



Part III Symmetry and Bonding Chapter 7 Normal Modes (简正模/简正振动模式)

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7. Normal modes (简正模)

- The state and the state of the
- 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 can be separated into contributions from *a finite number of special vibrations called normal modes*.
- *Each normal mode has a set of energy levels*, and the transitions between these levels give rise to *infra-red* spectra of the type.
- e.g., three *normal modes* of H_2O and their fundamental transitions



 $A_1 v_1 3652 \text{ cm}^{-1}$





Relative Transmittance

(https://webbook.nist.gov/chemistry)

3000



2000

Wavenumber (cm-1)

1000



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 <u>combination</u> bands.



7.1 Normal mode analysis



- Vibrations involve the physical displacement of atoms from their equilibrium positions.
- To analyse the symmetry of vibrations, we simply imagine a basis which consists of an x, y and z ulletdisplacement vector attached to each atom in the molecule. **3**N For the *i*th normal mode (vibration) of an *N*-atom molecule, $Q_i = \sum c_{ij} \vec{q}_j$ (q: 各原子位移基矢)

define its normal coordinate Q_i (简正坐标) as

• *Example*, H₂O ($C_{2\nu}$), basis (x, y and z displacement vectors on each atom).



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. 与之前对原子轨道做



7.1 Normal mode analysis



- OIE										- 1976
<i>y</i> •	► x O, y	● ● ● ● ● ● ● ● ● ● ●	C_{2v}	Ε	C_2^z	σ^{xz}	σ^{yz}			
			A_1	1	1	1	1	z	$x^2; y^2; z^2$	
Z	$H_1(y \oplus) \to H_{1,X}$	$H_2(y \oplus) \to H_2, x$	A_2	1	1	-1	-1	R_z	xy	
	\downarrow	\forall	B_1	1	-1	1	-1	$\begin{array}{c c} x & R_y \\ \end{array}$	XZ	
	¥	•	B_2	1	-1	-1	1	$y R_x$	yz	_
	п ₁ ,2	- (H Y H Y)	Γ	2	0	2	0	$=A_{1}$	ΘB_1	
Vector(s)	IR	$(\Pi_1, \Lambda, \Pi_2, \Lambda)$	-1	_			0	1		
O, <i>x</i>	B_1 (from the table)	(H_1, y, H_2, y)	Γ_2	2	0	-2	0	$=A_2$	$\mathcal{P}B_2$	
О,у	B_2	SALC Full set	(3N)				3 <i>A</i> - A	9 3R _A	A. @ 21	3.
\mathbf{O}, z A	A ₁	1 utt set	(311)			•				2
	$\Lambda \oplus R$	Translation	ıs (x,y,	<i>z</i>)			B ₁ , B ₂	A_1 (from	om the table)
(H_1, x, H_2, x)	$\mathbf{A}_1 \cup \mathbf{D}_1$	P otations (DD	D)		7				~
(H_1, z, H_2, z)	$A_1 \oplus B_1$	Kotations ($\mathbf{X}_{x}, \mathbf{X}_{y}$	\mathbf{N}_{z}			⁵ ₂ , ^B ₁	, A_2 (from	om the table	;)
(H_1, y, H_2, y)	$A_2 \oplus B_2$	Vibrations	(3N-	6)			$2A_1 \in$	$\mathcal{P} \boldsymbol{B}_{1}$		
Total 3A ₁		$B_2 \cdot 3N-6$	norma	l mo	odes	for r	non-li	near mo	lecules.	

3N-6 normal modes for non-linear molecules. ٠



15:31

7.1.1 Form of the normal modes

- 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
- H₂O has **two** *stretching* modes and **one** *angle bending* mode.





A₁ v₂ 1595 cm⁻¹





Ex.32





15:31

7.1.1 Form of the normal modes

Using internal (coordinate) displacements!

- First use the two O-H bond stretches (\vec{r}_1, \vec{r}_2) 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.

Example: H₂O y**(•)** $\mathbf{H}_{2} \mathbf{\vec{r}}_{2}$ σ^{xz} C_{2v} Ε C_2^z σ^{yz} $x^2; y^2; z^2$ A_1 Ζ. -1 A_2 -1 R_z xy -1 1 -1 B_1 R_{v} х XZ. -1 -1 B_2 R_x v yz2 0 2 0 $= A_1 \oplus B_1$ $\Gamma(2\vec{r})$ 1 1 $\Gamma(\alpha)$ 1 $= A_1$ A₁ v₂ 1595 cm⁻¹ B₁ v₁ 3756 cm⁻¹ A₁ v₁ 3652 cm⁻¹ Neither purely bending nor purely stretching.

The A_1 bending & symmetric stretching further mix!



7.1.2 Normal modes of H_3^+







X,1

- 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:* $(z, 1, z, 2, z, 3), (a, 1, a, 2, a, 3), and (b, 1, b, 2, b, 3) \rightarrow all 3-D reps.!$





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









Ex.33

- 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 <u>absorptions in the infra-red or</u> <u>vibrational Raman scattering (i.e. whether or not a mode is '*infra-red* or *Raman active*').
 </u>
- We will start out by looking at *the symmetry of the harmonic oscillator wavefunctions*, which are a <u>first approximation to the vibrational wavefunctions of the molecule</u>, and then move on to discuss the selection rules for transitions between them.



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).

$$\boldsymbol{E}_{\boldsymbol{v}_{i}} = \left(\boldsymbol{v}_{i} + \frac{1}{2}\right) \hbar \boldsymbol{\omega}_{i} \qquad \boldsymbol{v}_{i} = \boldsymbol{0}, \boldsymbol{1}, \boldsymbol{2} \dots$$

• 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.



Normal coordinate Q_i in the place of 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 *Q_i* (简正坐标) to describe the motion of *i*th normal mode. *Key point:* Γ^(Q_i) = Γ⁽ⁱ⁾



- For <u>a non-degenerate normal mode</u>, its ground-state wavefunction is $\psi_0 = exp \left(-\frac{1}{2}Q_i^2\right)$.
 - Q_i (as a basis) transforms as <u>a particular 1-D IR</u>, i.e.,
 - $\widehat{R}Q_i = \chi(\widehat{R})Q_i$ with $\chi(\widehat{R}) = +1$ or -1 (effect of symmetry operation \widehat{R} on Q_i)
- $\widehat{RQ_i^2} = [\chi(\widehat{R})Q_i]^2 = (+1)Q_i^2 \quad (\text{valid for arbitrary } \widehat{R} \text{ of the very point group!})$
- $\rightarrow Q_i^2$ 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*.



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





Symmetry of excited states: degenerate normal modes, For degenerate normal modes,



- The ground state (v = 0) transforms as *the totally symmetric IR*, and the first excited state (v = 1) transforms as *the same IR* as the normal mode.
- The symmetry properties of *higher excited states* follow a more complex pattern.
 e.g., for the Π_u(v₂) bending modes of CO₂, its second-excited state has symmetry,

$\mathcal{D}_{\infty h}$	Ε	$2C^{z}(\alpha)$		$\infty \sigma_v$	i	$2S^{z}(\alpha)$		∞C_2			$(\boldsymbol{\Pi}_{\boldsymbol{u}} \otimes \boldsymbol{\Pi}_{\boldsymbol{u}}) = \boldsymbol{\Sigma}_{\boldsymbol{g}}^{+} + \boldsymbol{\Delta}_{\boldsymbol{g}} + \boldsymbol{\Sigma}_{\boldsymbol{g}}^{-}$
$\begin{array}{ll} \Sigma_g^+ & (A_{1g}) \\ \Sigma_g^- & (A_{2g}) \\ \Pi_g & (E_{1g}) \\ \Delta_g & (E_{2g}) \\ \Phi_g & (E_{3g}) \end{array}$	1 1 2 2 2	1 1 2 cosα 2 cos2α 2 cos3α	···· ···· ····	$ \begin{array}{c} 1 \\ -1 \\ 0 \\ 0 \\ 0 \\ 0 \end{array} $	1 1 2 2 2	1 $-2\cos\alpha$ $2\cos 2\alpha$ $-2\cos 3\alpha$	···· ···· ····		$\begin{array}{c} R_z\\ (R_x,R_y)\end{array}$	$x^{2} + y^{2}; z^{2}$ (xz, yz) $(x^{2} - y^{2}, 2xy)$	Among which the state of Σ_g^+ symmetry mixes with the first excited
$\sum_{i=1}^{+} (A_{1,i})$	 1	 1	····	 1	 -1	 -1	· · ·	 —1	z		state (Σ_{g}^{+}) of the symmetric C-O
$ \begin{array}{c} \Sigma_u^- & (A_{2u}) \\ \Sigma_u^- & (A_{2u}) \\ \Pi_u & (E_{1u}) \\ \Delta_u & (E_{2u}) \end{array} $	1 2 2	$\frac{1}{2\cos\alpha}$	 	-1 0 0	-1 -2 -2	-1 $2\cos\alpha$ $-2\cos2\alpha$	 	1 0 0	(x,y)		stretching, giving rise to <i>combination</i>
Φ_u (E_{3u})	2	2 cos 3α	 	0	-2 	2 cos 3α	 	0 			<i>bands</i> in Raman spectrum.



7.2.3 Overall symmetry of the vibrational wavefunction



- The symmetry of *the overall vibrational wavefunction* (ψ_{tot}) for a molecule can be worked out straightforwardly using direct product. $\psi_{tot} = \prod \psi_{v_i}$
- Suppose the normal modes of a molecule are each at the energy level given below,

No.	<i>IR</i> of N.M.	Energy level (<i>quantum number</i>)	<i>IR</i> of the corresponding vibrational wavefunction
1	 <i>Γ</i> ⁽¹⁾	<i>v</i> ₁	$\Gamma_{v_1}^{(1)}$
2	 <i></i> 	<i>v</i> ₂	$\Gamma_{v_2}^{(2)}$
 i 		v _i	$\Gamma_{v_i}^{(i)}$

Normal modes of a molecule and their states

The *IR* of *the overall vibrational wavefunction* for this molecule is given by the direct product,

$$\Gamma_{tot} = \Gamma_{\nu_1}^{(1)} \otimes \Gamma_{\nu_2}^{(2)} \otimes \cdots \Gamma_{\nu_i}^{(i)} \otimes \cdots$$



7.2.3 Overall symmetry of the vibrational wavefunction



- For a molecule in which none of the vibrational modes are excited (all the v_i are zero), the overall vibrational wavefunction transforms as *the totally symmetric IR*.
- 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.
- In H₂O, suppose that for the three normal modes v₁=0, v₂=1 and v₃=1, the IRs for each of these wavefunctions are A₁, A₁ and B₁, respectively.
 - → The *IR* of the overall vibrational wavefunction is therefore $A_1 \otimes A_1 \otimes B_1 = B_1$.





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 q 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 Q_i changes about equilibrium. (2) $|\Delta v_i| = 1$. (the quantum number of only one mode is allowed to change by ± 1)
- Due to **anharmonicity**, transitions with *higher values of* $|\Delta v_i|$ are weakly allowed (**overtones**), as are transitions in which *more than one mode* changes quantum number (**combination bands**).
- 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 *I* of a transition between two vibrational levels, $v_i \rightarrow v'_i$, of normal mode *i* is proportional to the square of *the transition moment* $R_{v_iv'_i}$ between those levels,

$$I_{v_iv_i'} \propto R_{v_iv_i'}^2$$
, with $R_{v_iv_i'} = \int \psi_{v_i'} \widehat{\mu} \psi_{v_i} dQ_i$

 $\hat{\mu}$ 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,

$\Gamma^{(i)} \otimes \Gamma_{\cdots} \otimes \Gamma^{(i)}$	function/operator	$\psi_{\nu'_i}$	ĥ	ψ_{ν_i}
$(R_{v_iv_i'} = \int \psi_{v_i'} \hat{\mu} \psi_{v_i} dQ_i)$	irreducible representation	$\Gamma^{(i)}_{{ m u}'_i}$	$\Gamma_{\!\mu}$	$\Gamma^{(i)}_{ u_i}$

 $\begin{bmatrix} = \Gamma^{tot.sym.} (\bigoplus ...) \rightarrow R_{v_i v'_i} \neq 0 & v_i \rightarrow v'_i \text{ transition is symmetry allowed, i.e., infra-red active} \\ \neq \Gamma^{tot.sym.} (\bigoplus ...) \rightarrow R_{v_i v'_i} = 0 & v_i \rightarrow v'_i \text{ transition is symmetry forbidden, i.e., infra-red inactive} \end{bmatrix}$

- *The dipole moment operator* $\hat{\mu}$ ~ a function of *x*, *y* and *z*,
- $\rightarrow \Gamma_{\mu}$: either the *IR* of *x*, or of *y*, or of *z*, all three possibilities should be considered.



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



The fundamental transition

Example: **H**₂**O**





- 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 .
- All (three) fundamental transitions are *IR-active*!





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: H₂O,

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

ii) B_1 mode: *allowed* transitions are $A_1 \rightarrow A_1$, $A_1 \rightarrow B_1$, $B_1 \rightarrow A_1$ (hot band), and $B_1 \rightarrow B_1$. $\rightarrow A_1 \rightarrow A_1$ $\rightarrow A_1 \rightarrow B_1$ For a $B_1 \rightarrow B_1$ transition, the triple product is E overtones $\longrightarrow B_1 \rightarrow B_1$ B_1 $B_1 \otimes \Gamma_u \otimes B_1 = A_1$ (if $\Gamma_u = A_1$, z-like) A_1 Thus it is *IR-active*. B_1 A_1 • Hot bands are highly temperature-dependence. $v_3=0$ A_1 $v_1 = 0$ $v_2 = 0$ Mode $1, A_1$ Mode 3, B_1 Mode 2, A_1







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!
- > H₂O: The fundamentals of the A_1 , B_1 normal modes are observable in IR spectra.





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 H₂O the $0 \rightarrow 2$ 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 $\hat{\alpha}$

	$\mathbf{R}_{\boldsymbol{v}_i\boldsymbol{v}_i'} = \int$	$\int \psi_{v_i'} \widehat{\alpha} \psi_{v_i} dQ_i$	fı	inctio
<i>i</i> th normal mode	with $\hat{\alpha} \propto p$	$q(p,q \sim x,y,z)$	irreducibl	e repr
		quadratic function		

representation $\Gamma_{\nu_i}^{(i)}$ $\hat{\alpha}$ ψ_{ν_i} representation $\Gamma_{\nu_i}^{(i)}$ Γ_{α} $\Gamma_{\nu_i}^{(i)}$

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

- \rightarrow 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

 $\Gamma_{nm}^{(i)} \otimes \Gamma_{\alpha} \otimes \Gamma^{Tot.sym} = \Gamma^{Tot.sym} \text{ if } \Gamma_{nm}^{(i)} = \Gamma_{\alpha} \qquad (::\Gamma_{\nu=1}^{(i)} = \Gamma_{nm}^{(i)} \& \Gamma_{\nu=0}^{(i)} = \Gamma^{Tot.sym})$

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.

					• Normal modes 1&2: A, IR.
C_{2v}	$E C_2^z$	σ^{xz}	σ^{yz}		
A_1	1 1	1	1	z $x^2; y^2; z^2$	• Normal mode 3: $B_1 IR$,
A_2 B_1 B_2	$\begin{vmatrix} 1 & 1 \\ 1 & -1 \\ 1 & 1 \end{vmatrix}$	-1 1	$-1 \\ -1 \\ 1$	$\begin{array}{ccc} R_z & xy \\ x & R_y & xz \\ y & P & yz \end{array}$	• All three modes Raman acti
b ₂	1 -1	-1	1	$y K_x yz$	\longrightarrow A ₁ \rightarrow A ₁
					$ \rightarrow A_1 \rightarrow B_1 $
				3 — B ₁	
λβ	3	— A ₁		2 — A ₁	
	2 1 0	$-A_1$ $-A_1$ $-A_1$		$A_{1}^{1} = 0 \qquad B_{1}^{1}$	$\begin{array}{cccc} A_1 & 3 & & & \\ & 2 & & & & A_1 \\ & 2 & & & & A_1 \\ & 1 & & & & A_1 \\ & & & & & & A_1 \\ & & & & & & & A_1 \\ \end{array}$
15:31	mode 1,	 A ₁		mode 3, B ₁	$v_2 = 0$ v_1 energy zero $zero$



 z^2

 χZ

active!



7.3.3 Features (特征峰) 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, H₂O:

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

- The fundamental transitions of three normal modes of H_3^+
- A'₁ Raman active
 E' IR active Raman active
 → Raman spectrum ~ two features
 infra-red spectrum ~ one feature
- *Coincidence*: The same normal mode is active in both the infra-red and Raman, exhibiting a feature of the same frequency.
 - H_3^+ : one coincidence (from the *E'* mode).
 - H₂O: three coincidences

How can we use IR/Raman spectroscopy to identify the geometry of H_3^+ , bent, linear or triangular?



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





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 H₂O, the overall symmetry is

 $\mathbf{A}_1 \otimes \mathbf{A}_1 \otimes \mathbf{B}_1 = \mathbf{B}_1.$

 $A_1 \otimes A_1 \otimes A_1 = A_1$.

Q: Is the double-excitation transition, $(0,0,0) \rightarrow (1,0,1)$, in H₂O symmetry-allowed?

The overall symmetry of the ground state (0, 0, 0) is

We have shown that $A_1 \rightarrow B_1$ transition is allowed.



7.3.5 Rule of mutual exclusion



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

IRs labelled with a subscript **g**

~symmetric with respect to *i*

Functions $pq (p,q \sim x,y,z)$ $\hat{\iota}(pq) = (-p)(-q) = (+1)pq \rightarrow g$ -class IR

Raman scattering active normal modes match functions pq in **IR**. ~anti-symmetric with respect to *i Functions x, y, z*.

IRs labelled with a subscript **u**

 $\hat{\iota}q = (-1)q \rightarrow u\text{-}class IR$

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. E.g. 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}	у	active	inactive
B_{3u}	x	active	inactive
Q: Please	e work out th	ne symmetry al	lowed
overtone	s and combi	nation lines in	both types of
spectra.			

A _g	8 Q	B _{1g}	B _{2u}	B _{3u}
P	Q P	'like xy'	flike v'	'like x'

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	<i>z</i> .	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	<i>x</i>	



Overtones and combination lines of C-H stretches in C_2H_4





All Raman active!

• Combination line: $(0 \rightarrow 1 \& 0 \rightarrow 1)$

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

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

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

 $g \otimes g = g$ $g \otimes u = u$ $u \otimes u = g$



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 v_i to v'_i is allowed in the *infra-red* can be found by examining the direct product

$$\Gamma^{(i)}_{v'_i}\otimes\Gamma_\mu\otimes\Gamma^{(i)}_{v_i}$$

If this product contains the totally symmetric *IR* the transition is symmetry allowed. (Γ_{μ} itself transforms as *x*, *y* or *z*.)



7.4 Summary



• Whether or not a general transition from v_i to v'_i gives rise to Raman scattering can be found by examining the direct product

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

If this product contains the totally symmetric IR the transition is symmetry allowed. (Γ_{α} 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.



7.5 Normal modes of more complex molecules



- Classify the 15 vectors:
- i) Si,x; Si,y; Si,z;
- (H₁,x, H₂,x); (H₁,y, H₂,y); (H₁,z, H₂,z) (Cl₁,x, Cl₂,x); (Cl₁,y, Cl₂,y); (Cl₁,z, Cl₂,z) **15**:31SiH₂ similar to H₂O: $3A_1 \oplus 3B_1 \oplus A_2 \oplus 2B_2$

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
<i>B</i> ₂	1	-1	-1	1	у	R_x	уz
x, Cl_2, x) 2	0	0	-2	A	₽ ₿ 1	
y, Cl ₂ ,y) 2	0	0	2	A	, ⊕ B ₂	,
z, Cl ₂ ,z) 2	0	0	2	A	,⊕ B ₂	•
Full	set			5 A ₁ 6	∂ 4 E	3 ₁⊕ .	$2A_2 \oplus 4B_2$
Tran	slati	ons (x	:,y,z)	В ₁ , В	2, A ₁		
Full Tran Rote	set slation	ons (x	c,y,z) R R	5A ₁ 6 B ₁ , B B ₂ , B		B₁⊕ .	2A ₂ ⊕ 4B

Vibrations

 $4A_1 \oplus 2B_1 \oplus A_2 \oplus 2B_2$





Vibrational modes of SiH₂Cl₂

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 SiH₂Cl₂

• Two stretching modes of the SiCl₂ 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:

$$E \quad C_2 \quad \sigma_{xz} \quad \sigma_{yz}$$

$$\Gamma_{2SiCl} \quad 2 \quad 0 \quad 0 \quad 2 \quad \rightarrow \Gamma_{2SiCl} = A_1 \oplus B_2$$

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 SiH₂Cl₂

• Two stretching modes of the SiH₂ 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:

$$E \quad C_2 \quad \sigma_{xz} \quad \sigma_{yz}$$

$$\Gamma_{2SiH} \quad 2 \quad 0 \quad 2 \quad 0 \quad \rightarrow \Gamma_{2SiH} = A_1 \quad \bigoplus B_1$$

2) Get the combinations of bond stretchings:

 A_1 stretching = $(R_3 + R_4)/2$ ~symmetric stretching

 B_1 stretching = $(R_3 - R_4)/2$ ~anti-symmetric stretching











We now have:-

- two stretching modes of the SiCl₂ group: $A_1 \oplus B_2$ two of the SiH₂ group: $A_1 \oplus B_1$
- The remaining five modes must be deformations (angle bending vibrations)
- As with stretches, we must treat symmetry-related atoms together.
- Take SiH₂ (or SiCl₂) as a whole when considering the deformations (related to change of bond angles and dihedral angles).



SiCl₂ scissors: \angle Cl-S-Cl as a basis

E $C_2 \sigma_{xz} \sigma_{yz}$ +1 +1 +1 +1

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

We call the mode of vibration δ_{sym} SiCl₂ (or SiCl₂ scissors)









SiH₂ scissors: \angle H-Si-H as a basis

$$E \quad C_2 \quad \sigma_{xz} \quad \sigma_{yz}$$
$$+1 \quad +1 \quad +1 \quad +1$$





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

We call the mode of vibration δ_{sym} SiH₂ (or SiH₂ scissors)





• Concerted move of SiH₂ group ~ wag within the *xz* plane.





From the character table, this belongs to the symmetry species B_1

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







• Concerted move of the SiH₂ group~ rock within the yz plane.



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

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







 Concerted move of SiH₂ group ~ rotating around the zaxis.



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

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



Vibrational modes of SiH₂Cl₂

A Compared Former

Overall, we now have:-

two stretching modes of the SiCl2 group $A_1 \oplus B_2$ two of the SiH2 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: $4A_1 \oplus A_2 \oplus 2B_1 \oplus 2B_2$

• The aforementioned modes are just approximations of the exact normal modes of the molecule concerned. To obtain the exact forms of the normal modes, we need to mix those of the same IR!





