Distinguished Visiting Scientist Program

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Series Title: *Excitons*
Lecture-3: *Vibronic interaction and Exciton-Phonon Coupling*
Vibronic Interaction and Exciton-Phonon Coupling

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A separate molecule

\[ H_n \phi^i_n = \varepsilon_n^i \phi^i_n \]

- \( n \) enumerates molecules and \( i \) refers to the ground (0) or excited (1) states
Excitons in larger systems

\[ \psi^f = \sum_n c_{fn} \phi_n^1 \prod_{m \neq n} \phi_m^0 \]

\[ H_{ij} = \delta_{ij} \varepsilon_j + V_{ij} \]

\[ \vec{\mu}_f = \sum_n c_{fn} \vec{\mu}_n \]

- Exciton wave function
- Hamiltonian
- Transition dipole moment
Translational symmetry

$C_{fn} \propto e^{i\vec{k}\vec{r}_n}$

$\sum_{n=1}^{N} e^{i\vec{k}\vec{r}_n} = N\delta_{\vec{k},0}$

- $\vec{r}_n$ is the coordinate of the $n$-th molecule
- $k$ is the exciton quantum number
Molecules in adiabatic (Born-Oppenheimer) approximation

Molecule:

\[ H = H_e + H_{\text{nuc}} \]

where \( H_e = T_e + V_{e-e} + V_{e-\text{nuc}} \), \( H_{\text{nuc}} = T_{\text{nuc}} \)

Variables: \( \{r\}; \quad \{R\} \)

Small parameter: \( \frac{m_e}{M} \ll 1 \), thus
Molecules in adiabatic (Born-Oppenheimer) approximation

(I) \[ H_e(R)\varphi_n(r, R) = \varepsilon_n(R)\varphi_n(r, R) \]

(II) \[ H\Psi = E\Psi \]

Substituting:

\[ \Psi = \sum_n \Phi_n(R)\varphi_n(r, R) \]

we get:

\[ \sum_m [(T(R) + \varepsilon_n(R))\delta_{m,n} + \Lambda_{nm}]\Phi_m(R) = E_n\Phi_n(R) \]
Molecules in adiabatic (Born-Oppenheimer) approximation

where:

$$\Lambda_{nm} = -\frac{1}{2M} \left[ \int \phi_n^*(r, R) \frac{\partial^2}{\partial R^2} \phi_m(r, R) dr + \int \phi_m^*(r, R) \frac{\partial}{\partial R} \phi_m(r, R) dr \frac{\partial}{\partial R} \right]$$

is the adiabacity operator.

By neglecting nondiagonal terms of the adiabaticity operator, we will get:

$$T(R) + u_n(R) \Phi_n(R) = E_n \Phi_n(R)$$

is the Schrödinger equation in the adiabatic approximation.

Here

$$u_n(R) = \epsilon_n(R) + \Lambda_{nn}(R) .$$
Potential surfaces in the adiabatic approximation

$U^0(R)$ and $U^1(R)$ are the potential surfaces of the molecular electronic ground and excited states, respectively and

$$u_n(R) = u_n(R_0) + \frac{1}{2} \sum_{i,j} \frac{\partial^2}{\partial R_i \partial R_j} u_n(R_0)(R - R_{i0})(R - R_{j0})$$
Quantum oscillator

Expanding the potential by deviations of the nuclear coordinates from their equilibrium positions and applying the transformation of the coordinate system ($R \rightarrow Q$), we will get:

$$(T(Q) + \frac{1}{2} \sum_x M \omega_{nx}^2 Q_x^2) \Phi_n(Q) = E_n \Phi_n(Q)$$

By taking into account that

$$T(Q) = \frac{p^2}{2M}, \quad \text{where} \quad p_x = -i\hbar \frac{\partial}{\partial Q_x}.$$ 

Thus, we are dealing now with the quantum oscillator.
Quantum oscillator

The following commutation relation is satisfied:

\[ [Q_x, p_x] = i\hbar \]

By using the general formula of quantum mechanics in Heisenberg representation:

\[ \dot{A} = \frac{i}{\hbar} [H, A] \]

for the oscillator it follows:

\[ \dot{p} = -M\omega^2 Q, \quad \text{and} \quad \dot{Q} = \frac{p}{M} \]
Quantum oscillator

By combining both equations it follows, that

$$\ddot{Q} + \omega^2 Q = 0$$

Equations coincide with those of the classical oscillator.

Energy of quantum oscillators:

$$E_{n\nu} = \sum_x (\nu_x + \frac{1}{2}) \hbar \omega_{nx}$$

$$H_n = \sum_x \hbar \omega_{nx} [b_x^+ b_x + \frac{1}{2}]$$
Quantum oscillator

\[ \Phi_{nv}(Q) = \frac{\exp(-Q^2/2)}{\sqrt{2^v v! \sqrt{\pi}}} H_v(Q) \] • the oscillator wavefunction

\[ H_v(Q) = (-1)^v \exp(Q^2) \frac{d^v}{dQ^v} \exp(-Q^2) \] • the v-th order Hermitian polynomial
Vibronic interaction

\[ u_1(Q) - u_0(Q) = u_1(0) - u_0(0) + \frac{\hbar \omega_1}{2} (Q - a)^2 - \frac{\hbar \omega_0}{2} Q^2 = \]

\[ E_e + \lambda - a \hbar \omega_1 Q + \delta Q^2 \]

\[ E_e = u_1(0) - u_0(0) \]

\[ \lambda = \frac{a}{2} \hbar \omega_1 \]

\[ \delta = \frac{\hbar \omega_1 - \hbar \omega_0}{2} \]

- the excitation energy
- the Franck-Condon (or reorganization) energy
Vibronic interaction

• in terms of ground state oscillations

\[ H_1 = T + u_1(Q) = T + u_0(Q) + [u_1(Q) - u_0(Q)] = \]

\[ E_e + \lambda + \frac{\hbar \omega_0}{2} (Q^2 - \frac{\partial^2}{\partial Q^2}) - a\hbar \omega_1 Q + \delta Q^2 \]
Transition dipole moment

\[ \langle 1, \nu' | \mu | 0, \nu \rangle = e \int \int \Phi_{1\nu'}^*(Q) \varphi_1^*(r, Q) r \Phi_{0\nu}(Q) \varphi_0(r, Q) r dQ \]

\[ \mu_{10}(Q) = e \int \varphi_1^*(r, Q) r \varphi_0(r, Q) r dr \]  
  \hspace{1cm} \text{electronic transition}

\[ \mu_{10}(Q) = \mu_{10}(Q_0) + \left( \frac{\partial}{\partial Q} \mu_{10}(Q) \right)_{Q=Q_0} (Q - Q_0) \]

\[ \mu_{10}(Q) = \mu_{10}(Q_0) \]  
  \hspace{1cm} \text{if } Q\text{-dependence is weak}
  
  \hspace{1cm} \text{the so-called Franck-Condon approximation ,}
  
  \hspace{1cm} \text{The second term gives the Herzber-Teller approx.}
Transition dipole moment

\[ \langle 1, \nu' | \mu | 0, \nu \rangle = \mu_{10}(Q_0) FC_{\nu', \nu} \]

\[ FC_{\nu', \nu} = \int \Phi_{1\nu'}^*(Q) \Phi_{0\nu}(Q)dQ \]

- the Franck-Condon factor

\[ \sum_{\nu''} |FC_{\nu', \nu''}|^2 = 1 \]

- noramalization
Transition dipole moment

\[ FC_{v'v} = \sqrt{\frac{v!}{v'!}} e^{-\frac{S}{2}} \left(-\sqrt{S}\right)^{v'-v} L_{v'}^{v'-v}(S) \]

- In the case \( \delta=0 \)
- the Huang-Rhys factor
- the Laguerre polynomial

\[ S = \frac{a^2}{2} \]
Absorption spectrum

\[ d = |\mu_{10}|^2 \sum_{\nu,\nu'} \rho_{\nu} |FC_{\nu,\nu'}|^2 \]

- Defines the absorption spectrum at higher temperatures
- \( \rho_{\nu} \) is the population of the vibrational states

\[ \sigma_a(\omega) = \frac{|\mu_{10}|^2}{\pi} \text{Re} \int_0^\infty \exp[i(\omega - \omega_e)t - g(t)]dt \]

- \( g(t) \) is the line shape function

\[ \omega_e = \frac{E_e}{\hbar} \]
Absorption spectrum

\[ g(t) = \int_0^t dt_1 \int_0^{t_1} d\tau C(\tau) \]

- \( C(\tau) \) is the correlation function

\[ C(\tau) = 2S \omega_1 \langle Q(\tau)Q(0) \rangle \]

- For the linear interaction

\[ \langle Q(\tau)Q(0) \rangle = (n + 1) \exp(-i\omega_0 \tau) + n \exp(i\omega_0 \tau) \]

\[ n = \left[ \exp\left(\frac{\hbar \omega_0}{k_B T}\right) - 1 \right]^{-1} \]
Absorption spectrum

\[ g(t) = \int_{0}^{t} dt_1 \int_{0}^{t_1} d\tau C(\tau) \]

\[ g(t) = S[\coth \frac{\hbar \omega_0}{k_B T} (1 - \cos \omega_0 t) + i(\sin \omega_0 t - \omega_0 t)] \]

\[ \sigma_a(\omega) = |\mu_{10}|^2 \exp[-S \coth \frac{\hbar \omega_0}{2k_B T}] \times \]

\[ \sum_{n=-\infty}^{\infty} \exp \frac{n \hbar \omega_0}{2k_B T} I_n \left[ S \sqrt{\coth^2 \frac{\hbar \omega_0}{2k_B T} - 1} \right] \delta(\omega - \omega_e - n \omega_0) \]
Absorption spectrum

\[ \sigma_a (\omega) = |\mu_{10}|^2 \exp[-S \coth \frac{\hbar \omega_0}{2k_B T}] \times \]

\[ \sum_{n=-\infty}^{\infty} \exp \frac{n \hbar \omega_0}{2k_B T} I_n[S \sqrt{\coth^2 \frac{\hbar \omega_0}{2k_B T} - 1}] \delta(\omega - \omega_e - n \omega_0) \]

\[ \sigma_{00} \propto e^{-G} \delta(\omega - \omega_e) \]

- for 0-0 transition

\[ G = S(2n + 1) \equiv S \coth \frac{\hbar \omega_0}{2k_B T} \]

- Debye-Waller factor
Absorption spectrum

- At zero temperature we get:

\[ \sigma_a(\omega) = |\mu_0|^2 \exp(-S) \sum_{n=0}^{\infty} \frac{S^n}{n!} \delta(\omega - \omega_e - n\omega_0) \]
Absorption spectrum

In the case of low frequency vibrations

\[ g(t) = -iAt - 4Bt^2 \]

where

\[ A = S\omega_0 = \lambda \]

\[ B = 2S(2n+1)\omega_0^2 \]
Absorption spectrum

Thus

$$\sigma_a(\omega) = \frac{1}{\pi} \sqrt{\frac{\pi}{B}} \exp[-\frac{(\omega - \omega_e - \lambda)^2}{B}]$$

At high temperatures

$$B = 4\lambda k_B T$$
Absorption spectrum

Brownian oscillator

\[ m\ddot{Q}(t) + m\omega_0^2 Q(t) + m \int_{-\infty}^{t} \gamma(t - \tau) \dot{Q}(\tau) d\tau = f(t) + F(t) \]

The friction and the random force satisfy the relations:

\[ \langle f(t) \rangle = 0 \]
\[ \langle f(t) f(\tau) \rangle = 2mk_B T\gamma(t - \tau) \]
Absorption spectrum

In the case of overdamped oscillations, when $\gamma >> \omega$ and for initial conditions $Q(0) = \dot{Q}(0) = 0$

$$Q(t) = Q_0 [1 - \exp(-\Lambda t)]$$

Where

$$Q_0 = \frac{F}{m \omega_0^2} \quad \Lambda = \frac{\omega_0^2}{\gamma}$$
Absorption spectrum

In this case

\[ g(t) = \frac{2\lambda k_B T}{\Lambda^2} (e^{-\Lambda t} + \Lambda t - 1) \]

In short-time limiting case \( g(t) = \lambda k_B T t^2 \)

and thus

\[ \sigma_a(\omega) = \frac{1}{\sqrt{2\pi} \Delta} \exp\left[ -\frac{(\omega - \omega_e)^2}{2\Delta^2} \right] \]

\( \Delta^2 = 2\lambda k_B T \) is the inhomogeneous broadening
Absorption spectrum

In the opposite long time approximation

\[ g(t) = \Gamma t \]

where

\[ \Gamma = \frac{2\lambda k_B T}{\Lambda} \]

is the homogeneous bandwidth

Thus

\[ \sigma_a(\omega) = \frac{1}{\pi} \frac{\Gamma}{(\omega - \omega_e)^2 + \Gamma^2} \]
Vibronic spectrum of the crystal

\[ H = \sum_{n=1}^{N} (\varepsilon_n + q_n) |n\rangle\langle n| + \sum_{n,m=1}^{N} V_{nm} |n\rangle\langle m| + H_{ph} \]

\[ |k\rangle = \sum_{n=1}^{N} c_{kn} |n\rangle \]

• using transition into the exciton representation

\[ H = \sum_{k=1}^{N} (E_k + q_k) |k\rangle\langle k| + H_{ph} \]
Vibronic spectrum of the crystal

\[ H = \sum_{k=1}^{N} (E_k + q_k) |k\rangle \langle k| + H_{ph} \]

- \( H_{ph} \) is the hamiltonian of the ground state vibrations

\[ E_k = \sum_{n=1}^{N} |c_{kn}|^2 \varepsilon_n ; \quad q_k = \sum_{n=1}^{N} q_n |c_{kn}|^2 ; \]

\[ C_{kk} = C(\omega) \sum_{n=1}^{N} |c_{kn}|^4 \]
Pigments in LH2
Absorption spectrum of LH2
Absorption spectrum of LH2

- bandwidth of B800
- bandwidth of B850
Absorption spectrum of LH2

- 40K
- 100K
- 180K
Exciton-phonon coupling

\[
H(R) = \sum_n (\varepsilon + \Delta_n(R))|n\rangle\langle n| + \sum_{nm} V_{nm}(R)(|n\rangle\langle m| + |m\rangle\langle n|)
\]

- By expanding both terms into power of \( R \) and adding the ground state phonon hamiltonian

\[
H = H_{ex} + H_{ph} + H_{ex-oh}^{(1)} + H_{ex-ph}^{(2)}
\]
Exciton-phonon coupling

\[ H_{ex} = E_{ex}(k) \langle k | k \rangle \]

\[ H_{ph} = \sum_{q,s} \hbar \omega_s(q) [b_{s,q}^+ b_{s,q} + \frac{1}{2}] \]

\[ H_{ex-ph}^{(1)} = \frac{1}{\sqrt{N}} \sum_{k,q,s} F_s(k,q) \langle k + q | k \rangle \langle k | \varphi_s(q) \rangle \]

\[ H_{ex-ph}^{(2)} = \frac{1}{\sqrt{N}} \sum_{k,q,s} \chi_s(q) \langle k | k \rangle \langle k | \varphi_s(q) \rangle \]

\[ \varphi_s(q) = b_{s,q} + b_{s,-q}^+ \]

- \( s \) enumerates the phonon branches
- is the expansion term from the resonance interaction
- is the expansion term from the displacement energy
- is the phonon coordinate
Exciton-phonon coupling

\[ F_s (k, q) = \sum_{l,m} e^l_s (q) \sqrt{\frac{\hbar}{2M\omega_s (q)}} \left[ (\frac{\partial}{\partial R^l_0} + e^{iqm} \frac{\partial}{\partial R^0_m}) V_{0m} \right] e^{ikm} \]

\[ \chi_s (q) = \sum_{l,m} e^l_s (q) \sqrt{\frac{\hbar}{2M\omega_s (q)}} \left[ (\frac{\partial}{\partial R^l_0} + e^{iqm} \frac{\partial}{\partial R^0_m}) \Delta_{0m} \right] \]

- \( e^l_s (q) \) is the component of the unit vector of polarization of the \( s \)-component of phonons
Exciton-phonon coupling

\[ H_{ex-ph}^{(1)} \gg H_{ex-ph}^{(2)} \]

• weak exciton-phonon coupling, exciton scattering by phonons

\[ H_{ex-ph}^{(1)} \ll H_{ex-ph}^{(2)} \]

• strong exciton-phonon coupling, lattice deformation
Exciton-phonon coupling

- Free exciton formation in the rigid lattice
- Exciton self-trapping caused by the lattice deformation
- $E_{LR}$ is the energy loss caused by the lattice deformation
- $B = E_{band}/2$
Exciton-phonon coupling

- $g = \frac{E_{LR}}{B}$ is the measure for the strength of the exciton-phonon coupling, the constant of the exciton-phonon coupling
- $g < 1$, the exciton delocalization is most favorable
- $g > 1$, the exciton self-trapping is more probable
Excitons

Frenkel CT Vannier-Mott

\[ a_{\text{ex}} \ll a_L \quad a_{\text{ex}} \gg a_L \]

Self-trapped exciton
Exciton self-trapping
Exciton-phonon coupling

\[ \sigma_a(\omega) \propto \exp(-\sigma \frac{\omega_{00} - \omega}{k_B T}) \]

\[ \frac{\sigma}{k_B T} \]

\[ \sigma(T) = \sigma_0 \frac{2k_B T}{\hbar \omega_0} \tanh \frac{\hbar \omega_0}{k_B T} \]

\[ \sigma_0 = s / g \]

- Urbach-Martienssen rule
- describes the steepness on the low-energy side
- \( s \) is the steepness index
Polarization

- The Maxwell equation can be given by

\[
\frac{\partial^2}{\partial z^2} E(z,t) - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} E(z,t) = \frac{4\pi}{c^2} \frac{\partial^2}{\partial t^2} P(z,t)
\]

- where

\[
P(\vec{r},t) = P^{(1)}(\vec{r},t) + P_{NL}(\vec{r},t)
\]
Polarization

• The linear response function (or linear susceptibility):

\[ P^{(1)}(\vec{r},t) = \int_0^\infty \int S^{(1)}(\vec{r} - \vec{r}_1, t - t_1) E(\vec{r}_1, t_1) d\vec{r}_1 dt_1 \]

• For the linear polarization

\[ \frac{\partial^2}{\partial z^2} E(z,t) - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \int_0^\infty \int \epsilon(\vec{r} - \vec{r}_1, t - t_1) E(\vec{r}_1, t_1) d\vec{r}_1 dt_1 = 0 \]

where

\[ \epsilon(\vec{r} - \vec{r}_1, t - t_1) = \delta(\vec{r} - \vec{r}_1) \delta(t - t_1) + 4\pi S^{(1)}(\vec{r} - \vec{r}_1, t - t_1) \]
Polarization

- Upon substitution the plane wave

\[ E(z,t) = E_0 \exp(ikz - i\omega t) \]

into the Maxwell equation we get

\[ \frac{k^2 c^2}{\omega^2} = \varepsilon(k, \omega) \]

with

\[ \varepsilon(\vec{k}, \omega) = \int d\vec{r}_1 \int_0^\infty dt_1 \varepsilon(\vec{r} - \vec{r}_1, t_1) \exp(-ik\vec{r}_1 + i\omega t_1) \]
Polarization

• Thus

\[ \varepsilon(\vec{k}, \omega) = 1 + 4\pi\chi^{(1)}(\vec{k}, \omega) \]

• where linear susceptibility:

\[ \chi^{(1)}(\vec{k}, \omega) = \int d\vec{r}_1 \int dt_1 S^{(1)}(\vec{r} - \vec{r}_1, t_1) \exp(-i\vec{k}\vec{r}_1 + i\omega t_1) \]
Polarization

\[ \varepsilon(\vec{k}, \omega) = \varepsilon_0 + \frac{\hbar^2 \Omega_p^2 f^2}{E^2(\vec{k}) - (\hbar \omega + i \Gamma(\vec{k}))^2} \]

- the dielectric function for excitons

\[ \Omega_p = \sqrt{\frac{4\pi e^2}{mv}} \]

- is the plasmon frequency

- \( f \) is the oscillator strength
Polariton

- Curve 1 corresponds to the exciton dispersion,
- \( 2 \quad E = \frac{\hbar c k}{\sqrt{\varepsilon_0}} \)
- \( 3 \quad E = \frac{\hbar c k}{\sqrt{\varepsilon_\infty}} \)
- \( \hbar \Omega_\perp = E(0) \)
- \( \Omega_\parallel - \Omega_\perp = \frac{\Omega_p}{\sqrt{\varepsilon_0}} \)