Dalian ROA Lectures
June-July 2010
Lecture 3

Vibronic Theory of Raman Scattering

Far-From-Resonance, Near Resonance and Strong Resonance Theories

Outline

- Vibronic Theory of Raman Spectroscopy
- General Unrestricted Formalism
- Far-From-Resonance Formalism
- Near Resonance Formalism
- Single-Electronic-State Strong Resonance Formalism
- Dual-Electronic-State Strong Resonance Formalism

Vibronic Theory of Raman Scattering

General Raman Scattering Intensity for Samples of Isotropically Averaged Molecules

$$I\left(\tilde{e}^{d},\tilde{e}^{i}\right)=90K\left\langle\left|\tilde{e}_{\alpha}^{d*}\tilde{\alpha}_{\alpha\beta}\tilde{e}_{\beta}^{i}\right|^{2}\right\rangle$$

$$K=\frac{1}{90}\left(\frac{\omega_{s}^{2}\mu_{0}\tilde{E}^{(0)}}{4\pi R}\right)^{2} \qquad \hat{\mu}_{\alpha}=-e\sum_{j}r_{j\alpha}$$

$$\left(\tilde{\alpha}_{\alpha\beta}\right)_{mn}=\frac{1}{\hbar}\sum_{j\neq m,n}\left[\frac{\left\langle\tilde{\Psi}_{m}\left|\hat{\mu}_{\alpha}\right|\tilde{\Psi}_{j}\right\rangle\left\langle\tilde{\Psi}_{j}\left|\hat{\mu}_{\beta}\right|\tilde{\Psi}_{n}\right\rangle}{\omega_{jn}-\omega_{0}-i\Gamma_{j}}+\frac{\left\langle\tilde{\Psi}_{m}\left|\hat{\mu}_{\beta}\right|\tilde{\Psi}_{j}\right\rangle\left\langle\tilde{\Psi}_{j}\left|\hat{\mu}_{\alpha}\right|\tilde{\Psi}_{n}\right\rangle}{\omega_{jm}+\omega_{0}+i\Gamma_{j}}\right]$$

"Theory of Natural Raman Optical Activity I. Complete Circular Polarization Formalism" by L. Hecht and L.A. Nafie, *Mol. Phys*. **72,** 441-469 (1991).

"Theory and Measurement of Raman Optical Activity" by L.A. Nafie and D. Che, in *Modern Nonlinear Optics, Part 3*, M. Evans and S. Kielich eds., *Adv. Chem. Phys. Series* **85,** 105-149 (1994).

Raman Polarizability in the General Unrestricted Theory

$$\tilde{\alpha}_{\alpha\beta} = \frac{1}{\hbar}\sum_{j\neq m,n}\left[\frac{\langle m|\hat{\mu}_{\alpha}|j\rangle\langle j|\hat{\mu}_{\beta}|n\rangle}{\omega_{jn}-\omega_0-i\Gamma_j}+\frac{\langle m|\hat{\mu}_{\beta}|j\rangle\langle j|\hat{\mu}_{\alpha}|n\rangle}{\omega_{jm}+\omega_0+i\Gamma_j}\right]$$

Three Raman Invariants

Simplified Notation for wavefunctions

$$\alpha^2 = \frac{1}{9}\mathrm{Im}[(\tilde{\alpha}_{\alpha\alpha})^S(\tilde{\alpha}_{\beta\beta})^{S*}]$$

$$\beta_S(\tilde{\alpha})^2 = \frac{1}{2}\mathrm{Re}[3(\tilde{\alpha}_{\alpha\beta})^S(\tilde{\alpha}_{\alpha\beta})^{S*}-(\tilde{\alpha}_{\alpha\alpha})^S(\tilde{\alpha}_{\beta\beta})^{S*}]$$

$$\beta_A(\tilde{\alpha})^2 = \frac{1}{2}\mathrm{Re}[3(\tilde{\alpha}_{\alpha\beta})^A(\tilde{\alpha}_{\alpha\beta})^{A*}]$$

$$(T_{\alpha\beta})^S = \frac{1}{2}[(T_{\alpha\beta})+(T_{\beta\alpha})]$$

$$(T_{\alpha\beta})^A = \frac{1}{2}[(T_{\alpha\beta})-(T_{\beta\alpha})]$$

Born-Oppenheimer Approximation with Vibronic Detail

$$|\tilde{\Psi}_j(\boldsymbol{r},\boldsymbol{R})\rangle = |\Psi^A_{ev}(\boldsymbol{r},\boldsymbol{R})\rangle = |\psi^A_e(\boldsymbol{r},\boldsymbol{R})\phi_{ev}(\boldsymbol{R})\rangle = |e\rangle|\phi_{ev}\rangle$$

$$\left(\tilde{\alpha}_{\alpha\beta}\right)^a_{g1,g0} = \frac{1}{\hbar}\sum_{ev}\left[\frac{\langle\phi^a_{g1}|\langle g|\hat{\mu}_{\alpha}|e\rangle|\phi_{ev}\rangle\langle\phi_{ev}|\langle e|\hat{\mu}_{\beta}|g\rangle|\phi^a_{g0}\rangle}{\omega_{ev,g0}-\omega_0-i\Gamma_{ev}}\right.$$

Resonance Term

$$\left.+\frac{\langle\phi^a_{g1}|\langle g|\hat{\mu}_{\beta}|e\rangle|\phi_{ev}\rangle\langle\phi_{ev}|\langle e|\hat{\mu}_{\alpha}|g\rangle|\phi^a_{g0}\rangle}{\omega_{ev,g1}+\omega_0+i\Gamma_{ev}}\right]$$

Non-Resonance Term

Born-Oppenheimer Approximation with Vibronic Detail

Alternative expression for the denominator of the non-resonant term

$$\left(\tilde{\alpha}_{\alpha\beta}\right)^{a}_{g1,g0} = \frac{1}{\hbar}\sum_{ev}\left[\frac{\langle\phi^{a}_{g1}|\langle g|\hat{\mu}_{\alpha}|e\rangle|\phi_{ev}\rangle\langle\phi_{ev}|\langle e|\hat{\mu}_{\beta}|g\rangle|\phi^{a}_{g0}\rangle}{\omega_{ev,g0}-\omega_{0}-i\Gamma_{ev}}\right.$$

Resonance Term

$$\left.+\frac{\langle\phi^{a}_{g1}|\langle g|\hat{\mu}_{\beta}|e\rangle|\phi_{ev}\rangle\langle\phi_{ev}|\langle e|\hat{\mu}_{\alpha}|g\rangle|\phi^{a}_{g0}\rangle}{\omega_{ev,g0}+\omega_{s}+i\Gamma_{ev}}\right]$$

Non-Resonance Term

by using

$$\omega_{ev,g1}+\omega_{0}=\omega_{ev,g0}+\omega_{s}$$

Vibrational Dependence of Electronic Wavefunctions

$$\psi^{A}_{g}\left(Q_{a}\right)=\psi_{g,0}+\left(\frac{\partial\tilde{\psi}_{g}}{\partial Q_{a}}\right)_{0,0}Q_{a}+\ldots$$

Compact Notation

$$\langle g|\hat{\mu}_{\alpha}|e\rangle^{Q_{a}}_{0}=\left(\frac{\partial\langle g|\hat{\mu}_{\alpha}|e\rangle}{\partial Q_{a}}\right)_{0}=\left\langle\left(\frac{\partial\psi_{g}}{\partial Q_{a}}\right)_{0}\middle|\hat{\mu}_{\alpha}\middle|\psi_{e,0}\right\rangle+\left\langle\psi_{g,0}\middle|\hat{\mu}_{\alpha}\middle|\left(\frac{\partial\psi_{e}}{\partial Q_{a}}\right)_{0}\right\rangle$$

General Unrestricted (GU) Formalism

Vibronic Coupling Expression of GU Raman Tensor

$$\left(\tilde{\alpha}_{\alpha\beta}\right)_{g1,g0}^{Q_a} = \frac{1}{\hbar}\sum_{\substack{ev \\ e\neq g}}\left\{\left(\frac{\langle g|\hat{\mu}_\alpha|e\rangle_0\langle e|\hat{\mu}_\beta|g\rangle_0}{\omega_{ev,g0}-\omega_0-i\Gamma_{ev}}+\frac{\langle g|\hat{\mu}_\beta|e\rangle_0\langle e|\hat{\mu}_\alpha|g\rangle_0}{\omega_{ev,g1}+\omega_0+i\Gamma_{ev}}\right)\langle\phi_{g1}^a|\phi_{ev}\rangle\langle\phi_{ev}|\phi_{g0}^a\rangle\right.$$

$$+\left(\frac{\langle g|\hat{\mu}_\alpha|e\rangle_0^{Q_a}\langle e|\hat{\mu}_\beta|g\rangle_0}{\omega_{ev,g0}-\omega_0-i\Gamma_{ev}}+\frac{\langle g|\hat{\mu}_\beta|e\rangle_0^{Q_a}\langle e|\hat{\mu}_\alpha|g\rangle_0}{\omega_{ev,g1}+\omega_0+i\Gamma_{ev}}\right)\langle\phi_{g1}^a|Q_a|\phi_{ev}\rangle\langle\phi_{ev}|\phi_{g0}^a\rangle$$

$$\left.+\left(\frac{\langle g|\hat{\mu}_\alpha|e\rangle_0\langle e|\hat{\mu}_\beta|g\rangle_0^{Q_a}}{\omega_{ev,g0}-\omega_0-i\Gamma_{ev}}+\frac{\langle g|\hat{\mu}_\beta|e\rangle_0\langle e|\hat{\mu}_\alpha|g\rangle_0^{Q_a}}{\omega_{ev,g1}+\omega_0+i\Gamma_{ev}}\right)\langle\phi_{g1}^a|\phi_{ev}\rangle\langle\phi_{ev}|Q_a|\phi_{g0}^a\rangle\right\}$$

Far-From-Resonance Expression of Raman Tensor

Resonance Energy Denominator

$$\omega_{e\upsilon,g0} - \omega_0 - i\Gamma_{e\upsilon} \approx \omega_{eg}^0 - \omega_0$$

Non-Resonance Energy Denominator

$$\omega_{e\upsilon,g1} + \omega_0 + i\Gamma_{e\upsilon} \approx \omega_{eg}^0 + \omega_0$$

$$\left(\tilde{\alpha}_{\alpha\beta}\right)_{g1,g0}^a = \left\langle \phi_{g1}^a \right| \frac{1}{\hbar} \sum_e \left[\frac{\left\langle g \middle| \hat{\mu}_\alpha \middle| e \right\rangle \left\langle e \middle| \hat{\mu}_\beta \middle| g \right\rangle}{\omega_{eg}^0 - \omega_0} + \frac{\left\langle g \middle| \hat{\mu}_\beta \middle| e \right\rangle \left\langle e \middle| \hat{\mu}_\alpha \middle| g \right\rangle}{\omega_{eg}^0 + \omega_0} \right] \left| \phi_{g0}^a \right\rangle$$

No vibronic detail in energy denominator allow sum over all excited vibrational states

Far-From-Resonance Expression of Raman Tensor

Hermitian Property of Electronic Matrix Elements

$$\left\langle g \middle| \hat{\mu}_\beta \middle| e \right\rangle \left\langle e \middle| \hat{\mu}_\alpha \middle| g \right\rangle = \left\langle g \middle| \hat{\mu}_\alpha \middle| e \right\rangle^* \left\langle e \middle| \hat{\mu}_\beta \middle| g \right\rangle^* = \left\langle g \middle| \hat{\mu}_\alpha \middle| e \right\rangle \left\langle e \middle| \hat{\mu}_\beta \middle| g \right\rangle$$

Allows Combination of Resonance and Non-Resonance Terms

$$\left(\tilde{\alpha}_{\alpha\beta}\right)_{g1,g0}^a = \left\langle \phi_{g1}^a \right| \frac{1}{\hbar} \sum_e \left[\frac{\left\langle g \middle| \hat{\mu}_\alpha \middle| e \right\rangle \left\langle e \middle| \hat{\mu}_\beta \middle| g \right\rangle}{\omega_{eg}^0 - \omega_0} + \frac{\left\langle g \middle| \hat{\mu}_\alpha \middle| e \right\rangle \left\langle e \middle| \hat{\mu}_\beta \middle| g \right\rangle}{\omega_{eg}^0 + \omega_0} \right] \left| \phi_{g0}^a \right\rangle$$

$$\left(\tilde{\alpha}_{\alpha\beta}\right)_{g1,g0}^a = \left\langle \phi_{g1}^a \right| \frac{1}{\hbar} \sum_e \left\langle g \middle| \hat{\mu}_\alpha \middle| e \right\rangle \left\langle e \middle| \hat{\mu}_\beta \middle| g \right\rangle \left[\frac{1}{\omega_{eg}^0 - \omega_0} + \frac{1}{\omega_{eg}^0 + \omega_0} \right] \left| \phi_{g0}^a \right\rangle$$

Far-From-Resonance Expression of Raman Tensor

Combining the frequency denominators yields the expressions

$$\left(\alpha_{\alpha\beta}\right)^{a}_{g1,g0} = \left\langle \phi^{a}_{g1} \middle| \alpha_{\alpha\beta} \middle| \phi^{a}_{g0} \right\rangle = \left\langle \phi^{a}_{g1} \middle| \frac{2}{\hbar} \mathrm{Re} \sum_{e \neq g} \frac{\omega^{0}_{eg} \left\langle g \middle| \hat{\mu}_{\alpha} \middle| e \right\rangle \left\langle e \middle| \hat{\mu}_{\beta} \middle| g \right\rangle}{\left(\omega^{0}_{eg}\right)^{2} - \omega_{0}^{2}} \middle| \phi^{a}_{g0} \right\rangle$$

$$\alpha_{\alpha\beta} = \frac{2}{\hbar} \sum_{e \neq g} \frac{\omega^{0}_{eg}}{\left(\omega^{0}_{eg}\right)^{2} - \omega_{0}^{2}} \mathrm{Re}\left[\left\langle g \middle| \hat{\mu}_{\alpha} \middle| e \right\rangle \left\langle e \middle| \hat{\mu}_{\beta} \middle| g \right\rangle \right]$$

The polarizability tensor is now symmetric with respect to interchange of α and β.

GU verus FFR Invariants

GU – 3 Raman Invariants

$$\alpha^{2} = \frac{1}{9} \mathrm{Re}\left[\left(\tilde{\alpha}_{\alpha\alpha}\right)^{S} \left(\tilde{\alpha}_{\beta\beta}\right)^{S*} \right]$$

$$\beta_{S}\left(\tilde{\alpha}\right)^{2} = \frac{1}{2} \mathrm{Re}\left[3\left(\tilde{\alpha}_{\alpha\beta}\right)^{S} \left(\tilde{\alpha}_{\alpha\beta}\right)^{S*} - \left(\tilde{\alpha}_{\alpha\alpha}\right)^{S} \left(\tilde{\alpha}_{\beta\beta}\right)^{S*} \right]$$

$$\beta_{A}\left(\tilde{\alpha}\right)^{2} = \frac{1}{2} \mathrm{Re}\left[3\left(\tilde{\alpha}_{\alpha\beta}\right)^{A} \left(\tilde{\alpha}_{\alpha\beta}\right)^{A*} \right]$$

FFR – 2 Raman Invariants

$$\alpha^{2} = \frac{1}{9} \alpha_{\alpha\alpha} \alpha_{\beta\beta}$$

$$\beta\left(\alpha\right)^{2} = \frac{1}{2}\left(3\alpha_{\alpha\beta}\alpha_{\alpha\beta} - \alpha_{\alpha\alpha}\alpha_{\beta\beta} \right)$$

Overview of GU and FFR Raman/ROA Theories

GU Theory – Full Excited State Vibronic Detail

3 Raman Invariants
Beyond reach of current Raman/ROA intensity software

FFR Theory – No Excited State Vibronic Detail

2 Raman Invariants, 3 ROA Invariants
Software routines available commercially from Gaussian, Inc.

Near-Resonance (NR) Formalism

"Theory of Raman Scattering and Raman Optical Activity: Near-Resonance Theory and Levels of Approximation" by Laurence A. Nafie, *Theo. Chem. Acc.*, 119, 39-55 (2008).

Far-From Resonance (FFR) Raman Theory

GU Level for g0→g1

$$(\tilde{\alpha}_{\alpha\beta})^a_{g1,g0} = \frac{1}{\hbar}\sum_{ev}\left[\frac{\langle\phi^a_{g1}|\langle g|\hat{\mu}_\alpha|e\rangle|\phi_{ev}\rangle\langle\phi_{ev}|\langle e|\hat{\mu}_\beta|g\rangle|\phi^a_{g0}\rangle}{\omega_{ev,g0}-\omega_0-i\Gamma_e} + \frac{\langle\phi^a_{g1}|\langle g|\hat{\mu}_\beta|e\rangle|\phi_{ev}\rangle\langle\phi_{ev}|\langle e|\hat{\mu}_\alpha|g\rangle|\phi^a_{g0}\rangle}{\omega_{ev,g1}+\omega_0+i\Gamma_e}\right]$$

FFR Level for g0→g1

$$(\tilde{\alpha}_{\alpha\beta})^a_{g1,g0} = \langle\phi^a_{g1}|\frac{1}{\hbar}\sum_{e}\left[\frac{\langle g|\hat{\mu}_\alpha|e\rangle\langle e|\hat{\mu}_\beta|g\rangle}{\omega^0_{eg}-\omega_0} + \frac{\langle g|\hat{\mu}_\beta|e\rangle\langle e|\hat{\mu}_\alpha|g\rangle}{\omega^0_{eg}+\omega_0}\right]|\phi^a_{g0}\rangle$$

FFR Level with nuclear derivatives shown for g0→g1

$$(\tilde{\alpha}_{\alpha\beta})^{Q_a}_{g1,g0} = \frac{1}{\hbar}\sum_{e}\left[\frac{\langle g|\hat{\mu}_\alpha|e\rangle^{Q_a}_0\langle e|\hat{\mu}_\beta|g\rangle_0}{\omega^0_{eg}-\omega_0} + \frac{\langle g|\hat{\mu}_\alpha|e\rangle_0\langle e|\hat{\mu}_\beta|g\rangle^{Q_a}_0}{\omega^0_{eg}-\omega_0} + \frac{\langle g|\hat{\mu}_\beta|e\rangle^{Q_a}_0\langle e|\hat{\mu}_\alpha|g\rangle_0}{\omega^0_{eg}+\omega_0} + \frac{\langle g|\hat{\mu}_\beta|e\rangle_0\langle e|\hat{\mu}_\alpha|g\rangle^{Q_a}_0}{\omega^0_{eg}+\omega_0}\right]\langle\phi^a_{g1}|Q_a|\phi^a_{g0}\rangle$$

Near Resonance Raman (NR) Raman Theory

GU Level for g0→g1 with alternative non-resonance term denominator

$$\left(\tilde{\alpha}_{\alpha\beta}\right)^a_{g1,g0} = \frac{1}{\hbar}\sum_{e\upsilon}\left[\frac{\langle\phi^a_{g1}|\langle\tilde{g}|\hat{\mu}_\alpha|\tilde{e}\rangle|\phi^a_{g\upsilon}\rangle\langle\phi^a_{g\upsilon}|\langle\tilde{e}|\hat{\mu}_\beta|\tilde{g}\rangle|\phi^a_{g0}\rangle}{\omega_{e\upsilon,g0}-\omega_0-i\Gamma_{e\upsilon}} + \frac{\langle\phi^a_{g1}|\langle\tilde{g}|\hat{\mu}_\beta|\tilde{e}\rangle|\phi^a_{g\upsilon}\rangle\langle\phi^a_{g\upsilon}|\langle\tilde{e}|\hat{\mu}_\alpha|\tilde{g}\rangle|\phi^a_{g0}\rangle}{\omega_{e\upsilon,g0}+\omega_s+i\Gamma_{e\upsilon}}\right]$$

$$\omega_{e\upsilon,g1}+\omega_0 = \omega_{e\upsilon,g0}+\omega_s = \omega_{e\upsilon,g0}$$

$\omega_s = \omega_0 - \omega_a$ for Stokes scattering

Assume excited vibrational states same as the ground vibrational states

$$\phi_{e\upsilon} = \phi^a_{g\upsilon}$$

$$\left(\tilde{\alpha}_{\alpha\beta}\right)^a_{g1,g0} = \frac{1}{\hbar}\sum_{e\upsilon}\left[\frac{\langle\phi^a_{g1}|\langle\tilde{g}|\hat{\mu}_\alpha|\tilde{e}\rangle|\phi^a_{g\upsilon}\rangle\langle\phi^a_{g\upsilon}|\langle\tilde{e}|\hat{\mu}_\beta|\tilde{g}\rangle|\phi^a_{g0}\rangle}{\omega_{e\upsilon,g0}-\omega_0} + \frac{\langle\phi^a_{g1}|\langle\tilde{g}|\hat{\mu}_\beta|\tilde{e}\rangle|\phi^a_{g\upsilon}\rangle\langle\phi^a_{g\upsilon}|\langle\tilde{e}|\hat{\mu}_\alpha|\tilde{g}\rangle|\phi^a_{g0}\rangle}{\omega_{e\upsilon,g0}+\omega_s}\right]$$

$i\Gamma_{e\upsilon}$ is small, can be dropped

Near Resonance Raman (NR) Raman Theory

Only two excited vibronic states are important, ϕ_{g0}^{a} and ϕ_{g1}^{a}

$$(\tilde{\alpha}_{\alpha\beta})_{g1,g0}^{Q_a} = \frac{1}{\hbar}\sum_{e\neq g}\left[\left(\frac{\langle g|\hat{\mu}_\alpha|e\rangle_0^{Q_a}\langle e|\hat{\mu}_\beta|g\rangle_0}{\omega_{eg}^0-\omega_0}+\frac{\langle g|\hat{\mu}_\beta|e\rangle_0^{Q_a}\langle e|\hat{\mu}_\alpha|g\rangle_0}{\omega_{eg}^0+\omega_0-\omega_a}\right)\langle\phi_{g1}^a|Q_a|\phi_{g0}^a\rangle\langle\phi_{g0}^a|\phi_{g0}^a\rangle\right.$$

$$\left.+\left(\frac{\langle g|\hat{\mu}_\alpha|e\rangle_0\langle e|\hat{\mu}_\beta|g\rangle_0^{Q_a}}{\omega_{eg}^0+\omega_a-\omega_0}+\frac{\langle g|\hat{\mu}_\beta|e\rangle_0\langle e|\hat{\mu}_\alpha|g\rangle_0^{Q_a}}{\omega_{eg}^0+\omega_0}\right)\langle\phi_{g1}^a|\phi_{g1}^a\rangle\langle\phi_{g1}^a|Q_a|\phi_{g0}^a\rangle\right]$$

Detailed explanation of energy denominator in all four terms

For the ϕ_{g0}^{a} excited intermediate vibronic state

$$\omega_{e0,g0}-\omega_0=\omega_{eg}^0-\omega_0 \qquad \omega_{e0,g0}+\omega_s=\omega_{eg}^0+\omega_0-\omega_a=\omega_{eg}^0+\omega_s$$

For the ϕ_{g1}^{a} excited intermediate vibronic state

$$\omega_{e1,g0}-\omega_0=\omega_{eg}^0+\omega_a-\omega_0=\omega_{eg}^0-\omega_s$$

$$\omega_{e1,g0}+\omega_s=\omega_{eg}^0+\omega_a+\omega_0-\omega_a=\omega_{eg}^0+\omega_0$$

Near Resonance Raman (NR) Raman Theory

The vibrational matrix element reduce to the same expression giving

$$(\tilde{\alpha}_{\alpha\beta})_{g1,g0}^{Q_a} = \frac{1}{\hbar}\sum_{e\neq g}\left(\frac{\langle g|\hat{\mu}_\alpha|e\rangle_0^{Q_a}\langle e|\hat{\mu}_\beta|g\rangle_0}{\omega_{eg}^0-\omega_0}+\frac{\langle g|\hat{\mu}_\beta|e\rangle_0\langle e|\hat{\mu}_\alpha|g\rangle_0^{Q_a}}{\omega_{eg}^0+\omega_0}\right.$$

$$\left.+\frac{\langle g|\hat{\mu}_\alpha|e\rangle_0\langle e|\hat{\mu}_\beta|g\rangle_0^{Q_a}}{\omega_{eg}^0-\omega_s}+\frac{\langle g|\hat{\mu}_\beta|e\rangle_0^{Q_a}\langle e|\hat{\mu}_\alpha|g\rangle_0}{\omega_{eg}^0+\omega_s}\right)\langle\phi_{g1}^a|Q_a|\phi_{g0}^a\rangle$$

Near Resonance Raman (NR) Raman Theory

Using the Hermitian property of the electronic matrix elements

$$\langle g|\hat{\mu}_\beta|e\rangle_0 \langle e|\hat{\mu}_\alpha|g\rangle_0^{Q_a} = \langle g|\hat{\mu}_\alpha|e\rangle_0^{Q_a} \langle e|\hat{\mu}_\beta|g\rangle_0$$

$$\langle g|\hat{\mu}_\beta|e\rangle_0^{Q_a} \langle e|\hat{\mu}_\alpha|g\rangle_0 = \langle g|\hat{\mu}_\alpha|e\rangle_0 \langle e|\hat{\mu}_\beta|g\rangle_0^{Q_a}$$

The NR Raman tensor becomes

$$\left(\tilde{\alpha}_{\alpha\beta}\right)^a_{g1,g0} = \frac{1}{\hbar}\sum_e \Bigg[\langle g|\hat{\mu}_\alpha|e\rangle_0^{Q_a} \langle e|\hat{\mu}_\beta|g\rangle_0 \left(\frac{1}{\omega_{eg}^0 - \omega_0} + \frac{1}{\omega_{eg}^0 + \omega_0} \right) \langle g|\hat{\mu}_\beta|e\rangle_0^{Q_a} \langle e|\hat{\mu}_\alpha|g\rangle_0 \left(\frac{1}{\omega_{eg}^0 - \omega_s} + \frac{1}{\omega_{eg}^0 + \omega_s} \right) \Bigg]$$

NR Raman Tensor is simple but no long symmetric

$$\left(\tilde{\alpha}_{\alpha\beta}\right)^a_{g1,g0} \neq \left(\tilde{\alpha}_{\beta\alpha}\right)^a_{g1,g0}$$

Comparison of FFR Theory to NR Theory

FFR Theory (Symmetric Raman Tensor)

$$(\alpha_{\alpha\beta})^a_{g1,g0} = \langle \phi^a_{g1}|\alpha_{\alpha\beta}|\phi^a_{g0}\rangle = \left\langle \phi^a_{g1} \middle| \frac{2}{\hbar}\mathrm{Re}\sum_{e\neq g} \frac{\omega_{eg}\langle g|\hat{\mu}_\alpha|e\rangle\langle e|\hat{\mu}_\beta|g\rangle}{(\omega_{eg}^0)^2 - \omega_0^2} \middle| \phi^a_{g0} \right\rangle$$

NR Theory (Restores Asymmetry to Raman Tensor)

$$(\tilde{\alpha}_{\alpha\beta})^{Q_a}_{g1,g0} = \frac{2}{\hbar}\sum_{e\neq g}\Bigg[\frac{\omega_{eg}^0}{(\omega_{eg}^0)^2 - \omega_0^2}\mathrm{Re}\left[\langle g|\hat{\mu}_\alpha|e\rangle_0^{Q_a}\langle e|\hat{\mu}_\beta|g\rangle_0\right] + \frac{\omega_{eg}^0}{(\omega_{eg}^0)^2 - \omega_s^2}\mathrm{Re}\left[\langle g|\hat{\mu}_\alpha|e\rangle_0\langle e|\hat{\mu}_\beta|g\rangle_0^{Q_a}\right]\Bigg] \langle \phi^a_{g1}|Q_a|\phi^a_{g0}\rangle$$

$$\omega_{eg}^0 \pm (\omega_0 - \omega_a) = \omega_{eg}^0 \pm \omega_0(1 - \omega_a/\omega_0)$$

NR theory maintains time-reversal invariance of the Raman tensor. Stokes scattering using incident laser at ω_0 equals Raman tensor for anti-Stokes scattering using incident laser at ω_s.

Summary of GU, FFR and NR Raman Theories

GU Theory – Full Excited State Vibronic Detail

3 Raman Invariants
Time reversal invariant
Resonant to both incident and scattered radiation

FFR Theory – No Excited State Vibronic Detail

2 Raman Invariants
Not time reversal invariant
Resonance with only incident laser frequency

NR Theory – Simplified Excited State Vibronic Detail

3 Raman Invariants
Time reversal invariant
Resonance with both incident and scattered radiation

Single-Electronic-State (SES) Strong Resonance Formalism

General Vibronic Resonance Raman Theory

Need only one Resonance Term – General RR Expression

$$\left(\tilde{\alpha}_{\alpha\beta}\right)^{a}_{g1,g0} = \frac{1}{\hbar}\sum_{\upsilon}\frac{\left\langle \phi^{a}_{g1}\middle|\left\langle g\middle|\hat{\mu}_{\alpha}\middle|e\right\rangle\middle|\phi_{e\upsilon}\right\rangle\left\langle \phi_{e\upsilon}\middle|\left\langle e\middle|\hat{\mu}_{\beta}\middle|g\right\rangle\middle|\phi^{a}_{g0}\right\rangle}{\omega_{e\upsilon,g0}-\omega_{0}-i\Gamma_{e\upsilon}}$$

$$\left(\tilde{\alpha}_{\alpha\beta}\right)^{Q_a}_{g1,g0} = \left(A_{\alpha\beta}\right)^{Q_a}_{g1,g0} + \left(B_{\alpha\beta}\right)^{Q_a}_{g1,g0} + \left(C_{\alpha\beta}\right)^{Q_a}_{g1,g0}$$

RR Tensor is not symmetric – need vibronic detail

Franck-Condon or Albrecht A-Term

$$\left(A_{\alpha\beta}\right)^{Q_a}_{g1,g0} = \frac{1}{\hbar}\left\langle g\middle|\hat{\mu}_{\alpha}\middle|e\right\rangle_{0}\left\langle e\middle|\hat{\mu}_{\beta}\middle|g\right\rangle_{0}\sum_{\upsilon}\frac{\left\langle \phi^{a}_{g1}\middle|\phi_{e\upsilon}\right\rangle\left\langle \phi_{e\upsilon}\middle|\phi^{a}_{g0}\right\rangle}{\omega_{e\upsilon,g0}-\omega_{0}-i\Gamma_{e\upsilon}}$$

"Theory of Resonance Raman Optical Activity: The Single Electronic State Limit" by L.A. Nafie, *Chem. Phys*. **205**, 309-322 (1996).

General Vibronic Resonance Raman Theory

Albrecht B-Term

$$\left(B_{\alpha\beta}\right)^{Q_a}_{g1,g0} = \frac{1}{\hbar}\Bigg[\left\langle g\middle|\hat{\mu}_{\alpha}\middle|(e)^{Q_a}\right\rangle_{0}\left\langle e\middle|\hat{\mu}_{\beta}\middle|g\right\rangle_{0}\sum_{\upsilon}\frac{\left\langle \phi^{a}_{g1}\middle|Q_{a}\middle|\phi_{e\upsilon}\right\rangle\left\langle \phi_{e\upsilon}\middle|\phi^{a}_{g0}\right\rangle}{\omega_{e\upsilon,g0}-\omega_{0}-i\Gamma_{e\upsilon}}$$

$$+\left\langle g\middle|\hat{\mu}_{\alpha}\middle|e\right\rangle_{0}\left\langle (e)^{Q_a}\middle|\hat{\mu}_{\alpha}\middle|g\right\rangle_{0}\sum_{\upsilon}\frac{\left\langle \phi^{a}_{g1}\middle|\phi_{e\upsilon}\right\rangle\left\langle \phi_{e\upsilon}\middle|Q_{a}\middle|\phi^{a}_{g0}\right\rangle}{\omega_{e\upsilon,g0}-\omega_{0}-i\Gamma_{e\upsilon}}\Bigg]$$

Albrecht C-Term

$$\left(C_{\alpha\beta}\right)^{Q_a}_{g1,g0} = \frac{1}{\hbar}\Bigg[\left\langle (g)^{Q_a}\middle|\hat{\mu}_{\alpha}\middle|e\right\rangle_{0}\left\langle e\middle|\hat{\mu}_{\beta}\middle|g\right\rangle_{0}\sum_{\upsilon}\frac{\left\langle \phi^{a}_{g1}\middle|Q_{a}\middle|\phi_{e\upsilon}\right\rangle\left\langle \phi_{e\upsilon}\middle|\phi^{a}_{g0}\right\rangle}{\omega_{e\upsilon,g0}-\omega_{0}-i\Gamma_{e\upsilon}}$$

$$+\left\langle g\middle|\hat{\mu}_{\alpha}\middle|e\right\rangle_{0}\left\langle e\middle|\hat{\mu}_{\alpha}\middle|(g)^{Q_a}\right\rangle_{0}\sum_{\upsilon}\frac{\left\langle \phi^{a}_{g1}\middle|\phi_{e\upsilon}\right\rangle\left\langle \phi_{e\upsilon}\middle|Q_{a}\middle|\phi^{a}_{g0}\right\rangle}{\omega_{e\upsilon,g0}-\omega_{0}-i\Gamma_{e\upsilon}}\Bigg]$$

Herzberg-Teller Expansion of Nuclear Position Dependence of the Electronic Wavefunction

HT-Expansion

$$\psi_e(Q_a) = \psi_e^0 + \left(\frac{\partial \psi_e}{\partial Q_a}\right)_0 Q_a + \ldots$$

$$= \psi_e^0 + \sum_{s \neq e} \frac{\left\langle \psi_s^0 \middle| (\partial H_E / \partial Q_a)_0 \middle| \psi_e^0 \right\rangle}{E_e^0 - E_s^0} \psi_s^0 Q_a + \ldots$$

Compact Notation

$$\frac{\left\langle \psi_s^0 \middle| (\partial H_E / \partial Q_a)_0 \middle| \psi_e^0 \right\rangle}{E_e^0 - E_s^0} = \frac{h_{se,0}^a}{\hbar \omega_{es}^0}$$

B-Term Herzberg-Teller Expansion

HT-Expansion of B-Term

$$\left(B_{\alpha\beta}\right)_{g1,g0}^{Q_a} = \frac{1}{\hbar^2}\left[\sum_{s \neq e} \left\langle g \middle| \hat{\mu}_\alpha \middle| s \right\rangle_0 \frac{h_{se,0}^a}{\omega_{es}^0} \left\langle e \middle| \hat{\mu}_\beta \middle| g \right\rangle_0 \sum_{\upsilon} \frac{\left\langle \phi_{g1}^a \middle| Q_a \middle| \phi_{e\upsilon} \right\rangle \left\langle \phi_{e\upsilon} \middle| \phi_{g0}^a \right\rangle}{\omega_{e\upsilon,g0} - \omega_0 - i\Gamma_{e\upsilon}}\right.$$

$$\left. + \left\langle g \middle| \hat{\mu}_\alpha \middle| e \right\rangle_0 \frac{h_{es,0}^a}{\omega_{es}^0} \left\langle s \middle| \hat{\mu}_\beta \middle| g \right\rangle_0 \sum_{\upsilon} \frac{\left\langle \phi_{g1}^a \middle| \phi_{e\upsilon} \right\rangle \left\langle \phi_{e\upsilon} \middle| Q_a \middle| \phi_{g0}^a \right\rangle}{\omega_{e\upsilon,g0} - \omega_0 - i\Gamma_{e\upsilon}}\right]$$

Expansion of C-term is Similar but C-Term is Less Important for RR Scattering because

$$\omega_{es}^0 \ll \omega_{eg}^0$$

SES-RR Theory

Need only the A-Term since B- and C-Terms involve more than one excited electronic state through HT coupling

$$\left(\tilde{\alpha}_{zz}\right)_{g1,g0}^{Q_a} = \frac{1}{\hbar}\langle g|\hat{\mu}_z|e\rangle_0 \langle e|\hat{\mu}_z|g\rangle_0 \sum_{\upsilon} \frac{\langle \phi_{g1}^a|\phi_{e\upsilon}\rangle\langle \phi_{e\upsilon}|\phi_{g0}^a\rangle}{\omega_{e\upsilon,g0} - \omega_0 - i\Gamma_{e\upsilon}}$$

Chose the one electronic transition moment to be in the z-direction and hence there only one SES-RR tensor element

$$\left(\tilde{\boldsymbol{\alpha}}\right)_{g1,g0}^{a} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \left(\alpha_{zz}\right)_{g1,g0}^{a} \end{pmatrix}$$

Only polarized Raman modes are observed in RR=SES theory. Depolarized modes with zero isotropic invariant are not observed.

SES-RR Theory

There are only two non-zero Raman invariants and both take the same form from the single SES-RR tensor element

$$\alpha^2 = \frac{1}{9}\left|\left(\tilde{\alpha}_{zz}\right)_{g1,g0}^{Q_a}\right|^2 = \frac{1}{9\hbar^2}\left|\langle g|\hat{\mu}_z|e\rangle_0 \langle e|\hat{\mu}_z|g\rangle_0 \sum_{\upsilon} \frac{\langle \phi_{g1}^a|\phi_{e\upsilon}\rangle\langle \phi_{e\upsilon}|\phi_{g0}^a\rangle}{\omega_{e\upsilon,g0} - \omega_0 - i\Gamma_{e\upsilon}}\right|^2$$

$$= \frac{1}{9\hbar^2}\left|\langle e|\hat{\mu}_z|g\rangle_0\right|^4 U_{g1,g0}^a(\omega_0) = \frac{1}{9\hbar^2}\left(D_{eg}^0\right)^2 U_{g1,g0}^a(\omega_0)$$

$$\beta_S\left(\tilde{\alpha}\right)^2 = \left|\left(\tilde{\alpha}_{zz}\right)_{g1,g0}^{Q_a}\right|^2 = \frac{1}{\hbar^2}\left(D_{eg}^0\right)^2 U_{g1,g0}^a(\omega_0) \qquad D_{eg}^0 = \left|\langle e|\mu_z|g\rangle\right|^2$$

Here $U_{g1,g0}^a(\omega_0)$ is a line Lorentzian shape function from the complex vibronic resonance factor and the dipole strength of the g→e electronic transition is D_{eg}^0

SES-RR Lineshape and Depolarization Ratio

$$\left|\frac{1}{(\omega_{ev,g0}-\omega_0)-i\Gamma_{ev}}\right|^2=\frac{1}{(\omega_{ev,g0}-\omega_0)-i\Gamma_{ev}}\times\frac{1}{(\omega_{ev,g0}-\omega_0)+i\Gamma_{ev}}$$

$$=\frac{1}{(\omega_{ev,g0}-\omega_0)^2+\Gamma_{ev}^2}$$ Lorentzian shape

Depolarization Ratio for SES-RR Spectrum

$$\rho_l\left(90^0\right)=\frac{I_Z^X\left(90^0\right)}{I_X^X\left(90^0\right)}=\frac{3\beta_S\left(\tilde{\alpha}\right)^2+5\beta_A\left(\tilde{\alpha}\right)^2}{45\alpha^2+4\beta_S\left(\tilde{\alpha}\right)^2}$$

$$\rho_l=\frac{3\left|\left(\tilde{\alpha}_{zz}\right)_{g1,g0}^{Q_a}\right|^2}{45/9\left|\left(\tilde{\alpha}_{zz}\right)_{g1,g0}^{Q_a}\right|^2+4\left|\left(\tilde{\alpha}_{zz}\right)_{g1,g0}^{Q_a}\right|^2}=\frac{1}{3}$$

Dual-Electronic-State (DES) Strong Resonance Formalism

Two-Electronic-State Resonance Raman Theory

Need A- and B-Terms $$\left(\tilde{\alpha}_{\alpha\beta}\right)^a_{g1,g0} = \left(A_{\alpha\beta}\right)^a_{g1,g0} + \left(B_{\alpha\beta}\right)^a_{g1,g0}$$

Franck-Condon or Albrecht A-Term for First Excited State

$$\left(A_{\alpha\beta}\right)^a_{g1,g0} = \frac{1}{\hbar}\left\langle g\middle|\hat{\mu}_\alpha\middle|e\right\rangle_0 \left\langle e\middle|\hat{\mu}_\beta\middle|g\right\rangle_0 \sum_\upsilon \frac{\left\langle \phi^a_{g1}\middle|\phi_{e\upsilon}\right\rangle\left\langle \phi_{e\upsilon}\middle|\phi^a_{g0}\right\rangle}{\omega_{e\upsilon,g0} - \omega_0 - i\Gamma_{e\upsilon}}$$

Second Excited State Coupled to First by HT Coupling B-Term

$$\left(B_{\alpha\beta}\right)^a_{g1,g0} = \frac{1}{\hbar^2}\left[\left\langle g\middle|\hat{\mu}_\alpha\middle|s\right\rangle_0 \frac{h^a_{se,0}}{\omega^0_{es}}\left\langle e\middle|\hat{\mu}_\beta\middle|g\right\rangle_0 \sum_\upsilon \frac{\left\langle \phi^a_{g1}\middle|Q_a\middle|\phi_{e\upsilon}\right\rangle\left\langle \phi_{e\upsilon}\middle|\phi^a_{g0}\right\rangle}{\omega_{e\upsilon,g0} - \omega_0 - i\Gamma_{e\upsilon}}\right.$$

$$\left. + \left\langle g\middle|\hat{\mu}_\alpha\middle|e\right\rangle_0 \frac{h^a_{es,0}}{\omega^0_{es}}\left\langle s\middle|\hat{\mu}_\beta\middle|g\right\rangle_0 \sum_\upsilon \frac{\left\langle \phi^a_{g1}\middle|\phi_{e\upsilon}\right\rangle\left\langle \phi_{e\upsilon}\middle|Q_a\middle|\phi^a_{g0}\right\rangle}{\omega_{e\upsilon,g0} - \omega_0 - i\Gamma_{e\upsilon}}\right]$$

Two-Electronic-State Resonance Raman Theory

Raman Tensor has no simplifications and simplicity diagonal symmetry of the SES theory is lost

$$\left(\tilde{\alpha}_{\alpha\beta}\right)^a_{g1,g0} = \frac{1}{\hbar^2}\left[\hbar\left\langle g\middle|\hat{\mu}_z\middle|e\right\rangle_0 \left\langle e\middle|\hat{\mu}_z\middle|g\right\rangle_0 \sum_\upsilon \frac{\left\langle \phi^a_{g1}\middle|\phi_{e\upsilon}\right\rangle\left\langle \phi_{e\upsilon}\middle|\phi^a_{g0}\right\rangle}{\omega_{e\upsilon,g0} - \omega_0 - i\Gamma_{e\upsilon}}\right.$$

$$+ \left\langle g\middle|\hat{\mu}_\alpha\middle|s\right\rangle_0 \frac{h^a_{se,0}}{\omega^0_{es}}\left\langle e\middle|\hat{\mu}_z\middle|g\right\rangle_0 \sum_\upsilon \frac{\left\langle \phi^a_{g1}\middle|Q_a\middle|\phi_{e\upsilon}\right\rangle\left\langle \phi_{e\upsilon}\middle|\phi^a_{g0}\right\rangle}{\omega_{e\upsilon,g0} - \omega_0 - i\Gamma_{e\upsilon}}$$

$$\left. + \left\langle g\middle|\hat{\mu}_z\middle|e\right\rangle_0 \frac{h^a_{es,0}}{\omega^0_{es}}\left\langle s\middle|\hat{\mu}_\beta\middle|g\right\rangle_0 \sum_\upsilon \frac{\left\langle \phi^a_{g1}\middle|\phi_{e\upsilon}\right\rangle\left\langle \phi_{e\upsilon}\middle|Q_a\middle|\phi^a_{g0}\right\rangle}{\omega_{e\upsilon,g0} - \omega_0 - i\Gamma_{e\upsilon}}\right]$$