CHEMISTRY 273
SPECTROSCOPY
(BOHM CH. 18, SEC. 16-20)

1. $\hat{\mathcal{H}}\Psi(\vec{r}, \vec{\sigma}_e;\ \vec{R}_N,\ \vec{\sigma}_N,\ t) = -\frac{\hbar}{i}\frac{\partial \Psi}{\partial t}$

(a) If $\hat{\mathcal{H}}$ is independent of t

$$\Psi = \psi(\vec{r}, \vec{\sigma}_e;\ \vec{R}_N,\ \vec{\sigma}_N)\, e^{-i\mathbf{E}t/\hbar} \qquad \hat{H}\psi = E\psi$$

(b) If $\hat{\mathcal{H}}$ depends on t use time dependent perturbation theory

$$\hat{\mathcal{H}} = \hat{H}^o + \hat{H}'(t)$$

$$\Psi_\alpha^0 = \psi_\alpha^0 e^{-(i E_\alpha^o/\hbar)t}$$

$$\hat{H}^o\, \Psi_\alpha^o = -\frac{\hbar}{i}\frac{\partial \Psi_\alpha^o}{\partial t} \qquad \hat{H}^o \psi_\alpha^o = E_\alpha^o \psi_\alpha^o$$

assume expansion $\Psi = \sum_\alpha c_\alpha(t)\Psi_a^o = \sum_\alpha c_\alpha(t)\psi_\alpha^o e^{-i(E_\alpha^0/\hbar)t}$

Find c_α's by substituting $\hat{\mathcal{H}}\ \Psi = -\frac{\hbar}{i}\frac{\partial \Psi}{\partial t}$

$$\hat{H}^o\left(\sum_\alpha c_\alpha(t)\Psi_\alpha^o\right) + \hat{H}'\left(\sum_\alpha c_\alpha(t)\Psi_\alpha^o\right) = -\frac{\hbar}{i}\frac{\partial}{\partial t}\left(\sum_\alpha c_\alpha(t)\Psi_\alpha^o\right)$$

$$\underbrace{\hat{H}^o\left(\sum_\alpha c_\alpha(t)\Psi_\alpha^o\right)}_{I} + \underbrace{\hat{H}'\left(\sum_\alpha c_\alpha(t)\Psi_\alpha^o\right)}_{II} = \underbrace{-\frac{\hbar}{i}\sum_\alpha\left(\frac{\partial c_\alpha}{\partial t}\Psi_\alpha^o\right)}_{III} + \underbrace{\sum_\alpha c_\alpha\left(-\frac{\hbar}{i}\frac{\partial \Psi_\alpha^o}{\partial t}\right)}_{IV}$$

I = IV by above

$$\underbrace{\sum_\alpha c_\alpha(t)\hat{H}'(t)\Psi_\alpha^o}_{II} = \underbrace{-\frac{\hbar}{i}\sum_\alpha \Psi_\alpha^o\frac{\partial c_\alpha}{\partial t}}_{III}$$

II = III

multiply by $(\Psi_\beta^o)^*$ and integrate over space

$$\sum_{\alpha} c_{\alpha}(t)\left\langle \Psi^{o}_{\beta}\middle|\hat{H}'(t)\middle|\Psi^{o}_{\alpha}\right\rangle = -\frac{\hbar}{i}\sum_{\alpha}\left\langle \Psi^{o}_{\beta}\middle|\Psi^{o}_{\alpha}\right\rangle \frac{\partial c_{\alpha}}{\partial t}$$

$$\left(\psi^{o}_{\beta}e^{-i\left(E^{o}_{\beta}/\hbar\right)t}\right)^{*} \qquad \psi^{o}_{\alpha}e^{-i\left(E^{o}_{\alpha}/\hbar\right)t} \qquad \delta_{\alpha\beta}$$

$$\sum_{\alpha} c_{\alpha}(t)e^{i(E^{o}_{\beta}-E^{o}_{\alpha})t/\hbar}H'_{\beta\alpha} = -\frac{\hbar}{i}\frac{\partial c_{\beta}}{\partial t}$$

$$\int_{\text{space}} (\psi^{o}_{\beta})^{*}\hat{H}'(t)\psi^{o}_{\alpha}d\tau$$

system starts in state α at time $t = t_o$

then $c_{\alpha}(t_o) = 1$ $\qquad$ $c_{\alpha\neq\beta}(t_o) = 0$

at $t = t_o$ $\qquad$ $-\frac{\hbar}{i}\frac{\partial c_{\beta}}{\partial t} = e^{i(E^{o}_{\beta}-E^{o}_{\alpha})t/\hbar}H'_{\beta\alpha}$

at later time $\qquad$ $\boxed{c_{\beta} = -\frac{i}{\hbar}\int_{t_o}^{t} e^{i\frac{(E^{o}_{\beta}-E^{o}_{\alpha})}{\hbar}t''}H'_{\beta\alpha}dt''}$

I. In weak electromagnetic field

$\hat{H}' = -\frac{e}{2mc}(\vec{A}\cdot\vec{p}+\vec{p}\cdot\vec{A})$ where $\vec{A}$ is vector potential:

wave in z-direction with electric field in x direction.

$$\vec{A} = A_o\cos(kz-\omega t)\vec{i} \qquad \nabla\times\vec{A} = \vec{B} = \mu\,\vec{H}$$

$$\omega = 2\pi\nu \qquad \vec{\mathcal{E}} = -\frac{1}{c}\frac{\partial\vec{A}}{\partial t}$$

$$k = \frac{2\pi}{\lambda}$$

or kept explicitly in terms of the electric and magnetic field interactions

$$\psi^* \vec{\mathcal{E}} \psi \quad \text{and} \quad \psi^* (\vec{v} \times \vec{B}) \psi$$

see McQ. p. 472-475.

$$\vec{B} = -A_o k \sin(kz - \omega t)\vec{j} = -A_o \frac{\omega}{c} \sin(kz - \omega t)\vec{j}$$

$$\vec{\mathcal{E}} = -A_o \frac{\omega}{c} \sin(kz - \omega t)\,\vec{i}$$

Result #1 for single frequency ν

$$|c_\beta|^2 = \frac{e^2}{m^2c^2} A_o^2 \, |Q_{\alpha\beta}|^2 \sin^2 \frac{\left[\frac{(E_\beta - E_\alpha - h_\nu)(t - t_o)}{2k}\right]}{(E_\beta - E_\alpha - h\nu)^2}$$

$$Q_{\alpha\beta} = \int \psi_\alpha^o \hat{p}_x e^{ikz} \psi_\beta^o d\tau$$

Result #2 for a small spread of frequencies with intensities $I(\nu)$ centered around $\nu_o \approx \nu_{\alpha\beta}$

$$|c_\beta|^2 = \frac{2\pi e^2}{m^2 c\hbar^2} \; \frac{I(\nu_o)}{\omega_{\beta\alpha}} \; |Q_{\beta\alpha}|^2 (t - t_0)$$

[see handout for proofs of above arguments]

Probability of transition per unit time

$$P_{\beta\leftarrow\alpha} = \frac{2\pi e^2 |Q_{\beta\alpha}|^2}{\omega_{\alpha\beta}^2 m^2 c\hbar^2}$$

(probability for x-polarized light traveling in z-direction.)

$$Q_{\beta\alpha} = \int (\psi_\beta^o)^* \left(-\frac{\hbar}{i}\frac{\partial}{\partial x} e^{ikz} \psi_\alpha^o\right) d\tau$$

$$Q_{\beta\alpha} = \int (e^{ikz})(\psi_{\beta)}^o)^* \hat{p}_x \psi_\alpha^o d\tau$$

for molecule at $z = z_o$

$$Q_{\beta\alpha} = \int \left[1 + ik(z - z_o) - \frac{k^2}{2}(z - z_o)^2 \ldots \right] (\psi_\beta^o)^* \hat{p}_x \psi_\alpha^o d\tau$$

1) Dipole approximation: extent of molecule so small compared to wavelength of light, $k(z - z_o)$ is small in region of interest. $\left(k = \frac{2\pi}{\lambda} \right)$

$$Q_{\beta\alpha} \approx \int \psi_\beta^o \hat{p}_x \psi_\alpha^o d\tau$$ momentum transition moment

$$\int \psi_\beta^o \hat{p}_x \psi_\alpha^o d\tau = i\omega_{\beta\alpha} m \int \psi_\beta^o \hat{x} \psi_\alpha^o d\tau$$ position transition moment [see handout]

$$= \frac{-i\omega_{\beta\alpha}}{e} m \, \mu_{\beta\alpha}$$ $$\langle \vec{\mu} \rangle_{\beta\alpha} = \int \psi_\beta (-e\vec{r}) \, \psi_\alpha d\tau$$

$$P_{\beta\alpha} = \frac{2\pi}{c\hbar^2} \langle \mu_x \rangle^2$$

for *random* alignment of light and molecule

$$\overline{P}_{\beta\alpha} = \frac{2}{3} \frac{\pi}{c\hbar^2} \left[\langle \mu_x \rangle^2 + \langle \mu_y \rangle^2 + \langle \mu_z \rangle^2 \right]$$

$$f = \frac{2\nu_o \hbar m c}{e^2} \overline{P}_{\alpha\beta} = 4.315 \times 10^{-9} \int \varepsilon \ d\nu$$

oscillator strength (unitless) ↑

$$\| \quad \frac{4\pi\nu_o m}{3\hbar e^2} \left| \vec{\mu}_{\beta\alpha} \right|^2$$

ε: mol^{-1} L cm^{-1} ; ν: cm^{-1}

$$\boxed{P_{\beta\alpha} = \frac{2}{3} \frac{\pi}{c\hbar^2} \left| \vec{\mu}_{\beta\alpha} \right|^2 \qquad \vec{\mu}_{\beta\alpha} = \int \psi_\beta^o (-e\vec{r}) \psi_\alpha^o d\tau}$$

for one electron.