

## 6.0. A Classical Description of Spectroscopy

The traditional quantum mechanical treatment of spectroscopy is often a rather static representation of the rather dynamic process of light interacting with matter. The dynamic picture emerges from a time-domain description, which is similar to the classical treatment of spectroscopy. Much of the physical intuition that is helpful in understanding the nature of light-matter interaction in spectroscopy naturally emerges from the classical view. Let's review that:

The classical view begins with the observation that atoms and molecules are composed of charged particles, and these charges are the handle by which an electromagnetic field exerts a force on the atom or molecule. The force exerted on the molecules depends on the strength of the field, the magnitude of the charges, and how far the charges move.

The simplest elements of a model that captures what happens in absorption spectroscopy require us to consider a charged particle in a bound potential interacting with a harmonic driving force. The matter can be expressed in terms of a particle with charge  $q$  under the influence of a harmonic potential (the leading term in the expansion of any bound potential in the coordinate  $Q$ ):

$$V(t) = \frac{1}{2}kQ^2, \quad (1)$$

The light field we will take as plane electromagnetic waves. The simplest expression for the light-matter interaction potential is

$$V(t) = -\bar{\mu} \cdot \bar{E}(t), \quad (2)$$

the electric field interacting with the dipoles of the system.

The classical description of this system starts with Newton's equation of motion  $F=ma$ , which we write as

$$m \frac{\partial^2 Q}{\partial t^2} = F_{res} + F_{damp} + F_{ext} \quad (3)$$

On the right hand side of eq. (3) there are three forces: the harmonic restoring force, a damping force, and the external driving force exerted by the light. Remembering that

$$F = -\frac{\partial V}{\partial Q} \quad (4)$$

We can write eq. (4) as

$$m \frac{\partial^2 Q}{\partial t^2} = -kQ - b \frac{\partial Q}{\partial t} + F_0 \cos(\omega t) \quad (5)$$

Here, for the field, we have only considered the time-dependence  $\bar{E}(t) = \bar{E}_0 \cos(\omega t)$  and the amplitude of the driving force

$$F_0 = \left( \frac{\partial \bar{\mu}}{\partial Q} \right) \cdot \bar{E}_0. \quad (6)$$

Eq. (6) indicates that increasing the force on the oscillator is achieved by raising the magnitude of the field, increasing how much the charge is displaced, or improving the alignment between the electric field polarization and the transition dipole moment.

We can re-write eq. (5) as the driven harmonic oscillator equation:

$$\frac{\partial^2 Q}{\partial t^2} + 2\gamma \frac{\partial Q}{\partial t} + \omega_0^2 Q = \frac{F_0}{m} \cos(\omega t) \quad (7)$$

Here the damping constant  $\gamma = b/2m$  and the harmonic resonance frequency  $\omega_0 = \sqrt{k/m}$ .

Let's first look at the solution to eq. (7) for a couple of simple cases. First, for the case that there is no damping or driving force ( $\gamma = F_0 = 0$ ), we have simple harmonic solutions in which oscillate at a frequency  $\omega_0$ :  $Q(t) = A \sin(\omega_0 t) + B \cos(\omega_0 t)$ . Let's just keep the *sin* term for now. Now if you add damping to the equation:  $Q(t) = A e^{-\gamma t} \sin \Omega_0 t$ . The coordinate oscillates at a reduced frequency  $\Omega_0 = \sqrt{\omega_0^2 - \gamma^2}$ . As we continue, let's assume a case with weak damping for which  $\Omega_0 \approx \omega_0$ .

The full solution to eq. (7) takes the form

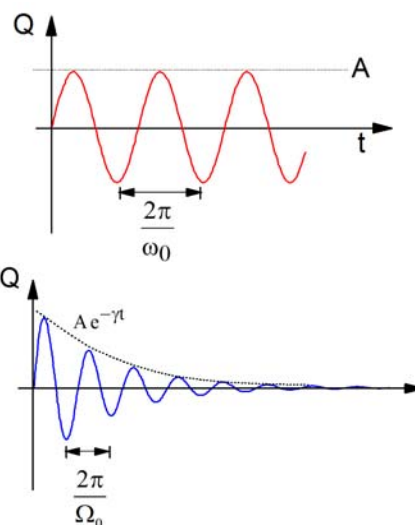
$$Q(t) = \frac{F_0/m}{\sqrt{(\omega_0^2 - \omega^2)^2 + 4\gamma^2 \omega^2}} \sin(\omega t + \beta) \quad (8)$$

Where  $\tan \beta = \omega_0^2 - \omega^2 / 2\gamma\omega$ . (9)

So this solution to the displacement of the particle says that the amplitude certainly depends on the magnitude of the driving force, but more importantly on the resonance condition. The frequency of the driving field should match the natural resonance frequency of the system,  $\omega_0 \approx \omega$  ...like pushing someone on a swing. When you drive the system at the resonance frequency there will be an efficient transfer of power to the oscillator, but if you push with arbitrary frequency, nothing will happen. Indeed, that is what an absorption spectrum is: a measure of the power absorbed by the system from the field.

Notice that the coordinate oscillates at the driving frequency  $\omega$  and not at the resonance frequency  $\omega_0$ . Also, the particle oscillates as a *sin*, that is,  $90^\circ$  out-of-phase with the field when driven on resonance. This reflects the fact that the maximum force can be exerted on the particle when it is stationary at the turning points. The phase shift  $\beta$ , depends varies with the detuning from resonance.

Now we can make some simplifications to eq. (8) and calculate the absorption spectrum. For weak damping  $\gamma \ll \omega_0$  and near resonance  $\omega_0 \approx \omega$ , we can write

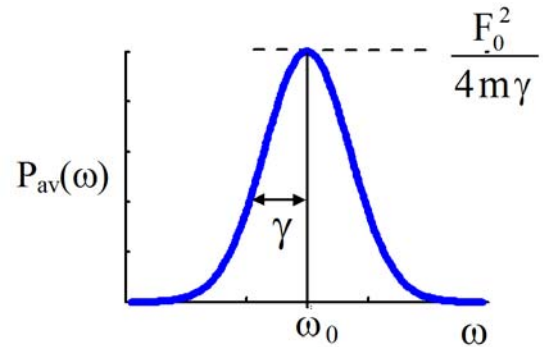


$$(\omega_0^2 - \omega^2)^2 = (\omega_0 - \omega)^2 (\omega_0 + \omega)^2 \approx 4\omega_0^2 (\omega_0 - \omega)^2 \quad (10)$$

The absorption spectrum is a measure of the power transferred to the oscillator, so we can calculate it by finding the power absorbed from the force on the oscillator times the velocity, averaged over a cycle of the field.

$$\begin{aligned} P_{avg} &= \left\langle F(t) \cdot \frac{\partial Q}{\partial t} \right\rangle_{avg} \\ &= \frac{\gamma F_0^2}{2m} \frac{1}{(\omega - \omega_0)^2 + \gamma^2} \end{aligned} \quad (11)$$

This is the Lorentzian lineshape, which is peaked at the resonance frequency and has a line width of  $2\gamma$  (full width half-maximum, FWHM). The area under the lineshape is  $\pi F_0^2 / 4m$ .



## 6.1. Time-Correlation Function Description of Absorption Lineshape

The interaction of light and matter as we have described from Fermi's Golden Rule gives the rates of transitions between discrete eigenstates of the material Hamiltonian  $H_0$ . The frequency dependence to the transition rate is proportional to an absorption spectrum. We also know that interaction with the light field prepares superpositions of the eigenstates of  $H_0$ , and this leads to the periodic oscillation of amplitude between the states. Nonetheless, the transition rate expression really seems to hide any time-dependent description of motions in the system. An alternative approach to spectroscopy is to recognize that the features in a spectrum are just a frequency domain representation of the underlying molecular dynamics of molecules. For absorption, the spectrum encodes the time-dependent changes of the molecular dipole moment for the system, which in turn depends on the position of electrons and nuclei.

A time-correlation function for the dipole operator can be used to describe the dynamics of an equilibrium ensemble that dictate an absorption spectrum. We will make use of the transition rate expressions from first-order perturbation theory that we derived in the previous section to express the absorption of radiation by dipoles as a correlation function in the dipole operator. Let's start with the rate of absorption and stimulated emission between an initial state  $|k\rangle$  and final state  $|\ell\rangle$  induced by a monochromatic field

$$w_{k\ell} = \frac{\pi E_0^2}{2\hbar^2} \left| \langle k | \hat{\epsilon} \cdot \vec{\mu} | \ell \rangle \right|^2 \left[ \delta(\omega_{k\ell} - \omega) + \delta(\omega_{k\ell} + \omega) \right] \quad (6.1)$$

We would like to use this to calculate the experimentally observable absorption coefficient (cross-section) which describes the transmission through the sample

$$T = \exp[-\Delta N \alpha(\omega) L]. \quad (6.2)$$

The absorption cross section describes the rate of energy absorption per unit time relative to the intensity of light incident on the sample

$$\alpha = \frac{\dot{E}_{rad}}{I}. \quad (6.3)$$

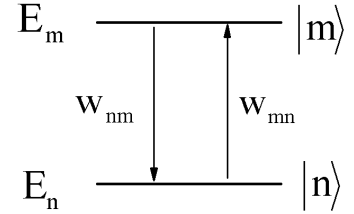
The incident intensity is

$$I = \frac{c}{8\pi} E_0^2. \quad (6.4)$$

If we have two discrete states  $|m\rangle$  and  $|n\rangle$  with  $E_m > E_n$ , the rate of energy absorption is proportional to the absorption rate and the transition energy

$$\dot{E}_{rad} = w_{nm} \cdot \hbar \omega_{nm}. \quad (6.5)$$

For an ensemble this rate must be scaled by the probability of occupying the initial state. More generally, we want to consider the rate of energy loss from the field as a result of the difference in rates of absorption and stimulated emission between states populated with a thermal distribution. So, summing all possible initial and final states  $|\ell\rangle$  and  $|k\rangle$  over all possible upper and lower states  $|m\rangle$  and  $|n\rangle$  with  $E_m > E_n$



$$\begin{aligned} \dot{E}_{rad} &= \sum_{\ell, k=m, n} p_{\ell} w_{k\ell} \hbar \omega_{k\ell} \\ &= \frac{\pi E_0^2}{2\hbar} \sum_{\ell, k=m, n} \omega_{k\ell} p_{\ell} \left| \langle k | \hat{\epsilon} \cdot \bar{\mu} | \ell \rangle \right|^2 \left[ \delta(\omega_{k\ell} - \omega) + \delta(\omega_{k\ell} + \omega) \right]. \end{aligned} \quad (6.6)$$

The cross section including absorption  $|n\rangle \rightarrow |m\rangle$  and stimulated emission  $|m\rangle \rightarrow |n\rangle$  terms is:

$$\alpha(\omega) = \frac{4\pi^2}{\hbar c} \sum_{n, m} \left[ \omega_{mn} p_n \left| \langle m | \hat{\epsilon} \cdot \bar{\mu} | n \rangle \right|^2 \delta(\omega_{mn} - \omega) + \omega_{nm} p_m \left| \langle n | \hat{\epsilon} \cdot \bar{\mu} | m \rangle \right|^2 \delta(\omega_{nm} + \omega) \right] \quad (6.7)$$

To simplify this we note:

- 1) Since  $\delta(x) = \delta(-x)$ ,  $\delta(\omega_{nm} + \omega) = \delta(-\omega_{nm} + \omega) = \delta(\omega_{mn} - \omega)$ .
- 2) The matrix elements squared in the two terms are the same:  $\left| \langle n | \hat{\epsilon} \cdot \bar{\mu} | m \rangle \right|^2 = \left| \langle m | \hat{\epsilon} \cdot \bar{\mu} | n \rangle \right|^2$  For shorthand we will write  $|\bar{\mu}_{mn}|^2$
- 3)  $\omega_{mn} = -\omega_{nm}$ .

So,

$$\alpha(\omega) = \frac{4\pi^2}{\hbar c} \sum_{n, m} \omega_{mn} (p_n - p_m) |\bar{\mu}_{mn}|^2 \delta(\omega_{mn} - \omega) \quad (6.8)$$

Here we see that the absorption coefficient depends on the population difference between the two states. This is expected since absorption will lead to loss of intensity, whereas stimulated emission

leads to gain. With equal populations in the upper and lower state, no change to the incident field would be expected. Since  $p_\ell = \exp[-\beta E_\ell]/Z$

$$p_n - p_m = p_n (1 - \exp[-\beta \hbar \omega_{nm}]) \quad (6.9)$$

$$\alpha(\omega) = \frac{4\pi^2}{\hbar c} \omega (1 - e^{-\beta \hbar \omega}) \sum_{n,m} p_n |\bar{\mu}_{nm}|^2 \delta(\omega_{nm} - \omega) \quad (6.10)$$

Note, that the two  $\omega_{nm}$  factors in eq. (6.8) have just been replaced with  $\omega$  because the delta function enforces this equality. We can now separate  $\alpha$  into a product of factors that represent the field, and the matter, where the matter is described by  $\sigma(\omega)$ , the absorption lineshape.

$$\alpha(\omega) = \frac{4\pi^2}{\hbar c} \omega (1 - e^{-\beta \hbar \omega}) \sigma(\omega) \quad (6.11)$$

$$\sigma(\omega) = \sum_{n,m} p_n |\bar{\mu}_{nm}|^2 \delta(\omega_{nm} - \omega) \quad (6.12)$$

We have already indicated that expressions of the form (6.12) can be expressed as a correlation function in the operator  $\mu$ , so following our earlier derivation,

$$\sigma(\omega) = \int_{-\infty}^{+\infty} dt e^{-i\omega t} \langle \hat{\epsilon} \cdot \bar{\mu}_l(0) \hat{\epsilon} \cdot \bar{\mu}_l(t) \rangle \quad (6.13)$$

Here, I added back the light field polarization for a moment. If you assume an isotropic light field, then you can show that (6.13) can be written as

$$\sigma(\omega) = \frac{1}{3} \int_{-\infty}^{+\infty} dt e^{-i\omega t} \langle \bar{\mu}_l(0) \bar{\mu}_l(t) \rangle \quad (6.14)$$

or

$$\sigma(\omega) = \frac{1}{3} \int_{-\infty}^{+\infty} dt e^{i\omega t} \langle \bar{\mu}_l(t) \bar{\mu}_l(0) \rangle \quad (6.15)$$

The absorption lineshape is given by the Fourier transform of the dipole correlation function. The correlation function describes the time-dependent behavior or spontaneous fluctuations in the dipole moment in absence of  $E$  field and contains information on states of system and broadening due to relaxation.

## 6.2. Examples

So the absorption spectrum in any frequency region is given by the Fourier transform over the dipole correlation function that describes the time-evolving charge distributions in molecules, solids, and nanosystems. Let's consider how this manifests itself in a few different spectroscopies, which have different contributions to the dipole operator. In general the dipole operator is a relatively simple representation of the charged particles of the system:

$$\bar{\mu} = \sum_i q_i (\bar{r}_i - \bar{r}_0). \quad (6.16)$$

The complexity arises from the time-dependence of this operator, which evolves under the full Hamiltonian for the system:

$$\bar{\mu}(t) = e^{iH_0 t} \bar{\mu}(0) e^{-iH_0 t} \quad (6.17)$$

$$H_0 = H_{elec} + H_{vib} + H_{rot} + H_{spin} + \dots + H_{bath} + \dots \quad (6.18)$$

The full Hamiltonian accounts for the dynamics of all electronic, nuclear, and spin degrees of freedom. It is expressed in eq. (6.18) in terms of separable contributions from those degrees of freedom and a bath Hamiltonian that contains all of the dark degrees of freedom not explicitly included in the dipole operator. (For now, I've left out terms such as  $H_{elec-vib}$  and  $H_{vib-rot}$  that involve pairwise couplings between different degrees of freedom). If we can write the Hamiltonian in this form, then the wavefunction for the system can be written as product states of the wavefunctions for the different degrees of freedom,

$$|\psi\rangle = |\psi_{elec} \psi_{vib} \psi_{rot} \dots \psi_{bath}\rangle \quad (6.19)$$

and the correlation function can be separated into a product of correlation functions from various sources:

$$C_{\mu\mu}(t) = C_{elec}(t) C_{vib}(t) C_{rot}(t) \dots \quad (6.20)$$

$$C_{vib}(t) = \sum_{n(vib)} p_n \langle \psi_{vib,n} | e^{iH_{vib} t} \mu e^{-iH_{vib} t} \mu | \psi_{vib,n} \rangle \quad (6.21)$$

The net correlation function will have oscillatory components at many frequencies and its Fourier transform will give the full absorption spectrum from the ultraviolet to the microwave regions of the spectrum. Generally speaking the highest frequency contributions (electronic or UV/Vis) will be modulated by contributions from lower frequency motions (...such as vibrations and rotations). However, we can separately analyze each of these contributions to the spectrum.

## Atomic transitions

$H_0 = H_{atom}$ . For hydrogenic orbitals,  $|n\rangle \rightarrow |n \ell m_\ell\rangle$ .

## Rotational spectroscopy

From a classical perspective, the dipole moment can be written in terms of a permanent dipole moment with amplitude and direction

$$\bar{\mu} = \mu_0 \hat{u} \quad (6.22)$$

$$\sigma(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{-i\omega t} \mu_0^2 \langle \hat{\varepsilon} \cdot \hat{u}(0) \hat{\varepsilon} \cdot \hat{u}(t) \rangle \quad (6.23)$$

The lineshape is the Fourier transform of the rotational motion of the permanent dipole vector in the laboratory frame. The frequency of the resonance would depend on the rate of rotation – the angular momentum and the moment of inertia. Collisions or other damping would lead to the broadening of the lines.

Quantum mechanically we expect a series of rotational resonances that mirror the thermal occupation and degeneracy of rotational states for the system. Taking a case with cylindrical symmetry as an example, the Hamiltonian is

$$H_{rot} = \frac{\bar{L}^2}{2I} \quad (6.24)$$

and the wavefunctions are spherical harmonics are described by

$$\begin{aligned} \bar{L}^2 |Y_{J,M}\rangle &= \hbar^2 J(J+1) |Y_{J,M}\rangle \\ L_Z |Y_{J,M}\rangle &= M\hbar |Y_{J,M}\rangle \end{aligned} \quad (6.25)$$

If we take a dipole operator in the form of eq. (6.22), then the far-infrared rotational spectrum will be described by the correlation function

$$C_{rot}(t) = \sum_{J,M} p_{J,M} |\mu_0|^2 \langle Y_{J,M} | e^{iH_{rot}t} (\hat{u} \cdot \hat{\varepsilon}) e^{-iH_{rot}t} (\hat{u} \cdot \hat{\varepsilon}) | Y_{J,M} \rangle. \quad (6.26)$$

Here the evaluation of this correlation function involves an orientational average. For instance, the matrix element

$$\langle Y_{J',M'} | (\hat{u} \cdot \hat{\varepsilon}_Z) | Y_{J,M} \rangle = \int_0^{2\pi} d\varphi \int_0^\pi \sin\theta d\theta Y_{J',M'}^* \cos\theta Y_{J,M}. \quad (6.27)$$

These functions are readily evaluated using reduction formulas such as

$$\cos\theta |Y_{J,M}\rangle = c_+ |Y_{J+1,M}\rangle + c_- |Y_{J-1,M}\rangle \quad (6.28)$$

$$c_+ = \sqrt{\frac{(J+1)^2 - M^2}{4(J+1)^2 - 1}} \quad c_- = \sqrt{\frac{J^2 + M^2}{4J^2 - 1}} \quad (6.29)$$

and the orthogonality of spherical harmonics

$$\langle Y_{J',M'} | Y_{J,M} \rangle = 4\pi \delta_{J',J} \delta_{M',M}. \quad (6.30)$$

These expressions in eq. (6.26) lead to the correlation function

$$C_{rot}(t) = \frac{1}{Z_{rot}} \sum_J (2J+1) e^{-\beta \bar{B}J(J+1)} \left[ e^{-i(J+1)2\bar{B}t} + e^{iJ2\bar{B}t} \right] \quad (6.31)$$

where the rotational constant is

$$\bar{B} = \frac{\hbar}{4\pi I c}. \quad (6.32)$$

Fourier transforming eq. (6.31) leads to the lineshape

$$\sigma_{rot}(\omega) = \frac{1}{2\pi Z_{rot}} \sum_J (2J+1) e^{-\beta \bar{B}J(J+1)} \left[ \delta(\omega - i2\bar{B}(J+1)) + \delta(\omega + i2\bar{B}J) \right]. \quad (6.33)$$

The two terms reflect the fact that each thermally populated level with  $J > 0$  contributes both to absorptive and stimulated emission processes, and the observed intensity reflects the difference in populations.

## **IR Vibrational Spectroscopy**

Vibrational spectroscopy can be described by taking the dipole moment to be weakly dependent on the displacement of vibrational coordinates  $q$

$$\bar{\mu} = \bar{\mu}_0 + \left. \frac{\partial \bar{\mu}}{\partial q} \right|_{q=q_0} q + \dots \quad (6.34)$$

Here the first expansion term is the permanent dipole moment and the second term is the transition dipole moment. If we are performing our ensemble average over vibrational states, the lineshape becomes the Fourier transform of a correlation function in the vibrational coordinate

$$\sigma(\omega) = \left| \frac{\partial \bar{\mu}}{\partial q} \right|^2 \int_{-\infty}^{+\infty} dt e^{-i\omega t} \langle q(0)q(t) \rangle \quad (6.35)$$

The vector nature of the transition dipole has been dropped here. So the time-dependent dynamics of the vibrational coordinate dictate the IR lineshape.

This approach holds for the classical and quantum mechanical cases. In the case of quantum mechanics, the change in charge distribution in the transition dipole moment is replaced with the equivalent transition dipole matrix element. If we take the vibrational Hamiltonian to be that of a harmonic oscillator,

$$H_{vib} = \frac{1}{2m} p^2 + \frac{1}{2} m \omega_0^2 q^2 = \hbar \omega_0 \left( a^\dagger a + \frac{1}{2} \right), \quad (6.36)$$

then the time-dependence of the vibrational coordinate, expressed as raising and lowering operators is

$$q(t) = \sqrt{\frac{\hbar}{2m\omega_0}} \left( a^\dagger e^{i\omega_0 t} + a e^{-i\omega_0 t} \right). \quad (6.37)$$

The absorption lineshape is then obtained from eq. (6.35).

$$\sigma_{vib}(\omega) = \left| \frac{\partial \bar{\mu}}{\partial q} \right|^2 \frac{1}{Z_{vib}} \sum_n e^{-\beta \hbar n \omega_0} \left[ (n+1) \delta(\omega - \omega_0) + n \delta(\omega + \omega_0) \right] \quad (6.38)$$

or for the low temperature limit applicable to most vibrations under ambient conditions:

$$\sigma_{vib}(\omega) = \left| \frac{\partial \bar{\mu}}{\partial q} \right|^2 \delta(\omega - \omega_0). \quad (6.39)$$

### **Raman Spectroscopy**

Technically, we need second-order perturbation theory to describe Raman scattering, because transitions between two states are induced by the action of two light fields whose frequency difference equals the energy splitting between states. But much the same result is obtained if we replace the dipole operator with an induced dipole moment generated by the incident field:  $\bar{\mu} \Rightarrow \bar{\mu}_{ind}$ . The incident field  $E_i$  polarizes the molecule,

$$\bar{\mu}_{ind} = \bar{\alpha} \cdot \bar{E}_i(t). \quad (6.40)$$

( $\bar{\alpha}$  is the polarizability), and the scattered light field results from the interaction with this induced dipole

$$\begin{aligned} V(t) &= -\bar{\mu}_{ind} \cdot \bar{E}_s(t) \\ &= \bar{E}_s(t) \cdot \bar{\alpha} \cdot \bar{E}_i(t) \\ &= E_s(t) E_i(t) (\hat{\epsilon}_s \cdot \bar{\alpha} \cdot \hat{\epsilon}_i) \end{aligned} \quad (6.41)$$

Here we have written the polarization components of the incident ( $i$ ) and scattered ( $s$ ) light projecting onto the polarizability tensor  $\bar{\bar{\alpha}}$ . Equation (6.41) leads to an expression for the Raman lineshape as

$$\begin{aligned}\sigma(\omega) &= \int_{-\infty}^{+\infty} dt e^{-i\omega t} \langle \hat{\epsilon}_s \cdot \bar{\bar{\alpha}}(0) \cdot \hat{\epsilon}_i \hat{\epsilon}_s \cdot \bar{\bar{\alpha}}(t) \cdot \hat{\epsilon}_i \rangle \\ &= \int_{-\infty}^{+\infty} dt e^{-i\omega t} \langle \bar{\bar{\alpha}}(0) \bar{\bar{\alpha}}(t) \rangle\end{aligned}\quad (6.42)$$

To evaluate this, the polarizability tensor can also be expanded in the nuclear coordinates

$$\bar{\bar{\alpha}} = \bar{\bar{\alpha}}_0 + \left. \frac{\partial \bar{\bar{\alpha}}}{\partial q} \right|_{q=q_0} q + \dots \quad (6.43)$$

where the leading term would lead to Rayleigh scattering and rotational Raman spectra, and the second term would give vibrational Raman scattering.

Also remember that the polarizability tensor is a second rank tensor that tells you how well a light field polarized along  $i$  can induce a dipole moment (light-field-induced charge displacement) in the  $s$  direction. For cylindrically symmetric systems which have a polarizability component  $\alpha_{\parallel}$  along the principal axis of the molecule and a component  $\alpha_{\perp}$  perpendicular to that axis, this usually takes the form

$$\bar{\bar{\alpha}} = \begin{pmatrix} \alpha_{\parallel} & & \\ & \alpha_{\perp} & \\ & & \alpha_{\perp} \end{pmatrix} = \alpha \mathbf{I} + \frac{1}{3} \beta \begin{pmatrix} 2 & & \\ & -1 & \\ & & -1 \end{pmatrix} \quad (6.44)$$

where  $\alpha$  is the isotropic component of polarizability tensor and  $\beta$  is the anisotropic component.

### 6.3. Ensemble Averaging and Line-Broadening

We have seen that an absorption lineshape can represent the dynamics of the dipole or be broadened by energy relaxation (i.e., coupling to continuum). However, there are numerous processes that can influence the lineshape. These can be broken into intrinsically molecular and ensemble average effects. These can be further separated by dynamic processes (homogeneous broadening) and static effects (inhomogeneous broadening). Let's review the phenomenological description. The separation of these effects is a

#### 1. Homogeneous broadening

Several homogeneous (dynamic) line broadening mechanisms are possible, which are qualitatively captured by a time-scale  $T_2$ . If these processes are independent, the exponential rates for different contributions add:

$$\frac{1}{T_2} = \frac{1}{T_1} + \frac{1}{T_2^*} + \frac{1}{\tau_{or}} \quad (6.45)$$

##### a. Molecular processes

**Population Relaxation.** Population relaxation  $T_1$  refers to amplitude decay in the coherent superposition created by the light field as a result of its finite lifetime. This can have contributions from radiative decay (spontaneous emission processes) or non-radiative processes (i.e., coupling to continuum and IVR)

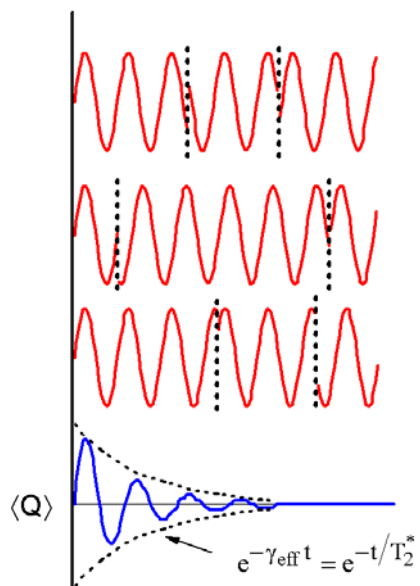
$$\frac{1}{T_1} = \frac{1}{\tau_{rad}} + \frac{1}{\tau_{NR}} \quad (6.46)$$

In this case, ensemble averaging doesn't change the measurement. All members of ensemble behave identically and the experimentally measured decay is the microscopic lifetime.

The observed population relaxation time depends on both the relaxation times of the upper and lower states ( $m$  and  $n$ ) being coupled by the field:  $1/T_1 = w_{mn} + w_{nm}$ . When the energy splitting is high, only the downward rate contributes, which is why the rate is often written  $1/2T_1$ .

## b. Ensemble processes

**Pure Dephasing.** Pure dephasing is characterized by a time constant  $T_2^*$  that characterizes the randomization of phase within an ensemble as a result of molecular interactions. This is a dynamic ensemble averaging effect in which the phase relationship of oscillation between members of the ensemble is gradually destroyed. Examples include collisions in a dense gas, or fluctuations induced by a solvent.

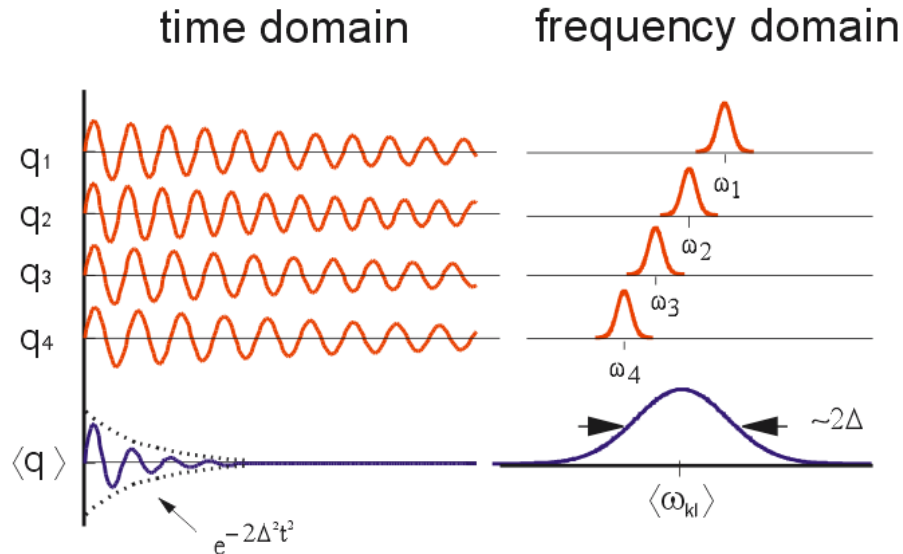


Orientational relaxation ( $\tau_{or}$ ) also leads to relaxation of the dipole correlation function and to line broadening. Since the correlation function depends on the projection of the dipole onto a fixed axis in the laboratory frame, randomization of the initial dipole orientations is an ensemble averaged dephasing effect. In solution, this process is commonly treated as an orientational diffusion problem in which  $\tau_{or}$  is proportional to the diffusion constant.

## 2. Inhomogeneous Broadening

Absorption lineshapes can also be broadened by a static distribution of frequencies. If molecules within the ensemble are influenced static environmental variations more than other processes, then the observed lineshape reports on the distribution of environments. This inhomogeneous

broadening is a static ensemble averaging effect, which hides the dynamical content in the homogeneous linewidth. The origin of the inhomogeneous broadening can be molecular (for instance a distribution of defects in crystals) or macroscopic (i.e. an inhomogeneous magnetic field in NMR).



The inhomogeneous linewidth is dictated the width of the distribution  $\Delta$ .

### Total Linewidth

The total observed broadening of the absorption lineshape reflects the contribution of all of these effects:

$$\langle \mu(0)\mu(t) \rangle \propto \exp\left[-t\left(\frac{1}{T_2^*} + \frac{1}{2T_1} + \frac{1}{\tau_{or}}\right)\right] e^{-\Delta^2 t^2/2} \quad (6.47)$$

These effects can be wrapped into a lineshape function  $g(t)$ . The lineshape for the broadening of a given transition can be written as the Fourier transform over the oscillating transition frequency damped and modulated by a complex  $g(t)$ :

$$\sigma(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{-i\omega t} e^{i\omega_{mn}t - g(t)} \quad (6.48)$$

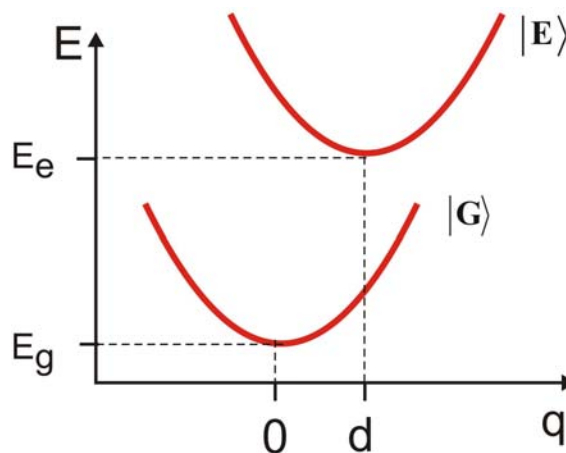
All of these effects can be present simultaneously in an absorption spectrum.

## 6.4 ELECTRONIC SPECTROSCOPY: DISPLACED HARMONIC OSCILLATOR MODEL<sup>1</sup>

Here we will start with one approach to a class of widely used models for the coupling of nuclear motions to an electronic transition that takes many forms and has many applications. We will look at the specific example of electronic absorption experiments, which leads to insight into the vibronic structure in absorption spectra. Spectroscopically, it is also used to describe wavepacket dynamics; coupling of electronic and vibrational states to intramolecular vibrations or solvent; or coupling of electronic states in solids or semiconductors to phonons. Further extensions of this model can be used to describe fundamental chemical rate processes, interactions of a molecule with a dissipative or fluctuating environment, and Marcus Theory for non-adiabatic electron transfer.

### Two-electronic states as displaced harmonic oscillators

We are interested in describing the electronic absorption spectrum for the case that the electronic energy depends on nuclear configuration. The simplified model for this is two identical harmonic oscillators potentials displaced from one another along a nuclear coordinate, and whose 0-0 energy splitting is  $E_e - E_g$ . We will calculate the electronic absorption spectrum in the interaction picture ( $H = H_0 + V(t)$ ) using the time-correlation



function for the dipole operator. The Hamiltonian for the matter represents two Born-Oppenheimer surfaces

$$H_0 = |G\rangle H_G \langle G| + |E\rangle H_E \langle E| \quad (6.1)$$

where the Hamiltonian describing the ground and excited states have contributions from the nuclear energy and the electronic energy

$$\begin{aligned} H_G &= E_g + H_g \\ H_E &= E_e + H_e \end{aligned} \quad (6.2)$$

The harmonic vibrational Hamiltonian has the same curvature in the ground and excited states, but the excited state is displaced by  $d$  relative to the ground state.

$$H_g = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 q^2 \quad (6.3)$$

$$H_e = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 (q-d)^2 \quad (6.4)$$

Now we are in a position to evaluate the dipole correlation function

$$C_{\mu\mu}(t) = \sum_{n=E,G} p_n \langle n | e^{iH_0 t/\hbar} \bar{\mu} e^{-iH_0 t/\hbar} \bar{\mu} | n \rangle. \quad (6.5)$$

with the time propagator

$$e^{-iH_0 t/\hbar} = |G\rangle e^{-i(H_g + E_g)t/\hbar} \langle G| + |E\rangle e^{-i(H_e + E_e)t/\hbar} \langle E| \quad (6.6)$$

We begin by making two approximations:

- 1) **Born-Oppenheimer Approximation**. Although this is implied in eq. (6.2) when we write the electronic energy as independent of  $q$ , specifically it means that we can write the state of the system as a product state in the electronic and nuclear configuration:

$$|G\rangle = |g, n\rangle \quad (6.7)$$

- 2) **Condon Approximation**. This approximation states that there is no nuclear dependence for the dipole operator. It is only an operator in the electronic states.

$$\bar{\mu} = |g\rangle \mu_{ge} \langle e| + |e\rangle \mu_{eg} \langle g| \quad (6.8)$$

Under all reasonable conditions, the system will only be on the ground electronic state at equilibrium,  $|g, n\rangle$ , and with the expression for the dipole operator (6.8), we find:

$$C_{\mu\mu}(t) = |\mu_{eg}|^2 e^{-i(E_e - E_g)t/\hbar} \langle e^{iH_g t/\hbar} e^{-iH_e t/\hbar} \rangle \quad (6.9)$$

Here the oscillations at the electronic energy gap are separated from the nuclear dynamics in the final factor, sometimes known as the dephasing function:

$$\begin{aligned} F(t) &= \langle e^{iH_g t/\hbar} e^{-iH_e t/\hbar} \rangle \\ &= \langle U_g^\dagger U_e \rangle \end{aligned} \quad (6.10)$$

Note that physically the dephasing function describes the time-dependent overlap of the initial nuclear wavefunction on the ground state with the time-evolution of the same wavepacket on the when initially projected onto the excited state

$$F(t) = \langle \varphi_g(t) | \varphi_e(t) \rangle. \quad (6.11)$$

This is a perfectly general expression that does not depend on the particular form of the potential. If you have knowledge of the nuclear and electronic eigenstates or the nuclear dynamics on your ground and excited state surfaces, this expression is your route to the absorption spectrum.<sup>2</sup>

To evaluate  $F(t)$ , it helps to realize that we can write the nuclear Hamiltonians as

$$H_g = \hbar\omega_0 \left( a^\dagger a + \frac{1}{2} \right) \quad (6.12)$$

$$H_e = \hat{D}^\dagger H_g \hat{D}. \quad (6.13)$$

Here  $D$  is the spatial displacement operator

$$\hat{D} = \exp(-ipd/\hbar) \quad (6.14)$$

which shifts an operator in space:

$$\hat{D}^\dagger q \hat{D} = q + d. \quad (6.15)$$

This allows us to express the excited state Hamiltonian in terms of a shifted ground state Hamiltonian in eq. (6.13), but also allows us to relate the time-propagators on the ground and excited states

$$e^{-iH_e t/\hbar} = \hat{D}^\dagger e^{-iH_g t/\hbar} \hat{D}. \quad (6.16)$$

Substituting eq. (6.16) into eq. (6.10) allows us to write

$$\begin{aligned} F(t) &= \langle U_g^\dagger e^{-idp/\hbar} U_g e^{idp/\hbar} \rangle \\ &= \langle e^{-idp(t)/\hbar} e^{idp(0)/\hbar} \rangle \end{aligned} \quad (6.17)$$

since

$$p(t) = U_g^\dagger p(0) U_g. \quad (6.18)$$

Up to now, everything we've written is general to any form of the potential, but here we will continue by evaluating the results for the specific case of a harmonic nuclear potential. The time-evolution of  $p$  is obtained by evaluating eq. (6.18) by applying eq. (6.12) to

$$p = \frac{i}{\sqrt{2}} (a^\dagger - a) \sqrt{m\hbar\omega_0}. \quad (6.19)$$

Remembering  $a^\dagger a = n$ , we find

$$\begin{aligned}
 U_g^\dagger a U_g &= e^{i n \omega_0 t} a e^{-i n \omega_0 t} = a e^{i(n-1)\omega_0 t} e^{-i n \omega_0 t} = a e^{-i \omega_0 t} \\
 U_g^\dagger a^\dagger U_g &= a^\dagger e^{+i \omega_0 t}
 \end{aligned}
 \tag{6.20}$$

which gives

$$p(t) = i \sqrt{\frac{m \hbar \omega_0}{2}} (a^\dagger e^{i \omega_0 t} - a e^{-i \omega_0 t}).
 \tag{6.21}$$

So for the dephasing function we now have

$$F(t) = \left\langle \exp\left[\underline{d} (a^\dagger e^{i \omega_0 t} - a e^{-i \omega_0 t})\right] \exp\left[-\underline{d} (a^\dagger - a)\right] \right\rangle,
 \tag{6.22}$$

where we have defined a dimensionless displacement variable

$$\underline{d} = d \sqrt{\frac{m \omega_0}{2 \hbar}}.
 \tag{6.23}$$

Since  $a^\dagger$  and  $a$  do not commute ( $[a^\dagger, a] = -1$ ), we split the exponential operators using the identities

$$e^{\hat{A} + \hat{B}} = e^{\hat{A}} e^{\hat{B}} e^{-\frac{1}{2}[\hat{A}, \hat{B}]}
 \tag{6.24}$$

$$e^{\lambda a^\dagger + \mu a} = e^{\lambda a^\dagger} e^{\mu a} e^{\frac{1}{2} \lambda \mu}.
 \tag{6.25}$$

This leads to

$$\begin{aligned}
 F(t) &= \left\langle \exp\left[\underline{d} a^\dagger e^{i \omega_0 t}\right] \exp\left[-\underline{d} a e^{-i \omega_0 t}\right] \exp\left[-\frac{1}{2} \underline{d}^2\right] \right. \\
 &\quad \left. \times \exp\left[-\underline{d} a^\dagger\right] \exp\left[\underline{d} a\right] \exp\left[-\frac{1}{2} \underline{d}^2\right] \right\rangle
 \end{aligned}
 \tag{6.26}$$

Now to simplify our work, let's specifically consider the low temperature case in which we are only in the ground vibrational state at equilibrium  $|n\rangle = |0\rangle$ . Since  $a|0\rangle = 0$  and  $\langle 0|a^\dagger = 0$ ,

$$e^{-\lambda a} |0\rangle = |0\rangle
 \tag{6.27}$$

$$\langle 0|e^{\lambda a^\dagger} = \langle 0|$$

and

$$F(t) = e^{-\underline{d}^2} \left\langle 0 \left| \exp\left[-\underline{d} a e^{-i \omega_0 t}\right] \exp\left[-\underline{d} a^\dagger\right] \right| 0 \right\rangle.
 \tag{6.28}$$

Since the operator defined through an expansion in raising operators, this expression is a bit tough to evaluate, as is. However, the evaluation becomes as easy as the previous step if we can exchange order of operators. Since

$$e^{\hat{A}} e^{\hat{B}} = e^{\hat{B}} e^{\hat{A}} e^{-[\hat{B}, \hat{A}]},
 \tag{6.29}$$

we write

$$\begin{aligned}
 F(t) &= e^{-\tilde{d}^2} \langle 0 | \exp[-\tilde{d} a^\dagger] \exp[-\tilde{d} a e^{-i\omega_0 t}] \exp[\tilde{d}^2 e^{-i\omega_0 t}] | 0 \rangle \\
 &= \exp[\tilde{d}^2 (e^{-i\omega_0 t} - 1)]
 \end{aligned}
 \tag{6.30}$$

So finally, we have the dipole correlation function:

$$C_{\mu\mu}(t) = |\mu_{eg}|^2 \exp[-i\omega_{eg}t + D(e^{-i\omega_0 t} - 1)] \tag{6.31}$$

$D$  is known as the Huang-Rhys parameter, and is a dimensionless factor related to the mean square displacement

$$D = \tilde{d}^2 = \frac{d^2 m \omega_0}{2\hbar} \tag{6.32}$$

It represents the strength of coupling to the nuclear degrees of freedom. Note we can write our correlation function as

$$C(t) = \sum_n p_n |\mu_{mn}|^2 e^{-i\omega_{mn}t - g(t)}. \tag{6.33}$$

Here  $g(t)$  is our lineshape function

$$g(t) = -D(e^{-i\omega_0 t} - 1). \tag{6.34}$$

## Absorption Lineshape and Franck-Condon Transitions

The absorption lineshape is obtained by Fourier transforming eq. (6.31)

$$\begin{aligned}\sigma_{abs}(\omega) &= \int_{-\infty}^{+\infty} dt e^{i\omega t} C_{\mu\mu}(t) \\ &= |\mu_{eg}|^2 e^{-D} \int_{-\infty}^{+\infty} dt e^{i\omega t} e^{-i\omega_{eg}t} \exp[De^{-i\omega_0 t}]\end{aligned}\quad (6.35)$$

If we now expand the final term as

$$\exp[De^{-i\omega_0 t}] = \sum_{j=0}^{\infty} \frac{1}{j!} D^j (e^{-i\omega_0 t})^j, \quad (6.36)$$

the lineshape is

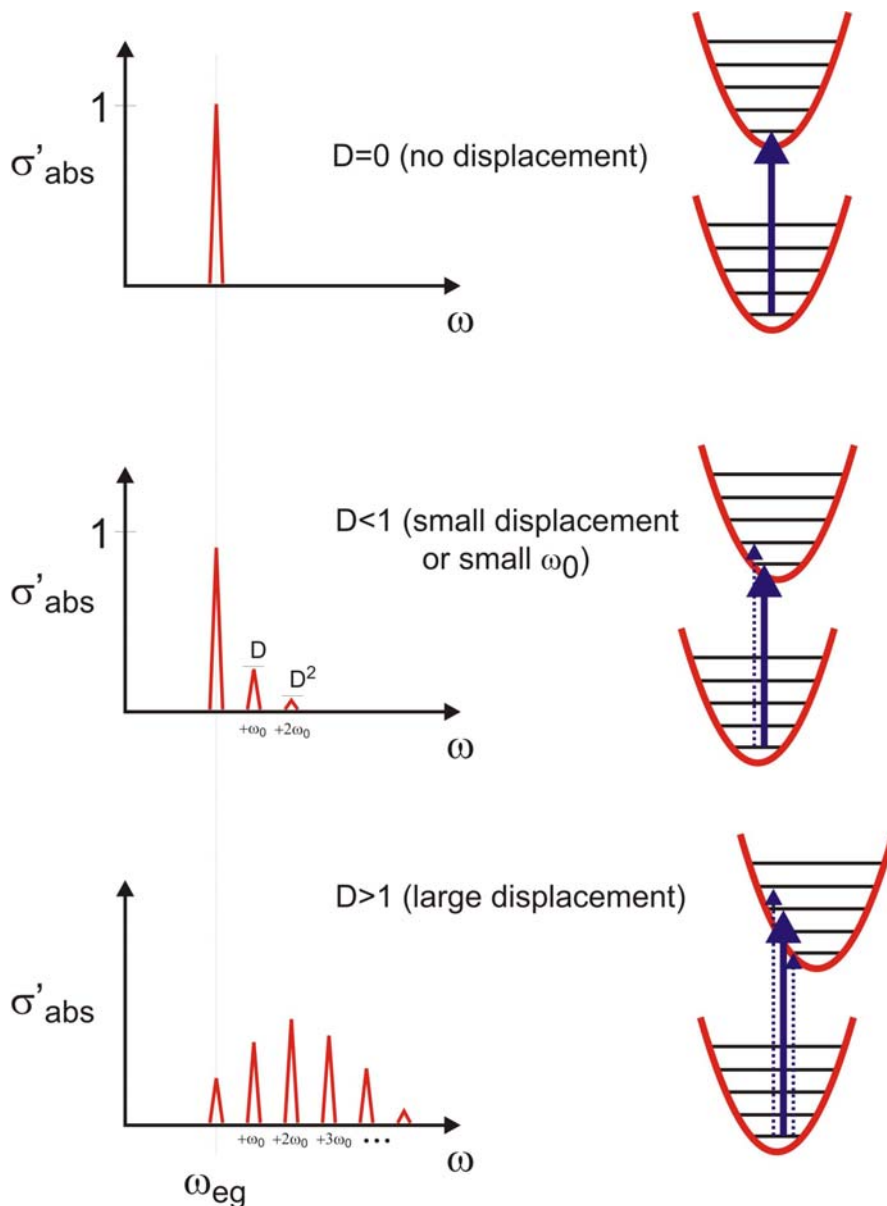
$$\sigma_{abs}(\omega) = |\mu_{eg}|^2 \sum_{j=0}^{\infty} e^{-D} \frac{1}{j!} D^j \delta(\omega - \omega_{eg} - j\omega_0). \quad (6.37)$$

The spectrum is a progression of absorption peaks rising from  $\omega_{eg}$ , separated by  $\omega_0$  with a Poisson distribution of intensities. This is a vibrational progression accompanying the electronic transition. The amplitude of each of these peaks are given by the Franck-Condon coefficients for the overlap of vibrational states in the ground and excited states

$$|\langle 0|v\rangle|^2 = e^{-D} \frac{1}{v!} D^v \quad (6.38)$$

The intensities of these peaks are dependent on  $D$ , which is a measure of the coupling strength between nuclear and electronic degrees of freedom.

Let's plot the normalized absorption lineshape  $\sigma'_{abs}(\omega) = \frac{\sigma_{abs}(\omega)}{e^{-D} |\mu_{eg}|^2}$  as a function of  $D$ .



For  $D < 1$ , the dependence of the energy gap on  $q$  is weak and the absorption maximum is at  $\omega_{eg}$  with  $n = 0$ , with the amplitude of the vibronic progression falling off at  $D^n$ . For  $D \gg 1$  (strong coupling), the transition with the maximum intensity is found for peak at  $n \approx D$ . So  $D$  corresponds roughly to the mean number of vibrational quanta excited from  $q = 0$  in the ground

state. This is the Franck-Condon principle, that transition intensities are dictated by the vertical overlap between nuclear wavefunctions in the two electronic surfaces.

To investigate the envelope for these transitions, we can perform a short time expansion of the correlation function applicable for  $t < 1/\omega_0$ . If we approximate the first term with damping

$$\exp(-i\omega_0 t) \approx 1 - i\omega_0 t - \frac{1}{2}\omega_0^2 t^2, \quad (6.39)$$

then the lineshape is

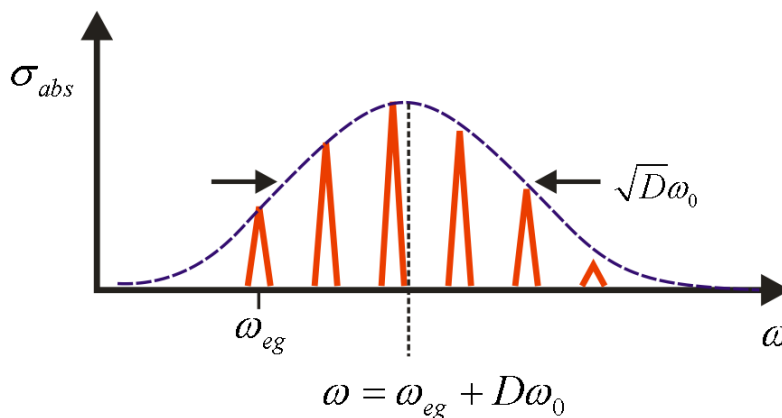
$$\begin{aligned} \sigma_{abs}(\omega) &= \left| \mu_{eg} \right|^2 \int_{-\infty}^{+\infty} dt e^{i\omega t} e^{-i\omega_{eg} t} e^{D(\exp(-i\omega_0 t) - 1)} \\ &\approx \left| \mu_{eg} \right|^2 \int_{-\infty}^{+\infty} dt e^{i(\omega - \omega_{eg} t)} e^{D[-i\omega_0 t - \frac{1}{2}\omega_0^2 t^2]} \\ &= \left| \mu_{eg} \right|^2 \int_{-\infty}^{+\infty} dt e^{i(\omega - \omega_{eg} - D\omega_0)t} e^{-\frac{1}{2}D\omega_0^2 t^2} \end{aligned} \quad (6.40)$$

This can be solved by completing the square, giving

$$\sigma_{abs}(\omega) = \sqrt{\pi} \left| \mu_{eg} \right|^2 \exp \left[ -\frac{(\omega - \omega_{eg} - D\omega_0)^2}{2D\omega_0^2} \right]. \quad (6.41)$$

The envelope has a Gaussian profile which is centered at Franck-Condon vertical transition

$$\omega = \omega_{eg} + D\omega_0. \quad (6.42)$$



Thus we can equate  $D$  with the mean number of vibrational quanta excited in  $|E\rangle$  on absorption from the ground state. Also, we can define the vibrational energy in  $|E\rangle$  on excitation at  $q = 0$

$$\lambda = D\hbar\omega_0 = \frac{1}{2}m\omega_0^2 d^2. \quad (6.43)$$

$\lambda$  is known as the reorganization energy. This is the energy that must be dissipated for vibrational relaxation on the excited state surface.





## 6.5. DISPLACED HARMONIC OSCILLATOR MODEL: COUPLING TO A BATH AND TEMPERATURE DEPENDENCE

### Coupling to a Harmonic Bath

It is worth noting a similarity between the Hamiltonian for this displaced harmonic oscillator problem, and a general form for the coupling of an electronic “system” which is observed, and a harmonic oscillator “bath” whose degrees of freedom are dark to the observation, but which influence the behavior of the system. This is a preview of the concepts that we will develop more carefully later for the description of fluctuations in spectroscopy.

We demonstrated the electronic absorption lineshape derives from a dipole correlation function which describes the overlap between two wave packets evolving on the ground and excited surfaces  $|E\rangle$  and  $|G\rangle$ .

$$\begin{aligned} C_{\mu\mu}(t) &= \langle G | e^{iH_0 t} \mu e^{-iH_0 t} \mu | G \rangle \\ &= \langle G | e^{iH_G t} \mu e^{-iH_E t} \mu | G \rangle \\ &\approx |\mu_{eg}|^2 \langle \varphi_g(t) | \varphi_e(t) \rangle e^{-i(E_e - E_g)t} \end{aligned} \quad (6.45)$$

$$\langle \varphi_g(t) | = \langle g | e^{iH_g t} \quad | \varphi_e(t) \rangle = e^{-iH_e t} | e \rangle \quad (6.46)$$

This is a perfectly general expression, which indicates that the absorption spectrum is the Fourier transform of the time-dependent overlap between excited and ground state nuclear wave packets.

Expressed in a slightly different physical picture, we can also conceive of this process as nuclear motions that act to modulate the electronic energy gap  $\omega_{eg}$ . We can imagine re-writing the same problem in terms of a Hamiltonian that describes the electronic energy gap's dependence on  $q$ , i.e. its variation relative to  $\omega_{eg}$ . Defining an Energy Gap Hamiltonian:

$$H_{eg} = H_E - H_G - \hbar\omega_{eg} = H_e - H_g \quad (6.47)$$

We can see that this leads to a problem for an electronic transition linearly coupled to a harmonic oscillator:

$$\begin{aligned} H_0 &= H_e + E_e + H_g + E_g \\ &= \hbar\omega_{eg} + H_{eg} + 2H_g \end{aligned} \quad (6.48)$$

Noting that

$$H_g = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 q^2 \quad (6.49)$$

we see

$$\begin{aligned} H_{eg} &= \frac{1}{2}m\omega_0^2 (q-d)^2 - \frac{1}{2}m\omega_0^2 q^2 \\ &= -m\omega_0^2 d q + \frac{1}{2}m\omega_0^2 d^2 \\ &= c q + \lambda \end{aligned} \quad (6.50)$$

The Energy Gap Hamiltonian describes a linear coupling between the electronic transition and a harmonic oscillator. The strength of the coupling is  $c$  and the Hamiltonian has a constant energy offset value given by the reorganization energy.

This discussion illustrates how the displaced harmonic oscillator and Energy Gap Hamiltonian are isomorphic with a Hamiltonian for an electronic “system” coupled to a harmonic oscillator “bath”:

$$H_0 = H_S + H_B + H_{SB} \quad (6.51)$$

$$H_S = |e\rangle(E_e + \lambda)\langle e| + |g\rangle E_g \langle g|$$

$$H_B = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 q^2 \quad (6.52)$$

$$H_{SB} = m\omega_0^2 d q$$

Here  $H_{SB}$  describes the interaction of the electronic system ( $H_S$ ) with the vibrational bath ( $H_B$ ). It is a linear coupling Hamiltonian, meaning that it is linear in the bath coordinate has a strength-of-coupling term ( $m\omega_0^2 d$ ).

### Coupling to Multiple Vibrations or a Continuum

The Hamiltonians we have written so far describe coupling to a single bath degree of freedom, but the results can be generalized to many vibrations or a continuum of nuclear motions. This approach is used to treat the spectroscopy of dissipative systems, through the interaction of a system with a continuum of states that are dark to the field, and which we treat in a statistical manner, in addition to describing fluctuations in spectroscopy.

So, what happens if the electronic transition is coupled to many vibrational coordinates, each with its own displacement? The extension is straightforward if the modes are independent,

i.e. we can conceive of the bath vibrations as harmonic normal modes. We imagine an electronic transition coupled to a set of normal modes for the molecule or lattice. Then we write the state of the system as product states in the electronic and nuclear occupation, i.e.  $|G\rangle = |g; n_1, n_2, \dots, n_i\rangle$ .

The dipole correlation function is then

$$\begin{aligned} C_{\mu\mu}(t) &= |\mu_{eg}|^2 e^{-i\omega_{eg}t} \cdot F_1(t) \cdot F_2(t) \cdots F_N(t) \\ &= |\mu_{eg}|^2 e^{-i\omega_{eg}t} \left[ \prod_{i=1}^N \exp\left[D_i(e^{-i\omega_i t} - 1)\right] \right] \\ &= |\mu_{eg}|^2 e^{-i\omega_{eg}t - g(t)} \end{aligned} \quad (6.53)$$

with

$$g(t) = \sum_i D_i (e^{-i\omega_i t} - 1) \quad (6.54)$$

For independent modes, the dipole correlation function is just a product of multiple dephasing functions that characterize the time-evolution of the different vibrations. In the time-domain this would lead to a complex beating pattern, which in the frequency domain appears as a spectrum with several superimposed vibronic progressions that follow the rules developed above.

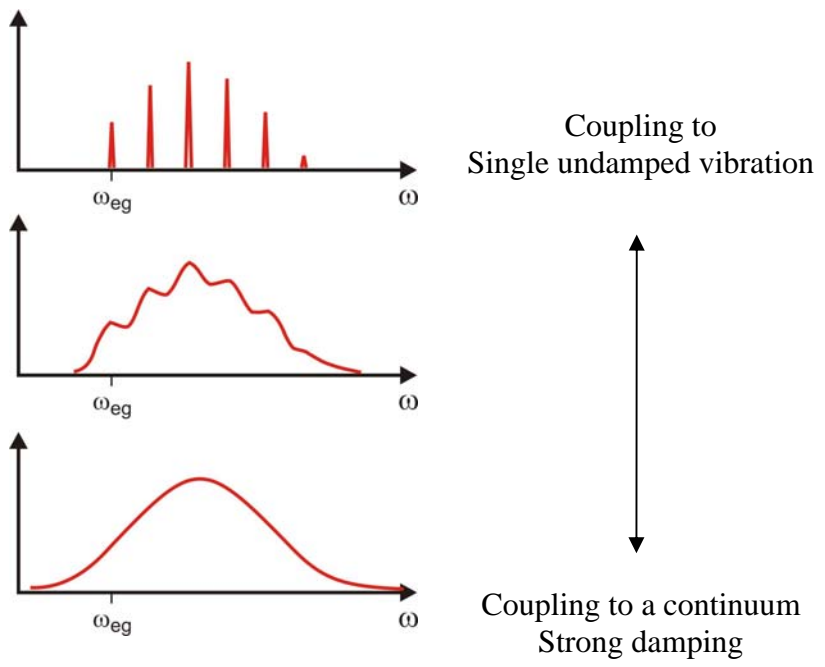
Taking this a step further, the generalization to a continuum of nuclear states should be apparent. This approach describes the absorption lineshape that results from dephasing or irreversible relaxation induced by coupling to a continuum. Given that we have a continuous frequency distribution of normal modes characterized by a density of states,  $W(\omega)$ , and a frequency dependent coupling,  $D(\omega)$ , we can change the sum in eq. (6.54) to an integral over the distribution

$$g(t) = \int d\omega W(\omega) D(\omega) (e^{-i\omega t} - 1). \quad (6.55)$$

Here the product  $W(\omega) D(\omega)$  can be considered a coupling-weighted density of states, sometimes referred to as a spectral density.

What this treatment does is provide a way of introducing a bath of states that the spectroscopically interrogated transition couples with. You can see that if the distribution of states is very broad and coupling is a constant, we can associate  $g(t)$  with a constant  $\Gamma$ , and we obtain a Lorentzian lineshape. So coupling to a continuum or bath provides a way of introducing relaxation effects or damping of the electronic coherence in the absorption spectrum. More

generally the lineshape function will be complex, where the real part describes damping and the imaginary part modulates the primary frequency and leads to fine structure.



### Displaced Harmonic Oscillator Model at Finite Temperature

If you solve the problem for coupling to a single vibrational mode at finite temperatures, where excited vibrational levels in the ground state are initially populated, you find

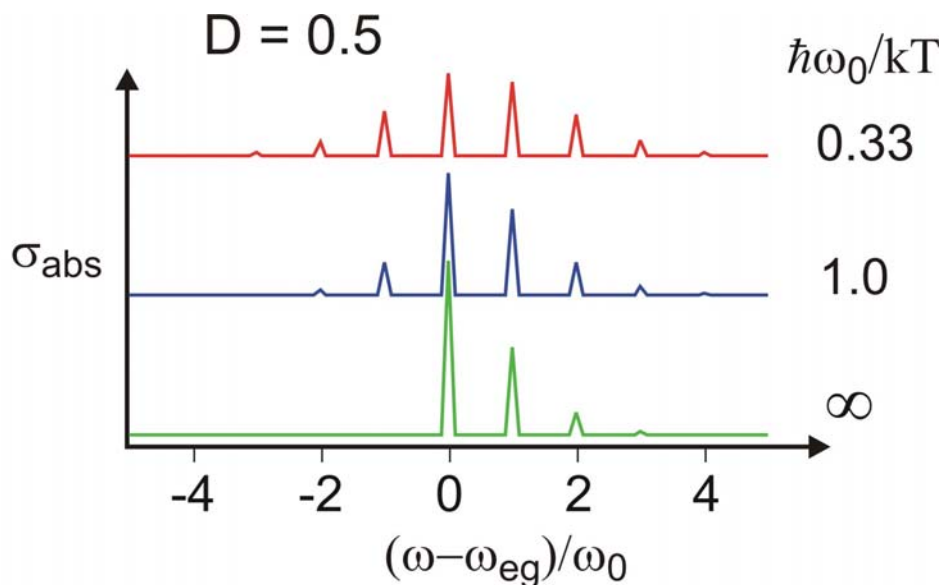
$$C_{\mu\mu}(t) = |\mu_{eg}|^2 e^{-i\omega_{eg}t} \exp\left[D\left[(\bar{n}+1)(e^{-i\omega_0 t} - 1) + \bar{n}(e^{+i\omega_0 t} - 1)\right]\right]. \quad (6.56)$$

$$\bar{n} = (e^{\beta\hbar\omega_0} - 1)^{-1} \quad (6.57)$$

$\bar{n}$  is the thermally averaged occupation number of the harmonic vibrational mode. Now, let's calculate the lineshape. Expanding exponentials in the dephasing function and Fourier transforming gives

$$\sigma_{abs}(\omega) = |\mu_{eg}|^2 e^{-D(2\bar{n}+1)} \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} \left(\frac{D^{j+k}}{j!k!}\right) (\bar{n}+1)^j \bar{n}^k \delta(\omega - \omega_{eg} - (j-k)\omega_0) \quad (6.58)$$

The first summation over  $j$  (setting all  $k$  to zero) looks as before, but the second summation now includes “hot bands”: transitions upward from thermally populated vibrational states with a net decrease in vibrational quantum number on excitation. Note their amplitudes depend on the thermal occupation.



We can extend this description to describe coupling to a many independent nuclear modes or coupling to a continuum. We write the state of the system in terms of the electronic state and the nuclear quantum numbers, i.e.  $|E\rangle = |e; n_1, n_2, n_3 \dots\rangle$ , and from that:

$$F(t) = \exp \left[ \sum_j D_j \left[ (\bar{n}_j + 1) (e^{-i\omega_j t} - 1) + \bar{n}_j (e^{+i\omega_j t} - 1) \right] \right] \quad (6.59)$$

or changing to an integral over a continuous frequency distribution of normal modes characterized by a density of states,  $W(\omega)$

$$F(t) = \exp \left[ \int d\omega W(\omega) D(\omega) \left[ (\bar{n}(\omega) + 1) (e^{-i\omega t} - 1) + \bar{n}(\omega) (e^{i\omega t} - 1) \right] \right] \quad (6.60)$$

$D(\omega)$  is the frequency dependent coupling. Let's look at the envelope of the nuclear structure on the transition by doing a short-time expansion on the complex exponential as in eq. (6.39)

$$F(t) = \exp \left[ \int d\omega D(\omega) W(\omega) \left( -i\omega t - (2\bar{n} + 1) \frac{\omega^2 t^2}{2} \right) \right]. \quad (6.61)$$

The lineshape is calculated from

$$\sigma_{abs}(\omega) = \int_{-\infty}^{+\infty} dt e^{i(\omega - \omega_{eg})t} \exp[-i\langle\omega\rangle t] \exp\left[-\frac{1}{2}\langle\omega^2\rangle t^2\right] \quad (6.62)$$

where we have defined the mean vibrational excitation on absorption

$$\begin{aligned} \langle\omega\rangle &= \int d\omega W(\omega) D(\omega) \omega \\ &= \lambda / \hbar \end{aligned} \quad (6.63)$$

and

$$\langle\omega^2\rangle = \int d\omega W(\omega) D(\omega) \omega^2 (2\bar{n}(\omega) + 1). \quad (6.64)$$

$\langle\omega^2\rangle$  reflects the thermally averaged distribution of accessible vibrational states. Completing the square, eq. (6.62) gives

$$\sigma_{abs}(\omega) = |\mu_{eg}|^2 \sqrt{\frac{\pi}{\langle\omega^2\rangle}} \exp \left[ \frac{-(\omega - \omega_{eg} - \langle\omega\rangle)^2}{2\langle\omega^2\rangle} \right] \quad (6.65)$$

The lineshape is Gaussian, with a transition maximum at the electronic resonance plus reorganization energy. The width of the Gaussian is temperature-dependent and given by eq. (6.64).

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## Readings

1. See also:

Mukamel, S. *Principles of Nonlinear Optical Spectroscopy* (Oxford University Press, New York, 1995), p. 217, also p. 189.

Nitzan, A. *Chemical Dynamics in Condensed Phases* (Oxford University Press, New York, 2006). Chapter 12, Sec. 5.

2. For further on this see:

Chapter 9 of Schatz, G. C. & Ratner, M. A. *Quantum Mechanics in Chemistry* (Dover Publications, Mineola, NY, 2002).

Also, Reimers, JR, Wilson, KR, Heller, EJ Complex time dependent wave packet technique for thermal equilibrium systems: Electronic spectra. *J. Chem. Phys.* **79**, 4749 (1983).