Theoretical Treatment

Raman Spectrum

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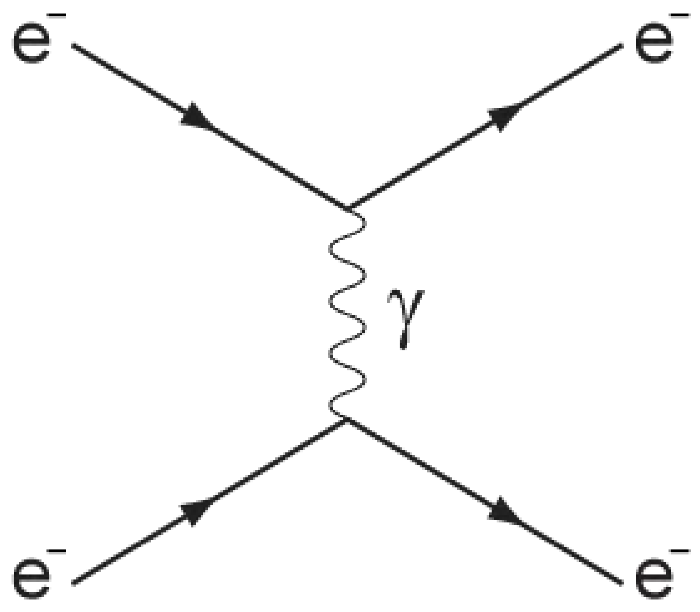
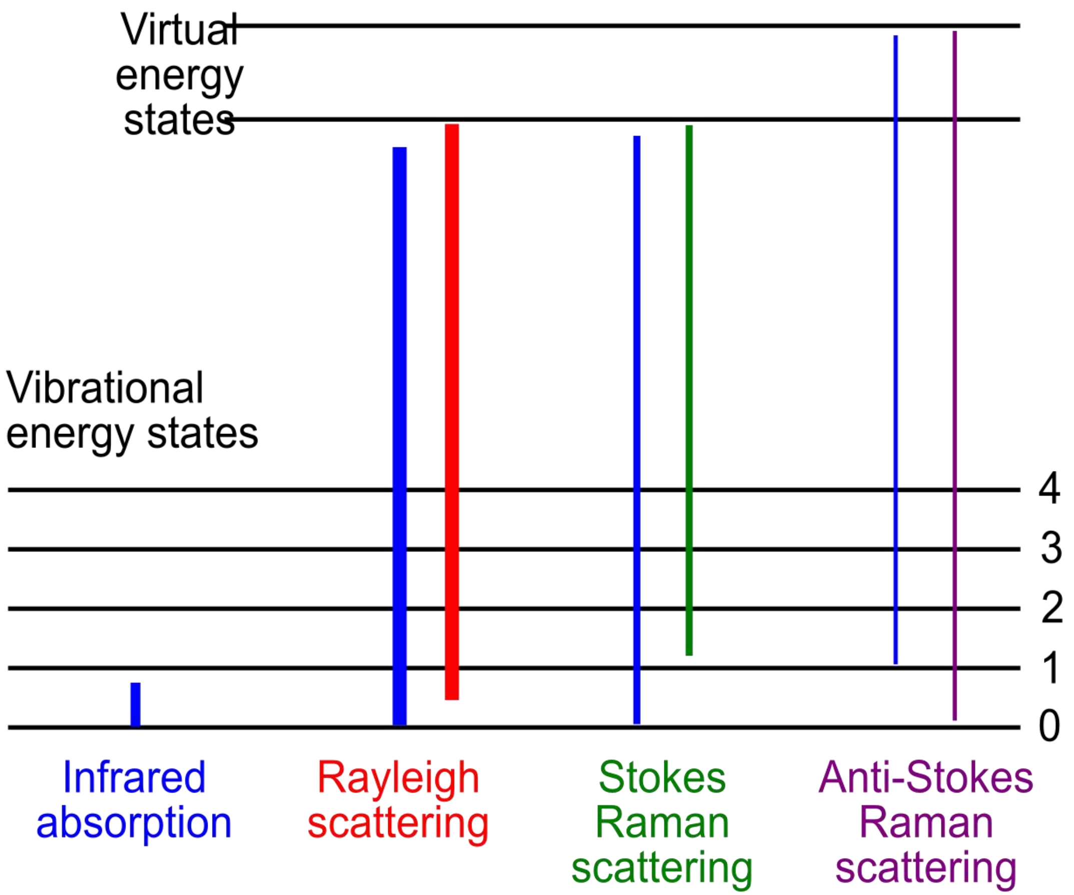
Catalogue

Introduction: Photon Scattering



Elastic: Rayleigh Scattering

Inelastic: Raman Scattering

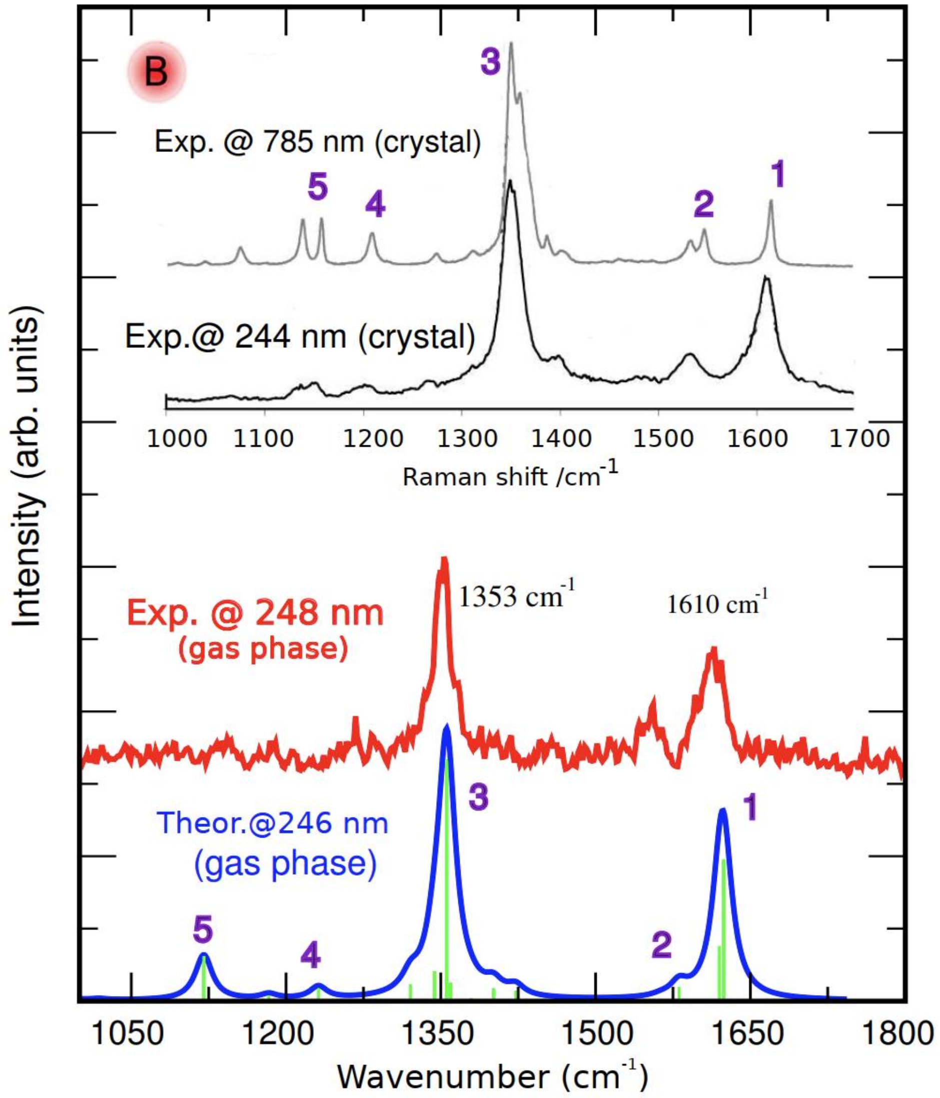


Introduction: Spectrum

Spectrum,

is to express intensity as a function of frequency:

$$I(\omega)$$



Introduction: Assumption

ASSUMPTION I: plane monochromatic wave.

ASSUMPTION II: interaction contains only electric dipole.

ASSUMPTION III: classical expression for incident light.

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1(t), \quad \mathcal{H}_1(t) = \boldsymbol{p} \cdot \boldsymbol{E}(t) = -\sum_\sigma p_\sigma E_\sigma(t)$$

$$E_\sigma(t) = E_\sigma(0) e^{-i(\omega t - \boldsymbol{k} \cdot \boldsymbol{r})}$$

Introduction: Radiation

ASSUMPTION IV: **classical radiation formula in electrodynamics**

$$I = k'_\omega \omega_s^4 p_0^2 \sin^2\theta$$

$$k'_\omega = \frac{1}{32\pi^2 \varepsilon_0 c_0^3}$$

$$\Rightarrow \quad \boldsymbol{p}(\omega)$$

Linear Approximation: Introduction

Approximation: Linear Response

$$p_\rho(\omega) = \boxed{\alpha_{\rho\sigma}(\omega)E_\sigma(\omega)} + \frac{1}{2}\beta_{\rho\sigma\tau}(\omega)E_\sigma(\omega)E_\tau(\omega) + \frac{1}{6}\gamma_{\rho\sigma\tau\eta}(\omega)E_\sigma(\omega)E_\tau(\omega)E_\eta(\omega) + \cdots$$

Comments: Given frequency, amplitude of the response is determined by an linear transformation (amplification & direction change) of the amplitudes of environmental factors.

Linear Approximation: Polarizability

$$p_\rho(\omega) = \underline{\alpha_{\rho\sigma}(\omega)} E_\sigma(\omega)$$

KEY VALUE

Classical Treatment: Normal Modes

Normal Modes:

$$Q_k = Q_{k_0} \cos\left(\omega_k t + \delta_k\right)$$

polarizability depend on shape change:

$$\alpha_{\rho\sigma} = (\alpha_{\rho\sigma})_0 + \sum_k \left(\frac{\partial \alpha_{\rho\sigma}}{\partial Q_k}\right)_0 Q_k + \frac{1}{2}\sum_{k,l}\left(\frac{\partial^2 \alpha_{\rho\sigma}}{\partial Q_k \partial Q_l}\right)_0 Q_k Q_l \ldots$$

Classical Treatment: Normal Modes

Harmonic Oscillator:

$$P_\rho = \alpha_{\rho\sigma}(E_\sigma)_0 \cos\omega t + \sum_k \left(\alpha'_{\rho\sigma}\right)_k (E_\sigma)_0 (Q_k)_0 \cos\left(\omega_k t + \delta_k\right)\cos\omega t$$

$$\begin{aligned} P_\rho = & \alpha_{\rho\sigma}(E_\sigma)_0 \cos\omega t \\ & + \frac{1}{2}\sum_k \left(\alpha'_{\rho\sigma}\right)_k (E_\sigma)_0 (Q_k)_0 \cos\left(\omega_k t + \delta_k + \omega t\right) \\ & + \frac{1}{2}\sum_k \left(\alpha'_{\rho\sigma}\right)_k (E_\sigma)_0 (Q_k)_0 \cos\left(\omega_k t + \delta_k - \omega t\right) \end{aligned}$$

$$(\alpha_{\rho\sigma}) = (\alpha_{\rho\sigma})_0 + \sum_k \left(\alpha'_{\rho\sigma}\right)_k Q_k$$

$$\left(\alpha'_{\rho\sigma}\right)_k = \left(\frac{\partial \alpha_{\rho\sigma}}{\partial Q_k}\right)_0$$

$$\cos A \cos B = \frac{1}{2}\{\cos(A+B) + \cos(A-B)\}$$

Classical Treatment: Beat Frequency

Harmonic Oscillator:

$$P_\rho = \alpha_{\rho\sigma}(E_\sigma)_0 \cos \omega t$$

Rayleigh

$$+ \frac{1}{2} \sum_k \left(\alpha'_{\rho\sigma}\right)_k (E_\sigma)_0 (Q_k)_0 \cos\left(\omega_k t + \delta_k + \omega t\right)$$

Anti-Stokes Raman

$$+ \frac{1}{2} \sum_k \left(\alpha'_{\rho\sigma}\right)_k (E_\sigma)_0 (Q_k)_0 \cos\left(\omega_k t + \delta_k - \omega t\right)$$

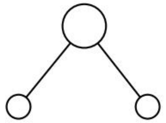
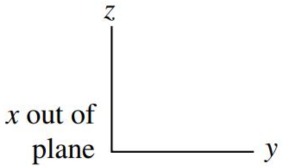
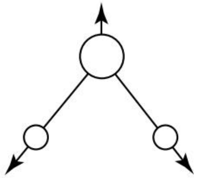
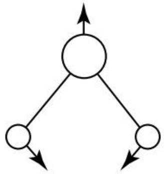
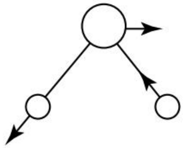
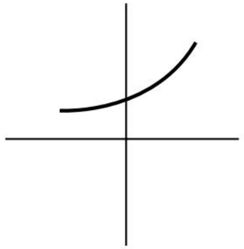
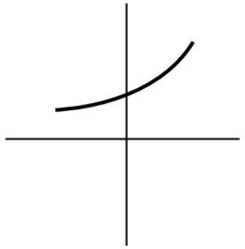
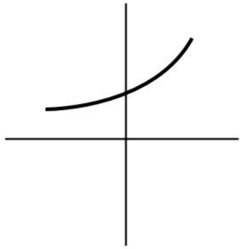
Stokes Raman

Comments: the frequencies observed in Raman scattering are beat frequencies between the radiation frequency ω and the molecular frequency ωk.

Classical Treatment: Selection Rules

$$(\alpha_{\rho\sigma}) = (\alpha_{\rho\sigma})_0 + \sum_k (\alpha'_{\rho\sigma})_k Q_k$$

$$(\alpha'_{\rho\sigma})_k = \left(\frac{\partial \alpha_{\rho\sigma}}{\partial Q_k}\right)_0$$

Molecule			
Mode of vibration			
Variation of polarizability with normal coordinate (schematic)			
Polarizability derivative at equilibrium position	$\neq 0$	$\neq 0$	$\neq 0$
Raman activity	Yes	Yes	Yes

Quantum Treatment: LRT

Linear Response: time domain

$$p_\rho(t) = \int_{-\infty}^{\infty} dt' \alpha_{\rho\sigma}\left(t - t'\right) E_\sigma\left(t'\right)$$

$$\alpha_{\rho\sigma}\left(t - t'\right) = \frac{\delta p_\rho(t)}{\delta E_\sigma\left(t'\right)}$$

Quantum Treatment: LRT

Linear Response: time domain

$$|\Psi(t_2)\rangle = U(t_2, t_1)\,|\Psi(t_1)\rangle$$

$$U(t_2, t_1) = \mathcal{T}\exp\left\{-\frac{i}{\hbar}\int_{t_1}^{t_2} dt\mathcal{H}(t)\right\}$$

$$\frac{\delta U(t_2, t_1)}{\delta E_\sigma(t)} = \frac{i}{\hbar}U(t_2, t)\,E_\sigma U(t, t_1)$$

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1(t), \quad \mathcal{H}_1(t) = \boldsymbol{p}\cdot\boldsymbol{E}(t) = -\sum_\sigma p_\sigma E_\sigma(t)$$

Quantum Treatment: LRT

Linear Response: time domain

$$\frac{\delta U\left(t_2, t_1\right)}{\delta E_\sigma(t)} = \frac{i}{\hbar} U\left(t_2, t\right) E_\sigma U\left(t, t_1\right)$$

$$\left.\frac{\delta|\Psi(t)\rangle}{\delta E_\sigma\left(t'\right)}\right|_{\{\forall t, \sigma, E_\sigma(t)=0\}} = \frac{i}{\hbar} e^{-i\mathcal{H}_0\left(t-t'\right)/\hbar} E_\sigma e^{-i\mathcal{H}_0\left(t'-t_0\right)/\hbar}\left|\Psi\left(t_0\right)\right\rangle \Theta\left(t-t'\right)$$

$$= \frac{i}{\hbar} e^{-i\mathcal{H}_0 t/\hbar} E_\sigma\left(t'\right) e^{+i\mathcal{H}_0 t_0/\hbar}\left|\Psi\left(t_0\right)\right\rangle \Theta\left(t-t'\right)$$

where: $E_\sigma(t') \equiv e^{i\mathcal{H}_0 t'/\hbar} E_\sigma e^{-i\mathcal{H}_0 t'/\hbar}$

Quantum Treatment: LRT

Linear Response: time domain

$$\begin{aligned}
\alpha_{\rho\sigma}(t-t') &= \frac{\delta}{\delta E_\sigma(t')}\langle\Psi(t)|\hat{p}_\rho|\Psi(t)\rangle \\
&= \frac{\delta\langle\Psi(t)|}{\delta E_\sigma(t')}\hat{p}_\rho|\Psi(t)\rangle + \langle\Psi(t)|\hat{p}_\rho\frac{\delta|\Psi(t)\rangle}{\delta E_\sigma(t')} \\
&= \Big\{-\frac{i}{\hbar}\langle\Psi(t_0)|e^{-i\mathcal{H}_0 t_0/\hbar}\hat{p}_\sigma(t')e^{+i\mathcal{H}_0 t/\hbar}\hat{p}_\rho|\Psi(t)\rangle \\
&\qquad +\frac{i}{\hbar}\langle\Psi(t)|\hat{p}_\rho e^{-i\mathcal{H}_0 t/\hbar}\hat{p}_\sigma(t')e^{+i\mathcal{H}_0 t_0/\hbar}|\Psi(t_0)\rangle\Big\}\Theta(t-t') \\
&= \frac{i}{\hbar}\langle[\hat{p}_\rho(t),\hat{p}_\sigma(t')]\rangle\Theta(t-t'),
\end{aligned}$$

Quantum Treatment: LRT

Linear Response: frequency domain

$$\int_0^\infty dt e^{i(\omega-\Omega+i\Gamma)t} = \frac{i}{\omega-\Omega+i\Gamma}$$

$$\begin{aligned}
p_\rho(\omega) &= \langle\psi_f|\hat{p}_i(\omega)|\psi_i\rangle = \langle\psi_f|\hat{\alpha}_{\rho\sigma}(\omega)E_\sigma(\omega)|\psi_i\rangle \\
&= \langle\psi_f|\left[\frac{i}{\hbar}\int_0^\infty dt e^{i\omega t}\left[\hat{p}_\rho(t),\hat{p}_\sigma(0)\right]\right]E_\sigma(\omega)|\psi_i\rangle \\
&= \langle\psi_f|\left[\frac{i}{\hbar}\int_0^\infty dt e^{i\omega t}\left[\hat{p}_\rho(t),\hat{p}_\sigma(0)\right]\right]E_\sigma(\omega)|\psi_i\rangle \\
&= \frac{i}{\hbar}\int_0^\infty dt e^{i\omega t}\sum_r\left\{\langle\psi_f|\hat{p}_\rho|\psi_r\rangle\langle\psi_r|\hat{p}_\sigma|\psi_i\rangle e^{+i(\omega_f-\omega_r)t}\right. \\
&\quad\left.-\langle\psi_f|\hat{p}_\sigma|\psi_r\rangle\langle\psi_r|\hat{p}_\rho|\psi_i\rangle e^{+i(\omega_r-\omega_i)t}\right\}E_\sigma(\omega)
\end{aligned}$$

Quantum Treatment: LRT

Linear Response: frequency domain

$$(\alpha_{\rho\sigma})_{fi} = \frac{1}{\hbar}\sum_r \left\{ \frac{\langle\psi_f|\hat{p}_\rho|\psi_r\rangle\langle\psi_r|\hat{p}_\sigma|\psi_i\rangle}{\omega_{ri}-\omega-\mathrm{i}\Gamma_r} + \frac{\langle\psi_f|\hat{p}_\sigma|\psi_r\rangle\langle\psi_r|\hat{p}_\rho|\psi_i\rangle}{\omega_{rf}+\omega+\mathrm{i}\Gamma_r} \right\}$$

Require wave functions, energies, lifetimes

Barrier to further progress

Simplification: Decomposition

Symmetric part & Anti-symmetric part

$$(\alpha_{\rho\sigma})^{\mathrm{s}}_{fi} = \frac{1}{2\hbar} \sum_{r \neq i,f} \frac{(\omega_{ri} + \omega_{rf})}{(\omega_{ri} - \omega_1 - \mathrm{i}\Gamma_r)(\omega_{rf} + \omega_1 + \mathrm{i}\Gamma_r)} \times \{\langle f|\hat{p}_\rho|r\rangle\langle r|\hat{p}_\sigma|i\rangle + \langle f|\hat{p}_\sigma|r\rangle\langle r|\hat{p}_\rho|i\rangle\}$$

$$(\alpha_{\rho\sigma})^{\mathrm{a}}_{fi} = \frac{1}{2\hbar} \sum_{r \neq i,f} \frac{(2\omega_1 + \omega_{if} + 2i\Gamma_r)}{(\omega_{ri} - \omega_1 - \mathrm{i}\Gamma_r)(\omega_{rf} + \omega_1 + \mathrm{i}\Gamma_r)} \times \{\langle f|\hat{p}_\rho|r\rangle\langle r|\hat{p}_\sigma|i\rangle - \langle f|\hat{p}_\sigma|r\rangle\langle r|\hat{p}_\rho|i\rangle\}$$

Simplification: Decomposition

Real part & Imaginary part

$$(\alpha_{\rho\sigma})^{\mathrm{s}}_{fi} = \frac{1}{2\hbar}\sum_{r\neq i,f}\frac{(\omega_{ri}+\omega_{rf})}{(\omega_{ri}-\omega_1)(\omega_{rf}+\omega_1)}$$
$$\times\,\mathrm{Re}(\langle f|\hat{p}_\rho|r\rangle\langle r|\hat{p}_\sigma|i\rangle + \langle f|\hat{p}_\sigma|r\rangle\langle r|\hat{p}_\rho|i\rangle)$$

$$(\alpha_{\rho\sigma})^{\mathrm{a}}_{fi} = \frac{1}{2\hbar}\sum_{r\neq i,f}\frac{(2\omega_1+\omega_{if})}{(\omega_{ri}-\omega_1)(\omega_{rf}+\omega_1)}$$
$$\times\,\mathrm{Re}(\langle f|\hat{p}_\rho|r\rangle\langle r|\hat{p}_\sigma|i\rangle - \langle f|\hat{p}_\sigma|r\rangle\langle r|\hat{p}_\rho|i\rangle)$$

$$(\alpha'_{\rho\sigma})^{\mathrm{s}}_{fi} = -\frac{1}{2\hbar}\sum_{r\neq i,f}\frac{(\omega_{ri}+\omega_{rf})}{(\omega_{ri}-\omega_1)(\omega_{rf}+\omega_1)}$$
$$\times\,\mathrm{Im}(\langle f|\hat{p}_\rho|r\rangle\langle r|\hat{p}_\sigma|i\rangle + \langle f|\hat{p}_\sigma|r\rangle\langle r|\hat{p}_\rho|i\rangle)$$

$$(\alpha'_{\rho\sigma})^{\mathrm{a}}_{fi} = -\frac{1}{2\hbar}\sum_{r\neq i,f}\frac{(2\omega_1+\omega_{if})}{(\omega_{ri}-\omega_1)(\omega_{rf}+\omega_1)}$$
$$\times\,\mathrm{Im}(\langle f|\hat{p}_\rho|r\rangle\langle r|\hat{p}_\sigma|i\rangle - \langle f|\hat{p}_\sigma|r\rangle\langle r|\hat{p}_\rho|i\rangle)$$

Simplification: B-O Approximation

Born-Oppenheimer: $|j\rangle = \left|e^j v^j R^j\right\rangle = \left|e^j\right\rangle \left|v^j\right\rangle \left|R^j\right\rangle$

$$\omega_{e^j v^j R^j} = \omega_{e^j} + \omega_{v^j} + \omega_{R^j}$$

$$\hat{\alpha}_{\rho\sigma}\left(e^r, v^r, R^r\right) = \frac{1}{\hbar} \sum_{\substack{e^r v^r R^r \neq e^i v^i R^i, \\ e^f v^f R^f}} \left\{ \frac{\hat{p}_\rho \left|e^r\right\rangle \left|v^r\right\rangle \left|R^r\right\rangle \left\langle R^r\right| \left\langle v^r\right| \left\langle e^r\right| \hat{p}_\sigma}{\omega_{e^r e^i} + \omega_{v^r v^i} + \omega_{R^r R^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r R^r}} \right.$$

$$\left. + \frac{\hat{p}_\sigma \left|e^r\right\rangle \left|v^r\right\rangle \left|R^r\right\rangle \left\langle R^r\right| \left\langle v^r\right| \left\langle e^r\right| \hat{p}_\rho}{\omega_{e^r e^f} + \omega_{v^r v^f} + \omega_{R^r R^f} + \omega_1 + \mathrm{i}\Gamma_{e^r v^r R^r}} \right\}$$

Simplification: B-O Approximation

Assumption:

$$\omega_1 \gg \omega_{v^r v^i} + \omega_{R^r R^i}$$

$$e^i = e^g$$

Effect: get rid of rotation:

$$\hat{\alpha}_{\rho\sigma}\left(e^r, v^r\right) = \frac{1}{\hbar} \sum_{\substack{e^r v^r \neq e^g v^i \\ e^f v^f}} \left\{ \frac{\hat{p}_\rho \left|e^r\right\rangle \left|v^r\right\rangle \left\langle v^r\right| \left\langle e^r\right| \hat{p}_\sigma}{\omega_{e^r e^g} + \omega_{v^r v^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r}} + \frac{\hat{p}_\sigma \left|e^r\right\rangle \left|v^r\right\rangle \left\langle v^r\right| \left\langle e^r\right| \hat{p}_\rho}{\omega_{e^r e^f} + \omega_{v^r v^f} + \omega_1 + \mathrm{i}\Gamma_{e^r v^r}} \right\}$$

$$\left(\alpha_{\rho\sigma}\right)_{e^f v^f : e^g v^i} = \frac{1}{\hbar} \sum_{\substack{e^r v^r \neq e^g v^i \\ e^f v^f}} \left\{ \frac{\left\langle v^f \left| \left\langle e^f \left| \hat{p}_\rho \right| e^r \right\rangle \right| v^r \right\rangle \left\langle v^r \left| \left\langle e^r \left| \hat{p}_\sigma \right| e^g \right\rangle \right| v^i \right\rangle}{\omega_{e^r e^g} + \omega_{v^r v^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r}} + \frac{\left\langle v^f \left| \left\langle e^f \left| \hat{p}_\sigma \right| e^r \right\rangle \right| v^r \right\rangle \left\langle v^r \left| \left\langle e^r \left| \hat{p}_\rho \right| e^g \right\rangle \right| v^i \right\rangle}{\omega_{e^r e^f} + \omega_{v^r v^f} + \omega_1 + \mathrm{i}\Gamma_{e^r v^r}} \right\}$$

Herzberg–Teller Vibronic Coupling

Coordinates Dependence:

$$\hat{H}_{\mathrm{e}}(Q) = (\hat{H}_{\mathrm{e}})_0 + \sum_k \left(\frac{\partial \hat{H}_{\mathrm{e}}}{\partial Q_k}\right)_0 Q_k + \frac{1}{2}\sum_{k,l}\left(\frac{\partial^2 \hat{H}_{\mathrm{e}}}{\partial Q_k \partial Q_l}\right) Q_k Q_l + \dots$$

Perturbation Theory:

$$|e^{r'}(Q_0)\rangle = |e^r(Q_0)\rangle + \frac{1}{\hbar}\sum_{e^s \neq e^r}\sum_k \frac{h^k_{e^s e^r}}{\omega_{e^r} - \omega_{e^s}} Q_k |e^s(Q_0)\rangle$$

$$h^k_{e^s e^r} = \langle \psi_{e^s}(Q_0)|(\partial \hat{H}_e/\partial Q_k)_0|\psi_{e^r}(Q_0)\rangle$$

Herzberg–Teller Vibronic Coupling

plug in and multiply out:

$$\langle e^{r'}|\hat{p}_\sigma|e^{g'}\rangle = \left\{\langle e^r| + \frac{1}{\hbar}\sum_{e^s \neq e^r}\sum_k \langle e^s|\frac{h^k_{e^r e^s}}{\omega_{e^r} - \omega_{e^s}}Q_k\right\}|\hat{p}_\sigma|\left\{|e^g\rangle + \frac{1}{\hbar}\sum_{e^t \neq e^g}\sum_k \frac{h^k_{e^t e^g}}{\omega_{e^g} - \omega_{e^t}}Q_k|e^t\rangle\right\}$$

$$(p_\sigma)_{e^{r'} e^{g'}} = (p_\sigma)^0_{e^r e^g} + \frac{1}{\hbar}\sum_{e^s \neq e^r}\sum_k \frac{h^k_{e^r e^s}}{\omega_{e^r} - \omega_{e^s}}Q_k (p_\sigma)^0_{e^s e^g}$$
$$+ \frac{1}{\hbar}\sum_{e^t \neq e^g}\sum_k (p_\sigma)^0_{e^r e^t}\frac{h^k_{e^t e^g}}{\omega_{e^g} - \omega_{e^t}}Q_k$$

Herzberg–Teller Vibronic Coupling

illustration:

$$(p_\sigma)_{e^{r'}e^{g'}} = (p_\sigma)^0_{e^r e^g} + \frac{1}{\hbar}\sum_{e^s \neq e^r}\sum_k \frac{h^k_{e^r e^s}}{\omega_{e^r} - \omega_{e^s}} Q_k (p_\sigma)^0_{e^s e^g}$$
$$+ \frac{1}{\hbar}\sum_{e^t \neq e^g}\sum_k (p_\sigma)^0_{e^r e^t} \frac{h^k_{e^t e^g}}{\omega_{e^g} - \omega_{e^t}} Q_k$$

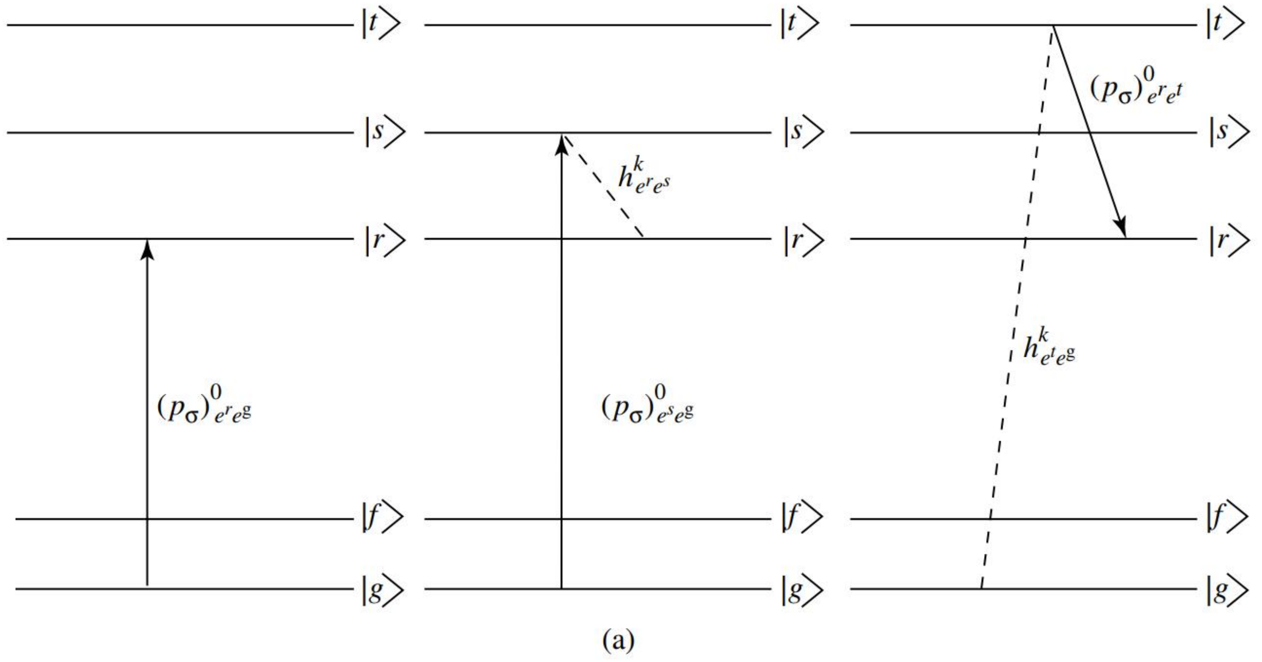


Figure 4.5(a) The three contributions to $(p_\sigma)_{e^{r'}e^{g'}}$ which arise from Herzberg–Teller coupling of the states $|s\rangle$ and $|r\rangle$, and $|t\rangle$ and $|g\rangle$ via Q_k.

Herzberg–Teller Vibronic Coupling

take back to polarizability:

$$(\alpha_{\rho\sigma})_{e^f v^f : e^g v^i} = A^{\mathrm{I}} + B^{\mathrm{I}} + C^{\mathrm{I}} + D^{\mathrm{I}}$$

more cases:

II. resonance & non-resonance case

III. normal electronic and vibronic scattering

IV. pure vibrational scattering

V. electronic and vibronic resonance scattering

VI. vibrational resonance scattering

Conclusion

$$(\alpha_{\rho\sigma})_{e^f v^f : e^g v^i} = A^{\mathrm{I}} + B^{\mathrm{I}} + C^{\mathrm{I}} + D^{\mathrm{I}}$$

Linear Response Theory

General Polarizability Tensor

Symmetry

B-O approximation

Vibronic Coupling