

# CHM 502 - Module 8 - Spectroscopic Selection Rules

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We will now use the dipole time correlation function to derive spectroscopic selection rules for microwave, infrared, and Raman spectroscopy. We will explicitly evaluate the absorption lineshapes of the rotational and vibrational motion of diatomic molecules, within the rigid rotor and harmonic oscillator approximations.

Recall our expression for the absorption lineshape, which describes the spectrum of allowed transitions and their relative strengths:

$$\begin{aligned} S(\omega) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_i p_i \langle \psi_i | \hat{\underline{\mu}}(0) \cdot \underline{\xi} \cdot \hat{\underline{\mu}}(t) \cdot \underline{\xi} | \psi_i \rangle \\ &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_i p_i \langle \psi_i | \hat{\underline{\mu}} \cdot \underline{\xi} \cdot e^{+i\hat{H}t/\hbar} \cdot \hat{\underline{\mu}} \cdot \underline{\xi} \cdot e^{-i\hat{H}t/\hbar} | \psi_i \rangle \end{aligned} \quad (1)$$

Where  $\underline{\xi}$  is a unit vector describing the linear polarization axis of the electric field, which we will often take to be the unit vector  $\hat{z}$ .

## 1 Rotational spectroscopy

We will start by deriving the selection rules for microwave spectroscopy by treating the rotational dynamics of a diatomic molecule as that of a rigid rotor.

The eigenfunctions of the rigid rotor are the spherical harmonics, which have many nice properties. The expression for their energy eigenvalues is very simple and depends only on  $J$ :

$$\hat{H} Y_J^m(\theta, \phi) = E_J Y_J^m(\theta, \phi) \quad (2)$$

$$E_J = \frac{\hbar^2}{2I} J(J+1) \equiv BJ(J+1) \quad (3)$$

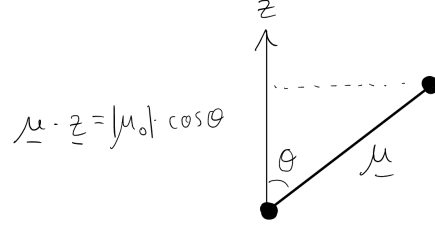
$$J = 0, \pm 1, \pm 2, \dots \quad m = \{-J, -J+1, \dots, J-1, J\}$$

where  $I = \mu r^2$  is the moment of inertia for a diatomic molecule with bond length  $r$  and reduced mass  $\mu$ .  $B = \frac{\hbar^2}{2I}$  is defined as the *rotational constant* for a given system (given here in Joules). The  $J^{\text{th}}$  energy level has degeneracy  $2J+1$ .

To apply Eqn. 1 to the rigid rotor, let's first take  $\underline{\xi}$  to be the unit vector  $\hat{z}$ . Therefore:

$$\hat{\underline{\mu}} \cdot \underline{\xi} = \hat{\underline{\mu}} \cdot \hat{z} = |\mu_0| \cos \theta \quad (4)$$

where  $\theta$  is the angle our rigid rotor makes with the  $z$  axis, and  $|\mu_0|$  is the magnitude of the molecule's permanent dipole.



Re-expressing Eqn. 1 for the case of the rigid rotor, we have:

$$S(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{J,m} p_{J,m} \langle Y_J^m | \mu_0 \cos \theta e^{+i\hat{H}_{rot}t/\hbar} \mu_0 \cos \theta e^{-\hat{H}_{rot}t/\hbar} | Y_J^m \rangle \quad (5)$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{J,m} p_{J,m} |\mu_0|^2 \langle Y_J^m | \cos \theta e^{+i\hat{H}_{rot}t/\hbar} \cos \theta e^{-\hat{H}_{rot}t/\hbar} | Y_J^m \rangle \quad (6)$$

Some useful properties of spherical harmonic wavefunctions include:

$$\hat{H}_{rot} | Y_J^m \rangle = B J(J+1) | Y_J^m \rangle \quad (7)$$

$$\langle Y_{J'}^{m'} | Y_J^m \rangle = \delta_{J,J'} \delta_{m,m'} \quad (8)$$

$$\cos \theta | Y_J^m \rangle = c_{J+} | Y_{J+1}^m \rangle + c_{J-} | Y_{J-1}^m \rangle \quad (9)$$

$$c_{J+} = \sqrt{\frac{(J+1)^2 - m^2}{4(J+1)^2 - 1}} \quad c_{J-} = \sqrt{\frac{J^2 + m^2}{4J^2 - 1}} \quad (10)$$

Eqn. 9 derives from the unique properties of Legendre polynomials.  $c_{J+}$  and  $c_{J-}$  are closely related to Clebsch-Gordan coefficients, but we will hand-wave them away here, since they are not essential to the major features of the microwave spectrum.

Forging ahead, let's start by evaluating the quantity

$$\langle Y_J^m | \cos \theta e^{+i\hat{H}_{rot}t/\hbar} \cos \theta e^{-i\hat{H}_{rot}t/\hbar} | Y_J^m \rangle = \langle Y_J^m | \cos \theta e^{+i\hat{H}_{rot}t/\hbar} \cos \theta | Y_J^m \rangle e^{-iE_J t/\hbar} \quad (11)$$

$$= \left[ c_{J+}^* \langle Y_{J+1}^m | + c_{J-}^* \langle Y_{J-1}^m | \right] e^{+i\hat{H}_{rot}t/\hbar} \left[ c_{J+} | Y_{J+1}^m \rangle + c_{J-} | Y_{J-1}^m \rangle \right] e^{-iE_J t/\hbar} \quad (12)$$

$$= \left[ c_{J+}^* \langle Y_{J+1}^m | + c_{J-}^* \langle Y_{J-1}^m | \right] \left[ c_{J+} | Y_{J+1}^m \rangle e^{+iE_{J+1}t/\hbar} + c_{J-} | Y_{J-1}^m \rangle e^{+iE_{J-1}t/\hbar} \right] e^{-iE_J t/\hbar} \quad (13)$$

$$= \left[ |c_{J+}|^2 e^{+iB(J+1)(J+2)t/\hbar} + |c_{J-}|^2 e^{+iB(J-1)Jt/\hbar} \right] e^{-iBJ(J+1)t/\hbar} \quad (14)$$

$$= |c_{J+}|^2 e^{+2iB(J+1)t/\hbar} + |c_{J-}|^2 e^{-2iBJt/\hbar} \quad (15)$$

Now, moving back to the full lineshape expression:

$$S(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{J,m} p_{J,m} |\mu_0|^2 \left[ |c_{J+}|^2 e^{+2iB(J+1)t/\hbar} + |c_{J-}|^2 e^{-2iBJt/\hbar} \right] \quad (16)$$

We will assume a thermal Boltzmann distribution with  $\beta = 1/k_B T$  and rotational partition function  $Q_{rot}$ , so the probability that a molecule is found with rotational angular momentum quantum number of  $J$  is given by:

$$p_J = \frac{(2J+1)e^{-\beta E_J}}{Q_{rot}} \quad (17)$$

where we also use the fact that each  $J$  level has degeneracy  $(2J+1)$  due to the  $m$  sub-levels. We will also ignore the  $m$ -dependence of the  $c_{J\pm}$  coefficients – this is an approximation, but not a dire one. Therefore:

$$S(\omega) = \frac{1}{2\pi} |\mu_0|^2 \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_J \frac{(2J+1)e^{-\beta E_J}}{Q_{rot}} \left[ |c_{J+}|^2 e^{+2iB(J+1)t/\hbar} + |c_{J-}|^2 e^{-2iBJt/\hbar} \right] \quad (18)$$

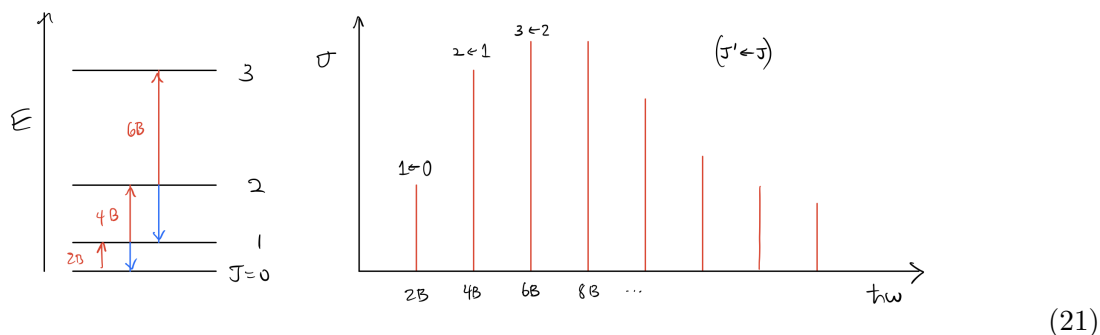
$$= \frac{1}{2\pi} \frac{|\mu_0|^2}{Q_{rot}} \sum_J (2J+1) e^{-\beta E_J} \int_{-\infty}^{\infty} dt \left[ |c_{J+}|^2 e^{+2iB(J+1)t/\hbar} + |c_{J-}|^2 e^{-2iBJt/\hbar} \right] e^{-i\omega t} \quad (19)$$

And finally, recalling that the Fourier transform of a complex sinusoid is a delta function centered at the carrier frequency:

$$S(\omega) \sim \frac{1}{2\pi} \frac{|\mu_0|^2}{Q_{rot}} \sum_J (2J+1) e^{-\beta E_J} \left[ |c_{J+}|^2 \underbrace{\delta(\hbar\omega - 2B(J+1))}_{\text{absorption}} + |c_{J-}|^2 \underbrace{\delta(\hbar\omega + 2BJ)}_{\text{emission}} \right] \quad (20)$$

Eqn. 20 encodes essentially everything about rotational spectroscopy of diatomic molecules within the rigid rotor approximation.

Pure rotational absorption and emission spectra consist of series of evenly spaced lines –  $\hbar\omega = 2B(J+1)$  in the absorption spectrum and  $\hbar\omega = 2BJ$  in the emission spectrum – reflecting transitions between neighboring pairs of  $J$  states for  $J = 0, 1, 2, \dots$ . The relative intensities of these spectral lines largely reflect the Boltzmann population in the initial  $J$  state.



Rotational transitions give rise to a molecule's microwave spectrum because the transition energies spaced by  $2B$  typically fall at microwave frequencies (100s of MHz to 100s of GHz). For instance, the CO molecule has a  $B$  value in the ballpark of 60 GHz ( $2 \text{ cm}^{-1}$ ).

We can also take away some information here about selection rules, which dictate which pairs of states feature dipole-allowed transitions. Here we glean the following rules:

- In order to have a rotational spectrum, a rigid rotor must have a finite permanent dipole moment,  $\mu_0 > 0$ . Homonuclear diatomic molecules like  $H_2$  or  $N_2$  do not have a microwave spectrum within the rigid rotor approximation.
- The only transitions which contribute to the spectrum are between  $|J, m\rangle$  and  $|J \pm 1, m\rangle$  states. Therefore,  $\Delta J = \pm 1$  and  $\Delta m = 0$  during an allowed rotational transition for a rigid diatomic molecule. In practice, these selection rules arise because the factor of  $\cos \theta$  in  $\underline{\hat{\mu}} \cdot \underline{\hat{\xi}}$  mixes spherical harmonics that differ in one quantum of  $J$  (as seen in Eqn. 9).

*Note:* Finding  $S(\omega)$  allowed us to solve for the entire, Boltzmann-weighted rotational spectrum at once. Alternatively, we could find just the selection rules by evaluating the transition rate between states  $|Y_J^m\rangle$  and  $|Y_{J'}^{m'}\rangle$ , which we know from time-dependent perturbation theory to be proportional to the square of the matrix element:

$$\Gamma_{J', m' \leftarrow J, m} \propto |\langle Y_J^m | \underline{\hat{\mu}} \cdot \underline{\hat{\xi}} | Y_{J'}^{m'} \rangle|^2 \quad (22)$$

This will yield the same answer. See McQuarrie Section 6.7 for a full worked example.

## 2 Vibrational spectroscopy

We now move on to consider the dynamics of the relative motion of the two nuclei in a diatomic molecule. We can approximate the vibration of a diatomic molecule as a harmonic oscillator (HO). Within the ladder operator formalism, we can write the Hamiltonian as:

$$\hat{H} = \hbar\omega_0 \left[ \hat{a}^\dagger \hat{a} + \frac{1}{2} \right] \equiv \hbar\omega_0 \left[ \hat{N} + \frac{1}{2} \right] \quad \omega_0 \equiv \sqrt{\frac{k}{m}} \quad (23)$$

where

$$\hat{a}^\dagger = \frac{1}{\sqrt{2\hbar m\omega_0}} \left[ m\omega_0 \hat{q} + i\hat{p}_q \right] \quad \text{raising/creation operator} \quad (24)$$

$$\hat{a} = \frac{1}{\sqrt{2\hbar m\omega_0}} \left[ m\omega_0 \hat{q} - i\hat{p}_q \right] \quad \text{lowering/annihilation operator} \quad (25)$$

and therefore

$$\hat{q} = \sqrt{\frac{\hbar}{2m\omega_0}} \left[ \hat{a}^\dagger + \hat{a} \right] \quad (26)$$

$$\hat{p}_q = i\sqrt{\frac{\hbar m\omega_0}{2}} \left[ \hat{a}^\dagger - \hat{a} \right] \quad (27)$$

and where

$$\hat{a}^\dagger |\psi_n\rangle = \sqrt{n+1} |\psi_{n+1}\rangle \quad (28)$$

$$\hat{a} |\psi_n\rangle = \sqrt{n} |\psi_{n-1}\rangle \quad (29)$$

$$\hat{a}^\dagger \hat{a} |\psi_n\rangle = \hat{N} |\psi_n\rangle = n |\psi_n\rangle \quad (30)$$

## 2.1 Heisenberg ladder operators

In preparation for calculating the absorption spectrum of our HO, it's useful to write down the time-dependent forms of the ladder operators within the Heisenberg picture:

$$\hat{a}(t) \equiv e^{i\hat{H}t/\hbar} \hat{a} e^{-i\hat{H}t/\hbar} = e^{i\omega_0(\hat{N}+\frac{1}{2})t} \hat{a} e^{-i\omega_0(\hat{N}+\frac{1}{2})t} = e^{i\omega_0\hat{N}t} \hat{a} e^{-i\omega_0\hat{N}t} \quad (31)$$

We can therefore evaluate  $\hat{a}(t)$ :

$$\hat{a}(t)|\psi_n\rangle = e^{i\omega_0\hat{N}t} \hat{a} e^{-i\omega_0\hat{N}t} |\psi_n\rangle \quad (32)$$

$$= e^{i\omega_0\hat{N}t} \hat{a} |\psi_n\rangle e^{-i\omega_0 n t} \quad (33)$$

$$= e^{i\omega_0\hat{N}t} \sqrt{n} |\psi_{n-1}\rangle e^{-i\omega_0 n t} \quad (34)$$

$$= \sqrt{n} |\psi_{n-1}\rangle e^{i\omega_0(n-1)t} e^{-i\omega_0 n t} \quad (35)$$

$$= \hat{a} |\psi_n\rangle e^{-i\omega_0 t} \quad (36)$$

$$\rightarrow \boxed{\hat{a}(t) = e^{-i\omega_0 t} \hat{a}} \quad (37)$$

Following a similar process, we can also find

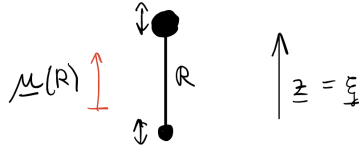
$$\boxed{\hat{a}^\dagger(t) = e^{i\omega_0 t} \hat{a}^\dagger} \quad (38)$$

## 2.2 Selection rules for infrared spectroscopy

Let's now evaluate the absorption lineshape for transitions between HO wavefunctions:

$$S(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_n p_n \langle \psi_n | \hat{\mu}_z(0) \cdot \hat{\mu}_z(t) | \psi_n \rangle \quad (39)$$

Where again we have assumed a laser field polarized along the lab frame  $z$  axis. For the moment, let's neglect rotational motion and assume that our molecule is oriented along the  $z$  axis, so we have already swapped  $\hat{\mu}$  with  $\hat{\mu}_z$ .



We need an expression for  $\hat{\mu}_z(t)$  that accounts for the vibrational dynamics of the system. For a diatomic molecule,  $\hat{\mu}_z$  lies along the bond axis and its magnitude may be modulated as the bond length  $R$  oscillates.

We take the nuclear dipole moment to be weakly dependent on vibrational displacement by Taylor expanding  $\hat{\mu}$  about its equilibrium value  $\hat{\mu}_0$  at equilibrium bond length  $R_e$ :

$$\hat{\mu}(R) = \hat{\mu}_0 + \left( \frac{d\hat{\mu}}{dR} \right)_{R_e} (R - R_e) + \frac{1}{2} \left( \frac{d^2\hat{\mu}}{dR^2} \right)_{R_e} (R - R_e)^2 + \dots \quad (40)$$

$$\rightarrow \hat{\mu}(q) \equiv \hat{\mu}_0 + \left( \frac{d\hat{\mu}}{dq} \right)_0 q + \dots \quad \rightarrow \boxed{\Delta\hat{\mu}(q) \equiv \hat{\mu}(x) - \hat{\mu}_0 \simeq \left( \frac{d\hat{\mu}}{dq} \right)_0 q} \quad (41)$$

where  $q \equiv R - R_e$ . We can truncate our expansion to first-order in  $x$  for small displacements.

We now want to find an expression for  $\hat{\mu}(t)$  in the Heisenberg picture. We will work with  $\Delta\hat{\mu}(t)$  rather than  $\hat{\mu}(t)$ , which contains all the time-dependent information necessary to evaluate  $S(\omega)$ .

$$\Delta\hat{\mu}(t) = \left(\frac{d\hat{\mu}}{dq}\right)_0 \hat{q}(t) \quad (42)$$

$$= \left(\frac{d\hat{\mu}}{dq}\right)_0 \sqrt{\frac{\hbar}{2m\omega_0}} [\hat{a}^\dagger(t) + \hat{a}(t)] \quad (43)$$

$$= \left(\frac{d\hat{\mu}}{dq}\right)_0 \sqrt{\frac{\hbar}{2m\omega_0}} [\hat{a}^\dagger \cdot e^{i\omega_0 t} + \hat{a} \cdot e^{-i\omega_0 t}] \quad (44)$$

Let's consider the inner product:

$$\langle \psi_n | \Delta\hat{\mu}(0) \cdot \Delta\hat{\mu}(t) | \psi_n \rangle \quad (45)$$

$$= \langle \psi_n | \left(\frac{d\hat{\mu}}{dq}\right)_0 \cdot \sqrt{\frac{\hbar}{2m\omega_0}} [\hat{a}^\dagger + \hat{a}] \cdot \left(\frac{d\hat{\mu}}{dq}\right)_0 \cdot \sqrt{\frac{\hbar}{2m\omega_0}} [\hat{a}^\dagger \cdot e^{i\omega_0 t} + \hat{a} \cdot e^{-i\omega_0 t}] | \psi_n \rangle \quad (46)$$

$$= \frac{\hbar}{2m\omega_0} \left(\frac{d\mu}{dq}\right)_0^2 \langle \psi_n | [\hat{a}^\dagger \hat{a}^\dagger e^{i\omega_0 t} + \hat{a}^\dagger \hat{a} e^{-i\omega_0 t} + \hat{a} \hat{a}^\dagger e^{i\omega_0 t} + \hat{a} \hat{a} e^{-i\omega_0 t}] | \psi_n \rangle \quad (47)$$

$$= \frac{\hbar}{2m\omega_0} \left(\frac{d\mu}{dq}\right)_0^2 [\langle \psi_n | \hat{a}^\dagger \hat{a} | \psi_n \rangle e^{-i\omega_0 t} + \langle \psi_n | \hat{a} \hat{a}^\dagger | \psi_n \rangle e^{i\omega_0 t}] \quad (48)$$

$$= \frac{\hbar}{2m\omega_0} \left(\frac{d\mu}{dq}\right)_0^2 [n e^{-i\omega_0 t} + (n+1) e^{i\omega_0 t}] \quad (49)$$

Because the  $|\psi_n\rangle$  states form an orthonormal basise, the only terms which survive are the cross terms involving both  $\hat{a}^\dagger$  and  $\hat{a}$ , which connect  $|\psi_n\rangle$  to  $|\psi_{n\pm 1}\rangle$ , then return it to itself.

Let's now return to evaluating the entire expression for  $S(\omega)$ , plugging in Eqn. 49:

$$S(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_n p_n \langle \psi_n | \Delta\hat{\mu}(0) \cdot \Delta\hat{\mu}(t) | \psi_n \rangle \quad (50)$$

$$= \frac{\hbar}{4\pi m\omega_0} \left(\frac{d\mu}{dq}\right)_0^2 \sum_n \frac{e^{-\beta\hbar\omega_0(n+\frac{1}{2})}}{Q_{vib}} \int_{-\infty}^{+\infty} dt e^{-i\omega t} [n e^{-i\omega_0 t} + (n+1) e^{i\omega_0 t}] \quad (51)$$

$$= \frac{\hbar}{4\pi m\omega_0} \left(\frac{d\mu}{dq}\right)_0^2 \sum_n \frac{e^{-\beta\hbar\omega_0(n+\frac{1}{2})}}{Q_{vib}} \left[ n \underbrace{\delta(\omega + \omega_0)}_{\text{emission}} + (n+1) \underbrace{\delta(\omega - \omega_0)}_{\text{absorption}} \right] \quad (52)$$

At reasonably low temperatures we will have  $k_B T < \hbar\omega_0$  the population will be nearly entirely in the ground vibrational state. In this regime, which is valid at room temperature for most vibrations, we can consider only the  $n = 0$  term in the sum, so:

$$S(\omega) \propto \left(\frac{d\mu}{dq}\right)_0^2 \delta(\omega - \omega_0) \quad (53)$$

From our expression for  $S(\omega)$ , we can glean the major selection rules of vibrational spectroscopy within the harmonic oscillator limit:

- $\left(\frac{d\mu}{dq}\right)_0^2 \neq 0$ . Motion along the vibrational coordinate  $q$  must change the dipole moment of the molecule in order to observe an infrared spectrum. Homonuclear diatomics like  $\text{H}_2$  or  $\text{N}_2$  therefore feature no dipole-allowed infrared spectrum.
- Transitions only occur when the driving frequency  $\omega$  is resonant with the HO state spacing  $\omega_0$ . This indicates that transitions are only allowed between neighboring levels, with  $\Delta n = \pm 1$ . This is because to first order, the  $\hat{\mu}$  operator only connects states on adjacent rungs of the ladder. Two phenomena can relax this selection rule: (a) higher order terms in the dipole expansion, and (b) anharmonicity of the vibrational potential well. In most cases, the “fundamental”  $\Delta n = \pm 1$  transitions always have vastly larger probabilities than “overtone” transitions with  $\Delta n = \pm 2, \pm 3, \dots$ .

### 3 Raman scattering

Raman scattering is another common form of vibrational spectroscopy which does not involve direct absorption or emission of radiation. Instead, it involves the inelastic scattering of incident radiation accompanied by a change in the internal state of the molecule. In the following, we will use  $\omega_i$  to represent the frequency of the incident radiation,  $\omega_s$  to represent the frequency of the scattered radiation which appears in the lineshape of the detected spectrum, and  $\omega_0$  to represent our molecular vibrational frequency within the HO approximation.

Technically we need higher-order perturbation theory to describe Raman scattering, because transitions between pairs of states are induced by the action of *two* light fields of different frequencies: the incident, and the scattered. However, we can describe Raman scattering quite accurately if we replace the molecular dipole moment with an *induced dipole moment* generated by the incident field.

The incident light with electric field  $\underline{E}(t) = \underline{E} \cos(\omega_i t)$  polarizes the molecule according to the molecule’s electric polarizability tensor  $\underline{\alpha}$ :

$$\hat{\mu}_I = \underline{\hat{\alpha}} \cdot \underline{E} \cos(\omega_i t) \quad (54)$$

$$\begin{bmatrix} \mu_{Ix} \\ \mu_{Iy} \\ \mu_{Iz} \end{bmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} \cos(\omega_i t) \quad (55)$$

$\underline{\alpha}$  which describes the ease with which the distribution of charges in a molecule is distorted by an external electric field. It is a second rank tensor whose matrix elements  $\alpha_{jk}$  describe how well a light field polarized along axis  $j$  can induce a dipole moment along axis  $k$ . Note that in a spherically symmetric atom, the polarizability can be expressed by a single scalar quantity. For molecules with lower-than-spherical symmetry, the polarizability is anisotropic and requires the use of a tensor.

To simplify our considerations here, we will take our driving field polarized along the lab-frame  $z$  axis:  $\underline{E} = |E| \hat{z}$ . We will additionally only look for outgoing light polarized along  $z$ , which can only interact with the  $z$  component of the induced dipole:

$$\hat{\mu}_{Iz}(t) = \hat{\alpha}_{zz} \cdot |E| \cos(\omega_i t) \quad (56)$$

In order to treat the dynamics of this induced dipole as the molecule vibrates, we will follow much the same procedure that we did for the HO infrared absorption spectrum. We take the polarizability to be a weak function of vibrational displacement  $\hat{q}$ :

$$\hat{\alpha}_{zz} = \hat{\alpha}_{zz,0} + \left( \frac{d\hat{\alpha}_{zz}}{dq} \right)_0 \hat{q} + \dots \quad (57)$$

$$\rightarrow \hat{\mu}_{Iz}(t) \approx \left[ \hat{\alpha}_{zz,0} + \left( \frac{d\hat{\alpha}_{zz}}{dq} \right)_0 \hat{q} \right] |E| \cos(\omega_i t) \quad (58)$$

We can now begin to evaluate the lineshape of scattered light as:

$$S(\omega_s) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega_s t} \sum_n p_n \langle \psi_n | \hat{\mu}_{Iz}(0) \cdot \hat{\mu}_{Iz}(t) | \psi_n \rangle \quad (59)$$

It's easier to evaluate just the bra-ket term first:

$$\langle \psi_n | \hat{\mu}_{Iz}(0) \cdot \hat{\mu}_{Iz}(t) | \psi_n \rangle \quad (60)$$

$$= \langle \psi_n | \left[ \hat{\alpha}_{zz,0} + \left( \frac{d\hat{\alpha}_{zz}}{dq} \right)_0 \hat{q}(0) \right] |E| \cos(\omega_i t) \cdot \left[ \hat{\alpha}_{zz,0} + \left( \frac{d\hat{\alpha}_{zz}}{dq} \right)_0 \hat{q}(t) \right] |E| \cos(\omega_i t) | \psi_n \rangle \quad (61)$$

$$= |\alpha_{zz,0}|^2 |E|^2 \cos(\omega_i t) + \left( \frac{d\alpha_{zz}}{dq} \right)_0^2 |E|^2 \cos(\omega_i t) \langle \psi_n | \hat{q}(0) \cdot \hat{q}(t) | \psi_n \rangle \quad (62)$$

Note that we've dropped the cross terms which only feature one multiple of  $\hat{q}(0)$  or  $\hat{q}(t)$  because  $\langle \psi_n | \hat{q} | \psi_n \rangle = 0$  for all HO eigenfunctions.

We know from our previous infrared spectroscopy calculations that:

$$\langle \psi_n | \hat{q}(0) \cdot \hat{q}(t) | \psi_n \rangle = \frac{\hbar}{2m\omega_0} \langle \psi_n | \left[ \hat{a}^\dagger + \hat{a} \right] \cdot \left[ \hat{a}^\dagger \cdot e^{i\omega_0 t} + \hat{a} \cdot e^{-i\omega_0 t} \right] | \psi_n \rangle \quad (63)$$

$$= \frac{\hbar}{2m\omega_0} \left[ n e^{-i\omega_0 t} + (n+1) e^{i\omega_0 t} \right] \quad (64)$$

Therefore, Eqn. 62 becomes:

$$|\alpha_{zz,0}|^2 |E|^2 \cos(\omega_i t) + \frac{\hbar}{2m\omega_0} \left( \frac{d\alpha_{zz}}{dq} \right)_0^2 |E|^2 \cos(\omega_i t) \left[ n e^{-i\omega_0 t} + (n+1) e^{i\omega_0 t} \right] \quad (65)$$

$$\approx |\alpha_{zz,0}|^2 |E|^2 \cos(\omega_i t) + \frac{\hbar}{2m\omega_0} \left( \frac{d\alpha_{zz}}{dq} \right)_0^2 |E|^2 (n+1) \left[ \cos((\omega_i + \omega_0)t) + \cos((\omega_i - \omega_0)t) \right] \quad (66)$$



Putting this all together in Eqn. 59, we find:

$$S(\omega_s) \approx \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega_s t} \left[ \sum_n p_n |\alpha_{zz,0}|^2 |E|^2 \cos(\omega_i t) \right. \quad (67)$$

$$\left. + p_n \frac{\hbar}{2m\omega_0} \left( \frac{d\alpha_{zz}}{dq} \right)_0^2 |E|^2 (n+1) \left[ \cos((\omega_i + \omega_0)t) + \cos((\omega_i - \omega_0)t) \right] \right]$$

$$= \frac{1}{2\pi} \sum_n p_n |\alpha_{zz,0}|^2 |E|^2 \underbrace{\delta(\omega_s - \omega_i)}_{\text{Rayleigh}} \quad (68)$$

$$+ p_n \frac{\hbar}{2m\omega_0} \left( \frac{d\alpha_{zz}}{dq} \right)_0^2 |E|^2 (n+1) \left[ \underbrace{\delta(\omega_s - (\omega_i + \omega_0))}_{\text{anti-Stokes}} + \underbrace{\delta(\omega_s - (\omega_i - \omega_0))}_{\text{Stokes}} \right]$$

The big takeaways are:

- The zeroth order components of the polarizability like  $\alpha_{zz,0}$  give rise to elastic Rayleigh scattering, where the incident and scattered fields have the same frequency, and the vibrational state of the molecule is left unchanged.
- For proper Raman scattering, the vibrational quantum number of the molecule can be changed by  $\Delta n = \pm 1$  just as we saw for infrared absorption.  $\Delta n = +1$  corresponds to Stokes shifted Raman scattering, where the molecule absorbs energy and scatters a photon of a lower frequency, while  $\Delta n = -1$  corresponds to anti-Stokes shifted Raman scattering, where the molecule gives up energy to the scattered field.
- Raman scattering can only lead to transitions in vibrational modes whose displacement changes the polarizability of the molecule, e.g.  $\left( \frac{d\alpha}{dq} \right)_0 \neq 0$ . In polyatomic molecules, vibrational modes of different symmetries can enable Raman scattering along different polarization axes.

