

Vibrational Selection Rules

Introduction

- in the last few lectures we have used a number of "rules" to determine if a mode was infrared or Raman active
 - the dipole moment must change for a vibration to be infrared active, and to determine this we used the symmetry of the translational vectors
 - the polarization must change for a vibration to be Raman active, and to determine this we examined the symmetry of the binary functions
- there is a second selection rule for vibrational spectroscopy that the quantum number v can only vary by $\Delta v \pm 1$
- in this section the origin of the rules for infrared and Raman activity will be explained, as will the $\Delta v \pm 1$ selection rule
- the Einstein coefficients tell us the probability for a transition

$$B_{if} = B_{fi} = \frac{|\mu_{if}|^2}{6\epsilon_0\hbar^2}$$

Equation 1

- this contains the transition dipole moment μ_{fi} and thus the transition dipole moment *must be non-zero for a transition to occur* (or for a peak to be present in an experimental spectrum)

$$\mu_{fi} = \int \Psi_f \mu \Psi_i d\tau = \langle f | \mu | i \rangle \neq 0$$

Equation 2

The Transition Dipole Moment

- the dipole moment can be a permanent dipole moment $\mu = \mu_0$ or an induced dipole moment dependent on the polarizability $\mu = \alpha\epsilon$.
- the **total molecular wavefunction** is composed of electronic, vibrational, rotational and translational components

$$\Psi_{total} = \psi_{el} \psi_{vib} \psi_{rot} \psi_{trans}$$

Equation 3

- we assume separability of the wavefunction and the associated Schrödinger equations, (including the BO approximation) allow us to "ignore" parts of the equation.
- we will now only be working with the $\psi_{el}\psi_{vib}$ part of these equations
- from now on I will use:
 - ψ for electronic and χ for nuclear wavefunctions
 - subscript f=final state and subscript i=initial state
- applying the BO approximation and assuming that the dipole moment can be written in terms of separate electronic and nuclear components we have:

$$\begin{aligned} \mu_{fi} &= \int \psi_f \chi_f (\mu_e + \mu_n) \psi_i \chi_i d\tau_e d\tau_n \\ &= \int \psi_f \chi_f (\mu_e) \psi_i \chi_i d\tau_e d\tau_n + \int \psi_f \chi_f (\mu_n) \psi_i \chi_i d\tau_e d\tau_n \\ &= \int \chi_f \left[\int \psi_f (\mu_e) \psi_i d\tau_e \right] \chi_i d\tau_n + \int \psi_f \left[\int \chi_f (\mu_n) \chi_i d\tau_n \right] \psi_i d\tau_e \\ &= \int \chi_f \langle \mu_e \rangle \chi_i d\tau_n + \int \psi_f \langle \mu_n \rangle \psi_i d\tau_e \end{aligned}$$

Equation 4

- we now need to distinguish between transitions on the same electronic state and those between different electronic states
- a transition between vibrational states on the **same electronic state** is experimentally “measured” by IR and Raman spectroscopy
 - the first component is zero because the integrand is an odd function

$$\int \chi_f \langle \mu_e \rangle \chi_i d\tau_n = \int \chi_f \left[\int \psi_i(\mu_e) \psi_i d\tau_n \right] \chi_i d\tau_e = 0$$

$$\text{because } \int \psi_i(\mu_e) \psi_i d\tau_n = \int \psi_i e \hat{r} \psi_i d\tau_e = \int e \hat{r} \psi_i^2 d\tau_e = 0$$

Equation 5

- and we need to evaluate the second component

$$\int \psi_i \langle \mu_n \rangle \psi_i d\tau_e$$

$$= \int \psi_i \left[\int \chi_f(\mu_n) \chi_i d\tau_n \right] \psi_i d\tau_e = \int \psi_i \psi_i d\tau_e \cdot \int \chi_f(\mu_n) \chi_i d\tau_n$$

$$= \int \chi_f(\mu_n) \chi_i d\tau_n \quad \text{because } \int \psi_i \psi_i d\tau_e = 1$$

Equation 6

- a transition between **different electronic states** is experimentally “measured” by UV-vis spectroscopy, however the effects of vibrational transitions can sometimes be seen as fine-structure
 - in this case the second component is zero because the electronic states are orthogonal

$$\int \psi_f \langle \mu_n \rangle \psi_i d\tau_e$$

$$= \int \psi_f \left[\int \chi_f(\mu_n) \chi_i d\tau_n \right] \psi_i d\tau_e = \int \psi_f \psi_i d\tau_e \cdot \int \chi_f(\mu_n) \chi_i d\tau_n = 0$$

$$\text{because } \int \psi_f \psi_i d\tau_e = 0 \quad \text{if } f \neq i$$

Equation 7

- and we will need to evaluate the first component, this is something we will consider in due course

$$\int \chi_f \langle \mu_e \rangle \chi_i d\tau_n = \int \chi_f \left[\int \psi_f(\mu_e) \psi_i d\tau_n \right] \chi_i d\tau_e$$

Equation 8

- now we will consider vibrational transitions on the same electronic state, **Equation 8.**

$$\mu_{fi} = \int \chi_f(\mu_n) \chi_i d\tau_n = \int \chi_f \left(e \sum_n Z_n R_n \right) \chi_i d\tau_n$$

Equation 9

- to progress we need to understand what is “under the hood” of this integral and we need to know how to determine if the integral is zero or not.
- an advantage of spectroscopy is that we don’t need to evaluate the integral! We just need to know if it is zero (no peak in the spectrum) or not zero (a peak will be evident in the spectrum)
- at the moment we say nothing about how intense the peak will be!

The Nuclear Vibrational Wavefunction

- first we need to know the form of the nuclear (or vibrational) wavefunction
- you have met the harmonic oscillator (HO) potential before **Figure 1** shows a picture of the solutions and the functional form of these solutions

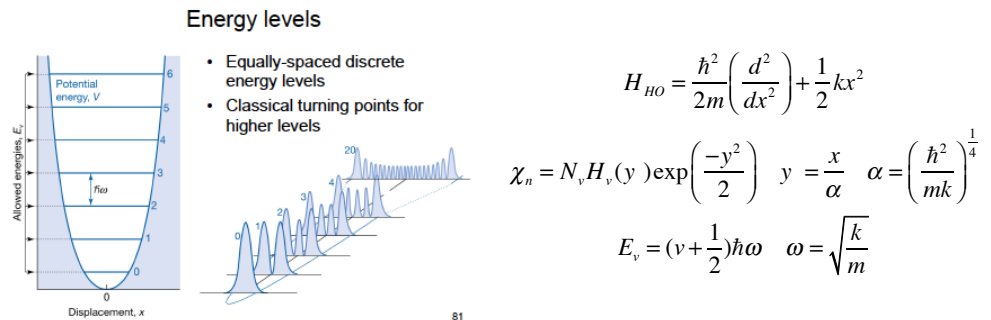


Figure 1 the HO Hamiltonian and wavefunctions

- these solutions take the form of a polynomial multiplied by an exponential,
 - the polynomial “looks after” the function going to zero (the oscillations)
 - the exponential “looks after” the decay properties of the functions (decaying to zero outside of the potential).
- $H_v(y)$ are **Hermite polynomials**, these are a set of functions (polynomials) with a special name because they satisfy a set of specific rules.

$$\begin{aligned} H_0(x) &= 1 \\ H_1(x) &= 2x \\ H_2(x) &= 4x^2 - 2 \\ H_3(x) &= 8x^3 - 12x \\ H_4(x) &= 16x^4 - 48x^2 + 12 \\ H_5(x) &= 32x^5 - 160x^3 + 120x \\ H_6(x) &= 64x^6 - 480x^4 + 720x^2 - 120 \end{aligned}$$

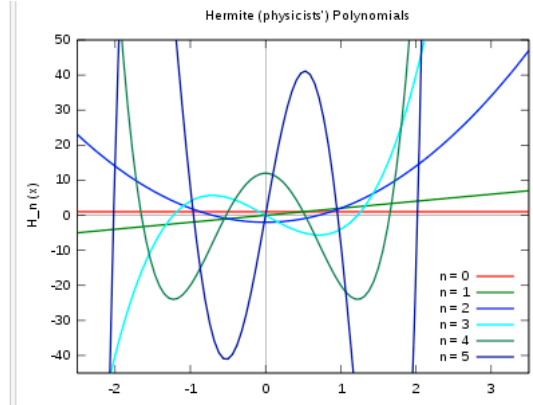


Figure 2 Hermite polynomials¹

- You have met other special types of function before, Bessel functions and spherical harmonics (angular solutions of electronic Schrödinger equation) as well as associated Laguerre functions (radial solution of the electronic equation), **there is a reminder of the radial electronic solutions in the OPTIONAL additional notes on-line.**
- Hermite polynomials satisfy certain rules:

$$\text{Recursion relation } H_{v+1}(y) = 2yH_v(y) - 2vH_{v-1}(y)$$

$$\text{Differential equation } H_v''(y) - 2yH_v'(y) + 2vH_v(y) = 0$$

$$\text{Orthogonality relation } \int_{-\infty}^{+\infty} H_v(y)H_{v'}(y)e^{-y^2} dy = 0 \quad v \neq v'$$

$$\text{Normalisation } \int_{-\infty}^{+\infty} H_v(y)H_v(y)e^{-y^2} dy = \pi^{\frac{1}{2}} 2^v v!$$

Equation 10

these will be provided if you need them in an exam!

¹ http://en.wikipedia.org/wiki/Hermite_polynomials

- the harmonic oscillator solutions given above are those for a single vibration, or single normal mode Q_i
 - the normal modes Q_i are just the vibrations we have already seen, ie the vector diagrams we generated in Lecture 3 which are also the coordinates that diagonalise the Hessian (second derivative matrix).
 - *each normal mode* has its own associated set of vibrational quantum numbers v_i .
 - to differentiate between the total vibrational wavefunction (χ) and the individual HO solutions for each Q_i I will refer to the individual solutions as $\varphi_{v_i}(Q_i)$
- in a molecule there are $3N-6$ vibrations and so the total nuclear wavefunction is made from a **product** of individual HO solutions for each normal mode:

$$\chi_n = \prod_i \varphi_i(Q_i) = \varphi_{v_1}(Q_1)\varphi_{v_2}(Q_2)\varphi_{v_3}(Q_3)\cdots$$

Equation 11

The Nuclear Dipole Moment

- we don't make a coordinate transformation to the normal modes for the dipole moment, so continue to think of this as a vector with μ_x , μ_y and μ_z components
- the nuclear dipole moment varies with the vibrational displacements of the nuclei, thus we use a Taylor expansion in terms of the normal modes (Q_k)

IMPORTANT

$$\mu_n = \mu_0 + \sum_k \left(\frac{\partial \mu_n}{\partial Q_k} \right)_0 Q_k + \frac{1}{2} \sum_k \left(\frac{\partial^2 \mu_n}{\partial Q_k^2} \right)_0 Q_k^2 + \cdots$$

Equation 12

- the first term gives the dipole moment when the displacement of atoms is zero, ie the static dipole moment, μ_0 .
- the second and larger terms describe the change in the dipole moment as the atoms move during a vibration

The Vibrational Selection Rules

- inserting μ_n into the equation for the transition dipole moment μ_{fi} generates:

$$\mu_{fi} = \langle \chi_f | \mu_0 | \chi_i \rangle + \sum_k \left(\frac{\partial \mu_n}{\partial Q_k} \right)_0 \langle \chi_f | Q_k | \chi_i \rangle + \frac{1}{2} \sum_k \left(\frac{\partial^2 \mu_n}{\partial Q_k^2} \right)_0 \langle \chi_f | Q_k^2 | \chi_i \rangle + \cdots$$

Equation 13

- in the **zero order term** μ_0 is a constant and can be brought out of the integral. By definition the vibrational states (on the same electronic state) are orthogonal and because we are examining an excitation this integral must be zero. Thus this term is eliminated

$$\langle \chi_f | \mu_0 | \chi_i \rangle = \mu_0 \langle \chi_f | \chi_i \rangle = \mu_0 \delta_{fi} = 0$$

Equation 14

- the **second order** and higher terms are assumed to be minimal

$$\frac{1}{2} \sum_k \left(\frac{\partial^2 \mu}{\partial Q_k^2} \right)_0 \langle \chi_f | Q_k^2 | \chi_i \rangle + \cdots \approx 0$$

Equation 15

- which leaves the **first order term** as the only significant contributor

$$\mu_{fi} = \sum_k \left(\frac{\partial \mu}{\partial Q_k} \right)_0 \langle \chi_f | Q_k | \chi_i \rangle$$

Equation 16

IMPORTANT

- the first order term has two components, both of these must be non-zero for the transition dipole moment to be **non-zero**

$$\left(\frac{\partial \mu}{\partial Q_k}\right)_0 \neq 0 \quad \text{and} \quad \langle \chi_f | Q_k | \chi_i \rangle \neq 0 \quad \text{Equation 17}$$

- the first of these indicates that to be vibrationally active the *nuclear dipole moment must change* or vary when the position of the atoms (nuclei) change within the normal mode Q_k . **This is the first selection rule for molecular vibrations.**
- we can explore the second expression further
 - first we think about the individual integrals

$$\begin{aligned} \chi_i &= \varphi_{v1}^i(Q_1) \varphi_{v2}^i(Q_2) \cdots \varphi_a^i(Q_a) \varphi_b^i(Q_b) \cdots \varphi_{v3n-6}^i(Q_{3n-6}) \\ \chi_f &= \varphi_{v1}^f(Q_1) \varphi_{v2}^f(Q_2) \cdots \varphi_a^f(Q_a) \varphi_b^f(Q_b) \cdots \varphi_{v3n-6}^f(Q_{3n-6}) \\ \langle \chi_f | Q_k | \chi_i \rangle &= \int (\varphi_{v1}^f(Q_1) \cdots \varphi_k^f(Q_k) \cdots) Q_k (\varphi_{v1}^i(Q_1) \cdots \varphi_k^i(Q_k) \cdots) dQ_1 \cdots dQ_k \cdots \\ &= \underbrace{\int \varphi_{v1}^f(Q_1) \varphi_{v1}^i(Q_1) dQ_1}_{=1} \cdots \int \varphi_k^f(Q_k) Q_k \varphi_k^i(Q_k) dQ_k \cdots \end{aligned} \quad \text{Equation 18}$$

only one integral will not be 1, that for the Q_k component

$$\begin{aligned} &= \int \varphi_k^f(Q_k) Q_k \varphi_k^i(Q_k) dQ_k \\ &\Rightarrow \langle \varphi_k^f(Q_k) | Q_k | \varphi_k^i(Q_k) \rangle \end{aligned}$$

- this integral can be evaluated using the harmonic oscillator solutions and **annihilation and creation operators** which are well beyond the scope of this course.
- a simpler justification for this rule can be determined from the recursion relationship of Hermite polynomials: $2yH_i(y) = H_{i+1}(y) + 2H_{i-1}(y)$:

$$\begin{aligned} |\varphi_i\rangle &\propto H_i(Q) \\ \langle \varphi_f | Q_k | \varphi_i \rangle &\propto \langle \varphi_f | Q_k H_i(Q) \rangle \\ 2QH_i(Q) &= H_{i+1}(Q) + 2H_{i-1}(Q) \quad \text{recursion relation} \\ \langle \varphi_f | Q_k | \varphi_i \rangle &\propto \frac{1}{2} \langle \varphi_f | H_{i+1}(Q) + 2H_{i-1}(Q) \rangle \\ &\propto \langle \varphi_f | H_{i+1}(Q) \rangle + \langle \varphi_f | H_{i-1}(Q) \rangle \\ &\propto \underbrace{\langle \varphi_f | \varphi_{i+1} \rangle}_{=0 \text{ unless } f=i+1} + \underbrace{\langle \varphi_f | \varphi_{i-1} \rangle}_{=0 \text{ unless } f=i-1} \end{aligned} \quad \text{Equation 19}$$

IMPORTANT

- two components result, the only way one of these components can be non-zero (due to the orthogonality of the harmonic oscillator solutions) is if $f=i+1$ or $f=i-1$.
- thus this *integral is only non-zero when the vibrational quantum numbers of the initial and final states differ by ± 1* , and we arrive at **the second selection rule for vibrational spectroscopy: $\Delta v = \pm 1$.**

- to determine if a Raman vibration is allowed we follow a similar procedure to that covered for the static dipole moment:
 - expand the polarizability with respect to the molecular vibrations or normal modes (Q_k) in a Taylor series
 - eliminate various terms until only the first order term is left

$$\mu_{fi} = \sum_k \left(\frac{\partial \alpha}{\partial Q_k} \right)_0 \langle \chi_f | Q_k | \chi_i \rangle \varepsilon \neq 0 \quad \text{Equation 20}$$

- the first factor of this term indicates that for a vibration to be Raman active the polarizability must change or vary with the vibrating nuclei.
- the second factor is identical to that obtained for an infrared vibration to be active and we arrive at the second selection rule that $\Delta v = \pm 1$.

The Direct Product and Integral Symmetry

- luckily to progress we don't need to compute the value of the transition dipole moment integral! We only need to know if the transition dipole is non-zero. This is where **symmetry is particularly powerful tool**.

$$\langle \chi_f | \lambda | \chi_i \rangle \neq 0 \quad \lambda = \alpha, \mu \quad \text{Equation 21}$$

- we now need two new pieces of information relating to symmetry groups and these are:
 - the direct product
 - odd and even functions and their integrals
- when two irreducible representations are combined as a product, the operation is called a **direct product** and is represented by the symbol $\otimes$
 - to form the direct product the characters of each symmetry operator of the representation are multiplied together
 - for example the direct product $A_1 \otimes A_2$ for the C_{3v} point group is A_2 :

C_{3v}	E	$2C_3$	$3\sigma_v$		C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1		A_1	1	1	1
A_2	1	1	-1		A_2	1	1	-1
E	2	-1	0		$A_1 \otimes A_2$	1	1	-1 = A_2

$A_1 \otimes A_2 = A_2$

Figure 3 Forming a direct product

- the irreducible representations of a point group are always orthonormal
 - another way of stating this property is to say that the sum of characters for a direct product of different IRs is always zero, and that the sum of characters for the same direct product IRs (divided by the order of the group) is always one (expand out the columns of point group first!)
 - for the example above:

$$\underbrace{[(1 \cdot 1)]}_E + \underbrace{[(2 \cdot 1)]}_{C_3} + \underbrace{[(3 \cdot -1)]}_{\sigma_v} = 0 \quad \text{Equation 22}$$

- the direct product does not necessarily behave the way we are used to! For example the direct product $E \otimes E$ for the C_{3v} point group is $\{A_1 + A_2 + E\}$ and it contains multiple components.

- To determine the direct product for degenerate IRs, first form the direct product and then reduce it using the reduction formula

C_{3v}	E	$2C_3$	$3\sigma_v$	
E	2	-1	0	
E	2	-1	0	
$E \otimes E$	4	1	0	

C_{3v}	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	$\Rightarrow n_{A_1} = \frac{1}{6}[(1 \cdot 4 \cdot 1) + (2 \cdot 1 \cdot 1) + (3 \cdot 0 \cdot 1)] = \frac{6}{6} = 1$
A_2	1	1	-1	$\Rightarrow n_{A_2} = \frac{1}{6}[(1 \cdot 4 \cdot 1) + (2 \cdot 1 \cdot 1) + (3 \cdot 0 \cdot -1)] = \frac{6}{6} = 1$
E	2	-1	0	$\Rightarrow n_{A_2} = \frac{1}{6}[(1 \cdot 4 \cdot 2) + (2 \cdot 1 \cdot -1) + (3 \cdot 0 \cdot 0)] = \frac{6}{6} = 1$
$E \otimes E$	4	1	0	

thus $E \otimes E = \{A_1 + A_2 + E\}$

Figure 4 Forming a direct product between degenerate IR

- there are short-cuts to working out a direct product these are listed with your character tables.
 - for example $A_1 \otimes A_2 = A_2$ since $A \otimes A = A$ and $1 \otimes 2 = 2$

In-Class Activity

- form the product $A_2 \otimes B_1$ for the C_{2v} point group explicitly by multiplying the characters, then check your answer by using the "rules" in your hand-out.

Determination of Non-Zero Integrals

IMPORTANT

- **functions that are totally symmetric have a non-zero integral**, while any functions that are not totally symmetric have zero integrals
- this is a key fact that we will be using extensively

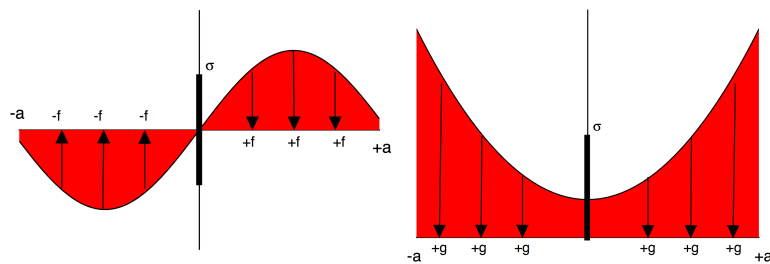


Figure 5 odd function f and even function g

- if f is antisymmetric about $x=0$ then $f(-x) = -f(x)$, and f is an "odd" function and will have an integral of zero over a symmetric range $-a$ to $+a$, **Figure 5a**

- if g is symmetric about $x=0$ then $g(-x) = g(x)$, and g is an "even" function and will have a non-zero integral over a symmetric range $-a$ to $+a$, **Figure 5b**
- if we consider the sign of the function over the interval a to $-a$, then the sign of these functions belongs to the C_s point group:

C_s	E	σ
A'	1	1
A''	1	-1

Figure 6 odd and even functions f and g

- the sign of the odd function f spans the irreducible representation A'' and the sign of the even function g spans the irreducible representation A'
- thus functions that are totally symmetric have a non-zero integral, while any functions that are not totally symmetric have zero integrals
- saying the same thing but more formally:

If an integrand is not a basis for the totally symmetric IR of the group, then the integral is necessarily zero.

- there is one caveat, a function that has a non-zero integral by symmetry may have a zero integral accident!

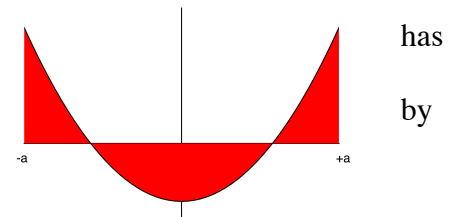


Figure 7 an integral is zero "by accident"

- consider first an integrals of the form $\int f^2 d\tau$ in the point group C_s

$$\begin{array}{lll}
 f \text{ spans } A'' & g \text{ spans } A' & g \text{ spans } A' \text{ and } f \text{ spans } A'' \\
 \therefore f^2 = f \times f & \therefore g^2 = g \times g & \therefore gf = g \times f \\
 \text{spans } A'' \otimes A'' = A' & \text{spans } A' \otimes A' = A' & \text{spans } A' \otimes A'' = A'' \\
 \text{Equation 23}
 \end{array}$$

- the irreducible representation spanned by the square of a function is always totally symmetric and will therefore have a non-zero integral by symmetry (it can still be accidentally zero!)
- the irreducible representation spanned by a product of functions belonging to different irreducible representations will not be totally symmetric and will therefore have a zero integral by symmetry
- there is an additional level of complexity introduced by functions that span degenerate irreducible representations, in this case the reduced representation must contain the totally symmetric component.
 - [there is a little more detail for this in the OPTIONAL additional notes on-line.](#)

- now we are ready to determine when a general integral is zero using symmetry.
 - an integral can only be non-zero if it has an integrand (the central functions inside the integral) that contains a totally symmetric component
 - first evaluate the direct product of all the components of the integral
 - if this is a reducible representation, reduce it to the component IR
 - identify if there is a totally symmetric component

$$\begin{aligned}
 I &= \int f_i f_j f_k d\tau \\
 \Gamma_R &= \Gamma(f_i) \otimes \Gamma(f_j) \otimes \Gamma(f_k) \\
 \Gamma_R &= n_1 \Gamma_1^{IR} + n_2 \Gamma_2^{IR} + \dots
 \end{aligned}
 \tag{Equation 24}$$

- for example we can evaluate the integral $I = \langle d_{xy} | z | d_{x^2-y^2} \rangle$ under the C_{4v} point group. The d_{xy} function spans the B_2 IR, the $d_{x^2-y^2}$ function spans the B_1 IR, and the z function spans the A_1 IR. To be non-zero the direct product of these IR must be A_1 .

$$\begin{aligned}
 I &= \langle d_{xy} | z | d_{x^2-y^2} \rangle \rightarrow \Gamma = \{B_2 \otimes A_1 \otimes B_1\} \\
 \text{and } B_2 \otimes A_1 &= B_2 \quad \text{then } B_2 \otimes B_1 = A_2 \\
 \text{thus } \Gamma &= A_2 \quad I = 0
 \end{aligned}
 \tag{Equation 25}$$

Using Symmetry to Determine Infrared and Raman Activity

- now we are ready to apply this general principle to our specific example
- we require that the transition dipole moment or transition polarizability matrix be non-zero, ie that $\langle \chi_f | \lambda | \chi_i \rangle \neq 0 \quad \lambda = \alpha, \mu$
- for this integral to be non-zero at least one component must span the totally symmetric irreducible representation of the point group of the molecule
- this is determined by forming the direct product of the components:

$$\Gamma^{\langle \chi_f |} \otimes \Gamma^\lambda \otimes \Gamma^{|\chi_i \rangle} \text{ where } \lambda = \mu \text{ or } \alpha
 \tag{Equation 26}$$

IMPORTANT

- the ground vibrational state is always totally symmetric $\Gamma^{|\chi_i \rangle} = A$
 - the symmetry of the final state is the symmetry of the excited vibration $\Gamma^{\langle \chi_f |} = \Gamma(\text{vibration})$ (when we have a single excitation)
 - the symmetry of the λ components is known, they reflect the symmetry of the translational vectors for μ or the binary functions for α
- $$\Gamma^\mu = \begin{bmatrix} \Gamma(x) \\ \Gamma(y) \\ \Gamma(z) \end{bmatrix} \quad \Gamma^\alpha = \begin{bmatrix} \Gamma(x^2) \\ \Gamma(y^2) \\ \Gamma(z^2) \\ \Gamma(xz) \\ \Gamma(xy) \\ \Gamma(yz) \end{bmatrix}$$
- for example we deduced the vibrational modes of water to be $\Gamma_{\text{vib}} = 2A_1 + B_2$
 - we know the ground vibrational state is totally symmetric $\Gamma^{|\chi_i \rangle} = A_1$
 - we know that the final vibrational state can be $\Gamma^{\langle \chi_f |} = A_1$ or B_2
 - we know that μ spans the IRs $x \Rightarrow B_1$ $y \Rightarrow B_2$ and $z \Rightarrow A_1$

- we know that α components span all the IRs (ie there is a binary function associated with all of the IR)
- thus for $\Gamma^{\langle \chi_f |} = A_1$ we require the direct product to contain the A_1 IR:

$$\left\{ \Gamma^{\langle \chi_f |} \otimes \Gamma^{|\chi_i \rangle} \right\} \otimes \Gamma^\lambda = \{A_1 \otimes A_1\} \otimes \begin{bmatrix} B_1 \\ B_2 \\ A_1 \end{bmatrix} = A_1 \otimes \begin{bmatrix} B_1 \\ B_2 \\ A_1 \end{bmatrix} = \{B_1, B_2, A_1\}$$

Equation 27

- I have used a “vector” notation to represent the dipole moment IRs
- I have used a “set” notation to indicate that the final integral will contain components $\{B_1, B_2, A_1\}$
- only one of these components needs to be the A_1 IR for the integral to be non-zero
- thus we find that the A_1 vibration is allowed $\Rightarrow$ we will see an A_1 peak in the infrared spectrum of water

In-Class Activity

- determine if excitation of the B_2 vibration of H_2O is allowed for IR spectra:

- a similar process is followed for Raman activity, thus for $\Gamma^{\langle \chi_f |} = A_1$ we require the direct product below to contain the A_1 IR:

$$\left\{ \Gamma^{\langle \chi_f |} \otimes \Gamma^{|\chi_i \rangle} \right\} \otimes \Gamma^\alpha = \{A_1 \otimes A_1\} \otimes \begin{bmatrix} A_1 \\ A_1 \\ A_1 \\ B_1 \\ A_2 \\ B_2 \end{bmatrix} = A_1 \otimes \begin{bmatrix} A_1 \\ B_1 \\ A_2 \\ B_2 \end{bmatrix} = \{A_1, B_1, A_2, B_2\}$$

Equation 28

- as above I have used the a “vector” notation to represent the all the IRs spanned by the binary functions. I have also used a “set” notation to indicate that the final integral will contain components $\{A_1, A_2, B_1, B_2\}$
- it is not necessary to include all the tensor components, we just need to know the different IRs so if one IR is repeated we don’t need to repeat it in the equations.
- only one of these components needs to be the A_1 IR for the integral to be non-zero. Thus the A_1 vibration is allowed $\Rightarrow$ we will see an A_1 peak in the Raman spectrum of water

In-Class Activity

- determine if excitation of the B_2 vibration is allowed for Raman spectra:

Phrasing of the Selection Rule

- the selection "rule" that we have previously been presented with was slightly different, it was stated that a mode is
 - infrared active if the IR of the vibration is the same as one of the translational vectors
 - Raman active if the IR of the vibration is the same as one of the binary functions
- to arrive at this form of the rules we must note:
 - the translational vectors have the same symmetry as the x, y and z coordinate axes which form the components of the nuclear dipole moment
 - the binary functions have the same symmetry as the matrix components of the polarizability tensor.
 - the totally symmetric mode is similar to the "identity" in matrix mechanics and thus $\{\Gamma^{(f)} \otimes \Gamma^{(i)}\} = \{\Gamma^{(f)} \otimes A_1\} = \Gamma^{(f)}$ always spans the IR of the final state as the initial state is totally symmetric
 - that only "the direct product square" of an IR will generate the totally symmetric IR $\Gamma^m \otimes \Gamma^m \in A_1$ (plus some other components if the IR is degenerate)
 - thus $\{\Gamma^{(f)} \otimes \Gamma^{(i)}\} \otimes \Gamma^\lambda = \Gamma^{(f)} \otimes \Gamma^\lambda$ only contains the A_1 IR when $\Gamma^f = \Gamma^\lambda$
- thus we can only have an "allowed" transition when the vibration has the same IR as the translational vectors (infrared) or binary functions (Raman)!

IMPORTANT

Key Points

- be able to explain the simplifications we have applied to the full transition dipole moment equation
- be able to explain and discuss the general components of the harmonic oscillator nuclear wavefunctions
- be able to show using a Taylor expansion the origin of the rule that "the *molecular dipole moment must change* for infrared activity" and be able to show the appropriate relationship for Raman activity
- be able to explain using equations the origin of the $\Delta v = \pm 1$ selection rule for vibrational spectroscopy
- be able to demonstrate the direct product of IRs giving examples, both the "long way" by explicit multiplication or IRs and using short-cuts
- be able to determine if an integral is zero or non-zero by symmetry

- starting from an expression of the form $\lambda_\alpha = \langle \chi_f | \lambda | \chi_i \rangle \neq 0$ $\lambda = \alpha, \mu$, be able to explain using direct products the origin of the vibrational selection "rules" that a mode is infrared active only if the IR of the vibration is the same as one of those for the translational vectors or a mode is Raman active only if the IR of the vibration is the same as one of those for the binary functions
- be able to determine when a mode is IR or Raman active using the expression

$$\left\{ \Gamma^{\langle \chi_f |} \otimes \Gamma^{|\chi_i \rangle} \right\} \otimes \Gamma^\lambda \text{ where } \lambda = \mu \text{ or } \alpha$$

Self-Study / Tutorial / Exam Preparation Problems

- show that the A_1 and A_2 IRs of the C_{3v} point group are orthonormal
- show that the irreducible representations of the point group C_3 are orthonormal (hint, don't forget that the pre-multiplied character is the complex conjugate!)

C_3	E	C_3^1	C_3^2
A_1	1	1	1
$E \left\{ \right.$	1	ε	ε^*
$\left. \right\}$	1	ε^*	ε

$\varepsilon = \exp(2\pi i/3)$

- form the direct product $A_2 \otimes B_2 \otimes B_1$ for the C_{2v} point group using both a character table and the crib sheet
- determine the irreducible representations spanned by $(x, y, z)^2$ under the C_{3v} point group
- form a direct product $E_1 \otimes T_1 \otimes T_2$ for the tetrahedral point group
- use the equation given below to identify and show which irreducible representations of the C_{4v} point group relate to modes that are IR active or inactive.

$$A_1 \in \left\{ \Gamma^{\langle \chi_f |} \otimes \Gamma^{|\chi_i \rangle} \otimes \Gamma^\mu \right\}$$