

# Notes of **Advanced Physical Chemistry II**

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## Introduction

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## 12 Group Theory: the Exploitation of Symmetry

### Matrices

$\det(\mathbf{A}) = 0 \Rightarrow \mathbf{A}$  is a singular matrix.

### 12.1 The Exploitation of the Symm of a Mol Can Be Used to Significantly Simplify Numerical Calculations

### 12.2 The Symm of Mols Can Be Described by a Set of Symm Elements

$E$	
$C_n$	Rotation by $360^\circ/n$
$\sigma$	
$i$	
$S_n$	

Table 1: Symmetry elements and operators

### Identity

### Rotation

$\sigma_h$	horizontal
$\sigma_v$	vertical
$\sigma_d$	diagonal (vertical and bisects the angle between $C_2$ axis)

Table 2

### Reflection

### Inversion

### Rotation Reflection

$$\hat{S}_n = \hat{\sigma}_h \times \hat{C}_n \quad (12.1)$$

### 12.2.1 Point Groups of Interest to Chemists

$C_{nv}$	Rotation by $360^\circ/n$
$C_{nh}$	
$D_{nh}$	
$D_{nv}$	
$D_{nd}$	
$T_d$	

Table 3: Symmetry elements and operators

## 12.3 The Symm Operators of a Mol Form a Group

A set of operators form a group if they satisfy:

1. closed under multiplication 乘法封闭
2. associative multiplication 乘法结合律
3. only one identity operator 单位元
4. everyone has only one inverse 逆元

### 12.3.1 Point Group for Some Mols

No Symm Axis

$C_1$  – nothing

$C_s$  –  $\sigma$

$C_i$  –  $i$

$C_n$

$S_n$

$C_{nv}$  –  $C_n$  and  $n\sigma_v$

$C_{nh}$  –  $C_n$  and  $\sigma_h$

$D_n$  –  $C_n$  and  $nC_2 \perp C_n$

e.g. 一点点交错的  $C_3H_6$ ,  $C_2$  在 3 个角平分线处

$D_{nd}$  –  $C_n$ (also  $S_{2n}$ ) and  $nC_2 \perp C_n$  and  $n\sigma_d$

$D_{nh}$  –  $C_n$  and  $nC_2 \perp C_n$  and  $\sigma_h$

$T_d$  主轴是  $S_4$

$O_h$

$I_h$

#### 12.4 Symm Operators Can Be Represented by Matrices

#### 12.5 The $C_{3v}$ Point Group Has a 2-D Irreducible Representation

#### 12.6 The Most Important Summary of the Properties of a Point Group Is Its Character Table

basis

class same characters – in a class.

# of class = # of irred representn.

notations

1.  $A_1, B_1, E:2D, T:3D$
2.  $A_1$ : symm wrt  $C_2/\sigma_v$ ,  $A_2$ : antisymm wrt that.
3.  $A'$ : symm wrt  $\sigma_h$ ,  $A''$ : antisymm wrt that.
4.  $A_g, A_u$ :

#### 12.7 Several Mathematical Relations Involve the Characters of Irreducible Representation

notations

XU G.X.	McQuarrie	
$D^{(\nu)}(R)$		
$\chi^{(\nu)}(R)$	$\chi_j(R)$	
$n_\nu$	$d_j$	dimension of repr matrix
$a_\nu$	$a_j$	
$g$	$h$	

Table 4

order

$$\sum_{\nu} n_{\nu}^2 = g \quad (12.2)$$

character

$$\sum_R D_{il}^{(\nu)} D_{jm}^{*(\mu)} = \frac{g}{n_{\nu}} \delta_{\mu\nu} \delta_{ij} \delta_{lm} \quad (12.3)$$

$$\sum_R \chi^{(\nu)}(R) \chi^{*(\mu)}(R) = g \delta_{\mu\nu} \quad (12.4)$$

$$\sum_R \chi^{(\nu)}(R) = 0 \quad (\nu \neq A_1) \quad (12.5)$$

reduce a given reducible repr  $\Gamma$

Suppose

$$\chi(R) = \sum_{\nu} a_{\nu} \chi^{(\nu)}(R) \quad (12.6)$$

thus

$$a_{\nu} = \frac{1}{g} \sum_R \chi(R) \chi^{(\nu)}(R) \quad (12.7)$$

12.8 Use Symm Arguments to Predict Which Elements in a Secular Det Equals 0

12.9 Generating Operators Are Used to Find LCAOs That Are Bases for IrRepr

$$\hat{\mathbf{P}}_j = \frac{d_j}{h} \sum_{\hat{\mathbf{R}}} \chi_j(\hat{\mathbf{R}}) \hat{\mathbf{R}} \quad (12.8)$$

## 13 Molecular Spectroscopy

### 13.1

	micro	far IR	IR	visible & UV
$f/\text{Hz}$				
$\lambda/\text{m}$				
$\tilde{\nu}/\text{cm}^{-1}$				
$E/\text{J mol}^{-1}$				
process				

Table 5

### 13.2 Rotational Transitions Accompany Vibrational Transitions

Vib & rot energy

$$\tilde{E} = G(\nu) + F(J) \quad (13.1)$$

$$= (v + 1/2)\tilde{\nu} + \tilde{B}J(J + 1) \quad (13.2)$$

selex rule:

$$\Delta v = \pm 1 \quad \Delta J = \pm 1 \quad (13.3)$$

P – left –  $\Delta J = -1$  – wide

R – right –  $\Delta J = +1$  – narrow

### 13.3

$$\tilde{B}_v = \tilde{B}_e - \tilde{\alpha}_e(v + 1/2) \quad (13.4)$$

$$\tilde{B}_0 > \tilde{B}_1 > \dots \quad (13.5)$$

which makes P-branches wider.

## 13.4

$$F(J) = \tilde{B}J(J+1) - \tilde{D}J^2(J+1)^2 \quad (13.6)$$

$\tilde{D}$ :

## 13.5 Overtones Are Observed in Vibrational Spectra

$$G(v) = \tilde{\nu}_e \left( v + \frac{1}{2} \right) - \tilde{x}_e \tilde{\nu}_e \left( v + \frac{1}{2} \right)^2 \quad (13.7)$$

$\tilde{x}_e$ : anharmonicity cons.

$$\tilde{\nu}_{obs} = \tilde{\nu}_e v - \tilde{x}_e \tilde{\nu}_e v(v+1) \quad (13.8)$$

$v = 1, 2, \dots$

## 13.6 Electronic Spectra Contains Electronic, Vibrational and Rotational Info

$$\tilde{E} = n\tilde{u}_{el} + \tilde{\nu}_e(v+1/2) - \tilde{x}_e \tilde{\nu}_e(v+1/2)^2 + \dots (rot) \quad (13.9)$$

vibronic transitions:

$0 \rightarrow 0$

$$\tilde{\nu}_{0,0} = \tilde{T}_e + \frac{1}{2}(\tilde{\nu}'_e - \tilde{\nu}''_e) - \frac{1}{4}(\tilde{x}'_e \tilde{\nu}'_e - \tilde{x}''_e \tilde{\nu}''_e) \quad (13.10)$$

## 13.7 Franck-Condon Principle Predicts the Relative Intensities of Vibronic Transitions

## 13.8 The Rotational Spectrum of a Polyatomic Mols Depends Upon the Principal Moments of Inertia of the Mol

$$\begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{xy} & I_{yy} & I_{yz} \\ I_{xz} & I_{yz} & I_{zz} \end{pmatrix} \xrightarrow{\text{diagonalization}} \begin{pmatrix} I_A & & \\ & I_B & \\ & & I_C \end{pmatrix} \quad (13.11)$$

	top	requisition
$I_C = I_B > I_A = 0$		
$I_C = I_B = I_A$	sph top	$2C_n, n \geq 3$
$I_C = I_B > I_A$	prolate symm top	
$I_C > I_B = I_A$	oblate symm top	
$I_C \neq I_B \neq I_A$	asymm	

Table 6

## 13.9 The Vibrations of Polyatomic Mols Are Represented by Normal Coordinates

## 13.10 Normal Coordinates Belong to Irreducible Representations of Mol Point Groups

Contribution to  $\chi(R)$  per unmoved atom



$\hat{\mathbf{R}}$ contribution per unmoved atom
--

Table 7

Now we get  $\Gamma_{3N}$ .

Subtract the irreducible representations corresponding to translational  $(x, y, z)$  and rotational  $(R_x, R_y, R_z)$  degrees of freedom, we get  $\Gamma_{vib}$ .

### 13.11 Selection Rules Are Derived from TD Perturbation Theory

Consider a mol interacting w/ EM radiation. The EM field

$$\mathbf{E} = \mathbf{E}_0 \cos 2\pi\nu t \quad (13.12)$$

$$\hat{\mathbf{H}}^{(1)} = -\boldsymbol{\mu} \cdot \mathbf{E} = -\boldsymbol{\mu} \mathbf{E}_0 (\mathrm{e}^{\mathrm{i} 2\pi\nu t} + \mathrm{e}^{-\mathrm{i} 2\pi\nu t})/2 \quad (13.13)$$

$$\Psi(t) = a_1(t)\Psi_1(t) + a_2(t)\Psi_2(t) \quad (13.14)$$

$$a_1(t)\hat{\mathbf{H}}^{(1)}\Psi_1 + a_2(t)\hat{\mathbf{H}}^{(1)}\Psi_2 = \mathrm{i}\hbar\left(\Psi_1\frac{\mathrm{d}a_1}{\mathrm{d}t} + \Psi_2\frac{\mathrm{d}a_2}{\mathrm{d}t}\right) \quad (13.15)$$

$$a_1(t)\left\langle\psi_2\left|\hat{\mathbf{H}}^{(1)}\right|\Psi_1\right\rangle + a_2(t)\left\langle\psi_2\left|\hat{\mathbf{H}}^{(1)}\right|\Psi_2\right\rangle = \mathrm{i}\hbar\left(0 + \frac{\mathrm{d}a_2}{\mathrm{d}t}\mathrm{e}^{-\mathrm{i}Et/\hbar}\right) \quad (13.16)$$

...

$$\mathrm{i}\hbar\frac{\mathrm{d}a_2}{\mathrm{d}t} = \mathrm{e}^{-\mathrm{i}(E_1-E_2)t/\hbar}\left\langle\psi_2\left|\hat{\mathbf{H}}^{(1)}\right|\psi_1\right\rangle \quad (13.17)$$

$$\frac{\mathrm{d}a_2}{\mathrm{d}t} \approx \dots \quad (13.18)$$

### 13.12 The Selection Rule in the Rigid-Rotator Approx Is $\Delta J = \pm 1$

$$\begin{aligned} \langle J', M' | \mu_z | J, M \rangle &= \int_0^{2\pi} \mathrm{d}\phi \int_0^\pi Y_{J'}^{M'*} \mu_z Y_J^M \sin\theta \mathrm{d}\theta \\ &= \dots \end{aligned} \quad (13.19)$$

### 13.13 The Harmonic-Oscillator Selection Rule Is $\Delta\nu = \pm 1$

## 14 Nuclear Magnetic Resonance Spectroscopy

### 14.1 Nuclei Have Intrinsic Spin Angular Momenta

### 14.2 Magnetic Moments Interact with Magnetic Fields

### 14.3

### 14.4 The Magnetic Field Acting upon Nuclei in Mols Is Shielded

### 14.5 Chemical Shifts Depend upon the Chemical Environment of the Nucleus

### 14.6 Spin-Spin Coupling

$$\hat{\mathbf{H}} = -\gamma B_0(1 - \sigma_1)\hat{\mathbf{I}}_{z1} - \gamma B_0(1 - \sigma_2)\hat{\mathbf{I}}_{z2} + 2\pi J_{12}\hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2 \quad (14.1)$$

$$\hat{H}^{(0)} = -\gamma B_0(1 - \sigma_1)\hat{I}_{z1} - \gamma B_0(1 - \sigma_2)\hat{I}_{z2} \quad \hat{H}^{(1)} = 2\pi J_{12}\hat{I}_1 \cdot \hat{I}_2 \quad (14.2)$$

$$\psi_1^{(0)} = \alpha(1)\alpha(2) \quad \psi_2^{(0)} = \beta(1)\alpha(2) \quad (14.3)$$

$$\psi_3^{(0)} = \alpha(1)\beta(2) \quad \psi_4^{(0)} = \beta(1)\beta(2) \quad (14.4)$$

$$E_1^{(0)} = -\gamma B_0 \left(1 - \frac{\sigma_1 + \sigma_2}{2}\right) \quad E_2^{(0)} = -\gamma B_0(\sigma_1 - \sigma_2) \quad (14.5)$$

$$E_3^{(0)} = \gamma B_0(\sigma_1 - \sigma_2) \quad E_4^{(0)} = \gamma B_0 \left(1 - \frac{\sigma_1 + \sigma_2}{2}\right) \quad (14.6)$$

perturbed to 1st order

$$E_1 = -\gamma B_0 \left(1 - \frac{\sigma_1 + \sigma_2}{2}\right) + \frac{2\pi J_{12}}{4} \quad (14.7)$$

$$E_2 = -\gamma B_0(\sigma_1 - \sigma_2) - \frac{2\pi J_{12}}{4} \quad (14.8)$$

$$E_3 = \gamma B_0(\sigma_1 - \sigma_2) - \frac{2\pi J_{12}}{4} \quad (14.9)$$

$$E_4 = \gamma B_0 \left(1 - \frac{\sigma_1 + \sigma_2}{2}\right) + \frac{2\pi J_{12}}{4} \quad (14.10)$$

Since

$$\nu_0 = \frac{\gamma B_0}{2\pi} \quad (14.11)$$

$$\nu_{1 \rightarrow 2} = \nu_0(1 - \sigma_1) - \frac{J_{12}}{2} \quad (14.12)$$

$$\nu_{1 \rightarrow 3} = \nu_0(1 - \sigma_2) - \frac{J_{12}}{2} \quad (14.13)$$

$$\nu_{2 \rightarrow 4} = \nu_0(1 - \sigma_2) + \frac{J_{12}}{2} \quad (14.14)$$

$$\nu_{3 \rightarrow 4} = \nu_0(1 - \sigma_1) + \frac{J_{12}}{2} \quad (14.15)$$

## 14.7 Spin-Spin Coupling Between Chemically Equivalent Protons

### 14.8 The $n + 1$ Rule

### 14.9 2nd-Order Spectra

Only for the case in which

$$J \ll \nu_0 |\sigma_1 - \sigma_2| \quad (14.16)$$

the  $n + 1$  spectra.

## 15 Lasers, Laser Spectroscopy and Photochemistry

### 15.1

### 15.2 The Dynamics of Spectroscopic Transitions between the Electronic States

absorption

$$-\frac{dN_1(t)}{dt} = B_{12}\rho_\nu(\nu_{12})N_1(t) \quad (15.1)$$

emission

### 15.3 Population Inversion, 2-Level System

### 15.4 Population Inversion, 3-Level System

### 15.5 What is Inside a Laser?

### 15.6 He-Ne Laser

### 15.7 High-Resolution Laser Spectroscopy

Hyperfine structure

### 15.8 The Dynamics of Photochemistry Process

def: quantum yield

$$\Phi = \frac{\# \text{ mols undergoing reaction}}{\# \text{ photons absorbed}} \quad (15.2)$$

## 16 The Properties of Gases

## 17 The Boltzmann Factor and Partition Functions

### 17.1

### 17.2 Partition Function

$$Q = \quad (17.1)$$

$$p_j = \frac{e^{-E_j\beta}}{Q} \quad (17.2)$$

### 17.3 Thermodynamic Quantities

#### 17.3.1 Energy

#### 17.3.2 Work and Heat

### 17.4 Pressure

#### 17.4.1 Heat Capacity

#### 17.4.2 Entropy

### 17.5

### 17.6 The Partition Function of a System of Independent, Distinguishable Mols

$$Q(N, V, T) = \sum_{i,j,k,\dots} e^{-\beta(\varepsilon_i + \varepsilon_j + \varepsilon_k)} = \sum_i e^{-\beta\varepsilon_i} \sum_j e^{-\beta\varepsilon_j} \dots \quad (17.3)$$

### 17.7 The Partition Function of a System of Independent, Indistinguishable Mols

$$Q(N, V, T) = \frac{q(V, T)^N}{N!} \quad (17.4)$$

### 17.8

$$\langle \varepsilon \rangle = \sum_j \frac{\varepsilon_j e^{-\beta\varepsilon_j}}{q} \quad (17.5)$$

$$\varepsilon = \varepsilon_i^{trans} + \varepsilon_j^{rot} + \varepsilon_k^{vib} + \varepsilon_l^{elec} \quad (17.6)$$

$$\pi_{ijkl} = \frac{e^{-\beta\varepsilon_i^{trans}} e^{-\beta\varepsilon_j^{rot}} e^{-\beta\varepsilon_k^{vib}} e^{-\beta\varepsilon_l^{elec}}}{q_{trans} q_{rot} q_{vib} q_{elec}} \quad (17.7)$$

## 18 Partition Functions and Ideal Gases

### 18.1 The Translational PF of Monatomic Ideal Gas

$$q_{trans} = \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} T \quad (18.1)$$

### 18.2 The Electronic PF

### 18.3

### 18.4 The Rotational PF

$$q_{rot} = \sum_{J=0} (2J+1) e^{-J(J+1)\Theta_{rot}/T} \quad (18.2)$$

where

$$\Theta_{rot} = \frac{\hbar^2}{2Ik_B} \quad (18.3)$$

At low  $\Theta_{rot}$

$$q_{rot} = \dots = \frac{T}{\Theta_{rot}} \quad (18.4)$$

Symmetry Number

$$q_{\text{rot}} = \frac{T}{\sigma \Theta_{\text{rot}}} \quad (18.5)$$

Spherical top

$$q_{\text{rot}} = \frac{\sqrt{\pi}}{\sigma} \left( \frac{T}{\Theta_{\text{rot}}} \right)^{3/2} \quad (18.6)$$

## 25 The Kinetic Theory of Gases

### 25.1

### 25.2 Speed Distribution

$$f(u_x) = \sqrt{\frac{m}{2\pi k_B T}} e^{-mu_x^2/2k_B T} \quad (25.1)$$

$$\langle u_x^2 \rangle = \frac{k_B T}{m} = \frac{RT}{M} \quad (25.2)$$

### 25.3 Maxwell Distribution

$$F(u) = 4\pi u^2 \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-mu^2/2k_B T} \quad (25.3)$$

$$\langle u \rangle = \sqrt{\frac{8k_B T}{\pi m}} \quad (25.4)$$

$$\langle u^2 \rangle = \frac{3k_B T}{m} \quad (25.5)$$

$$u_{mp} = \sqrt{\frac{2k_B T}{m}} \quad (25.6)$$

$$F(\varepsilon) = \frac{2\pi}{(\pi k_B T)^{3/2}} \varepsilon^{1/2} e^{-\varepsilon/k_B T} \quad (25.7)$$

$$\langle \varepsilon \rangle = \frac{3}{2} k_B T \quad (25.8)$$

### 25.4 The Frequency of Collisions with a Wall

$$dz = \frac{1}{A} \frac{dN}{dt} \quad (25.9)$$

freq per area

$$z = \frac{\rho}{4} \langle u \rangle \quad (25.10)$$

### 25.5 Inter-collision and MFP

$$z_A = \rho \sigma \langle u_r \rangle = \rho \sigma \sqrt{2} \langle u \rangle \quad (25.11)$$

$$l = \frac{u}{z_A} = \frac{1}{\sqrt{2} \rho \sigma} \quad (25.12)$$

$$p(x) dx = \frac{1}{l} e^{-x/l} dx \quad (25.13)$$