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 $360°/n$
σ	
i	
S_n	

Table 1: Symmetry elements and operators

Identity

Rotation

σ_h	horizontal
σ_v	vertical
σ_d	diagonal (vertical and bisects the angle between C_2 axis)

Table 2

Reflection

Inversion

Rotation Reflection

$$\hat{S}_n = \hat{\sigma}_h \times \hat{C}_n \tag{12.1}$$

12.2.1 Point Groups of Interest to Chemists

C_{nv}	
C_{nh}	Rotation by $360°/n$
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 – σ
C_i – i

C_n

S_n

C_{nv} – C_n and $n\sigma_v$

C_{nh} – C_n and σ_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 σ_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 represtn.

notations

1. A:, B:, E:2D, T:3D
2. A_1: symm wrt C_2/σ_v, A_2: antisymm wrt that.
3. A': symm wrt σ_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_ν	d_j	dimension of repr matrix
a_ν	a_j	
g	h	

Table 4

order

$$\sum_\nu n_\nu^2 = g \tag{12.2}$$

character

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

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

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

reduce a given reducible repr Γ
Suppose

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

thus

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

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

$$\widehat{\mathbf{P}}_j = \frac{d_j}{h} \sum_{\widehat{\mathbf{R}}} \chi_j(\widehat{\mathbf{R}})\, \widehat{\mathbf{R}} \tag{12.8}$$

13 Molecular Spectroscopy

13.1

	micro	far IR	IR	visible & UV
f/Hz				
λ/m				
$\bar{\nu}/\mathrm{cm}^{-1}$				
$E/\mathrm{J\,mol}^{-1}$				
process				

Table 5

13.2 Rotational Transitions Accompany Vibrational Transitions

13.3

13.4

13.5 Overtones Are Observed in Vibrational Spectra

$$G(v) = \tilde{\nu}_e\left(v + \frac{1}{2}\right) - \tilde{x}_e\tilde{\nu}_e\left(v + \frac{1}{2}\right)^2 \tag{13.1}$$

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

13.6 Electronic Spectra Contains Electronic, Vibrational and Rotational Info

$$\tilde{v}_{obs} = \tilde{T}_e + ... \tag{13.2}$$

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

$$\begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{xy} & I_{yy} & I_{yz} \\ I_{xz} & I_{yz} & I_{zz} \end{pmatrix} \xrightarrow{\text{diagnalization}} \begin{pmatrix} I_A & & \\ & I_B & \\ & & I_C \end{pmatrix} \tag{13.3}$$

	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

$\widehat{\mathbf{R}}$	contribution per unmoved atom

Table 7

Now we get Γ_{3N}.
Subtract the irreducible representations corresponding to translational (x, y, z) and rotational (R_x, R_y, R_z) degrees of freedom, we get Γ_{vib}.

13.11 Selection Rules Are Derived from TD Perturbation Theory

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

$$\mathbf{E} = \mathbf{E}_0 \cos 2\pi\nu t \tag{13.4}$$

$$\widehat{\mathrm{H}}^{(1)} = -\boldsymbol{\mu} \cdot \mathbf{E} = -\boldsymbol{\mu}\mathbf{E}_0 \left(\mathrm{e}^{\mathrm{i}\, 2\pi\nu t} + \mathrm{e}^{-\mathrm{i}\, 2\pi\nu t}\right)/2 \tag{13.5}$$

$$\Psi(t) = a_1(t)\Psi_1(t) + a_2(t)\Psi_2(t) \tag{13.6}$$

$$a_1(t)\, \widehat{\mathrm{H}}^{(1)}\, \Psi_1 + a_2(t)\, \widehat{\mathrm{H}}^{(1)}\, \Psi_2 = \mathrm{i}\,\hbar \left(\Psi_1 \frac{\mathrm{d}a_1}{\mathrm{d}t} + \Psi_2 \frac{\mathrm{d}a_2}{\mathrm{d}t} \right) \tag{13.7}$$

$$a_1(t) \left\langle \psi_2 \middle| \widehat{\mathrm{H}}^{(1)} \middle| \Psi_1 \right\rangle + a_2(t) \left\langle \psi_2 \middle| \widehat{\mathrm{H}}^{(1)} \middle| \Psi_2 \right\rangle = \mathrm{i}\,\hbar \left(0 + \frac{\mathrm{d}a_2}{\mathrm{d}t}\, \mathrm{e}^{-\mathrm{i}\, Et/\hbar} \right) \tag{13.8}$$

...

$$\mathrm{i}\,\hbar \frac{\mathrm{d}a_2}{\mathrm{d}t} = \mathrm{e}^{-\mathrm{i}(E_1 - E_2)t/\hbar} \left\langle \psi_2 \middle| \widehat{\mathrm{H}}^{(1)} \middle| \psi_1 \right\rangle \tag{13.9}$$

$$\frac{\mathrm{d}a_2}{\mathrm{d}t} \approx ... \tag{13.10}$$

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

$$\begin{aligned}\langle J', M' \,|\, \mu_z \,|\, J, M\rangle &= \int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi} Y_{J'}^{M'*} \mu_z Y_J^M \sin\theta \mathrm{d}\theta \\ &= \ldots \end{aligned} \tag{13.11}$$

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

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

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

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

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

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

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

perturbed to 1st order

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

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

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

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

Since

$$\nu_0 = \frac{\gamma B_0}{2\pi} \tag{14.11}$$

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

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

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

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

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

$$J << \nu_0|\sigma_1 - \sigma_2| \tag{14.16}$$

the $n+1$ spectra.

15 Lasers, Laser Spectroscopy and Photochemistry

15.1

15.2 The Dynamics of Spectroscopic Transitions between the Electronic States

absorption

$$-\frac{\mathrm{d}N_1(t)}{\mathrm{d}t} = B_{12}\rho_\nu(\nu_{12})N_1(t) \tag{15.1}$$

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

$$\Phi = \frac{\#\text{ mols undergoing reaction}}{\#\text{ photons absorbed}} \tag{15.2}$$