MIT Department of Chemistry
5.74, Spring 2004: Introductory Quantum Mechanics II
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NUCLEAR MOTION COUPLED TO ELECTRONIC TRANSITION[*]

Vibronic structure is absorption spectra; wavepacket dynamics; coupling of electronic states to intramolecular vibrations or solvent; coupling of electronic excitation/excitons in solids/semiconductors to phonons. Also, extensions to Förster and Marcus Theories.

### Two-Electronic Level System: Displaced harmonic oscillators $(T = 0°)$

We will calculate the electronic absorption spectrum using T.C.F.

$$H = H_0 + V(t)$$

$$H_0 = |g\rangle H_g^{TOT} \langle g| \quad + \quad |e\rangle H_e^{TOT} \langle e|$$

$$H_g^{TOT} = T(Q) + W_g(Q) + E_g$$

$$H_e^{TOT} = T(Q) + W_e(Q) + E_e$$
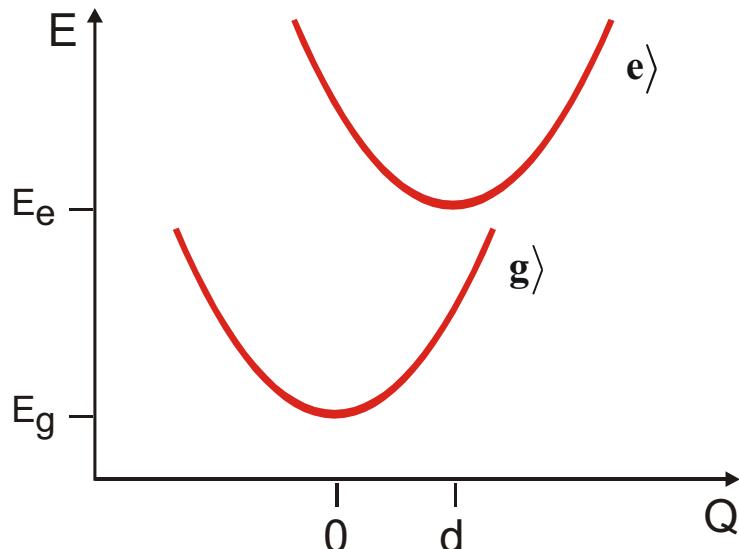
Our Model

$T(Q)$: Nuclear kinetic energy $\longrightarrow p^2/2m$

$W_g(Q)/W_e(Q)$: Potential energy $\longrightarrow \frac{1}{2}m\omega_0^2 Q^2$

$\longrightarrow \frac{1}{2}m\omega_0^2 (Q-d)^2$

$E_e - E_g$: Electronic energy gap

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[*] See Mukamel, p. 217, also p. 189.

$$H_e^{TOT} = \frac{p^2}{2m} + \tfrac{1}{2} m\omega_0^2 (Q-d)^2 + E_e \qquad\qquad = H_e + E_e$$

$$H_g^{TOT} = \frac{p^2}{2m} + \tfrac{1}{2} m\omega_0^2 Q^2 \qquad\qquad = H_g + E_g$$

1) **Born-Oppenheimer Approximation**

$$\left| \psi_g \right\rangle = \left| g \right\rangle \left| n \right\rangle$$

vibrational state

electronic state
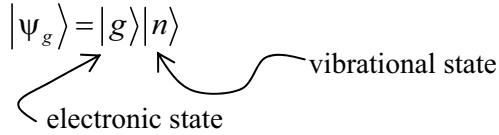
2) **Condon Approximation**
No Q dependence to $\bar{\mu}$ – No vibrational excitation accompanying electronic excitation

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

$$\bar{\mu} = \left| g \right\rangle \mu_{ge} \left\langle e \right| + \left| e \right\rangle \mu_{eg} \left\langle g \right|$$

Now let's calculate an absorption lineshape. Write dipole correlation function:

$$\left\langle \bar{\mu}_I (t) \bar{\mu}_I (0) \right\rangle = \sum_n p_n \left\langle n \left| \bar{\mu}_I (t) \bar{\mu}_I (0) \right| n \right\rangle$$

$$= \left\langle g, 0 \left| e^{iH_0 t/\hbar} \bar{\mu} e^{-iH_0 t/\hbar} \bar{\mu} \right| g, 0 \right\rangle \qquad \text{since at low T all population in } \left| g, 0 \right\rangle$$

By substituting our Hamiltonian H_0 and dipole operator $\bar{\mu}$ we find:

$$C_{\mu\mu}(t) = \left| \mu_{eg} \right|^2 \underbrace{\left\langle 0 \left| e^{iH_g t/\hbar} e^{-iH_e t/\hbar} \right| 0 \right\rangle}_{F(t)} e^{-i(E_e - E_g)t/\hbar}_{\quad e^{-i\omega_{eg}t}}$$

Note we can write our correlation function as $C(t) = \sum_n p_n \left| V_{mn} \right|^2 e^{i\omega_{mn}t - g(t)}$ where g(t) is our

lineshape function. Lets concentrate on $F(t) = exp(-g(t))$, sometimes known as the dephasing function:

$$F(t) = \left\langle 0 \left| e^{iH_g t/\hbar} e^{-iH_e t/\hbar} \right| 0 \right\rangle$$

From problem set 1: displacement operator

$$e^{i\alpha p} Q e^{-i\alpha p} = Q + \alpha\hbar$$

$$\therefore \quad H_e = e^{idp/\hbar} H_g e^{-idp/\hbar}$$

$$F(t) = \left\langle 0 \left| \underbrace{e^{iH_g t/\hbar} \overset{U_g^\dagger}{e^{-idp/\hbar}} e^{-iH_g t/\hbar}}_{} \overset{U_g}{e^{idp/\hbar}} \right| 0 \right\rangle$$

$$= \quad \left\langle 0 \left| e^{-idp(t)/\hbar} e^{idp(0)/\hbar} \right| 0 \right\rangle \qquad\qquad \text{since } p(t) = U_g^\dagger p(0) U_g$$

Now, using

$$H_g = \frac{p^2}{2m} + \tfrac{1}{2} m\omega_0^2 Q^2 = \hbar\omega_0\left(a^\dagger a + \tfrac{1}{2}\right) \qquad\qquad a^\dagger a = n$$

We have:

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

$$F(t) = \left\langle 0 \left| \exp\left[\underset{\sim}{d}\left(a^\dagger e^{i\omega_0 t} - a e^{-i\omega_0 t}\right)\right] \exp\left[-\underset{\sim}{d}\left(a^\dagger - a\right)\right] \right| 0 \right\rangle \qquad\qquad \text{with } \underset{\sim}{d} = d\sqrt{\frac{m\omega_0}{2\hbar}}$$

We can evaluate this using the identity $e^{\hat{A}+\hat{B}} = e^{\hat{A}} e^{\hat{B}} e^{-\frac{1}{2}\left[\hat{A},\hat{B}\right]}$. With $\left[a^\dagger, a\right] = -1$

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

So F(t) becomes

$$F(t) = e^{-d^2_{\sim}} \left\langle 0 \left| \exp\left[-d\, a\, e^{-i\omega_0 t} \right] \exp\left[d\, a^\dagger \right] \right| 0 \right\rangle \qquad \longleftarrow$$

where we have used $\ a|0\rangle = 0; \langle 0|a^\dagger = 0$

Note that operator defined through expansion!

To help evaluate, we want to exchange order of operators,

and since $\ e^{\hat{A}}\, e^{\hat{B}} = e^{\hat{B}}\, e^{\hat{A}}\, e^{-\left[\hat{B}, \hat{A} \right]}$

$$F(t) = e^{-d^2_{\sim}} \left\langle 0 \left| \exp\left[-d\, a^\dagger \right] \exp\left[d\, a\, e^{-i\omega_0 t} \right] \exp\left[d^2\, e^{-i\omega_0 t} \right] \right| 0 \right\rangle$$

$$= \exp\left[d^2 \left(e^{-i\omega_0 t} - 1 \right) \right]$$

$$\equiv e^{-g(t)} \qquad\qquad \text{(where } g(t) = -d^2_{\sim}\left(e^{-i\omega_0 t} - 1 \right)$$

$$\text{is the lineshape function)}$$

So we have the dipole correlation function:

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

Where $\ D = d^2_{\sim} = \dfrac{d^2 m \omega_0}{2\hbar}$ \qquad\qquad <u>Huang-Rhys parameter</u>

This represents the strength of coupling to the nuclear degrees of freedom.

Absorption Lineshape

$$\sigma_{abs}(\omega) = \int_{-\infty}^{+\infty} dt\, e^{i\omega t} \left| \mu_{eg} \right|^2 e^{-i\omega_{eg} t} \underbrace{\exp\left[D\left(e^{-i\omega_0 t} - 1 \right) \right]}_{expand\, exponential}$$

$$e^{-D} \sum_{j=0}^{\infty} \frac{1}{j!} D^j \left(e^{-i\omega_0 t} \right)^j$$

$$= \left| \mu_{eg} \right|^2 e^{-D} \sum_{j=0}^{\infty} \frac{1}{j!} D^j \, \delta\left(\omega - \omega_{eg} - j\omega_0 \right)$$

Spectrum is a progression of absorption peaks separated by ω_0 with a Poisson distribution of intensities $\rightarrow$ vibrational progression!

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

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

σ'_{abs} 1   D=0 (no displacement) ω

σ'_{abs} 1   D<1 (small displacement or small ω_0)   D D^2 $+\omega_0$ $+2\omega_0$ ω

σ'_{abs} D>1 (large displacement) $+\omega_0$ $+2\omega_0$ $+3\omega_0$ $\cdots$ ω ω_{eg}
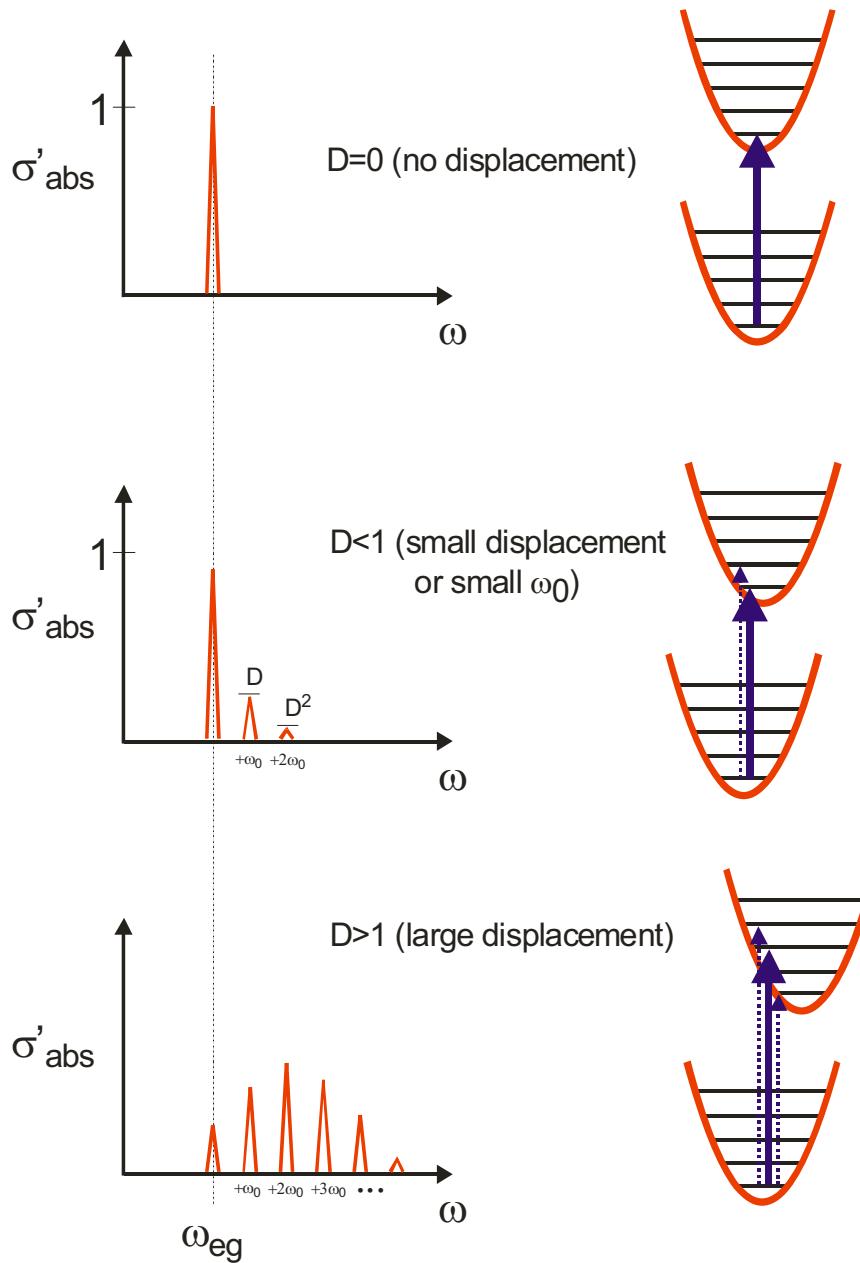
Franck-Condon Transitions

Note that for $D < 1$ peak absorption at $n = 0$. For $D \gg 1$ peak at $n \approx D$.
Note that D is the number of quanta excited at $Q = 0 \rightarrow$ Franck-Condon principle.

The envelope for these transitions is Gaussian:

Short time expansion: $t < \dfrac{1}{\omega_0}$.

$$\sigma_{abs}(\omega) = \left|\mu_{eg}\right|^2 \int_{-\infty}^{+\infty} dt\, e^{i\omega t}\, e^{-i\omega_{eg} t}\, e^{D(\exp(-i\omega_e t)-1)}$$

expand exponential for small t
(retain first three terms)

$$\approx \left|\mu_{eg}\right|^2 \int_{-\infty}^{+\infty} dt\, e^{i(\omega-\omega_{eg} t)}\, e^{D\left[-i\omega_0 t - \frac{1}{2}\omega_0^2 t^2\right]}$$

$$= \left|\mu_{eg}\right|^2 \int_{-\infty}^{+\infty} dt\, e^{i(\omega-\omega_{eq} - D\omega_0)t}\, e^{-\frac{1}{2}\omega_0^2 t^2}$$

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

Gaussian profile centered at Franck-Condon vertical transition.
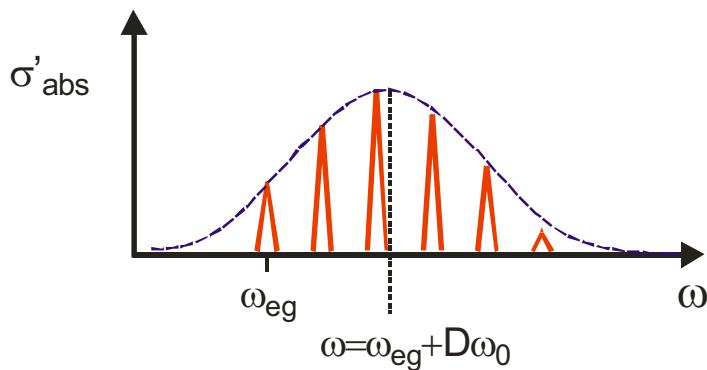
D: mean number of vibrational quanta excited in $|e\rangle$ on absorption.

$$\lambda = D\hbar\omega_0 = \tfrac{1}{2}m\omega_0^2 d^2 \quad = \quad \text{vibrational energy in } |e\rangle \text{ on excitation at } a = 0$$
$$= \quad \text{vibrational energy in } |g\rangle \text{ at } Q = d$$

reorganization energy

Absorption: $\hbar\left(\omega_{eg}+D\omega_0\right)$
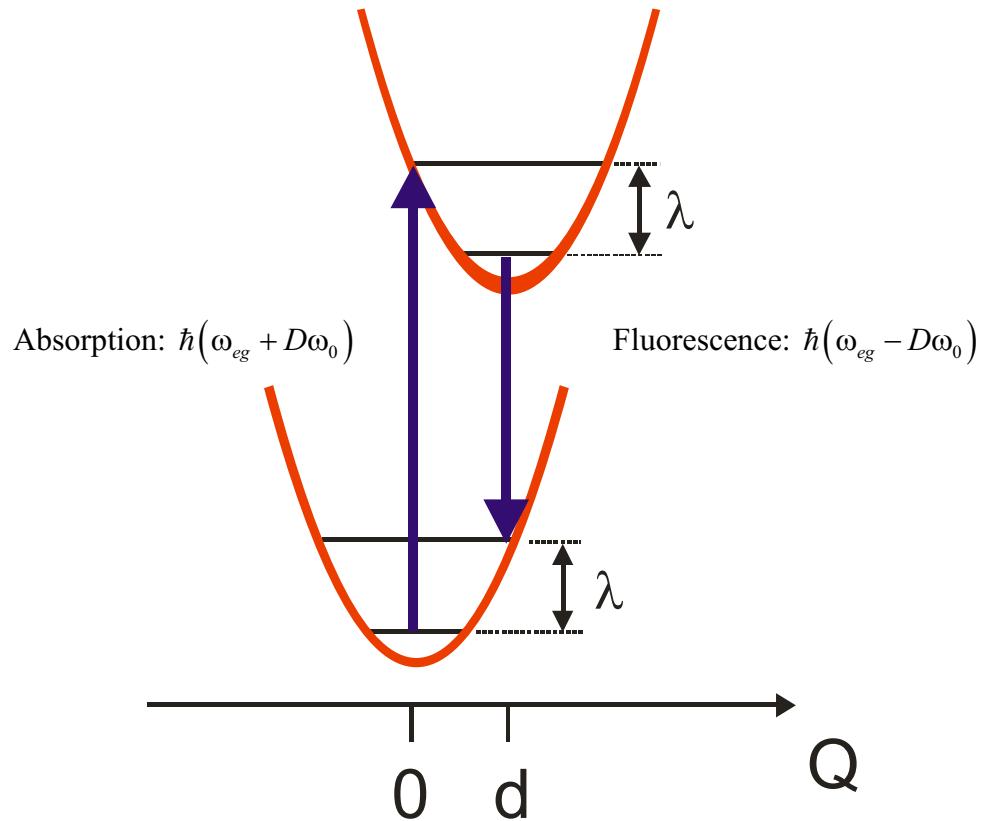
Fluorescence: $\hbar\left(\omega_{eg}-D\omega_0\right)$

Since vibrational energy on $|e\rangle$ is dissipated quickly, we expect fluorescence to be red-shifted by 2λ and have mirror symmetry:

$$\sigma_{abs}(\omega)=\int_{-\infty}^{+\infty}dt\,e^{i\left(\omega-\omega_{eg}\right)t-g(t)}$$

$$\sigma_{fluor}(\omega)=\int_{-\infty}^{+\infty}dt\,e^{i\left(\omega-\omega_{eg}-2\lambda\right)t-g^*(t)}$$

$$g(t)=D\left(e^{-i\omega_0 t}-1\right)$$

2λ: Stokes Shift
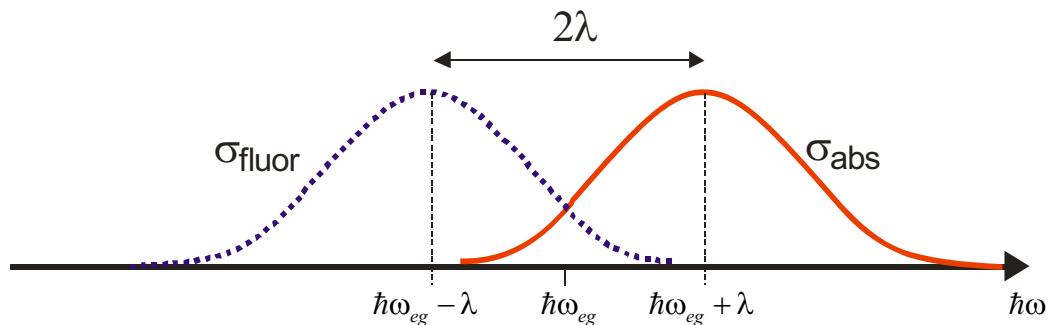
What if the electronic transition is coupled to many vibrational coordinates with own displacement?

Correlation function is easy (if the modes are independent). Then we write the state of the system as product states, i.e. $\left| g; n_1, n_2, ..., n_i \right\rangle$

$$C_{\mu\mu}(t) = \left| \mu_{eg} \right|^2 e^{-i\omega_{eg}t} \left[\prod_{i=1}^{N} exp\left[D_i \left(e^{-i\omega_i t} - 1 \right) \right] \right]$$

$$= \left| \mu_{eg} \right|^2 e^{-\omega_{eg}t - g(t)}$$

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

Relaxation—

We didn't include damping. Clearly, this will lead to broadening of delta function transitions.

We can also think of this as coupling to damped harmonic oscillators:

Coupling to undamped or weakly damped harmonic oscillators

Coupling to strongly (over-)damped harmonic oscillator
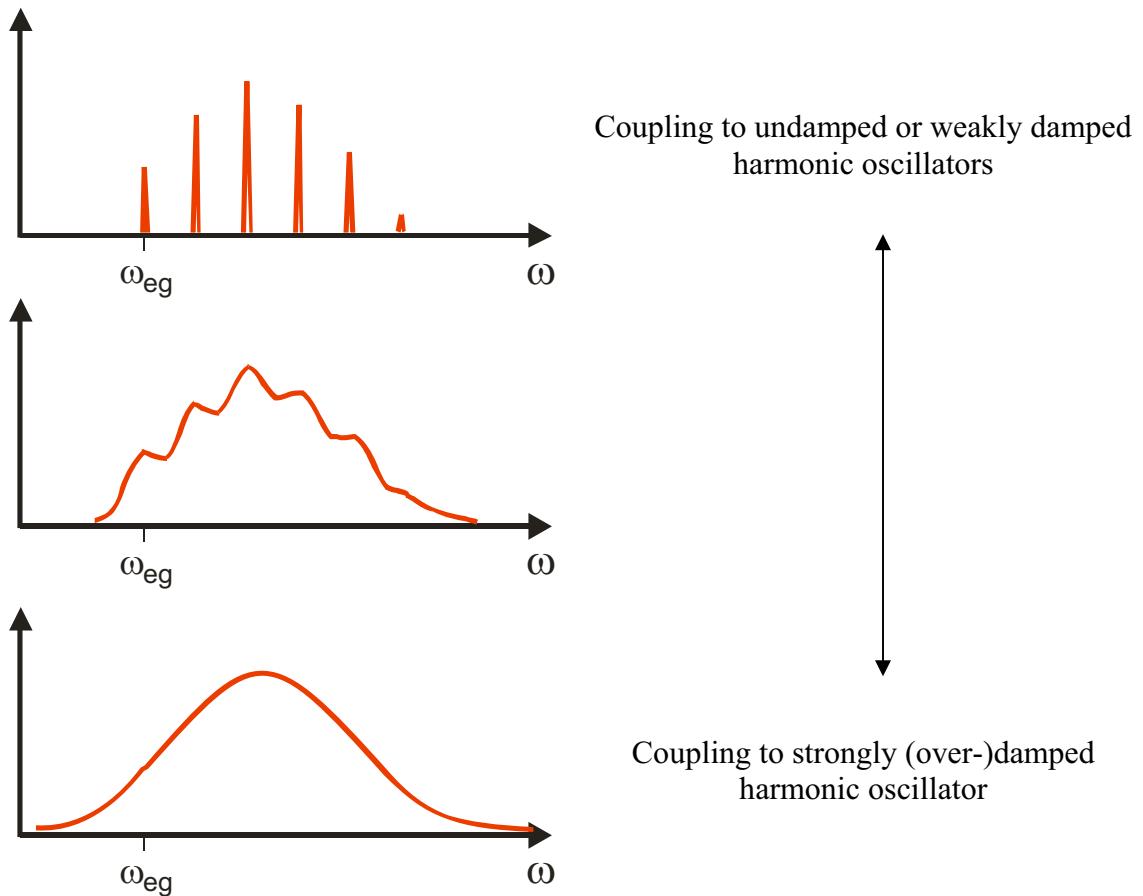
More on Displaced Harmonic Oscillator Model

If you want to solve the same problem at finite temperatures, where excited vibrational levels are populated, you find:

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

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

Calculating the lineshape, we would see "hot bands": transitions from thermally populated vibrational states. At low temperature the first term dominates – giving our previous result, and at high temperatures, we have additional contributions which gives a progression of transitions to frequencies below ω_{eg}.

For the coupling of electronic transitions to nuclear motion, we often want to describe coupling to a large number of modes. A continuous distribution can be used to describe relaxation processes—remember that coupling to a continuum leads to irreversible relaxation. If the nuclear degrees of freedom don't interact, we can write the state of the system in terms of the electronic state and the nuclear quantum numbers, i.e. $\left|e; n_1, n_2, n_3 \ldots\right\rangle$, and from that:

$$C_{\mu\mu}(t) \propto \exp\left[\sum_j D_j\left[(\bar{n}_j+1)\left(e^{-i\omega_j t}-1\right)+\bar{n}_j\left(e^{+i\omega_j t}-1\right)\right]\right]$$

or changing to an integral over a continuous distribution characterized by a density of states, $\rho(\omega)$.

$$C_{\mu\mu}(t) \propto \exp\left[\int dw \rho(\omega) D(\omega)\left[(\bar{n}(\omega)+1)\left(e^{-i\omega t}-1\right)+\bar{n}(\omega)\left(e^{i\omega t}-1\right)\right]\right]$$

Let's look at the lineshape by doing a short-time expansion on the complex exponential

$$e^{-i\omega t} = 1 - i\omega t - \frac{\omega^2 t^2}{2} + \ldots$$

Retaining the first three terms, we can write:

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

$$\sigma_{abs}(\omega) = \int_{-\infty}^{+\infty} dt\, e^{i(\omega-\omega_{eg})t}\ exp\left[-i\left\{\int d\omega \rho(\omega) D(\omega)\omega\right\} t\right] exp\left[-\tfrac{1}{2}\left\{\int d\omega \rho(\omega) D(\omega)\omega^2 \left(2\bar{n}(\omega)+1\right)\right\} t^2\right]$$
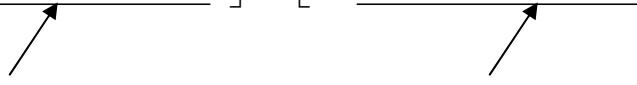
$\langle\omega\rangle = \lambda/\hbar$: mean
vibrational excitation!

$\langle\omega^2\rangle$ temperature
dependent! Damping!

Completing the square, we have:

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

Gaussian centered at electronic resonance plus reorganization energy. Width is temperature-dependent.

We can also use the displaced harmonic oscillator model to describe rates of energy or electron transfer.