PHY 745 Group Theory
11-11:50 AM MWF Olin 102

Plan for Lecture 9:

Evaluating transition matrix elements using character tables

Reading: Chapter 8 in DDJ

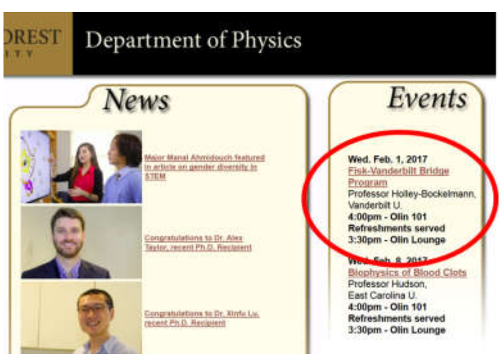
1. **Analysis of vibrational infrared spectra**
2. **Analysis of vibrational Raman spectra**

Note: In this lecture, some materials are taken from an electronic version of the Dresselhaus, Dresselhaus, Jorio text

Course schedule for Spring 2017

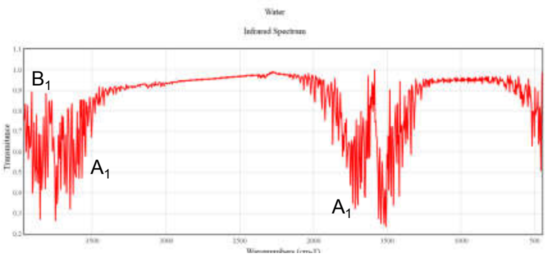
(Preliminary schedule -- subject to frequent adjustment.)

	Lecture date	DDJ Reading	Topic	HW	Due date
1	Wed: 01/11/2017	Chap. 1	Definition and properties of groups	#1	01/20/2017
2	Fri: 01/13/2017	Chap. 1	Theory of representations		
	Mon: 01/16/2017		*MLK Holiday - no class*		
3	Wed: 01/18/2017	Chap. 2	Theory of representations		
4	Fri: 01/20/2017	Chap. 2	Proof of the Great Orthonality Theorem	#2	01/23/2017
5	Mon: 01/23/2017	Chap. 3	Notion of character of a representation	#3	01/25/2017
6	Wed: 01/25/2017	Chap. 3	Examples of point groups	#4	01/27/2017
7	Fri: 01/27/2017	Chap. 4 & 8	Symmetry of vibrational modes	#5	01/30/2017
8	Mon: 01/30/2017	Chap. 4 & 8	Symmetry of vibrational modes	#6	02/01/2017
9	Wed: 02/01/2017	Chap. 8	Vibrational excitations	#7	02/03/2017
10	Fri: 02/03/2017				
11	Mon: 02/06/2017				
12	Wed: 02/08/2017				



Symmetry analysis of the coupling of electromagnetic waves to molecular vibrations

Infrared spectrum of gaseous H_2O from NIST



Fermi Golden Rule for absorption of electromagnetic radiation

$$R_{i \to f} = \frac{2\pi}{\hbar} \left| \langle \Psi_i | \Delta H | \Psi_f \rangle \right|^2 \rho_f$$

density of final states

In this case the perturbation matrix represents the coupling of an electric field $\mathbf{E}$ with the charges $\{q_j\}$ of the system:

$\Delta H = \mathbf{E} \cdot \mathbf{u}$ where dipole moment $\mathbf{u} = \sum_j q_j \mathbf{r}_j$

$\langle \Psi_i |$ Initial state; usually ground state characterized by identity representation

$| \Psi_f \rangle$ Final state

Note that radiation couples to molecules with net dipole moment

Using character tables to analyze interaction matrix elements

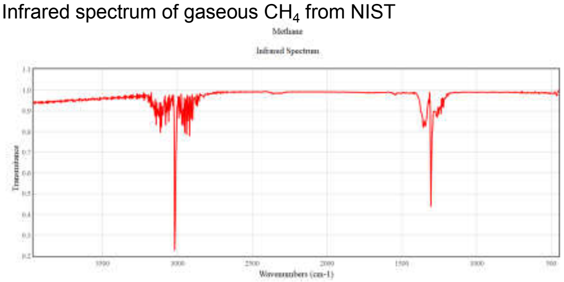
$$\langle \Psi_i | \Delta H | \Psi_f \rangle \Leftrightarrow \sum_k N_k \left(\chi^i(\mathcal{C}_k) \right)^* \chi^{\Delta H}(\mathcal{C}_k) \chi^f(\mathcal{C}_k)$$

Example of H_2O

C_{2v} (2mm)			E	C_2	σ_v	σ'_v
x^2, y^2, z^2	z	A_1	1	1	1	1
xy	R_z	A_2	1	1	−1	−1
xz	R_y, x	B_1	1	−1	1	−1
yz	R_x, y	B_2	1	−1	−1	1

$\langle \Psi_i \|$	ΔH	$\| \Psi_f \rangle$	
A_1	$E_z u_z$ (A_1)	A_1	
A_1	$E_x u_x$ (B_1)	B_1	
A_1	$E_y u_y$ (B_2)	B_2	0 (frequency mode)

Infrared spectrum of gaseous CH_4 from NIST



Example of CH_4

T_d ($\bar{4}3m$)		E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$
	A_1	1	1	1	1	1
	A_2	1	1	1	−1	−1
	E	2	−1	2	0	0
(R_x, R_y, R_z)	T_1	3	0	−1	−1	1
(x, y, z)	T_2	3	0	−1	1	−1

$$\langle \Psi_i | \quad \Delta H \quad | \Psi_f \rangle$$

$$A_1 \quad E_x, E_y, E_z \ (T_2) \quad ??$$

Vibrational modes excited by Raman scattering

Consider an induced dipole moment due to incident electric field:

$$\mathbf{u} = \boldsymbol{\alpha} \cdot \mathbf{E}_i \cos \omega t$$

Raman polarizability tensor having the form:

$$\boldsymbol{\alpha} = \boldsymbol{\alpha}_0 + \Delta\boldsymbol{\alpha} \cos \omega_v t$$

static polarizability

polarizability due to vibration at frequency ω_v

$$\mathbf{u} = \boldsymbol{\alpha} \cdot \mathbf{E}_i \cos \omega t = (\boldsymbol{\alpha}_0 + \Delta\boldsymbol{\alpha} \cos \omega_v t) \cdot \mathbf{E}_i \cos \omega t$$

$$= \boldsymbol{\alpha}_0 \cdot \mathbf{E}_i \cos \omega t + \frac{\Delta\boldsymbol{\alpha} \cdot \mathbf{E}_i}{2} \left(\cos[(\omega - \omega_v)t] + \cos[(\omega + \omega_v)t] \right)$$

Rayleigh interaction

Stokes interaction

anti-Stokes interaction

Raman interaction Hamiltonian:

$$\Delta H = -\frac{1}{2}\left(\Delta\boldsymbol{\alpha}\cdot\mathbf{E}_i\right)\cdot\mathbf{E}_S\cos\left[\left(\omega\pm\omega_v\right)t\right]$$

As before, we need to analyze matrix elements of the form

$$\left\langle\Psi_i\middle|\Delta H\middle|\Psi_f\right\rangle$$

$$x^2, y^2, z^2, xy, yz, xz$$

Example for H_2O

C_{2v} (2mm)			E	C_2	σ_v	σ_v'
x^2, y^2, z^2	z	A_1	1	1	1	1
xy	R_z	A_2	1	1	−1	−1
xz	R_y, x	B_1	1	−1	1	−1
yz	R_x, y	B_2	1	−1	−1	1

$\langle\Psi_i\|$	ΔH	$\|\Psi_f\rangle$	
A_1	x^2, y^2, z^2 (A_1)	A_1	
A_1	xy (A_2)	A_2	0 (frequency mode)
A_1	xz (B_1)	B_1	
A_1	yz (B_2)	B_2	0 (frequency mode)

Other examples

$D_{3h} = D_3 \otimes \sigma_h$ $(\bar{6}m2)$			E	σ_h	$2C_3$	$2S_3$	$3C_2'$	$3\sigma_v$	
x^2+y^2, z^2		A_1'	1	1	1	1	1	1	➔Raman
	R_z	A_2'	1	1	1	1	−1	−1	
		A_1''	1	−1	1	−1	1	−1	
	z	A_2''	1	−1	1	−1	−1	1	➔IR
(x^2-y^2, xy)	(x, y)	E'	2	2	−1	−1	0	0	➔IR+Raman
(xz, yz)	(R_x, R_y)	E''	2	−2	−1	1	0	0	➔Raman