

CHAPTER 5

Vibronic Spectroscopy

5.1 Absorption Spectra with Vibrational Structure

We can now use the vibronic states, which approximate energy eigenstates of the full molecular Hamiltonian, to obtain expressions for absorption, emission, and other processes that contain the vibrational structure.

The probability amplitude for absorption was found to be

$$U_{f, n_k^{\lambda-1}, i, n_k^{\lambda}} = -i \left[2\pi \hbar \omega_k n_k^{\lambda} \right]^{1/2} e^{i\vec{k} \cdot \vec{r}_0} \frac{\langle f | \hat{e}^{\lambda} \cdot \vec{\mu} | i \rangle}{\varepsilon_f - \varepsilon_i - \hbar \omega_k} \left(1 - e^{i(\varepsilon_f - \varepsilon_i - \hbar \omega)(t-t_0)/\hbar} \right),$$

where the states $|f\rangle$ and $|i\rangle$ in the equation are the exact molecular energy eigenstates. However, instead of the exact molecular eigenstates, we will use our first-order approximate vibronic states obtained in the last chapter. These are not the crude Born-Oppenheimer product states, $|l_v\rangle|\bar{u}\rangle$, which are our 0th order molecular stationary states. Instead we will use the stationary states $|l\rangle$ that are to first order given by

$$\begin{aligned} |l\rangle = |l_v\rangle|\bar{u}\rangle &- \sum_{j,\alpha} \sum_{\bar{w}} \sum_K \frac{\langle j_\alpha | \left(\frac{\partial H'}{\partial Q_K} \right)_0 | l_v \rangle \langle \bar{w} | Q_K | \bar{u} \rangle}{E_{l_v \bar{u}} - E_{j_\alpha \bar{w}}} | j_\alpha \rangle |\bar{u}\rangle f_{j_\alpha \bar{w}, l_v \bar{u}}(t_0) \\ &- \sum_{j,\alpha} \sum_{\bar{w}} \sum_{K,L} \frac{\langle j_\alpha | \left(\frac{\partial^2 H'}{\partial Q_K \partial Q_L} \right)_0 | l_v \rangle \langle \bar{w} | Q_K Q_L | \bar{u} \rangle}{E_{l_v \bar{u}} - E_{j_\alpha \bar{w}}} | j_\alpha \rangle |\bar{w}\rangle f_{j_\alpha \bar{w}, l_v \bar{u}}(t_0) \end{aligned}$$

+ *high order perturbation terms and high order Taylor series expansion terms,*

We will assume that at time t'_0 , the molecular system is prepared in a crude Born-Oppenheimer state $|i\rangle = |g\rangle|\bar{v}\rangle$, this state will evolve to the state $|i(t_0)\rangle$, at which point the interaction with the field is turned on, as described at the end of Chapter 4, giving the ground state analog of $|l\rangle$,

$$|g\bar{v}\rangle = |g\rangle|\bar{v}\rangle - \sum_{j,\alpha} \sum_{\bar{w}} \sum_K \frac{\langle j_\alpha | \left(\frac{\partial H}{\partial Q_K} \right)_0 | g \rangle \langle \bar{w} | Q_K | \bar{v} \rangle}{E_{g\bar{v}} - E_{j_\alpha \bar{w}}} | j_\alpha \rangle |\bar{w}\rangle f_{j_\alpha \bar{w}, g\bar{v}}(t_0 - t'_0)$$

$$-\sum_{j,\alpha} \sum_{\bar{w}} \sum_{K,L} \frac{\langle j_\alpha | \left(\frac{\partial^2 H'}{\partial Q_K \partial Q_L} \right)_0 | g \rangle \langle \bar{w} | Q_K Q_L | \bar{v} \rangle}{E_{g\bar{v}} - E_{j_\alpha \bar{w}}} | j_\alpha \rangle | \bar{w} \rangle f_{j_\alpha \bar{w}, g\bar{v}}(t_0).$$

Actually, to substitute into the expression for the U -matrix, we will need $\langle l_\nu \bar{u} |$ not $| l_\nu \bar{u} \rangle$, obtained by taking the adjoint, to give

$$\begin{aligned} \langle l_\nu \bar{u} | = \langle l_\nu | \langle \bar{u} | - \sum_{j,\alpha} \sum_{\bar{w}} \sum_K \frac{\langle l_\nu | \left(\frac{\partial H'}{\partial Q_K} \right)_0 | j_\alpha \rangle \langle \bar{w} | Q_K | \bar{u} \rangle}{E_{l_\nu \bar{u}} - E_{j_\alpha \bar{w}}} \langle j_\alpha | \langle \bar{u} | f_{l_\nu \bar{u}, j_\alpha \bar{w}} \\ - \sum_{j,\alpha} \sum_{\bar{w}} \sum_{K,L} \frac{\langle l_\nu | \left(\frac{\partial^2 H'}{\partial Q_K \partial Q_L} \right)_0 | j_\alpha \rangle \langle \bar{w} | Q_K Q_L | \bar{u} \rangle}{E_{l_\nu \bar{u}} - E_{j_\alpha \bar{w}}} \langle j_\alpha | \langle \bar{w} | f_{l_\nu \bar{u}, j_\alpha \bar{w}}. \end{aligned}$$

Substituting these expressions for the initial and final states $| g\bar{v} \rangle$ and $| l_\nu \bar{u} \rangle$ into the expression for the absorption probability amplitude, we have

$$U_{l_\nu \bar{u}, g\bar{v}}^{n_k^\lambda - 1, n_k^\lambda} = -i \left[2\pi \hbar \omega_k n_k^\lambda \right]^{1/2} e^{i\bar{k} \cdot \bar{r}_0} \frac{\langle l_\nu \bar{u} | \hat{e}^\lambda \cdot \bar{\mu} | g\bar{v} \rangle}{E_{l_\nu \bar{u}} - E_{g\bar{v}} - \hbar \omega_k} \left(1 - e^{i(E_{l_\nu \bar{u}} - E_{g\bar{v}} - \hbar \omega_k)(t-t_0)/\hbar} \right).$$

Neglecting the last term of the vibronic states, substitution will give four terms, and we will neglect the fourth term that is the product of the second terms of the state expansions (term with factors like $\langle \bar{w} | Q_k | \bar{v} \rangle \langle \bar{u} | Q_k | \bar{x} \rangle$). Thus, we obtain

$$\begin{aligned} U_{l_\nu \bar{u}, g\bar{v}}^{n_k^\lambda - 1, n_k^\lambda} = -i \left[2\pi \hbar \omega_k n_k^\lambda \right]^{1/2} e^{i\bar{k} \cdot \bar{r}_0} \left[\frac{\langle l_\nu | \hat{e}^\lambda \cdot \bar{\mu} | g \rangle \langle \bar{u} | \bar{v} \rangle}{E_{l_\nu \bar{u}} - E_{g\bar{v}} - \hbar \omega_k} \left(1 - e^{i(E_{l_\nu \bar{u}} - E_{g\bar{v}} - \hbar \omega_k)(t-t_0)/\hbar} \right) \right. \\ - \sum_{j_\alpha} \sum_{\bar{w}} \sum_K \frac{\left\langle l_\nu \left| \left(\frac{\partial H'}{\partial Q_K} \right)_0 \right| j_\alpha \right\rangle \langle \bar{w} | Q_K | \bar{u} \rangle f_{l_\nu \bar{u}, j_\alpha \bar{w}}(t_0 - t')}{E_{l_\nu \bar{u}} - E_{j_\alpha \bar{w}}} \frac{\langle j_\alpha | \hat{e}^\lambda \cdot \bar{\mu} | g \rangle \langle \bar{w} | \bar{v} \rangle}{E_{l_\nu \bar{u}} - E_{g\bar{v}} - \hbar \omega_k} \left(1 - e^{i(E_{l_\nu \bar{u}} - E_{g\bar{v}} - \hbar \omega_k)(t-t_0)/\hbar} \right) \\ - \sum_{j_\alpha} \sum_{\bar{w}} \sum_K \frac{\left\langle j_\alpha \left| \left(\frac{\partial H'}{\partial Q_K} \right)_0 \right| g \right\rangle \langle \bar{w} | Q_K | \bar{v} \rangle f_{j_\alpha \bar{w}, g\bar{v}}(t_0 - t')}{E_{g\bar{v}} - E_{j_\alpha \bar{w}}} \frac{\langle l_\nu | \hat{e}^\lambda \cdot \bar{\mu} | j_\alpha \rangle \langle \bar{u} | \bar{w} \rangle}{E_{l_\nu \bar{u}} - E_{g\bar{v}} - \hbar \omega_k} \left(1 - e^{i(E_{l_\nu \bar{u}} - E_{g\bar{v}} - \hbar \omega_k)(t-t_0)/\hbar} \right) \\ \left. + \text{terms in } Q_K Q_L \dots \right] \end{aligned}$$

The final state $|l, \vec{u}\rangle$ at time t can be a different vibrational level of the electronic ground state (infrared) or an excited electronic state (optical, NIR).

Here, we have approximated $\langle \vec{u} | \langle l_v | \hat{e}^\lambda \cdot \vec{\mu} | j_\alpha \rangle | \vec{w} \rangle$ by $\langle l_v | \hat{e}^\lambda \cdot \vec{\mu} | j_\alpha \rangle \langle \vec{u} | \vec{w} \rangle$. However, the dipole operator is defined by $\vec{\mu} \equiv \sum_\alpha Z_\alpha e \vec{r}_\alpha$, where α includes all charged particles of the molecule (electrons and nuclei), thus, we have ignored the nuclear coordinate dependence of $\vec{\mu}$. In this case, nuclear coordinate dependence will come entirely through the Q_K -dependence of the energy eigenstates. This is reasonable for optical frequencies of light since the field primarily interacts with the light electrons, but not the heavy and shielded nuclei. On the other hand for IR absorption, this approximation is not sufficient and we must keep the explicit nuclear coordinate dependence of $\vec{\mu}$.

Each state absorbs independently of the other states, thus, the probability of absorption to all molecular states is

$$P(\hbar\omega_k) = \sum_{l, \vec{v}} \left| U_{l, \vec{u}, g \vec{v}}^{n_k^\lambda - 1, n_k^\lambda} \right|^2.$$

Because the matrix elements like $\langle \vec{u} | \vec{v} \rangle$ and $\langle \vec{w} | Q_K | \vec{v} \rangle$ vanish for most cases, only a few terms of the U-matrix survive since $\langle \vec{u} | \vec{v} \rangle = \delta_{\vec{u}, \vec{v}}$ and $\langle \vec{w} | Q_K | \vec{v} \rangle = 0$, unless $w_K = v_K + 1$ or $v_K - 1$ and $w_L = v_L \quad \forall L \neq K$. In the case of $w_K = v_K + 1$,

$$\langle \vec{w} | Q_K | \vec{v} \rangle = \left[\frac{(v_K + 1) \hbar}{2\mu_K \Omega_K} \right]^{1/2},$$

and for $w_K = v_K - 1$,

$$\langle \vec{w} | Q_K | \vec{v} \rangle = \left[\frac{v_K \hbar}{2\mu_K \Omega_K} \right]^{1/2}.$$

Thus, the matrix elements of the time evolution operator for vanish for most final vibrational states.

(1) First, consider the case when $\vec{u} = \vec{v}$ and l is an electronic excited state; this is called the pure electronic or 0-0 transition. In this case, we have

$$U_{l, \vec{v}, g \vec{v}}^{n_k^\lambda - 1, n_k^\lambda} = i \left[2\pi \hbar \omega_k n_k^\lambda \right]^{1/2} e^{i\vec{k} \cdot \vec{r}_0} \frac{\langle l_v | \hat{e}^\lambda \cdot \vec{\mu} | g \rangle}{E_{l_v}^0 - E_g^0 - \hbar\omega_k} \left(1 - e^{i(E_{l_v}^0 - E_g^0 - \hbar\omega_k)(t-t_0)/\hbar} \right),$$

where the second and third terms vanish because

$$\langle \bar{w} | Q_K | \bar{u} \rangle \langle \bar{w} | \bar{v} \rangle = \langle \bar{w} | Q_K | \bar{u} \rangle \delta_{\bar{w}, \bar{v}} = \langle \bar{v} | Q_K | \bar{v} \rangle \delta_{\bar{w}, \bar{v}}$$

vanishes, and similarly,

$$\langle \bar{w} | Q_K | \bar{v} \rangle \langle \bar{w} | \bar{v} \rangle = 0 \text{ for } \bar{u} = \bar{v}.$$

(2) Next, consider the case, $|\bar{u}\rangle = |v_1, \dots, v_{L-1}, v_L + 1, \dots, v_{3N-6}\rangle \equiv |v_L + 1\rangle$, for which we have

$$\begin{aligned} U_{l, v_L+1, g v_L}^{n_k^2 - 1, n_k^2} &= -i \left[2\pi n_k^2 \hbar \omega_k \right]^{1/2} e^{i\bar{k} \cdot \bar{r}_0} \\ &\times \left[0 - \left[\frac{(v_L + 1) \hbar}{2\mu_L \Omega_L} \right]^{1/2} \sum_{j_\alpha} \frac{\left\langle l_\nu \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| j_\alpha \right\rangle \langle j_\alpha | \hat{e}^\lambda \cdot \bar{\mu} | g \rangle f_{l, v_L+1, j_\alpha v_L} \left(1 - e^{i(E_{l, \bar{v}} + \hbar \Omega_L - E_{g \bar{v}} - \hbar \omega_k)(t-t_0)/\hbar} \right)}{(E_{l, \bar{v}} + \hbar \Omega_L - E_{j_\alpha \bar{v}})(E_{l, \bar{v}} + \hbar \Omega_L - E_{g \bar{v}} - \hbar \omega_k)} \right. \\ &\quad \left. - \left[\frac{(v_L + 1) \hbar}{2\mu_L \Omega_L} \right]^{1/2} \sum_{j_\alpha} \frac{\left\langle j_\alpha \left| \left(\frac{\partial H'}{\partial Q_L} \right)_D \right| g \right\rangle \langle l_\nu | \hat{e}^\lambda \cdot \bar{\mu} | j_\alpha \rangle f_{j_\alpha v_L+1, g v_L} \left(1 - e^{i(E_{l, \bar{v}} + \hbar \Omega_L - E_{g \bar{v}} - \hbar \omega_k)(t-t_0)/\hbar} \right)}{(E_{g \bar{v}} - E_{j_\alpha \bar{v}} - \hbar \Omega_L)(E_{l, \bar{v}} + \hbar \Omega_L - E_{g \bar{v}} - \hbar \omega_k)} \right] \\ &= i \left[2\pi n_k^2 \hbar \omega_k \right]^{1/2} e^{i\bar{k} \cdot \bar{r}_0} \left[\frac{(v_L + 1) \hbar}{2\mu_L \Omega_L} \right]^{1/2} \\ &\quad \times \left[\sum_{j_\alpha} \frac{\left\langle l_\nu \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| j_\alpha \right\rangle \langle j_\alpha | \hat{e}^\lambda \cdot \bar{\mu} | g \rangle f_{l, v_L+1, j_\alpha v_L} \left(1 - e^{i(E_{l, \bar{v}}^0 - E_{g \bar{v}}^0 + \hbar \Omega_L - \hbar \omega_k)(t-t_0)/\hbar} \right)}{(E_{l, \bar{v}}^0 - E_{j_\alpha \bar{v}}^0 + \hbar \Omega_L)(E_{l, \bar{v}}^0 - E_{g \bar{v}}^0 + \hbar \Omega_L - \hbar \omega_k)} \right. \\ &\quad \left. + \sum_{j_\alpha} \frac{\left\langle j_\alpha \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| g \right\rangle \langle l_\nu | \hat{e}^\lambda \cdot \bar{\mu} | j_\alpha \rangle f_{j_\alpha v_L+1, g v_L} \left(1 - e^{i(E_{l, \bar{v}}^0 - E_{g \bar{v}}^0 + \hbar \Omega_L - \hbar \omega_k)(t-t_0)/\hbar} \right)}{(E_{g \bar{v}}^0 - E_{j_\alpha \bar{v}}^0 - \hbar \Omega_L)(E_{l, \bar{v}}^0 - E_{g \bar{v}}^0 + \hbar \Omega_L - \hbar \omega_k)} \right], \end{aligned}$$

which gives the final expression,

$$U_{l_v, v_L+1, g v_L}^{n_k^{\lambda}-1, n_k^{\lambda}} = i \left[\frac{2\pi n_k^{\lambda} \hbar \omega_k (v_L+1) \hbar}{2\mu_L \Omega_L} \right]^{1/2} e^{i\vec{k}\cdot\vec{r}_0} \frac{\left(1 - e^{i(E_{l_v}^0 - E_g^0 + \hbar\Omega_L - \hbar\omega_k)(t-t_0)/\hbar} \right)}{\left(E_{l_v}^0 - E_g^0 + \hbar\Omega_L - \hbar\omega_k \right)}$$

$$\times \sum_{j_\alpha} \left[\frac{\left\langle l_v \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| j_\alpha \right\rangle \langle j_\alpha | \hat{e}^\lambda \cdot \vec{\mu} | g \rangle f_{l_v, v_L+1, j_\alpha v_L}}{E_{l_v}^0 - E_{j_\alpha}^0 + \hbar\Omega_L} + \frac{\left\langle j_\alpha \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| g \right\rangle \langle l_v | \hat{e}^\lambda \cdot \vec{\mu} | j_\alpha \rangle f_{j_\alpha v_L+1, g v_L}}{E_g^0 - E_{j_\alpha}^0 - \hbar\Omega_L} \right].$$

(3) The only other case in which an element of U survives is when the final vibrational state is $|\vec{u}\rangle = |v_1, \dots, v_{L-1}, v_L-1, \dots, v_{3N-6}\rangle = |v_L-1\rangle$. In this case, we have

$$U_{l_v, v_L-1, g v_L}^{n_k^{\lambda}-1, n_k^{\lambda}} = i \left[2\pi n_k^{\lambda} \hbar \omega_k \right]^{1/2} e^{i\vec{k}\cdot\vec{r}_0}$$

$$\times \left[0 + \left(\frac{v_L \hbar}{2\mu_L \Omega_L} \right)^{1/2} \frac{\left\langle j_\alpha \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| l_v \right\rangle \langle j_\alpha | \hat{e}^\lambda \cdot \vec{\mu} | g \rangle f_{l_v, v_L-1, j_\alpha v_L} \left(1 - e^{i(E_{l_v} - \hbar\Omega_L - E_{g v} - \hbar\omega_k)(t-t_0)/\hbar} \right)}{\left(E_{l_v} - \hbar\Omega_L - E_{j_\alpha v} \right) \left(E_{l_v} - \hbar\Omega_L - E_{g v} - \hbar\omega_k \right)} \right.$$

$$\left. + \left(\frac{v_L \hbar}{2\mu_L \Omega_L} \right)^{1/2} \sum_{j_\alpha} \frac{\left\langle j_\alpha \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| g \right\rangle \langle l_v | \hat{e}^\lambda \cdot \vec{\mu} | j_\alpha \rangle f_{j_\alpha v_L-1, g v_L} \left(1 - e^{i(E_{l_v} - \hbar\Omega_L - E_{g v} - \hbar\omega_k)(t-t_0)/\hbar} \right)}{\left(E_{g v} - E_{j_\alpha v} + \hbar\Omega_L \right) \left(E_{l_v} - \hbar\Omega_L - E_{g v} - \hbar\omega_k \right)} \right]$$

$$= +i \left[2\pi n_k^{\lambda} \hbar \omega_k \right]^{1/2} e^{i\vec{k}\cdot\vec{r}_0} \left(\frac{v_L \hbar}{2\mu_L \Omega_L} \right)^{1/2}$$

$$\times \left[\frac{\left\langle j_\alpha \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| l_v \right\rangle \langle j_\alpha | \hat{e}^\lambda \cdot \vec{\mu} | g \rangle f_{l_v, v_L-1, j_\alpha v_L} \left(1 - e^{i(E_{l_v}^0 - E_g^0 - \hbar\Omega_L - \hbar\omega_k)(t-t_0)/\hbar} \right)}{\left(E_{l_v}^0 - E_{j_\alpha}^0 - \hbar\Omega_L \right) \left(E_{l_v}^0 - E_g^0 - \hbar\Omega_L - \hbar\omega_k \right)} \right.$$

$$\left. + \sum_{j_\alpha} \frac{\left\langle j_\alpha \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| g \right\rangle \langle l_v | \hat{e}^\lambda \cdot \vec{\mu} | j_\alpha \rangle f_{j_\alpha v_L-1, g v_L} \left(1 - e^{i(E_{l_v}^0 - E_g^0 - \hbar\Omega_L - \hbar\omega_k)(t-t_0)/\hbar} \right)}{\left(E_g^0 - E_{j_\alpha}^0 + \hbar\Omega_L \right) \left(E_{l_v}^0 - E_g^0 - \hbar\Omega_L - \hbar\omega_k \right)} \right],$$

and finally we obtain for the last case,

$$U_{l_v, \nu_L^{-1}, g \nu_L}^{n_k^{\lambda-1}, n_k^{\lambda}} = i \left[\frac{2\pi n_k^{\lambda} \hbar \omega_k \nu_L \hbar}{2\mu_L \Omega_L} \right]^{1/2} e^{i\vec{k} \cdot \vec{r}_0} \frac{\left(1 - e^{i(E_{l_v}^0 - E_g^0 - \hbar\Omega_L - \hbar\omega_k)(t-t_0)/\hbar} \right)}{\left(E_{l_v}^0 - E_g^0 - \hbar\Omega_L - \hbar\omega_k \right)}$$

$$\times \sum_{j_\alpha} \left[\frac{\left\langle j_\alpha \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| l_v \right\rangle \langle j_\alpha | \hat{e}^\lambda \cdot \vec{\mu} | g \rangle f_{l_v \nu_L^{-1}, j_\alpha \nu_L}}{E_{l_v}^0 - E_{j_\alpha}^0 - \hbar\Omega_L} + \frac{\left\langle j_\alpha \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| g \right\rangle \langle l_v | \hat{e}^\lambda \cdot \vec{\mu} | j_\alpha \rangle f_{j_\alpha \nu_L^{-1}, g \nu_L}}{E_g^0 - E_{j_\alpha}^0 + \hbar\Omega_L} \right].$$

Before we examine what these three expressions say about the vibrational structure in electronic absorption spectra, let's make one additional simplification. At **absolute zero temperature**, only the lowest lying vibrational state will be populated, *i.e.*, $|\vec{\nu}\rangle = |\vec{0}\rangle$, and under these conditions the three expressions become

$$U_{l_v, \vec{0}, g \vec{0}}^{n_k^{\lambda-1}, n_k^{\lambda}} = i \left[2\pi n_k^{\lambda} \hbar \omega_k \right]^{1/2} e^{i\vec{k} \cdot \vec{r}_0} \langle l_v | \hat{e}^\lambda \cdot \vec{\mu} | g \rangle \frac{\left(1 - e^{i(E_{l_v}^0 - E_g^0 - \hbar\omega_k)(t-t_0)/\hbar} \right)}{\left(E_{l_v}^0 - E_g^0 - \hbar\omega_k \right)}$$

$$U_{l_v, 1_L, g 0_L}^{n_k^{\lambda-1}, n_k^{\lambda}} = i \left[\frac{\pi n_k^{\lambda} \hbar \omega_k \hbar}{\mu_L \Omega_L} \right]^{1/2} e^{i\vec{k} \cdot \vec{r}_0} \frac{\left(1 - e^{i(E_{l_v}^0 - E_g^0 + \hbar\Omega_L - \hbar\omega_k)(t-t_0)/\hbar} \right)}{\left(E_{l_v}^0 - E_g^0 + \hbar\Omega_L - \hbar\omega_k \right)}$$

$$\times \sum_{j_\alpha} \left[\frac{\left\langle j_\alpha \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| l_v \right\rangle \langle j_\alpha | \hat{e}^\lambda \cdot \vec{\mu} | g \rangle f_{l_v 1_L, j_\alpha 0}}{E_{l_v}^0 - E_{j_\alpha}^0 + \hbar\Omega_L} + \frac{\left\langle j_\alpha \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| g \right\rangle \langle l_v | \hat{e}^\lambda \cdot \vec{\mu} | j_\alpha \rangle f_{j_\alpha 1_L, g 0}}{E_g^0 - E_{j_\alpha}^0 - \hbar\Omega_L} \right],$$

and for the third case

$$U_{l_v, (-1_L), g 0}^{n_k^{\lambda-1}, n_k^{\lambda}} = 0.$$

We now use these three expressions to evaluate vibronic effects on optical absorption spectra. First, we will look at the 0°K approximation. Then we evaluate what the expression for case (3), which vanishes in the 0°K approximation, says about absorption spectra in cases where the temperature is not zero.

When absorption is to an excited electronic state $|l_v\rangle$, one absorption band, given by $U_{l_v, \vec{0}, g \vec{0}}^{n_k^{\lambda-1}, n_k^{\lambda}}$, peaks at $E_{l_v}^0 - E_g^0 = \hbar\omega_k$, that is, when the exciting frequency matches the purely

electronic transition energy. The intensity at this peak is determined by the transition dipole matrix element, $\langle l_v | \hat{e}^\lambda \cdot \vec{\mu} | g \rangle$, the incident intensity $I_0 = n_k^2 \hbar \omega_k$, and the other factors in front of the sum. For an A_{1g} ground state $|g\rangle$, it is sufficient for $|l_v\rangle$ to transform as $x, y,$ or z so that the dipole matrix element does not necessarily vanish. (In our D_{4h} molecular symmetry example, that would be either an E_u or an A_{2u} state.)

We get additional vibronic peaks as determined by $U_{l_v, 1_L, g^0}^{n_k^2 - 1, n_k^2}$. The peaks occur when the frequency of the incident light is $\hbar \omega_k = E_{l_v}^0 - E_g^0 + \hbar \Omega_L$. This is when the light energy corresponds to the electronic energy level separation *plus* the energy of the vibrational quantum for the L^{th} normal mode. The intensity of this vibrational side band depends on the dipole matrix element as does the 0-0 absorption band. However, the intensity of the 0-1 absorption band also depends on the magnitude of the vibronic coupling matrix elements,

$$\left\langle j_\alpha \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| l_v \right\rangle.$$

Absorption processes are independent events so the spectrum is just the sum of all of the peaks, *i.e.*,

$$P(\hbar \omega_k) = \sum_{l_v} \sum_{\bar{u}} \left| U_{l_v, \bar{u}, g^0}^{n_k^2 - 1, n_k^2} \right|^2 = \sum_{l_v} \sum_K \left| U_{l_v, 1_L, g^0}^{n_k^2 - 1, n_k^2} \right|^2.$$

(See equations (11) and (12) in *J. Chem. Phys.* 1981, 74, 6644.)

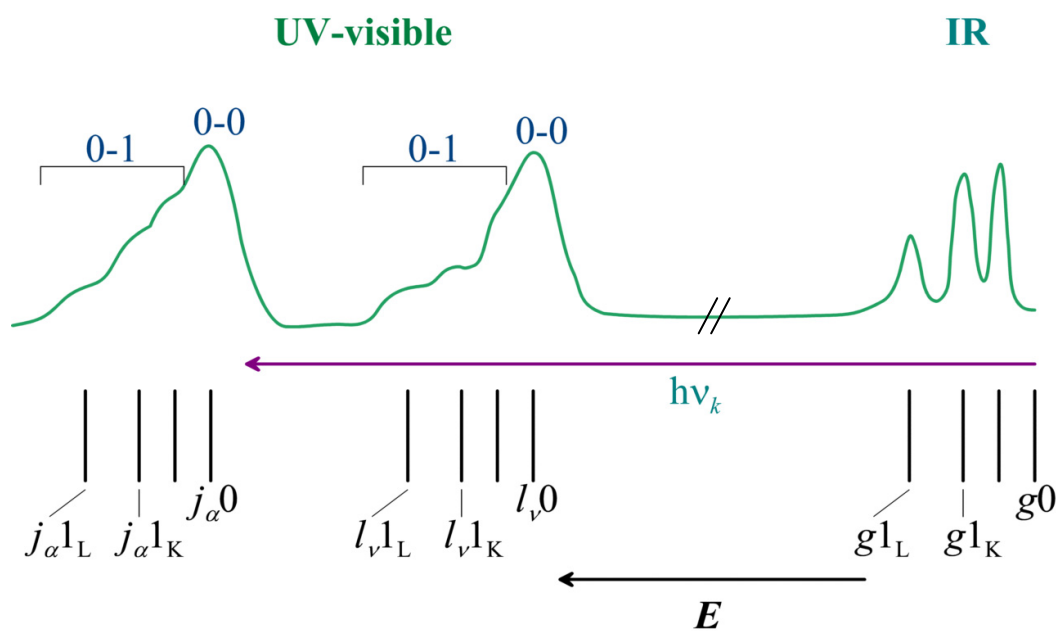


Figure 5.1. Vibronic structure in absorption spectra.

Thus, in this case the absorption spectrum, which is proportional to the probability of absorption, is composed of the 0-0 transition for each electronic state and a vibrational satellite band composed of the 0-1 absorption from each of the allowed normal coordinates. The normal coordinates that contribute to the spectrum is determined by the symmetry properties of the vibronic coupling matrix elements. In particular, the totally symmetric representation must belong to $\Gamma_{l_v} \times \Gamma_{j_\alpha} \times \Gamma_L$ if the coupling matrix above is to be nonzero.

5.2 Intensity Borrowing in Absorption Spectra

Ignoring the t -dependent factors, the intensity of the 0-0 absorption band is

$$I_{l_v, \bar{0}, g \bar{0}} = \frac{2\pi\hbar\omega_k n_k^\lambda \left| \langle l_v | \hat{e}^\lambda \cdot \vec{\mu} | g \rangle \right|^2}{\left(E_{l_v}^0 - E_g^0 - \hbar\omega_k \right)^2},$$

and the intensity of the contribution of L^{th} normal mode to the vibrational side band is

$$I_{l_v, 1_L, g 0} = \frac{\pi n_k^\lambda \hbar \omega_k}{\mu_L \Omega_L} \frac{1}{\left(E_{l_v}^0 - E_g^0 + \hbar\Omega_L - \hbar\omega_k \right)^2} \times \left[\sum_{j_\alpha} \left[\frac{\left\langle j_\alpha \left| \left(\frac{\partial H'}{\partial Q_L} \right) \right| l_v \right\rangle \langle j_\alpha | \hat{e}^\lambda \cdot \vec{\mu} | g \rangle f_{l_v, 1_L, j_\alpha 0}}{E_{l_v}^0 - E_{j_\alpha}^0 + \hbar\Omega_L} + \frac{\left\langle j_\alpha \left| \left(\frac{\partial H'}{\partial Q_L} \right) \right| g \right\rangle \langle l_v | \hat{e}^\lambda \cdot \vec{\mu} | j_\alpha \rangle f_{j_\alpha, 1_L, g 0}}{E_g^0 - E_{j_\alpha}^0 - \hbar\Omega_L} \right]^2 \right]$$

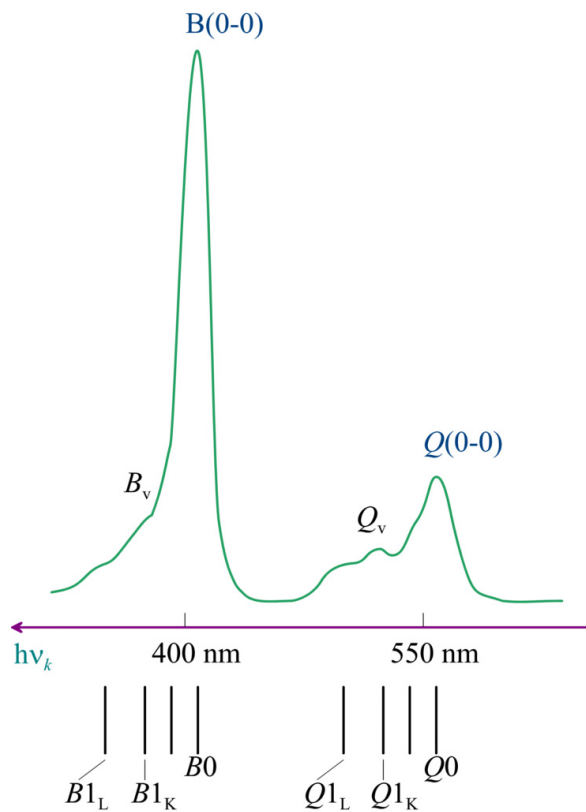
Clearly, the term of the sum with $j_\alpha = l_v$ will dominate, since it is included in the sum and the denominator gets very small ($\rightarrow \hbar\Omega_L$ for exact resonance). For electronic absorption, the energy denominator of the second term in the numerator is large, since

$$E_{j_\alpha}^0 - E_g^0 + \hbar\Omega_L > E_{j_\alpha}^0 - E_g^0 \gg \hbar\Omega_L.$$

Thus, we can neglect the second term in this case, and we have

$$I_{l_v, 1_L, g 0} = \frac{2\pi n_k^\lambda \hbar \omega_k \hbar}{\mu_L \Omega_L} \left| \sum_{j_\alpha} \frac{\left\langle j_\alpha \left| \left(\frac{\partial H'}{\partial Q_L} \right) \right| l_v \right\rangle \langle j_\alpha | \hat{e}^\lambda \cdot \vec{\mu} | g \rangle}{E_{l_v}^0 - E_{j_\alpha}^0 + \hbar\Omega_L} \right|^2 \frac{1}{\left(E_{l_v}^0 - E_g^0 + \hbar\Omega_L - \hbar\omega_k \right)^2}.$$

Figure 5.2. Typical metal porphyrin absorption spectrum illustrating the observed vibronic structure for the Q transition. The intensity of the vibrational side band is partly a consequence of intensity borrowing from the strong B transition.



Usually, the largest term will be from vibronic coupling within an electronic state $|l_v\rangle$, *i.e.*, the term for which $j_\alpha = l_v$, since this allows the denominator to get as small as $\hbar\Omega_L$. However, nearby electronic states for which $E_{j_\alpha}^0 - E_{l_v}^0 \approx \hbar\Omega_L$ can also give a large contribution. Moreover, even if an electronic state $|j_\alpha\rangle$ is farther away in energy (*i.e.*,

$E_{j_\alpha}^0 - E_{l_v}^0 > \hbar\Omega_L$) vibronic coupling to $|j_\alpha\rangle$ will contribute if its transition dipole $\langle j_\alpha | \hat{e}^\lambda \cdot \vec{\mu} | g \rangle$ is large enough to make up for the large denominator. When this occurs, it is called *intensity borrowing*.

The UV-visible absorption spectra of metalloporphyrins, illustrated in Figure 6.2, provide a good example of intensity borrowing. Part of the intensity in Q_v -band is due to vibronic coupling among the Q_x and Q_y components of the doubly degenerate E_u state (D_{4h} molecular symmetry), *i.e.*,

$$j_\alpha = l_v = Q_x, Q_y \quad (j = Q; \alpha = x, y),$$

through matrix elements such as

$$\left\langle Q_x \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| Q_x \right\rangle.$$

Another part of the intensity is a result of coupling of the Q states to the B_x and B_y states, *i.e.*, $j_\alpha = B_x, B_y$ and $l_v = Q_x, Q_y$ by matrix elements like

$$\left\langle Q_x \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| B_y \right\rangle.$$

Even though the separation between the Q and B states is large ($\sim 7000 \text{ cm}^{-1}$) compared to fundamental frequencies ($\sim 1500 \text{ cm}^{-1}$), the large extinction coefficient of B still allows it to contribute on par with the inter- Q state coupling.

We now consider the situation in which the **temperature is not zero**. In this case, the expressions determining the absorbance become

$$(1) \quad \text{for } |\vec{u}\rangle = |\vec{v}\rangle,$$

$$U_{l, \vec{u}, g^{\vec{v}}}^{n_k^{\vec{u}}-1, n_k^{\vec{v}}} = i \left[2\pi \hbar \omega_k n_k^{\vec{u}} \right]^{1/2} e^{i\vec{k} \cdot \vec{r}_0} \frac{\langle l_v | \hat{e}^\lambda \cdot \vec{\mu} | g \rangle \left(1 - e^{i(E_{l_v}^0 - E_g^0 - \hbar \omega_k)(t-t_0)/\hbar} \right)}{(E_{l_v}^0 - E_g^0 - \hbar \omega_k)},$$

$$(2) \quad \text{for } |\vec{u}\rangle = |v_L + 1\rangle,$$

$$U_{l, v_L+1, g^{v_L}}^{n_k^{\vec{u}}-1, n_k^{\vec{v}}} = i \left[\frac{2\pi n_k^{\vec{u}} \hbar \omega_k (v_L + 1) \hbar}{2\mu_L \Omega_L} \right]^{1/2} e^{i\vec{k} \cdot \vec{r}_0} \frac{\left(1 - e^{i(E_{l_v}^0 - E_g^0 + \hbar \Omega_L - \hbar \omega_k)(t-t_0)/\hbar} \right)}{(E_{l_v}^0 - E_g^0 + \hbar \Omega_L - \hbar \omega_k)} \\ \times \sum_{j_\alpha} \frac{\left\langle l_v \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| j_\alpha \right\rangle \langle j_\alpha | \hat{e}^\lambda \cdot \vec{\mu} | g \rangle f_{l, v_L+1, j_\alpha v_L}}{E_{l_v}^0 - E_{j_\alpha}^0 + \hbar \Omega_L},$$

where in omitting the “non-resonant” terms in the sums, we have assume all electronic excited states are far from the ground state. And, finally, we have

$$(3) \quad \text{for } |\vec{u}\rangle = |v_L - 1\rangle,$$

$$U_{l, v_L-1, g^{v_L}}^{n_k^{\vec{u}}-1, n_k^{\vec{v}}} = i \left[\frac{\pi n_k^{\vec{u}} \hbar \omega_k v_L \hbar}{\mu_L \Omega_L} \right]^{1/2} e^{i\vec{k} \cdot \vec{r}_0} \frac{\left(1 - e^{i(E_{l_v}^0 - E_g^0 - \hbar \Omega_L - \hbar \omega_k)(t-t_0)/\hbar} \right)}{(E_{l_v}^0 - E_g^0 - \hbar \Omega_L - \hbar \omega_k)} \\ \times \sum_{j_\alpha} \frac{\left\langle j_\alpha \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| l_v \right\rangle \langle j_\alpha | \hat{e}^\lambda \cdot \vec{\mu} | g \rangle f_{l, v_L-1, j_\alpha v_L}}{E_{l_v}^0 - E_{j_\alpha}^0 - \hbar \Omega_L},$$

where we again have assumed $E_{j_\alpha}^0 - E_g^0 \gg 0$ for all $|j_\alpha\rangle$.

Now let's look at the difference between the 0° K approximation and the $T > 0$ K result. There are three main points.

- The $l_\nu \bar{\nu} \leftarrow g \bar{\nu}$ transition (case (1) above), called the 0-0 transition, again gives a peak at the purely electronic transition $\hbar\omega_k = E_{l_\nu}^0 - E_g^0$.
- We also get a peak at $l_\nu \nu_L + 1 \leftarrow g \nu_L$, where $\hbar\omega_k = E_{l_\nu}^0 - E_g^0 + \hbar\Omega_L$ from case (2) above.
- Case (3) now gives us new peaks at $l_\nu \nu_L - 1 \leftarrow g \nu_L$ or where $\hbar\omega_k = E_{l_\nu}^0 - E_g^0 - \hbar\Omega_L$.

Thus, at $T > 0$, the absorption should look like the illustration in Figure 6.3. However, one must keep in mind that the presence of the third-term resonance requires that a vibrational state of the electronic ground state be excited (*i.e.*, population of the L^{th} vibrational mode, $\nu_L > 0$) or else this term vanishes. The Boltzmann factor, $e^{-\hbar\Omega_L/k_B T}$ determines the number of molecules with the first excited state of the L^{th} mode populated and only vibrational modes with $\hbar\Omega_L \approx k_B T$ will be significantly populated. At room temperature, $K_B T \approx 200 \text{ cm}^{-1}$. Fundamentals of molecular vibration are usually in the range from 100 cm^{-1} - 3000 cm^{-1} , so most normal modes will not be significantly populated at room temperature ($T = 300^\circ \text{ K}$). Thus, the spectrum will be effected only by the low frequency normal modes, $\hbar\Omega_L \approx 200 \text{ cm}^{-1}$. At higher temperature, the effect might be larger, but will still be somewhat obscured by line broadening.

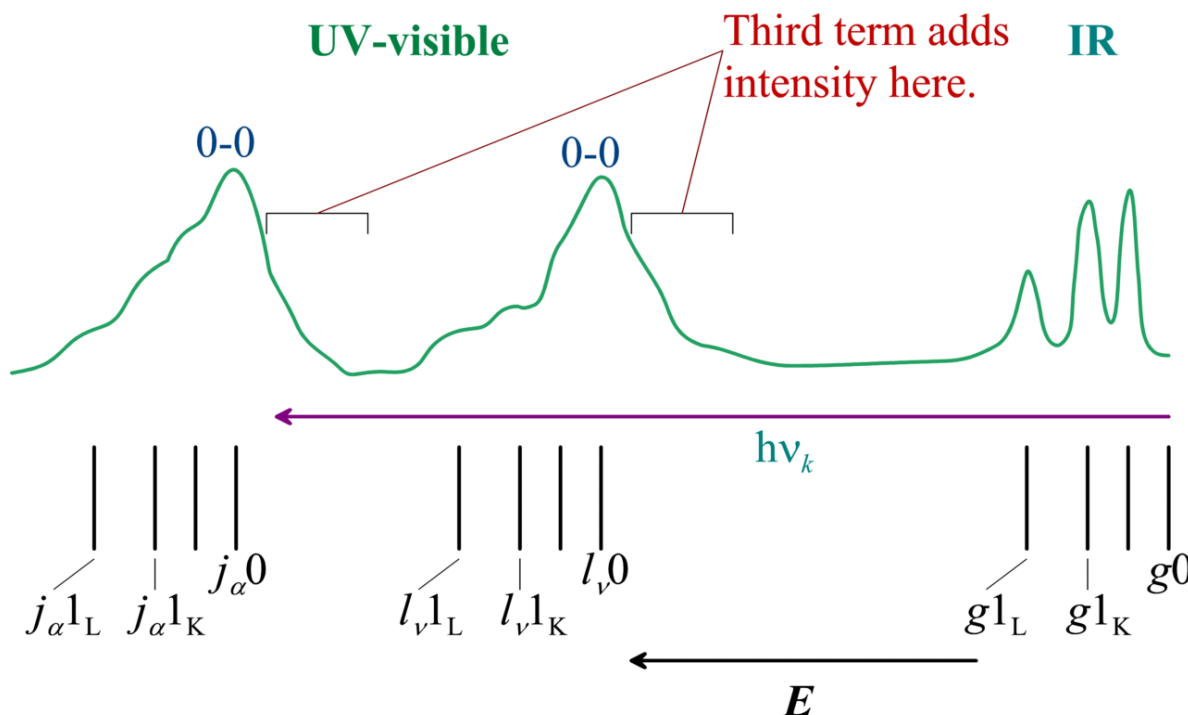


Figure 5.3. Effect of the third term contributions in the vibronic absorption spectra at $T > 0$.

5.3 Infrared Absorption Spectra

For infrared absorption, the final state is the ground electronic state ($|l_v\rangle = |g\rangle$), thus we have for the transition in which no vibrational modes are excited.

$$U_{g\vec{0},g\vec{0}}^{n_k^{\lambda}-1,n_k^{\lambda}} = i \left[2\pi n_k^{\lambda} \hbar \omega_k \right]^{1/2} e^{i\vec{k}\cdot\vec{r}_0} \langle g | \hat{e}^{\lambda} \cdot \vec{\mu} | g \rangle \frac{(1 - e^{i(-\hbar\omega_k)(t-t_0)/\hbar})}{\hbar\omega_k}.$$

This ($\vec{0}-\vec{0}$) term vanishes for a totally symmetric ground state because of the symmetry properties of the dipole matrix element.

For excitation of one quantum of the L^{th} normal mode, we have

$$U_{g^{1_L},g^{0_L}}^{n_k^{\lambda}-1,n_k^{\lambda}} = i \left[\frac{\pi n_k^{\lambda} \hbar \omega_k \hbar}{\mu_L \Omega_L} \right]^{1/2} e^{i\vec{k}\cdot\vec{r}_0} \frac{(1 - e^{i(\hbar\Omega_L - \hbar\omega_k)(t-t_0)/\hbar})}{\hbar\Omega_L - \hbar\omega_k} \\ \times \sum_{j_{\alpha}} \left[\frac{\left\langle j_{\alpha} \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| g \right\rangle \langle j_{\alpha} | \hat{e}^{\lambda} \cdot \vec{\mu} | g \rangle f_{g^{1_L},j_{\alpha}^0}}}{E_g^0 - E_{j_{\alpha}}^0 + \hbar\Omega_L} + \frac{\left\langle j_{\alpha} \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| g \right\rangle \langle g | \hat{e}^{\lambda} \cdot \vec{\mu} | j_{\alpha} \rangle f_{j_{\alpha}^1,g^0}}{E_g^0 - E_{j_{\alpha}}^0 - \hbar\Omega_L} \right]$$

If there are no low-lying excited electronic states, then the sum might be approximated by just one term, $|j_{\alpha}\rangle = |g\rangle$, and

$$U_{g^{1_L},g^{0_L}}^{n_k^{\lambda}-1,n_k^{\lambda}} = i \left[\frac{\pi n_k^{\lambda} \hbar \omega_k \hbar}{\mu_L \Omega_L} \right]^{1/2} e^{i\vec{k}\cdot\vec{r}_0} \frac{(1 - e^{i(\hbar\Omega_L - \hbar\omega_k)(t-t_0)/\hbar})}{\hbar\Omega_L - \hbar\omega_k} \\ \times \left[\frac{\left\langle g \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| g \right\rangle \langle g | \hat{e}^{\lambda} \cdot \vec{\mu} | g \rangle f_{g^{1_L},g^0}}{\hbar\Omega_L} + \frac{\left\langle g \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| g \right\rangle \langle g | \hat{e}^{\lambda} \cdot \vec{\mu} | g \rangle f_{g^{1_L},g^0}}{-\hbar\Omega_L} \right]$$

$$= 0.$$

Thus, to have IR absorption in this approximation we cannot neglect all the excited states. So we are left with only

$$U_{g^1, g^0}^{n_k^2-1, n_k^2} = -i \left[\frac{\pi n_k^2 \hbar^2 \omega_k}{\mu_L \Omega_L} \right] e^{i\vec{k} \cdot \vec{r}_0} \frac{(1 - e^{i(\hbar\Omega_L - \hbar\omega_k)(t-t_0)/\hbar})}{\hbar\Omega_L - \hbar\omega_k} \times \sum_{j_\alpha} \left[\frac{\left\langle g \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| j_\alpha \right\rangle \langle j_\alpha | \hat{e}^\lambda \cdot \vec{\mu} | g \rangle f_{g^1, j_\alpha^0}}{E_{j_\alpha}^0 - E_g^0 - \hbar\Omega_L} + \frac{\left\langle j_\alpha \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| g \right\rangle \langle g | \hat{e}^\lambda \cdot \vec{\mu} | j_\alpha \rangle f_{j_\alpha^1, g^0}}{E_{j_\alpha}^0 - E_g^0 + \hbar\Omega_L} \right].$$

Now, writing out the time-dependent factors, we have

$$U_{g^1, g^0}^{n_k^2-1, n_k^2} = -i \left[\frac{\pi n_k^2 \hbar^2 \omega_k}{\mu_L \Omega_L} \right] e^{i\vec{k} \cdot \vec{r}_0} \frac{(1 - e^{i(\hbar\Omega_L - \hbar\omega_k)(t-t_0)/\hbar})}{\hbar\Omega_L - \hbar\omega_k} \times \sum_{j_\alpha} \left[\frac{\left\langle g \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| j_\alpha \right\rangle \langle j_\alpha | \hat{e}^\lambda \cdot \vec{\mu} | g \rangle \left(1 - e^{-i(E_{j_\alpha}^0 - E_g^0 - \hbar\Omega_L)(t-t_0)/\hbar} \right)}{E_{j_\alpha}^0 - E_g^0 - \hbar\Omega_L} + \frac{\left\langle j_\alpha \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| g \right\rangle \langle g | \hat{e}^\lambda \cdot \vec{\mu} | j_\alpha \rangle \left(1 - e^{i(E_{j_\alpha}^0 - E_g^0 + \hbar\Omega_L)(t-t_0)/\hbar} \right)}{E_{j_\alpha}^0 - E_g^0 + \hbar\Omega_L} \right].$$

This is the equation that describes the amplitude for absorption of one IR photon resulting in excitation of the L^{th} normal mode. The factor,

$$\frac{(1 - e^{i(\hbar\Omega_L - \hbar\omega_k)(t-t_0)/\hbar})}{\hbar\Omega_L - \hbar\omega_k},$$

gives conservation of energy. Peaks will occur at photon energies $\hbar\omega_k$ equal to the energy of the L^{th} normal mode.

The intensity factor says that intermediate electronic states that are dipole allowed, *i.e.*, $\langle j_\alpha | \hat{e}^\lambda \cdot \vec{\mu} | g \rangle \neq 0$, contribute to the IR absorption in the ground state for modes, L , with symmetries for which

$$\left\langle j_\alpha \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| g \right\rangle$$

does not vanish. Furthermore,

$$\left(\frac{\partial H'}{\partial Q_L} \right)_0$$

has the symmetry of Q_L in electronic space, thus the irreducible representation to which Q_L belongs is the same as that of the electronic dipole, *i.e.*, the representations to which x , y , and z belong.

For example, assuming $|g\rangle$ is totally symmetric, the matrix element $\langle j_\alpha | \hat{e}^\lambda \cdot \vec{\mu} | g \rangle$ will not vanish if $|j_\alpha\rangle$ transforms like x , y , or z . (In D_{4h} , these are E_u and A_{2u} .) If $|j_\alpha\rangle$ transform like x , y , or z , then $\left\langle j_\alpha \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| g \right\rangle$ requires that the normal mode be of a symmetry Γ_L that when crossed with Γ_{j_α} will contain A_{1g} . That is, $A_{1g} \subseteq \Gamma_\sigma \otimes \Gamma_L \Rightarrow \Gamma_L = \Gamma_\sigma$, where $\sigma = x, y, z$. (In D_{4h} , x and y transform like E_u , and $E_u \otimes E_u$ contains A_{1g} , therefore, E_u modes will be IR active. Further, z transforms like A_{2u} , and $A_{2u} \otimes A_{2u} = A_{1g}$, so A_{2u} modes will also be IR active.

We must remember that we assumed that the electric dipole had no explicit dependence on the nuclear coordinates in the above discussion. This is not the case, for infrared light frequencies. Therefore, we have obtained only a part of the infrared intensities. The other part is obtained by expanding the dipole matrix element in a Taylor series in the normal coordinates, *i.e.*,

$$\hat{e}^\lambda \cdot \vec{\mu} = \hat{e}^\lambda \cdot \vec{\mu}^0 + \sum_K \left(\frac{\partial (\hat{e}^\lambda \cdot \vec{\mu})}{\partial Q_K} \right)_0 Q_K + \dots$$

This procedure gives matrix elements that are linear in the Q_K , such as

$$\langle j_\alpha \bar{w} | \hat{e}^\lambda \cdot \mu | g \bar{v} \rangle = \langle j_\alpha | \hat{e}^\lambda \cdot \mu^0 | g \rangle \langle \bar{w} | \bar{v} \rangle + \sum_K \langle j_\alpha | \left(\frac{\partial (\hat{e}^\lambda \cdot \mu)}{\partial Q_K} \right)_0 | g \rangle \langle \bar{w} | Q_K | \bar{v} \rangle.$$

These new terms add to similar terms in the expansion of the vibronic wave functions to give the total infrared absorbance. However, the essential features as described above are unaltered.

5.4 Vibrational Raman Scattering Tensor

For Raman scattering the transition probability amplitude is given by

$$U_{l_v, \bar{u}, g\bar{v}}^{n_k^{\lambda}-1, n_{\ell}^{\lambda'}+1, n_k^{\lambda}, n_{\ell}^{\lambda'}} = 2\pi \left[\hbar\omega_k n_k^{\lambda} \hbar\omega_{\ell} (n_{\ell}^{\lambda'} + 1) \right]^{1/2} e^{i(\bar{k}-\bar{l})\cdot\bar{r}_0} \frac{f_{l_v, \bar{u}, g\bar{v}}}{E_{l_v, \bar{v}} - E_{g\bar{v}} - (\hbar\omega_k - \hbar\omega_{\ell})} \sum_{\sigma} \sum_{\rho} (\beta_{l_v, \bar{u}, g\bar{v}})_{\sigma\rho},$$

where $(\beta_{l_v, \bar{u}, g\bar{v}})_{\sigma\rho}$ is the scattering tensor defined as

$$\beta_{l_v, \bar{u}, g\bar{v}} = \sum_{j_{\alpha}} \sum_{\bar{w}} \left[\frac{\left\langle l_v \bar{u} \left| e_{\sigma}^{\lambda'} \mu_{\sigma} \right| j_{\alpha} \bar{w} \right\rangle \left\langle j_{\alpha} \bar{w} \left| e_{\rho}^{\lambda} \mu_{\rho} \right| g\bar{v} \right\rangle}{E_{j_{\alpha} \bar{w}} - E_{g\bar{v}} - \hbar\omega_k} + \frac{\left\langle l_v \bar{u} \left| e_{\sigma}^{\lambda} \mu_{\sigma} \right| j_{\alpha} \bar{w} \right\rangle \left\langle j_{\alpha} \bar{w} \left| e_{\rho}^{\lambda'} \mu_{\rho} \right| g\bar{v} \right\rangle}{E_{j_{\alpha} \bar{w}} - E_{g\bar{v}} + \hbar\omega_{\ell}} \right].$$

We can get approximate expressions for $\beta_{l_v, \bar{u}, g\bar{v}}$ using our first-order approximate vibronic states,

$$|j_{\alpha} \bar{w}\rangle = |j_{\alpha}\rangle |\bar{w}\rangle - \sum_{n_{\gamma}} \sum_{\bar{x}} \sum_L \frac{\left\langle n_{\gamma} \left| \left(\frac{\partial H'}{\partial Q_L} \right) \right| j_{\alpha} \right\rangle \langle \bar{x} | Q_L | \bar{w} \rangle f_{n_{\gamma}, \bar{x}, j_{\alpha} \bar{w}}}{E_{j_{\alpha} \bar{w}} - E_{n_{\gamma} \bar{x}}} |n_{\gamma}\rangle |\bar{x}\rangle,$$

with similar expressions for $|l_v \bar{u}\rangle$ and $|g\bar{v}\rangle$.

For vibrational Rayleigh and Raman transitions in the ground electronic state, we are interested in the case where the final state $|l_v \bar{u}\rangle$ is $|g\bar{v}\rangle$, thus,

$$U_{g\bar{u}, g\bar{v}}^{n_k^{\lambda}-1, n_{\ell}^{\lambda'}-1, n_k^{\lambda}, n_{\ell}^{\lambda'}} = \frac{(1 - e^{iE_{g\bar{u}} - E_{g\bar{v}} - (\hbar\omega_k - \hbar\omega_{\ell})(t-t_0)/\hbar})}{E_{g\bar{u}} - E_{g\bar{v}} - (\hbar\omega_k - \hbar\omega_{\ell})} 2\pi \left[n_k^{\lambda} \hbar\omega_k (n_{\ell}^{\lambda'} + 1) \hbar\omega_{\ell} \right]^{1/2} e^{i(\bar{k}-\bar{l})\cdot\bar{r}_0} \sum_{\sigma} \sum_{\rho} (\beta_{g\bar{u}, g\bar{v}})_{\sigma\rho}$$

and

$$(\beta_{g\bar{u}, g\bar{v}})_{\sigma\rho} = \sum_{j_{\alpha}} \sum_{\bar{w}} \left[\frac{\langle g\bar{u} | P'_{\sigma} | j_{\alpha} \bar{w} \rangle \langle j_{\alpha} \bar{w} | P_{\rho} | g\bar{v} \rangle}{E_{j_{\alpha} \bar{w}} - E_{g\bar{v}} - \hbar\omega_k} + \frac{\langle g\bar{u} | P_{\sigma} | j_{\alpha} \bar{w} \rangle \langle j_{\alpha} \bar{w} | P'_{\rho} | g\bar{v} \rangle}{E_{j_{\alpha} \bar{w}} - E_{g\bar{v}} + \hbar\omega_{\ell}} \right].$$

These expressions comprise the Heisenberg-Dirac equation. The two terms (linear and quadratic in the Q_L) in the approximate vibronic states, when substituted into the four appearances of the vibronic states in $\beta_{l_v, \bar{u}, g\bar{v}}$, gives 16 terms for each of the two terms in $\beta_{l_v, \bar{u}, g\bar{v}}$.

5.5 Rayleigh Scattering

The lowest order term is

$$\left(\beta_{g\bar{u},g\bar{v}}^{(0)}\right)_{\sigma\rho} = \sum_{j_\alpha} \sum_{\bar{w}} \left[\frac{\langle g|P'_\sigma|j_\alpha\rangle \langle j_\alpha|P_\rho|g\rangle \langle \bar{u}|\bar{w}\rangle \langle \bar{w}|\bar{v}\rangle}{E_{j_\alpha\bar{w}} - E_{g\bar{v}} - \hbar\omega_k} + \frac{\langle g|P_\sigma|j_\alpha\rangle \langle j_\alpha|P'_\rho|g\rangle \langle \bar{u}|\bar{w}\rangle \langle \bar{w}|\bar{v}\rangle}{E_{j_\alpha\bar{w}} - E_{g\bar{v}} + \hbar\omega_\ell} \right]$$

$$= \begin{cases} \sum_{j_\alpha} \left[\frac{\langle g|P'_\sigma|j_\alpha\rangle \langle j_\alpha|P_\rho|g\rangle}{E_{j_\alpha}^0 - E_g^0 - \hbar\omega_k} + \frac{\langle g|P_\sigma|j_\alpha\rangle \langle j_\alpha|P'_\rho|g\rangle}{E_{j_\alpha}^0 - E_g^0 + \hbar\omega_\ell} \right], & |\bar{u}\rangle = |\bar{v}\rangle \\ 0, & |\bar{u}\rangle \neq |\bar{v}\rangle, \end{cases}$$

This is the Rayleigh scattering term, which describes elastic scattering of photons since no vibrational quanta of the molecule are excited at zeroth order. Remember that the scattering tensor is an intensity factor; the peaks still occur when

$$E_{g\bar{u}} - E_{g\bar{v}} = \hbar\omega_k - \hbar\omega_\ell = 0,$$

since $\bar{u} = \bar{v}$ and thus *the peak occurs when the incident laser frequency is equal to the scattered photon frequency*. (The line width will be narrow because both molecular state energies are for the ground state.)

Rayleigh scattering will be intense compared to the Raman intensities because the zeroth order states are involved. That is, there are no vibronic coupling matrix elements appearing in the expression with the associated small constant factor. The intensity of the Rayleigh scattering term is partially determined by the energy denominators of the scattering tensor. Resonance Rayleigh scattering will occur when the laser frequency, $\hbar\omega_k$, is equal to an electronic transition $E_{j_\alpha}^0 - E_g^0$ in the first resonant term of the scattering tensor. (This resonance will be broad since an excited electronic state is involved.) As above for infrared and UV-visible-NIR absorption, we have used the approximation that the electric dipole depends only on the electronic coordinates, not the nuclear coordinates. In most cases this approximation is valid since laser frequency is large compared to vibrational frequencies of the molecule.

5.6 Stokes Raman Scattering

Of the remaining 30 terms we will omit those that are quadratic or higher order in Q_K and Q_L , *i.e.*, we will retain only linear terms in Q_L . There are four such terms for each of the two terms in the expression for $\beta_{g\bar{u},g\bar{v}}$, and they will allow \bar{u} to differ from \bar{v} in only one quantum in the K^{th} mode.

The case for which $|\bar{u}\rangle = |v_K + 1\rangle$ is called *Stokes scattering*, and the expression for the scattering tensor is

$$\begin{aligned}
 & \left(\beta_{g^{v_K+1}, g^{v_K}}^{(1)} \right)_{\sigma\rho} \\
 &= - \sum_{j_\alpha} \sum_{\bar{w}} \sum_{n_\gamma} \sum_{\bar{x}} \sum_L \left[\frac{\langle g | P'_\sigma | j_\alpha \rangle \langle \bar{u} | \bar{w} \rangle \left\langle j_\alpha \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| n_\gamma \right\rangle \langle \bar{x} | Q_L | \bar{w} \rangle}{E_{j_\alpha \bar{w}} - E_{n_\gamma \bar{x}}} \langle n_\sigma | P_\rho | g \rangle \langle \bar{x} | \bar{v} \rangle f_{n_\gamma \bar{x}, j_\alpha \bar{w}} \right. \\
 & \quad + \frac{\langle g | P'_\sigma | n_\gamma \rangle \langle \bar{u} | \bar{x} \rangle \left\langle n_\gamma \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| j_\alpha \right\rangle \langle \bar{w} | Q_L | \bar{x} \rangle}{E_{j_\alpha \bar{w}} - E_{n_\gamma \bar{x}}} \langle j_\alpha | P_\rho | g \rangle \langle \bar{w} | \bar{v} \rangle f_{j_\alpha \bar{w}, n_\gamma \bar{x}} \\
 & \quad + \frac{\langle g | P'_\sigma | j_\alpha \rangle \langle \bar{u} | \bar{w} \rangle \langle j_\alpha | P_\rho | n_\gamma \rangle \left\langle n_\gamma \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| g \right\rangle \langle \bar{v} | Q_L | \bar{x} \rangle}{E_{j_\alpha \bar{w}} - E_{g \bar{v}} - \hbar \omega_k} \langle \bar{w} | \bar{x} \rangle f_{g \bar{v}, n_\gamma \bar{x}} \\
 & \quad + \frac{\left\langle g \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| n_\gamma \right\rangle \langle \bar{u} | Q_L | \bar{x} \rangle}{E_{g \bar{u}} - E_{n_\gamma \bar{x}}} \langle n_\sigma | P'_\sigma | j_\alpha \rangle \langle \bar{x} | \bar{w} \rangle \langle j_\alpha | P_\rho | g \rangle \langle \bar{w} | \bar{v} \rangle f_{g \bar{u}, n_\gamma \bar{x}} \\
 & \quad \left. + \text{the 4 non-resonant terms} \right] \\
 & - \sum_{j_\alpha} \sum_{n_\gamma} \left[\frac{\langle g | P'_\sigma | j_\alpha \rangle \langle n_\gamma | P_\rho | g \rangle \left\langle j_\alpha \left| \left(\frac{\partial H'}{\partial Q_K} \right)_0 \right| n_\gamma \right\rangle \frac{f_{n_\gamma v_K, j_\alpha v_K + 1}}{E_{j_\alpha}^0 - E_{n_\gamma}^0 + \hbar \Omega_K} \left[\frac{(v_K + 1) \hbar}{2 \mu_K \Omega_K} \right]^{1/2}}{E_{j_\alpha}^0 - E_g^0 + \hbar \Omega_K - \hbar \omega_k} \right]
 \end{aligned}$$

$$\begin{aligned}
& + \frac{\langle g | P'_\sigma | n_\gamma \rangle \langle j_\alpha | P_\rho | g \rangle \left\langle n_\gamma \left| \left(\frac{\partial H'}{\partial Q_K} \right)_0 \right| j_\alpha \right\rangle \frac{f_{j_\alpha v_K, n_\gamma v_K + 1}}{E_{j_\alpha}^0 - E_{n_\gamma}^0 - \hbar \Omega_K} \left[\frac{(v_K + 1) \hbar}{2 \mu_K \Omega_K} \right]^{1/2}}{E_{j_\alpha}^0 - E_g^0 - \hbar \omega_k} \\
& + \frac{\langle g | P'_\sigma | j_\alpha \rangle \langle j_\alpha | P_\rho | n_\gamma \rangle \left\langle n_\gamma \left| \left(\frac{\partial H'}{\partial Q_K} \right)_0 \right| g \right\rangle \frac{f_{g v_K, n_\gamma v_K + 1}}{E_g^0 - E_{n_\gamma}^0 - \hbar \Omega_K} \left[\frac{(v_K + 1) \hbar}{2 \mu_K \Omega_K} \right]^{1/2}}{E_{j_\alpha}^0 - E_g^0 + \hbar \Omega_K - \hbar \omega_k} \\
& + \frac{\langle n_\gamma | P'_\sigma | j_\alpha \rangle \langle j_\alpha | P_\rho | g \rangle \left\langle g \left| \left(\frac{\partial H'}{\partial Q_K} \right)_0 \right| n_\gamma \right\rangle \frac{f_{g v_K + 1, n_\gamma v_K}}{E_g^0 - E_{n_\gamma}^0 + \hbar \Omega_K} \left[\frac{(v_K + 1) \hbar}{2 \mu_K \Omega_K} \right]^{1/2}}{E_{j_\alpha}^0 - E_g^0 - \hbar \omega_k} \\
& + \text{the 4 non-resonant terms]
\end{aligned}$$

Let's assume that vibronic coupling between the ground state and all excited electronic states can be neglected, *i.e.*, $E_{j_\alpha}^0 \gg E_g^0$, $\forall j_\alpha$ and

$$\begin{aligned}
\left(\beta_{g, v_K + 1; g, v_K}^{(1)} \right)_{\sigma\rho} = & - \left[\frac{(v_K + 1) \hbar}{2 \mu_K \Omega_K} \right]^{1/2} \sum_{j_\alpha} \left[\frac{\sum_{n_\gamma} \langle g | P'_\sigma | j_\alpha \rangle \frac{f_{n_\gamma v_K, j_\alpha v_K + 1}}{E_{j_\alpha}^0 - E_{n_\gamma}^0 + \hbar \Omega_K} \left\langle j_\alpha \left| \left(\frac{\partial H'}{\partial Q_K} \right)_0 \right| n_\gamma \right\rangle \langle n_\gamma | P_\rho | g \rangle}{E_{j_\alpha}^0 - E_g^0 + \hbar \Omega_K - \hbar \omega_k} \right. \\
& \left. + \frac{\sum_{n_\gamma} \langle g | P'_\sigma | n_\gamma \rangle \frac{f_{j_\alpha v_K, n_\gamma v_K + 1}}{E_{j_\alpha}^0 - E_{n_\gamma}^0 - \hbar \Omega_K} \left\langle n_\gamma \left| \left(\frac{\partial H'}{\partial Q_K} \right)_0 \right| j_\alpha \right\rangle \langle j_\alpha | P_\rho | g \rangle}{E_{j_\alpha}^0 - E_g^0 - \hbar \omega_k} \right],
\end{aligned}$$

which is essentially Equation (13) in *J. Chem Phys.* **1981**, 74, 6644.

Now, let's examine the equation above to see what we can expect for Raman spectroscopy. Remember again, that $\beta_{g, v_K + 1; g, v_K}^{(1)}$ is the intensity (amplitude) factor, the energy conservation factor says that the peaks will occur at

$$E_{g\bar{u}} - E_{g\bar{v}} = E_g^0 - E_g^0 + \hbar \Omega_K = \hbar \Omega_K = \hbar \omega_k - \hbar \omega_\ell$$

Thus, the peaks will occur when the difference in the laser frequency and the emitted light frequency is equal to the fundamental frequency of a normal mode.

The intensity of the peak in the Raman spectrum depends on the scattering tensor. The Raman scattering will be less intense than the Rayleigh scattering because of the factor

$$\left[\frac{\hbar}{2\mu_K \Omega K} \right]^{1/2},$$

which comes in with the vibronic coupling matrix element. In addition, the energy denominator in the second term of $\beta^{(1)}$ say that there will be a peak in the intensity when

$$E_{j_\alpha}^0 - E_g^0 = \hbar\omega_k,$$

i.e., at the purely electronic transition energy for the excited state. Another maximum will occur when the resonance condition for the first term is met, that is at

$$E_{j_\alpha}^0 - E_g^0 + \hbar\Omega_K = \hbar\omega_k.$$

Thus, we obtain *two* peaks in the intensity of a Raman line as the exciting laser frequency is tuned through an electronic transition. And, this will occur for each electronic transition that is electric dipole allowed as illustrated in Figure 5.4.

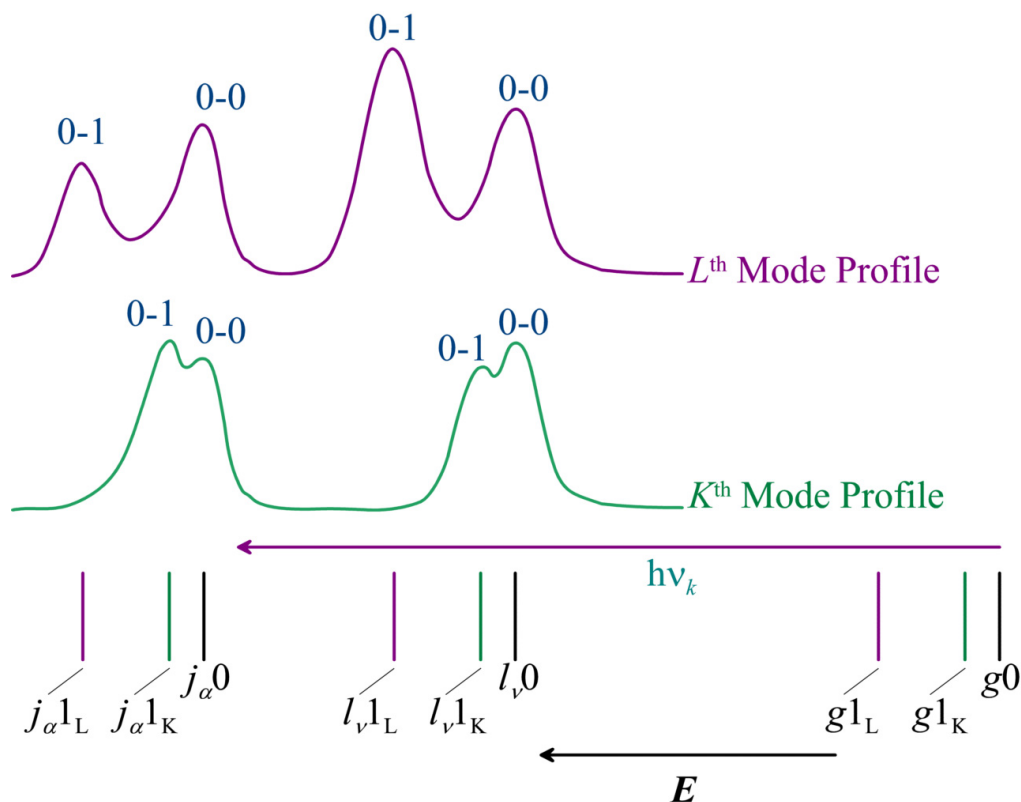


Figure 5.4. Raman excitation profiles showing resonances in the intensities of two Raman lines.

5.7 Interference Effects and Intensity Borrowing in Resonance Raman Spectra

Remember also that $\left(\beta_{g,\nu_k+1;g\nu_k}^{(l)}\right)_{\sigma\rho}$ must be squared to get the intensity, thus, cross terms between the 0-0 and 0-1 resonant terms also contribute to the intensity. These cross terms primarily act to raise or lower the intensity between the two peaks in the *excitation profiles of the Raman lines* (intensity as a function of laser frequency), depending on the relative sign between the two terms. A plus sign gives constructive interference; a minus sign gives destructive interference.

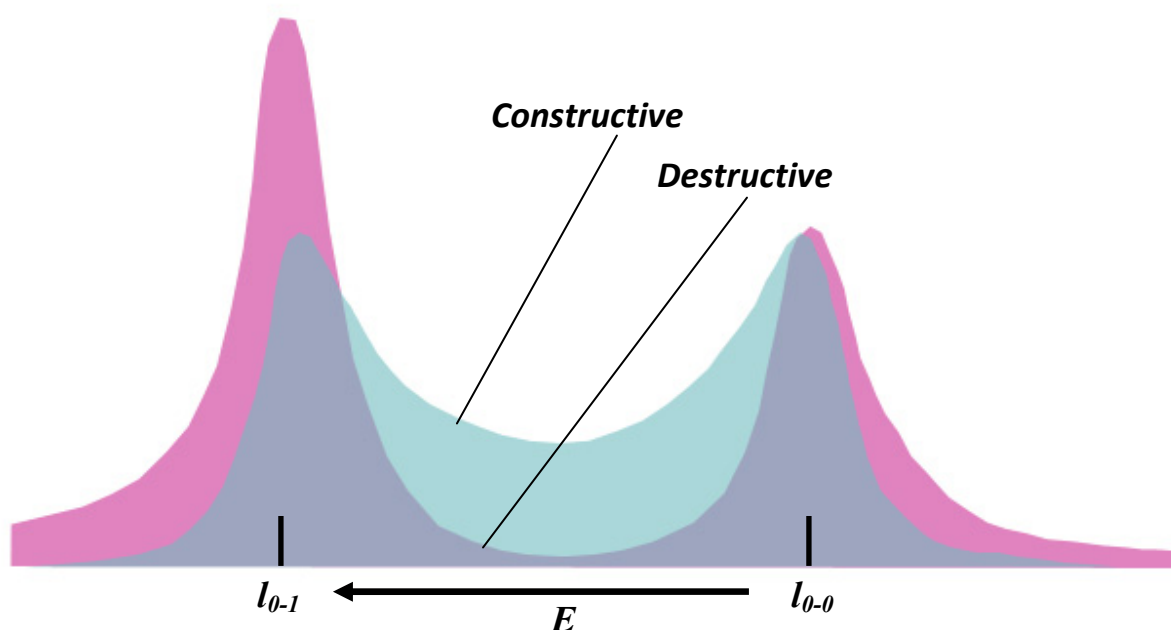


Figure 5.5. Raman excitation profiles with destructive interference (pink) and constructive interference (green).

We can also have intensity borrowing effects in the Raman excitation profiles just as we did in absorption spectra. This occurs because more than one state n_γ may lead to a significant contribution to the numerators of the 0-0 and 0-1 resonant terms of $\beta^{(l)}$. To see the effect of intensity borrowing, we first consider the relative intensities of the 0-0 and 0-1 peaks when only one state contributes, $l = n_\gamma = j_\alpha$. Then

$$\left(\beta_{g\nu_K+1, g\nu_K}^{(1)}\right)_{\sigma\rho} = - \left[\frac{(v_K+1)\hbar}{2\mu_K\Omega_K} \right]^{1/2} \left[\frac{\langle g|P'_\sigma|l\rangle \left\langle l \left| \left(\frac{\partial H'}{\partial Q_K} \right)_0 \right| l \right\rangle \langle l|P_\rho|g\rangle \frac{f_{l\nu_K, l\nu_K+1}}{+\hbar\Omega_K}}{E_l^0 - E_g^0 + \hbar\Omega_K - \hbar\omega_k} + \frac{\langle g|P'_\sigma|l\rangle \left\langle l \left| \left(\frac{\partial H'}{\partial Q_K} \right)_0 \right| l \right\rangle \langle l|P_\rho|g\rangle \frac{f_{l\nu_K, l\nu_K+1}}{-\hbar\Omega_K}}{E_l^0 - E_g^0 - \hbar\omega_k} \right]$$

Thus, the two maxima in the excitation profile of the l -band will be equal in intensity. In addition, the interference will be destructive, assuming l non-degenerate.

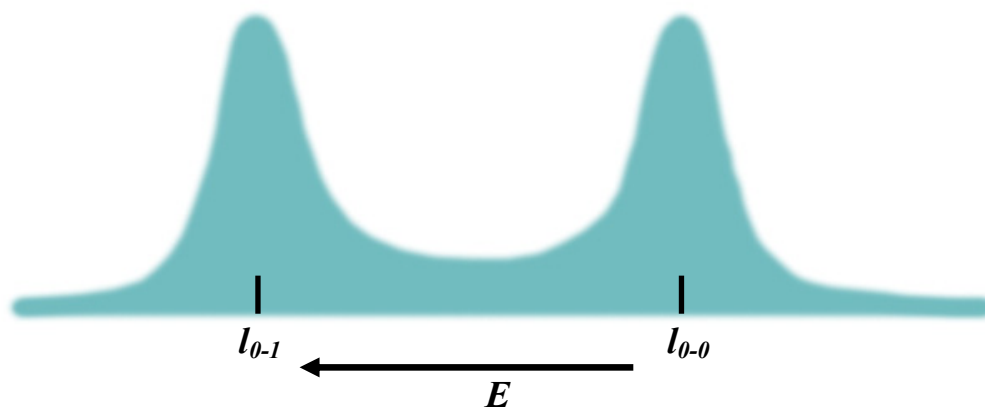
Now, consider the effect on the profile of the l state, when another allowed electronic state, say $|m\rangle$, is nearby. In this case,

$$\left(\beta_{g\nu_K+1, g\nu_K}^{(1)}\right)_{\sigma\rho} = - \left[\frac{(v_K+1)\hbar}{2\mu_K\Omega_K} \right]^{1/2} \left[\frac{\langle g|P'_\sigma|l\rangle \left\langle l \left| \left(\frac{\partial H'}{\partial Q_K} \right)_0 \right| l \right\rangle \frac{f_{l\nu_K, l\nu_K+1}}{\hbar\Omega_K} \langle l|P_\rho|g\rangle + \left\langle l \left| \left(\frac{\partial H'}{\partial Q_K} \right)_0 \right| m \right\rangle \frac{f_{m\nu_K, l\nu_K+1}}{E_l^0 - E_m^0 + \hbar\Omega_K} \langle m|P_\rho|g\rangle}{E_l^0 - E_g^0 + \hbar\Omega_K - \hbar\omega_k} + \frac{\langle g|P'_\sigma|l\rangle \frac{f_{l\nu_K, l\nu_K+1}}{-\hbar\Omega_K} \left\langle l \left| \left(\frac{\partial H'}{\partial Q_K} \right)_0 \right| l \right\rangle + \langle g|P'_\sigma|m\rangle \frac{f_{l\nu_K, m\nu_K+1}}{E_l^0 - E_m^0 - \hbar\Omega_K} \left\langle m \left| \left(\frac{\partial H'}{\partial Q_K} \right)_0 \right| l \right\rangle \langle l|P_\rho|g\rangle}{E_l^0 - E_g^0 - \hbar\omega_k} \right]$$

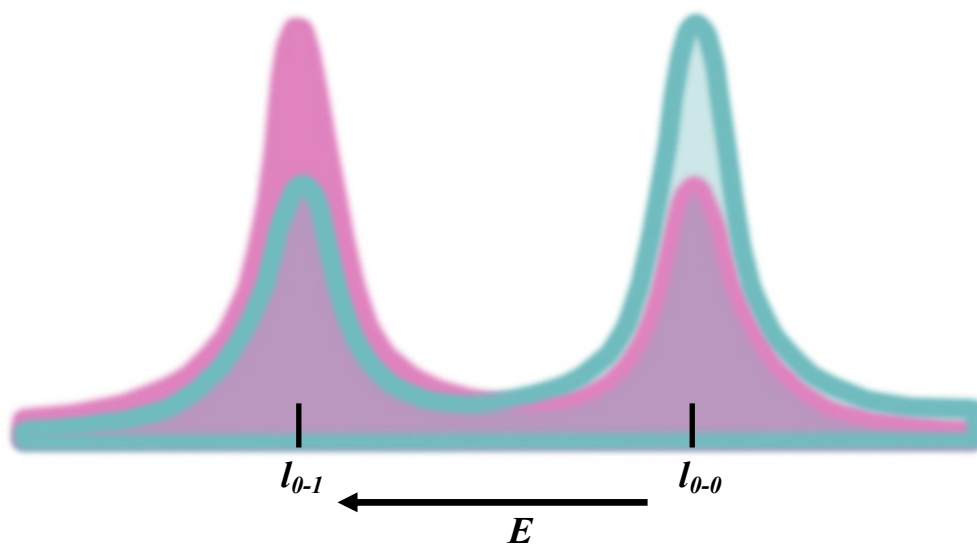
+ 2 m -state resonance terms.

The factor in parenthesis in the numerator of the two terms now gives unequal intensities at the 0-0 and 0-1 resonances. This is because the first term in the parenthesis adds in one case and subtracts in the other depending on the sign.

Summarizing, the Raman excitation profiles of the l -state with



(1) one contributing state, or



(2) two contributing states. In the latter case, we could similarly evaluate the Raman intensities in the region of the m -state.

5.8 Anti-Stokes Raman Scattering

Anti-Stokes Raman scattering is the name given to the case for which the final vibrational state is $|\vec{u}\rangle = |v_K - 1\rangle$. From the earlier expression for the scattering tensor for this case, we have

$$\begin{aligned}
\left(\beta_{g\nu_K-1, g\nu_K}^{(1)}\right)_{\sigma\rho} = & -\sum_{j_\alpha} \sum_{n_\gamma} \left[\frac{\langle g|P'_\sigma|j_\alpha\rangle \langle n_\gamma|P_\rho|g\rangle \frac{f_{n_\gamma\nu_K, j_\alpha\nu_K-1}}{E_{j_\alpha}^0 - E_{n_\gamma}^0 - \hbar\Omega_K} \left\langle j_\alpha \left| \left(\frac{\partial H'}{\partial Q_K} \right)_0 \right| n_\gamma \right\rangle \left[\frac{\nu_K \hbar}{2\mu_K \Omega_K} \right]^{1/2}}{E_l^0 - E_g^0 - \hbar\Omega_K - \hbar\omega_k} \right. \\
& + \frac{\langle g|P'_\sigma|n_\gamma\rangle \langle j_\alpha|P_\rho|g\rangle \left\langle n_\gamma \left| \left(\frac{\partial H'}{\partial Q_K} \right)_0 \right| j_\alpha \right\rangle \frac{f_{j_\alpha\nu_K, n_\gamma\nu_K-1}}{E_{j_\alpha}^0 - E_{n_\gamma}^0 + \hbar\Omega_K} \left[\frac{\nu_K \hbar}{2\mu_K \Omega_K} \right]^{1/2}}{E_{j_\alpha}^0 - E_g^0 - \hbar\omega_k} \\
& + \frac{\langle g|P'_\sigma|j_\alpha\rangle \langle j_\alpha|P_\rho|n_\gamma\rangle \frac{f_{g\nu_K, n_\gamma\nu_K-1}}{E_g^0 - E_{n_\gamma}^0 + \hbar\Omega_K} \left\langle n_\gamma \left| \left(\frac{\partial H'}{\partial Q_K} \right)_0 \right| g \right\rangle \left[\frac{\nu_K \hbar}{2\mu_K \Omega_K} \right]^{1/2}}{E_{j_\alpha}^0 - E_g^0 - \hbar\Omega_K - \hbar\omega_k} \\
& + \frac{\langle n_\gamma|P'_\sigma|j_\alpha\rangle \langle j_\alpha|P_\rho|g\rangle \frac{f_{g\nu_K-1, n_\gamma\nu_K}}{E_g^0 - E_{n_\gamma}^0 - \hbar\Omega_K} \left\langle g \left| \left(\frac{\partial H'}{\partial Q_K} \right)_0 \right| n_\gamma \right\rangle \left[\frac{\nu_K \hbar}{2\mu_K \Omega_K} \right]^{1/2}}{E_{j_\alpha}^0 - E_g^0 - \hbar\omega_k} \\
& \left. + 4 \text{ non-resonant terms} \right].
\end{aligned}$$

Neglecting coupling with the ground state, we get

$$\begin{aligned}
\left(\beta_{g\nu_K-1, g\nu_K}^{(1)}\right)_{\sigma\rho} = & -\left[\frac{\nu_K \hbar}{2\mu_K \Omega_K} \right]^{1/2} \sum_{j_\alpha} \left[\frac{\sum_{n_\gamma} \langle g|P'_\sigma|j_\alpha\rangle \frac{f_{n_\gamma\nu_K, j_\alpha\nu_K-1}}{E_{j_\alpha}^0 - E_{n_\gamma}^0 - \hbar\Omega_K} \left\langle j_\alpha \left| \left(\frac{\partial H'}{\partial Q_K} \right)_0 \right| n_\gamma \right\rangle \langle n_\gamma|P_\rho|g\rangle}{E_{j_\alpha}^0 - E_g^0 - \hbar\Omega_K - \hbar\omega_k} \right. \\
& \left. + \frac{\sum_{n_\gamma} \langle g|P'_\sigma|n_\gamma\rangle \frac{f_{j_\alpha\nu_K, n_\gamma\nu_K-1}}{E_{j_\alpha}^0 - E_{n_\gamma}^0 + \hbar\Omega_K} \left\langle n_\gamma \left| \left(\frac{\partial H'}{\partial Q_K} \right)_0 \right| j_\alpha \right\rangle \langle j_\alpha|P_\rho|g\rangle}{E_{j_\alpha}^0 - E_g^0 - \hbar\omega_k} \right]
\end{aligned}$$

Examining the tensor for anti-Stokes scattering, we see that peaks occur where

$$E_{g\bar{u}} - E_{g\bar{v}} = E_g^0 - E_g^0 - \hbar\Omega_K = -\hbar\Omega_K = \hbar\omega_k - \hbar\omega_\ell.$$

That is, peaks occur where the scattered photon energy $\hbar\omega_\ell$ is higher by the energy of one quantum in the K^{th} mode than the incident (laser) photon energy $\hbar\omega_k$.

Now, taking both Stokes and Anti-Stokes Scattering into consideration a Raman spectrum looks like:

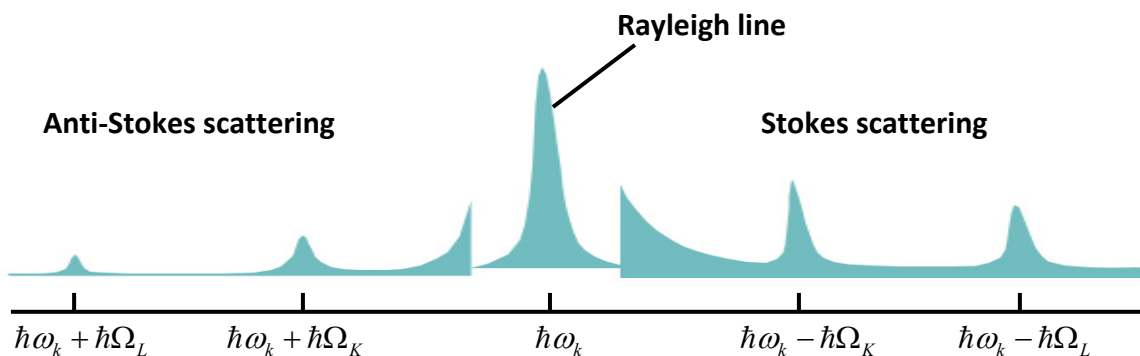


Figure 5.6. Stokes and anti-Stokes Raman scattering and Rayleigh scattering for incident laser light energy of $\hbar\omega_k$ for two vibrational modes with angular frequencies of $\hbar\Omega_K$ and $\hbar\Omega_L$.

The anti-Stokes line intensities are weighted by the Boltzmann factor since an excited vibrational level is necessarily the initial state $|\vec{v}\rangle$. This can be seen from the intensity (amplitude) factor $\beta^{(1)}$ (note $(\beta_{g^{v_k-1}, g^{v_k}}^{(1)})_{\rho\sigma} = 0$, if $v_k = 0$ for anti-stokes scattering, but $\neq 0$, for $v_k = 0$ for stokes scattering.)

Now, let's look into the intensities of the anti-Stokes lines. First, the maximum in the intensity of the anti-Stokes Raman lines occurs at

$$\hbar\omega_k = \begin{cases} E_{j_a}^0 - E_g^0 - \hbar\Omega_K \\ E_{j_a}^0 - E_g^0 \end{cases}$$

Figure 5.7. Intensity of two Raman lines as a function of incident laser frequency $\hbar\omega_k$.

As for the Stokes scattering, the intensities of the 0-0 and 0-1 maxima are equal and the interference is destructive, because the numerators of the two terms are equal, but have opposite signs.

If, two states, l and m , contribute in the sums over j_α and n_γ , then

$$\begin{aligned}
 \left(\beta_{g\nu_K^{-1}, g\nu_K}^{(l)} \right)_{\sigma\rho} = & - \left[\frac{\nu_K \hbar}{2\mu_K \Omega_K} \right]^{1/2} \left[\frac{\langle g | P'_\sigma | l \rangle \left(\left\langle l \left| \left(\frac{\partial H'}{\partial Q_K} \right)_0 \right| l \right\rangle \frac{\langle l | P_\rho | g \rangle}{-\hbar\Omega_K} + \left\langle l \left| \left(\frac{\partial H'}{\partial Q_K} \right)_0 \right| m \right\rangle \frac{\langle m | P_\rho | g \rangle}{E_l^0 - E_m^0 - \hbar\Omega_K} \right)}{E_l^0 - E_g^0 - \hbar\Omega_K - \hbar\omega_k} \right. \\
 & + \frac{\left(\frac{\langle g | P'_\sigma | l \rangle}{\hbar\Omega_K} \left\langle l \left| \left(\frac{\partial H}{\partial Q_K} \right)_0 \right| l \right\rangle + \frac{\langle g | P'_\sigma | m \rangle}{E_l^0 - E_m^0 + \hbar\Omega_K} \left\langle m \left| \left(\frac{\partial H}{\partial Q_K} \right)_0 \right| l \right\rangle \right) \langle l | P_\rho | g \rangle}{E_l^0 - E_g^0 - \hbar\omega_k} \\
 & + \frac{\langle g | P'_\sigma | m \rangle \left(\frac{\langle l | P_\rho | g \rangle}{E_m^0 - E_l^0 - \hbar\Omega_K} \left\langle m \left| \left(\frac{\partial H}{\partial Q_K} \right)_0 \right| l \right\rangle + \frac{\langle m | P_\rho | g \rangle}{-\hbar\Omega_K} \left\langle m \left| \left(\frac{\partial H}{\partial Q_K} \right)_0 \right| m \right\rangle \right)}{E_m^0 - E_g^0 - \hbar\Omega_K - \hbar\omega_k} \\
 & \left. + \frac{\left(\frac{\langle g | P'_\sigma | l \rangle}{E_m^0 - E_l^0 + \hbar\Omega_K} \left\langle l \left| \left(\frac{\partial H}{\partial Q_K} \right)_0 \right| m \right\rangle + \frac{\langle g | P'_\sigma | m \rangle}{\hbar\Omega_K} \left\langle m \left| \left(\frac{\partial H}{\partial Q_K} \right)_0 \right| m \right\rangle \right) \langle m | P_\rho | g \rangle}{E_m^0 - E_g^0 - \hbar\omega_k} \right],
 \end{aligned}$$

where, this time, we have retained the m -resonant terms. Thus, we have all four resonances, two 0-0 resonances (one for each electronic state) and two 0-1 resonances at one vibrational quantum *below* the 0-0 transition energy. In addition, the relative sign between the two terms in the numerator reverses for the 0-0 and 0-1 resonances for l and m electronic states.

To see the effect of the denominators of the terms in the numerator, let's assume

$$\langle g | P'_\sigma | l \rangle = \langle g | P_\rho | l \rangle = \langle g | P'_\sigma | m \rangle = \langle g | P_\rho | m \rangle = M,$$

and also assume

$$\left\langle l \left| \left(\frac{\partial H'}{\partial Q_K} \right)_0 \right| l \right\rangle = \left\langle m \left| \left(\frac{\partial H'}{\partial Q_K} \right)_0 \right| m \right\rangle = \left\langle l \left| \left(\frac{\partial H'}{\partial Q_K} \right)_0 \right| m \right\rangle = H$$

and

$$E_m^0 - E_l^0 = \Delta \gg \hbar\Omega_K > 0,$$

i.e., m is higher in energy than l . Then, the scattering tensor becomes

$$\left(\beta_{g\nu_K-1, g\nu_K}^{(1)} \right)_{\sigma\rho} = -M^2 H \left[\frac{\nu_K \hbar}{2\mu_K \Omega_K} \right]^{1/2} \left[\frac{\left(\frac{1}{-\hbar\Omega_K} + \frac{1}{-\Delta - \hbar\Omega_K} \right)}{E_l^0 - E_g^0 - \hbar\Omega_K - \hbar\omega_k} + \frac{\left(\frac{1}{\hbar\Omega_K} + \frac{1}{-\Delta + \hbar\Omega_k} \right)}{E_l^0 - E_g^0 - \hbar\omega_k} \right. \\ \left. + \frac{\left(\frac{1}{\Delta - \hbar\Omega_K} + \frac{1}{-\hbar\Omega_K} \right)}{E_m^0 - E_g^0 - \hbar\Omega_K - \hbar\omega_k} + \frac{\left(\frac{1}{\Delta + \hbar\Omega_K} + \frac{1}{\hbar\Omega_K} \right)}{E_m^0 - E_g^0 - \hbar\omega_k} \right]$$

Although the cross terms in the square play a role in the intensity at the resonances, the intensities at the peaks for the K^{th} mode are roughly proportion to the square of the numerator for each resonance. The numerators except for the sign have one of two forms,

$$a = \frac{1}{\hbar\Omega_K} + \frac{1}{\Delta + \hbar\Omega_K} > 0,$$

and

$$b = \frac{1}{\hbar\Omega_K} - \frac{1}{\Delta - \hbar\Omega_K} > 0,$$

Also notice that $a > b$. An approximate representation of the intensities and interference effects for this case are illustrated in Figure 5.X.

This kind of behavior can occur when the molecule has symmetry, because symmetry makes many of the matrix elements, such as M and H , related to each other. (Remember also that the anti-Stokes intensities are related to the Stokes profiles by the Boltzmann populations of the vibrational levels. This influence is not included in the above discussion, but must be taken into account.)

Similar Raman excitation profile behavior has been observe for the Stokes profiles for symmetrical molecules like the metalloporphyrins.

5.9 Overtones and Combination Line Raman Intensities

To obtain the intensities of overtones and combination lines in Raman spectra, we must go back to the original expression for the vibronic state and include the quadratic terms, *i.e.*,

$$|j_\alpha \bar{w}\rangle = |j_\alpha\rangle |\bar{w}\rangle - \sum_{n_\gamma} \sum_{\bar{x}} \sum_L \frac{\left\langle n_\gamma \left| \left(\frac{\partial H}{\partial Q_L} \right)_0 \right| j_\alpha \right\rangle \langle \bar{x} | Q_L | \bar{w} \rangle}{E_{j_\alpha \bar{w}} - E_{n_\gamma \bar{x}}} |n_\gamma\rangle |\bar{x}\rangle$$

$$- \sum_{n_\gamma} \sum_{\bar{x}} \sum_{L,K} \frac{\left\langle n_\gamma \left| \left(\frac{\partial^2 H}{\partial Q_K \partial Q_L} \right)_0 \right| j_\alpha \right\rangle \langle \bar{x} | Q_K Q_L | \bar{w} \rangle}{E_{j_\alpha \bar{w}} - E_{n_\gamma \bar{x}}} |n_\gamma\rangle |\bar{x}\rangle$$

which we will now write as

$$|j_\alpha \bar{w}\rangle = |j_\alpha\rangle |\bar{w}\rangle - \sum_{n_\gamma} \sum_{\bar{x}} \sum_L \frac{H_{n_\gamma j_\alpha}^L \langle \bar{x} | Q_L | \bar{w} \rangle}{E_{j_\alpha \bar{w}} - E_{n_\gamma \bar{x}}} |n_\gamma\rangle |\bar{x}\rangle - \sum_{n_\gamma} \sum_{\bar{x}} \sum_{L,K} \frac{H_{n_\gamma j_\alpha}^{KL} \langle \bar{x} | Q_K Q_L | \bar{w} \rangle}{E_{j_\alpha \bar{w}} - E_{n_\gamma \bar{x}}} |n_\gamma\rangle |\bar{x}\rangle$$

where

$$H_{n_\gamma j_\alpha}^{KL} \equiv \left\langle n_\gamma \left| \left(\frac{\partial^2 H}{\partial Q_K \partial Q_L} \right)_0 - f_K \delta_{K,L} \right| j_\alpha \right\rangle$$

The prime in the latter is a reminder that the diagonal elements represent the change in the force constant. In addition, when substituting these states into the expression for the scattering tensor, we must keep all terms up to quadratic terms in Q_K and Q_L . Thus, we must retain all of the constant and linear terms written so far for the scattering tensor, and we must add to these the quadratic terms. The quadratic terms come both from the quadratic terms in the expansion of the vibronic states and the bilinear products of the linear terms.

This is a lot of terms! However, we can simplify as before by neglecting the terms coming from expansion of the ground vibronic states (coupling to the ground state). In addition, let's restrict ourselves to overtones for the time being.

For Stokes scattering, we need

$$\begin{aligned}
\left(\beta_{g^{v_M+2}, g^{v_M}}^{(2)}\right)_{\rho\sigma}^{lin} &= \sum_{j_\alpha} \sum_{\bar{w}} \sum_{n_\gamma} \sum_{\bar{x}} \sum_{m_\delta} \sum_{\bar{z}} \sum_{K,L} \left[\frac{\langle g | P'_\sigma | m_\delta \rangle \left(\frac{H_{j_\alpha, m_\delta}^K \langle \bar{w} | Q_K | \bar{z} \rangle H_{j_\alpha, n_\gamma}^L \langle \bar{v} | Q_L | \bar{w} \rangle}{(E_{j_\alpha \bar{w}} - E_{m_\delta \bar{u}})(E_{j_\alpha \bar{w}} - E_{n_\gamma \bar{v}})} \right) \langle n_\gamma | P_\rho | g \rangle}{E_{j_\alpha \bar{w}} - E_{g \bar{v}} - \hbar \omega_k} \right] \\
\left(\beta_{g^{v_M+2}, g^{v_M}}^{(2)}\right)_{\rho\sigma}^{lin} &= \sum_{j_\alpha} \sum_{\bar{w}} \sum_{n_\gamma} \sum_{m_\delta} \left[\frac{\langle g | P'_\sigma | m_\delta \rangle \langle n_\gamma | P_\rho | g \rangle \left(\frac{H_{j_\alpha, m_\delta}^M \langle \bar{w} | Q_M | \bar{u} \rangle H_{j_\alpha, n_\gamma}^M \langle \bar{v} | Q_M | \bar{w} \rangle}{(E_{j_\alpha \bar{w}} - E_{m_\delta \bar{u}})(E_{j_\alpha \bar{w}} - E_{n_\gamma \bar{v}})} \right)}{E_{j_\alpha \bar{w}} - E_{g \bar{v}} - \hbar \omega_k} \right] \\
&= \sum_{j_\alpha} \sum_{n_\gamma} \sum_{m_\delta} \left[\frac{\langle g | P'_\sigma | m_\delta \rangle \langle n_\gamma | P_\rho | g \rangle \left(\frac{H_{j_\alpha, m_\delta}^M \left[\frac{(v_M + 2)\hbar}{2\mu_M \Omega_M} \right]^{1/2} H_{j_\alpha, n_\gamma}^M \left[\frac{(v_M + 1)\hbar}{2\mu_M \Omega_M} \right]^{1/2}}{(E_{j_\alpha}^0 - E_{m_\delta}^0 - \hbar \Omega_M)(E_{j_\alpha}^0 - E_{n_\gamma}^0 + \hbar \Omega_M)} \right)}{E_{j_\alpha}^0 - E_g^0 + \hbar \Omega_M - \hbar \omega_k} \right] \\
&= \frac{[(v_M + 2)(v_M + 1)]^{1/2} \hbar}{2\mu_M \Omega_M} \sum_{j_\alpha} \sum_{n_\gamma} \sum_{m_\delta} \left[\frac{\langle g | P'_\sigma | m_\delta \rangle \langle n_\gamma | P_\rho | g \rangle \left(\frac{H_{j_\alpha, m_\delta}^M H_{j_\alpha, n_\gamma}^M}{(E_{j_\alpha}^0 - E_{m_\delta}^0 - \hbar \Omega_M)(E_{j_\alpha}^0 - E_{n_\gamma}^0 + \hbar \Omega_M)} \right)}{E_{j_\alpha}^0 - E_g^0 + \hbar \Omega_M - \hbar \omega_k} \right]
\end{aligned}$$

This term is only the term resulting from the linear term of the vibronic states. We must also have the terms coming from the quadratic term of the vibronic states. There are two of these,

$$\begin{aligned}
\left(\beta_{g^{v_M+2}, g^{v_M}}^{(2)}\right)_{\rho\sigma}^{quad} &= -\sum_{j_\alpha} \sum_{\bar{w}} \sum_{n_\gamma} \sum_{\bar{x}} \sum_{K,L} \left[\frac{\langle g | P'_\sigma | j_\alpha \rangle \langle \bar{u} | \bar{w} \rangle \left(\frac{H'_{n_\gamma j_\alpha}{}^{KL} \langle \bar{x} | Q_K Q_L | \bar{w} \rangle}{E_{j_\alpha \bar{w}} - E_{n_\gamma \bar{x}}} \right) \langle n_\gamma | P_\rho | g \rangle \langle \bar{x} | \bar{v} \rangle}{E_{j_\alpha \bar{w}} - E_{g \bar{v}} - \hbar \omega_k} \right. \\
&\quad \left. + \frac{\langle g | P'_\sigma | n_\gamma \rangle \langle \bar{u} | \bar{x} \rangle \left(\frac{H'_{j_\alpha n_\gamma}{}^{KL} \langle \bar{w} | Q_K Q_L | \bar{x} \rangle}{E_{j_\alpha \bar{w}} - E_{n_\gamma \bar{x}}} \right) \langle n_\gamma | P_\rho | g \rangle \langle \bar{w} | \bar{v} \rangle}{E_{j_\alpha \bar{w}} - E_{g \bar{v}} - \hbar \omega_k} \right] \\
&= -\sum_{j_\alpha} \sum_{n_\gamma} \left[\frac{\left[\frac{\hbar(v_M+1)}{2\mu_M \Omega_M} \right] \langle g | P'_\sigma | m_\delta \rangle \left(\frac{H'_{n_\gamma j_\alpha}{}{MM}}{E_{j_\alpha}^0 - E_{n_\gamma}^0 + 2\hbar \Omega_M} \right) \langle n_\gamma | P_\rho | g \rangle}{E_{j_\alpha}^0 - E_g^0 + 2\hbar \Omega_M - \hbar \omega_k} \right. \\
&\quad \left. + \frac{\left[\frac{\hbar(v_M+1)}{2\mu_M \Omega_M} \right] \langle g | P'_\sigma | n_\gamma \rangle \left(\frac{H'_{j_\alpha n_\gamma}{}{MM}}{E_{j_\alpha}^0 - E_{n_\gamma}^0 - 2\hbar \Omega_M} \right) \langle j_\alpha | P_\rho | g \rangle}{E_{j_\alpha}^0 - E_g^0 - \hbar \omega_k} \right] \\
&= -\left[\frac{\hbar(v_M+1)}{2\mu_M \Omega_M} \right] \sum_{j_\alpha} \sum_{n_\gamma} \left[\frac{\langle g | P'_\sigma | m_\delta \rangle \langle n_\gamma | P_\rho | g \rangle \left(\frac{H'_{n_\gamma j_\alpha}{}{MM}}{E_{j_\alpha}^0 - E_{n_\gamma}^0 + 2\hbar \Omega_M} \right)}{E_{j_\alpha}^0 - E_g^0 + 2\hbar \Omega_M - \hbar \omega_k} \right. \\
&\quad \left. + \frac{\langle g | P'_\sigma | n_\gamma \rangle \langle j_\alpha | P_\rho | g \rangle \left(\frac{H'_{j_\alpha n_\gamma}{}{MM}}{E_{j_\alpha}^0 - E_{n_\gamma}^0 - 2\hbar \Omega_M} \right)}{E_{j_\alpha}^0 - E_g^0 - \hbar \omega_k} \right].
\end{aligned}$$

Now consider scattering from only one contributing electronic state $|j_\alpha\rangle$. We have

$$\begin{aligned}
\left(\beta_{g^{v_M+2}, g^{v_M}}^{(2)}\right)_{\rho\sigma} &= -\frac{[(v_M+2)(v_M+1)]^{1/2} \hbar \langle g|P'_\sigma|j_\alpha\rangle \langle j_\alpha|P_\rho|g\rangle \left(\frac{H_{j_\alpha, j_\alpha}^M}{(-\hbar\Omega_M)} \frac{H_{j_\alpha, j_\alpha}^M}{\hbar\Omega_M}\right)}{2\mu_M\Omega_M} \frac{1}{E_{j_\alpha}^0 - E_g^0 + \hbar\Omega_M - \hbar\omega_k} \\
&+ \frac{[(v_M+1)] \hbar}{2\mu_M\Omega_M} \left[\frac{\langle g|P'_\sigma|j_\alpha\rangle \langle j_\alpha|P_\rho|g\rangle \left(\frac{H_{j_\alpha, j_\alpha}^{MM}}{2\hbar\Omega_M}\right)}{E_{j_\alpha}^0 - E_g^0 + 2\hbar\Omega_M - \hbar\omega_k} + \frac{\langle g|P'_\sigma|j_\alpha\rangle \langle j_\alpha|P_\rho|g\rangle \left(\frac{H_{j_\alpha, j_\alpha}^{MM}}{-2\hbar\Omega_M}\right)}{E_{j_\alpha}^0 - E_g^0 - \hbar\omega_k} \right] \\
&= \frac{\hbar \langle g|P'_\sigma|j_\alpha\rangle \langle j_\alpha|P_\rho|g\rangle (v_M+1)^{1/2}}{2\mu_M\Omega_M} \left[\frac{(v_M+2)^{1/2} (-1) \left(\frac{H_{j_\alpha, j_\alpha}^M}{\hbar\Omega_M}\right)^2}{E_{j_\alpha}^0 - E_g^0 + \hbar\Omega_M - \hbar\omega_k} \right. \\
&\quad \left. + \frac{\frac{1}{2}(v_M+1)^{1/2} \frac{H_{j_\alpha, j_\alpha}^{MM}}{\hbar\Omega_M}}{E_{j_\alpha}^0 - E_g^0 + 2\hbar\Omega_M - \hbar\omega_k} - \frac{\frac{1}{2}(v_M+1)^{1/2} \frac{H_{j_\alpha, j_\alpha}^{MM}}{\hbar\Omega_M}}{E_{j_\alpha}^0 - E_g^0 - \hbar\omega_k} \right].
\end{aligned}$$

Figure 5.8.

Figure 5.9.

5.10 Non-resonance Raman Scattering

5.11 Multi-mode Phenomena