Notes of **Advanced Physical Chemistry II**

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Contents

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 $\Delta J = \pm 1$

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