

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 $360^\circ/n$
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

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

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 – 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 representn.

notations

1. $A_1, B_1, E:2D, T:3D$
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

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

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 Γ

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/Hz				
λ/m				
$\bar{\nu}/\text{cm}^{-1}$				
$E/\text{J mol}^{-1}$				
process				

Table 5

13.2 Rotational Transitions Accompany Vibrational Transitions

13.3

13.4

13.5 Overtones Are Observed in Vibrational Spectra

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

\tilde{x}_e : anharmonicity cons.

13.6 Electronic Spectra Contains Electronic, Vibrational and Rotational Info

$$\tilde{\nu}_{obs} = \tilde{T}_e + \dots \quad (13.2)$$

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

$$\begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{xy} & I_{yy} & I_{yz} \\ I_{xz} & I_{yz} & I_{zz} \end{pmatrix} \xrightarrow{\text{diagonalization}} \begin{pmatrix} I_A & & \\ & I_B & \\ & & I_C \end{pmatrix} \quad (13.3)$$

	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