\boldsymbol{\Gamma_\alpha}$ transforms as *pq*.)

- A symmetry-allowed transition may nevertheless not be observed on account of it having low intensity.
- The rule of mutual exclusion states that for a molecule with a centre of inversion the fundamental of a particular normal mode cannot both give rise to an absorption in the infra-red and vibrational Raman scattering.

7.1.4 Normal modes of more complex molecules

- Example: SiH_2Cl_2 (point group C_{2v})



3N-6=9 vibrational modes!

C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
A_1	1	1	1	1	z		$x^2; y^2; z^2$
A_2	1	1	−1	−1		R_z	xy
B_1	1	−1	1	−1	x	R_y	xz
B_2	1	−1	−1	1	y	R_x	yz
$\Gamma(Cl_1,x, Cl_2,x)$	2	0	0	-2	$A_2 \oplus B_1$		
$\Gamma(Cl_1,y, Cl_2,y)$	2	0	0	2	$A_1 \oplus B_2$		
$\Gamma(Cl_1,z, Cl_2,z)$	2	0	0	2	$A_1 \oplus B_2$		

- Classify the 15 vectors:

i) Si,x; Si,y; Si,z;

(H_1,x, H_2,x); (H_1,y, H_2,y) ; (H_1,z, H_2,z)

(Cl_1,x, Cl_2,x); (Cl_1,y, Cl_2,y) ; (Cl_1,z, Cl_2,z)

- SiH_2 similar to H_2O: $3A_1 \oplus 3B_1 \oplus A_2 \oplus 2B_2$

Full set	$5A_1 \oplus 4B_1 \oplus 2A_2 \oplus 4B_2$
Translations (x,y,z)	B_1, B_2, A_1
Rotations (R_x,R_y,R_z)	B_2, B_1, A_2
Vibrations	$4A_1 \oplus 2B_1 \oplus A_2 \oplus 2B_2$

Vibrational modes of SiH_2Cl_2

Two rules

(i) there is 1 stretching vibration per bond

(ii) we must treat symmetry-related atoms together

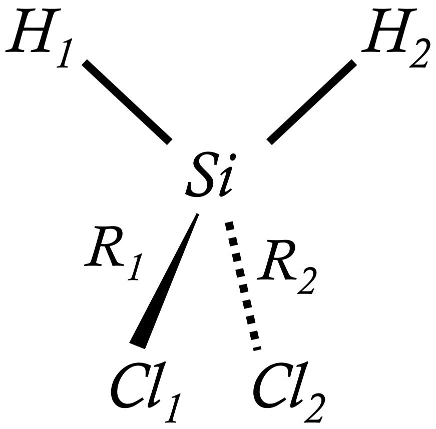
We therefore have:-

two stretching modes of the $SiCl_2$ group

two stretching modes of the SiH_2 group

The remaining five modes must be deformations (angle bending vibrations)

Vibrational modes of SiH_2Cl_2



- Two stretching modes of the $SiCl_2$ group

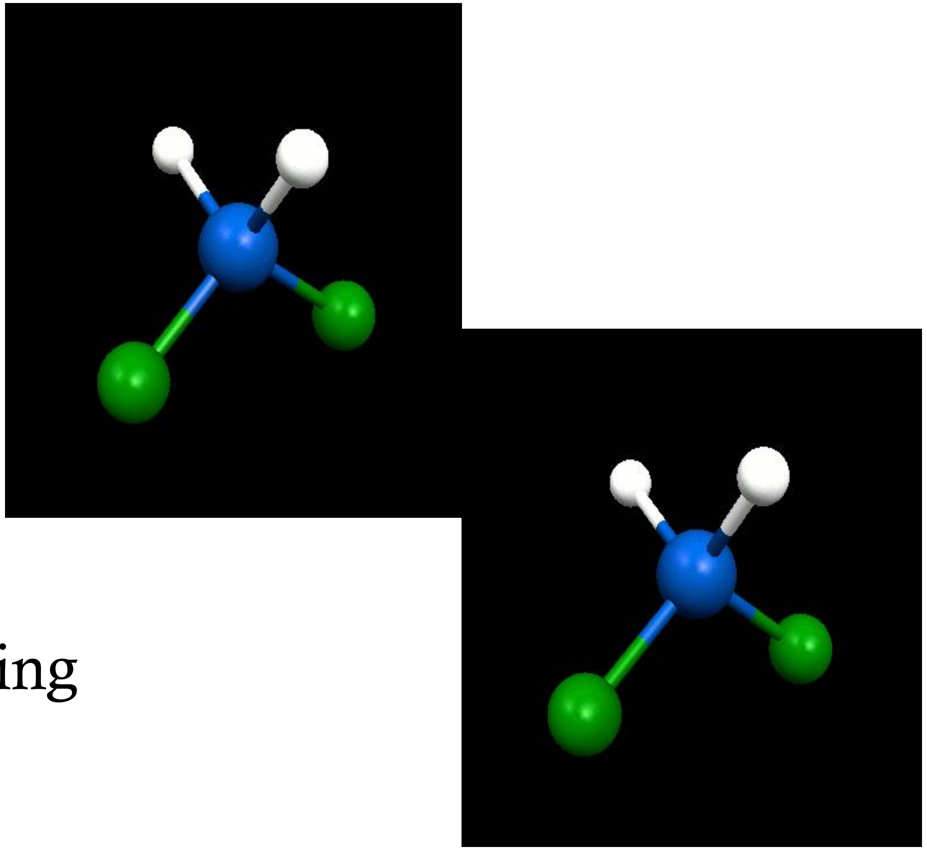
We can stretch the two Si-Cl bonds: together *in phase* or together *out of phase*!

1) use the two Si-Cl bond stretching as basis set:

	E	C_2	σ_{xz}	σ_{yz}
Γ_{2SiCl}	2	0	0	2

$\rightarrow \Gamma_{2SiCl} = A_1 \oplus B_2$

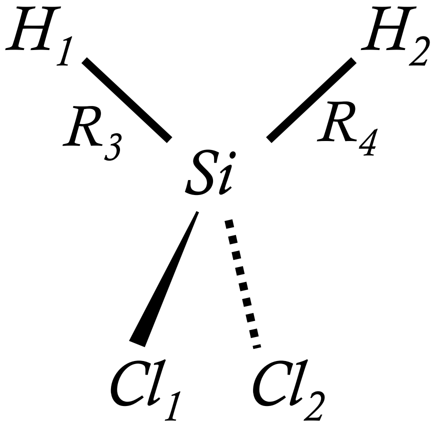
2) Get the combinations of bond stretching:



A_1 **stretching =** **$(R_1 + R_2)/2$** ~symmetric stretching

B_2 **stretching =** **$(R_1 - R_2)/2$** ~anti-symmetric stretching

Vibrational modes of SiH_2Cl_2



- Two stretching modes of the SiH_2 group

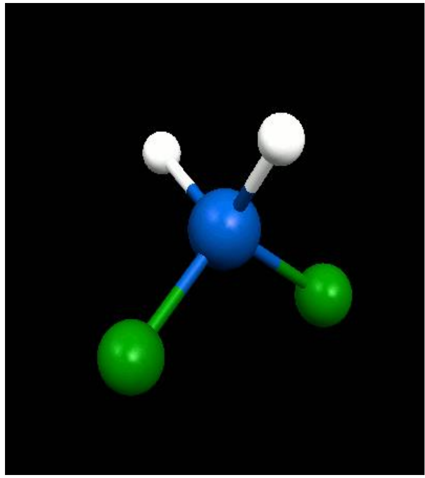
We can stretch the two Si-H bonds: together *in phase* or together *out of phase*!

1) use the two Si-H bond stretching as basis set:

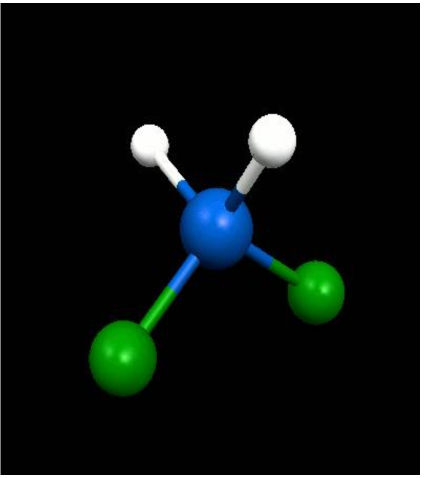
	E	C_2	σ_{xz}	σ_{yz}
Γ_{2SiH}	2	0	2	0

$\rightarrow \Gamma_{2SiH} = A_1 \oplus B_1$

2) Get the combinations of bond stretchings:



***A₁* stretching = (R₃ + R₄)/2** ~symmetric stretching



***B₁* stretching = (R₃ - R₄)/2** ~anti-symmetric stretching

Vibrational modes of SiH_2Cl_2

We now have:-

two stretching modes of the $SiCl_2$ group

two of the SiH_2 group

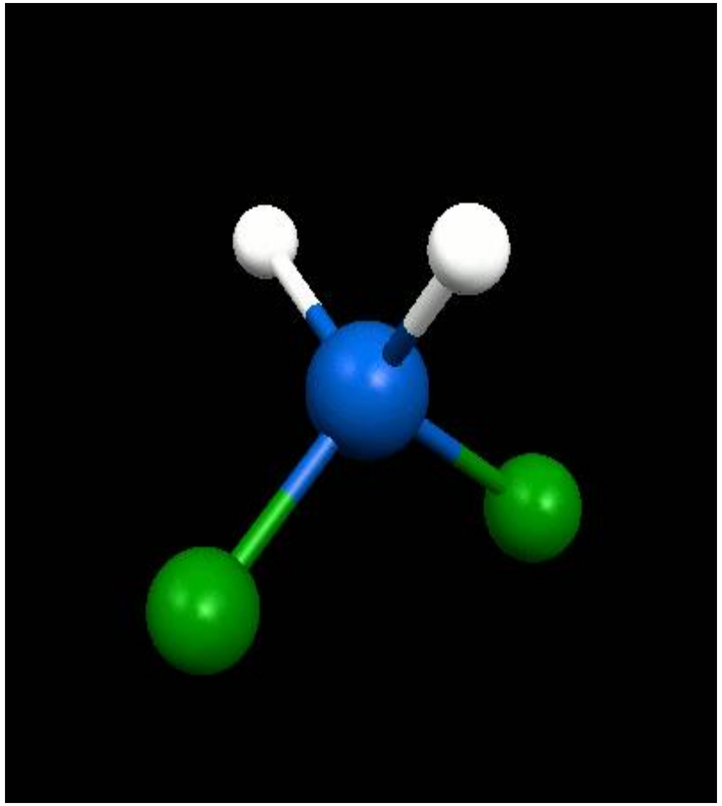
The remaining five modes must be deformations (angle bending vibrations)

As with stretches, we must treat symmetry-related atoms together.

- Take SiH_2 (or $SiCl_2$) as a whole when considering the deformations (related to change of bond angles and dihedral angles).

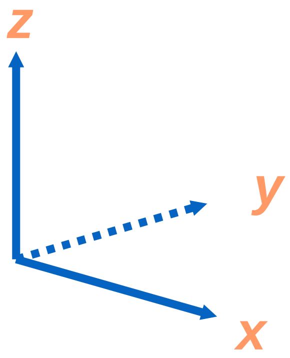
$SiCl_2$ scissors： ∠Cl-S-Cl as a basis

E	C_2	σ_{xz}	σ_{yz}
+1	+1	+1	+1



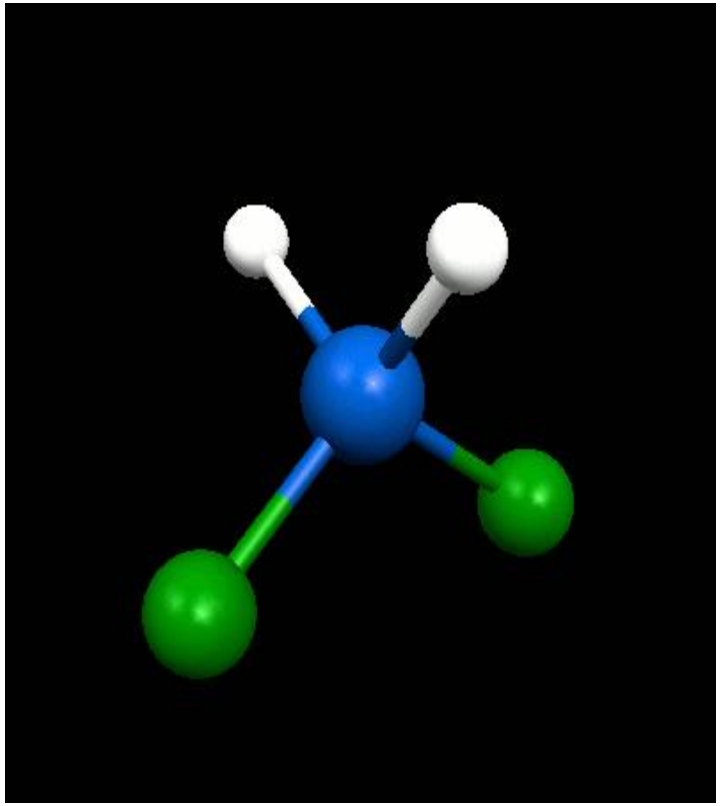
From the character table, this belongs to the symmetry species A_1

We call the mode of vibration δ_{sym} $SiCl_2$ (or $SiCl_2$ scissors)



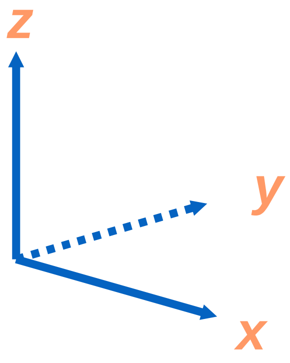
SiH_2 scissors： ∠H-Si-H as a basis

E	C_2	σ_{xz}	σ_{yz}
+1	+1	+1	+1



From the character table, this belongs to the symmetry species A_1

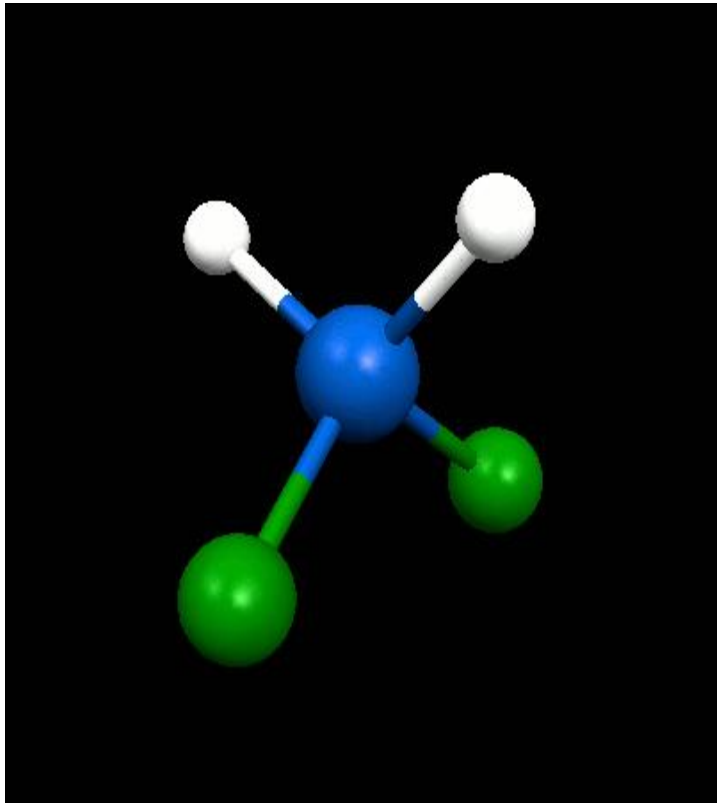
We call the mode of vibration δ_{sym} SiH_2 (or SiH_2 scissors)

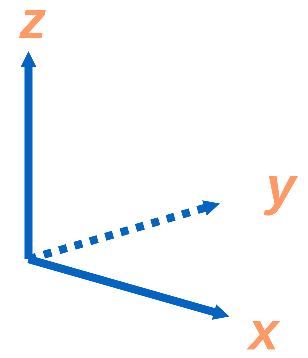


SiH$_2$ wag

- Concerted move of SiH$_2$ group ~ wag within the *xz* plane.

E	C_2	σ_{xz}	σ_{yz}
+1	-1	+1	-1





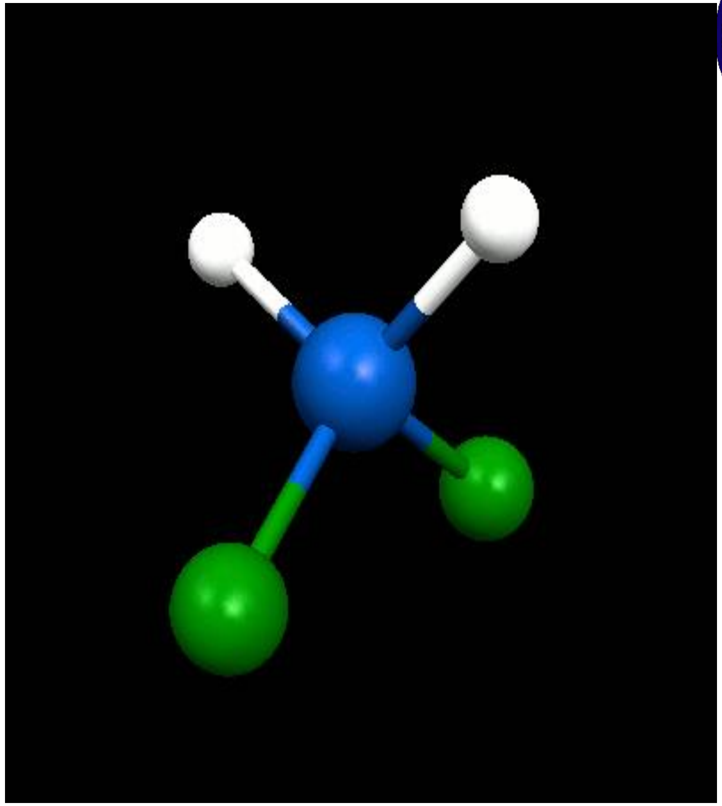
From the character table, this belongs to the symmetry species ***B$_1$***

We call the mode of vibration ω_{SiH2} (or SiH$_2$ wag).

SiH_2 rock

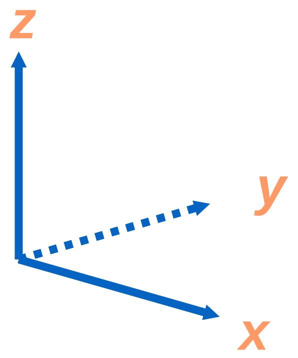
- Concerted move of the SiH_2 group~ rock within the yz plane.

E	C_2	σ_{xz}	σ_{yz}
+1	-1	-1	1



From the character table, this belongs to the symmetry species ***B_2***

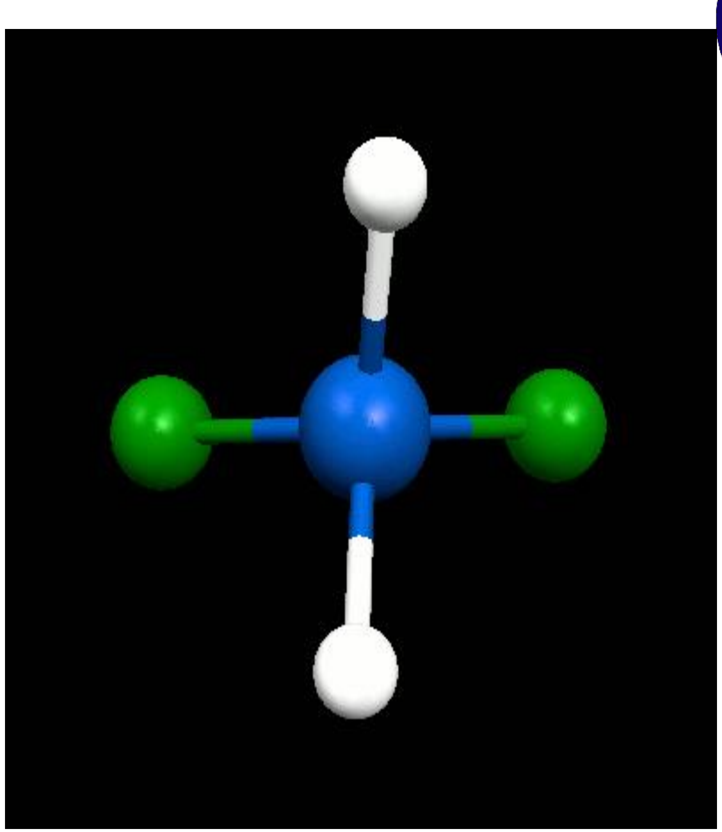
We call the mode of vibration ρ_{SiH2} (or SiH_2 rock).



SiH_2 twist

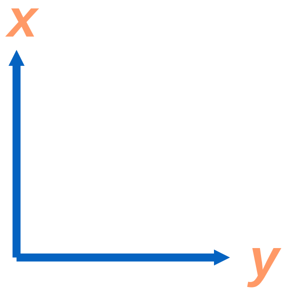
- Concerted move of SiH_2 group ~ rotating around the z-axis.

E	C_2	σ_{xz}	σ_{yz}
+1	+1	-1	-1



From the character table, this belongs to the symmetry species ***A_2***

We call the mode of vibration τ_{SiH2} (or SiH_2 twist).



Vibrational modes of SiH_2Cl_2

Overall, we now have:-

two stretching modes of the $SiCl_2$ group $A_1 \oplus B_2$

two of the SiH_2 group $A_1 \oplus B_1$

five deformation modes $2A_1 \oplus A_2 \oplus B_1 \oplus B_2$

Together, these account for all the modes we expect: $4A_1 \oplus A_2 \oplus 2B_1 \oplus 2B_2$