

Spectroscopy and Dynamics of Polarizable Optical Chromophores in Molecular Solvents

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- Electron Transfer Reactions
- Optical Spectra
- Polar Solvation
- Time-Resolved Fluorescence Spectroscopy

Spectroscopy and Dynamics in Liquids, March 23, 2003

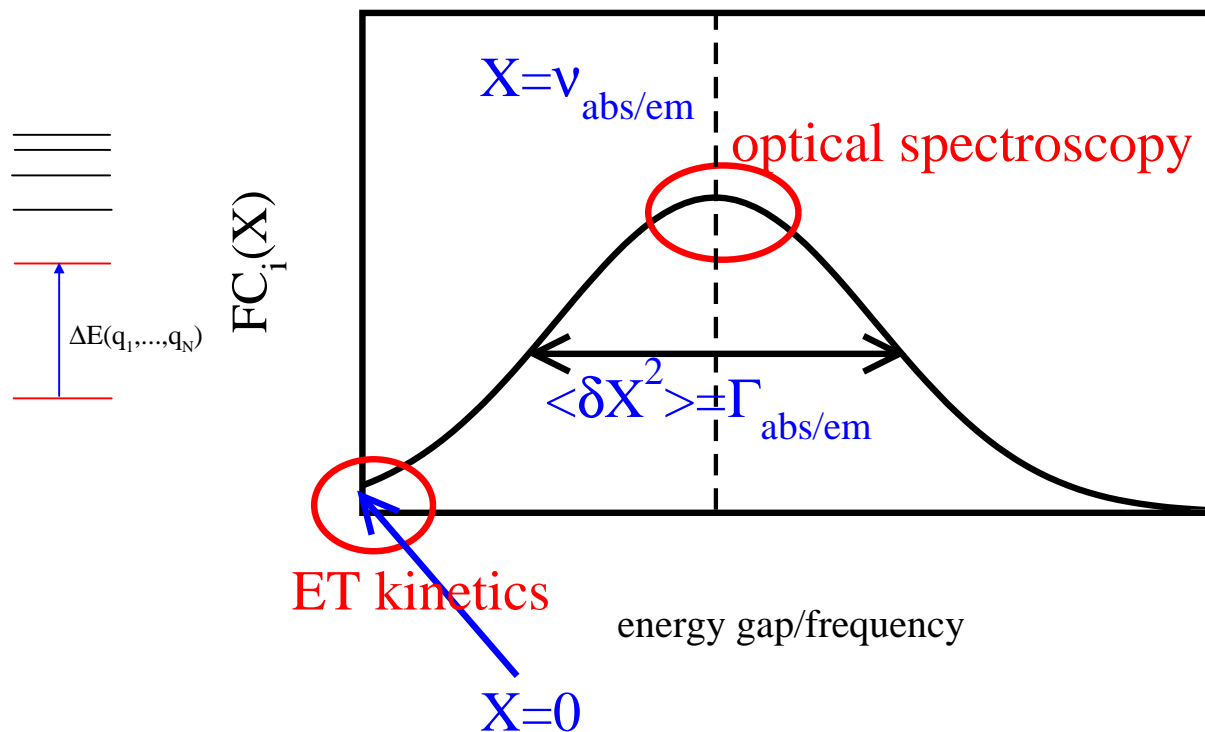
Charge-Transfer Processes in Condensed Phases

Density of energy gaps ($X = \hbar\omega$):

$$FC_i(\omega) = \hbar \langle \delta(\hbar\omega - \Delta E(\mathbf{q})) \rangle_{\mathbf{q},i} = e^{-\beta F_i(\hbar\omega)}$$

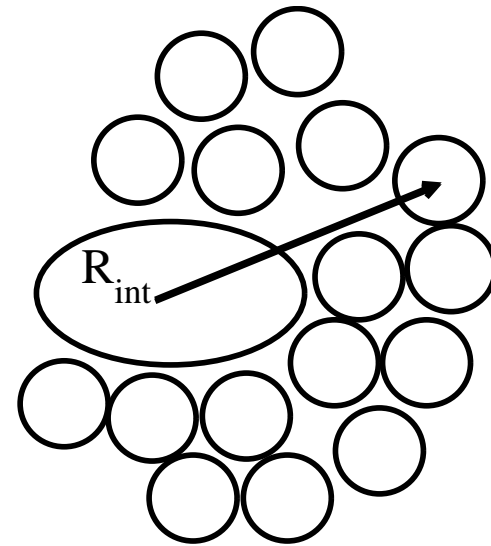
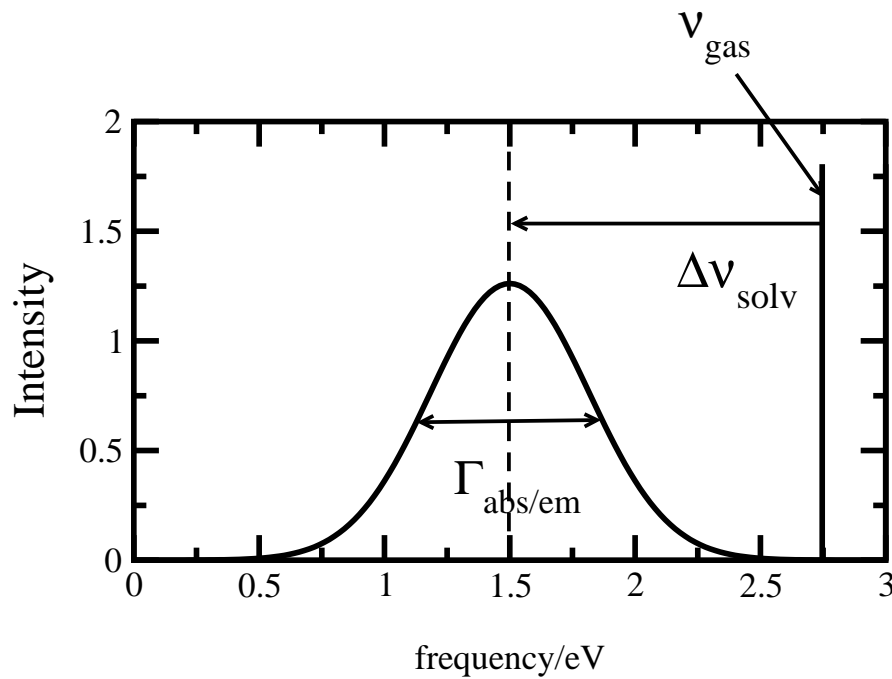
↓
spectroscopy

↓
charge transfer



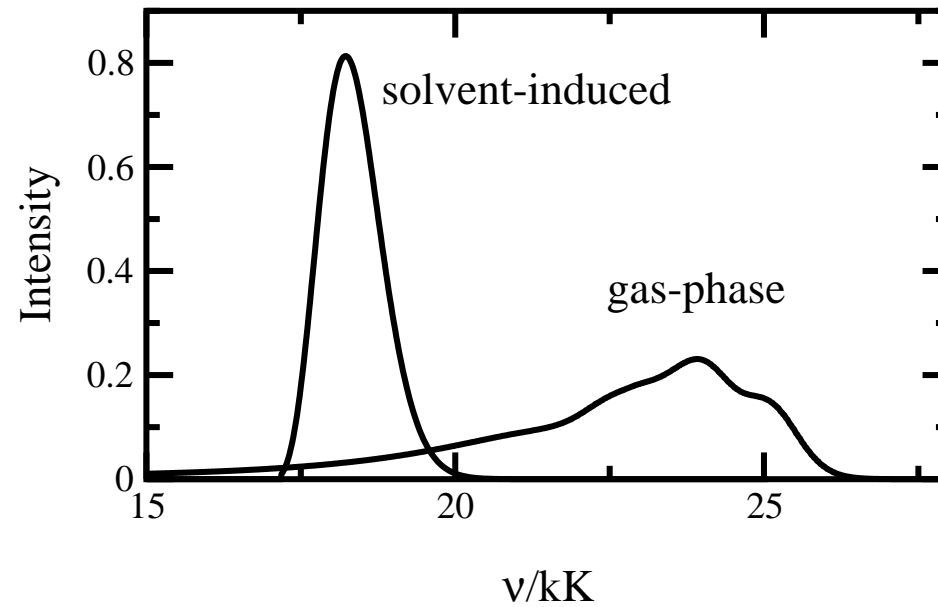
Inhomogeneous Solvent-Induced Broadening

$$I_{\text{abs/em}}(\nu) = [2\pi\sigma_{\text{abs/em}}^2]^{-1/2} \exp\left(-\frac{(\nu - \nu_{\text{abs/em}})^2}{2\sigma_{\text{abs/em}}^2}\right)$$



$$\sigma_{\text{abs/em}}^2 = \frac{\Gamma_{\text{abs/em}}^2}{8 \ln(2)}$$

Spectral Band-Shape

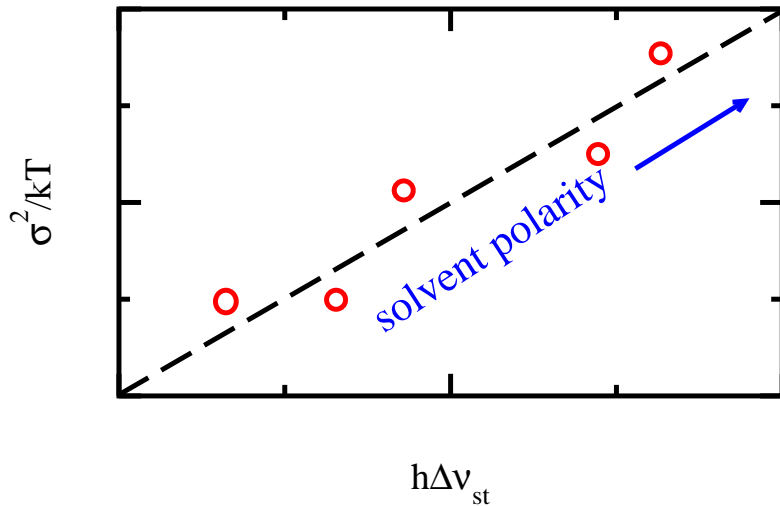


Convolution of gas-phase and solvent-induced bands:

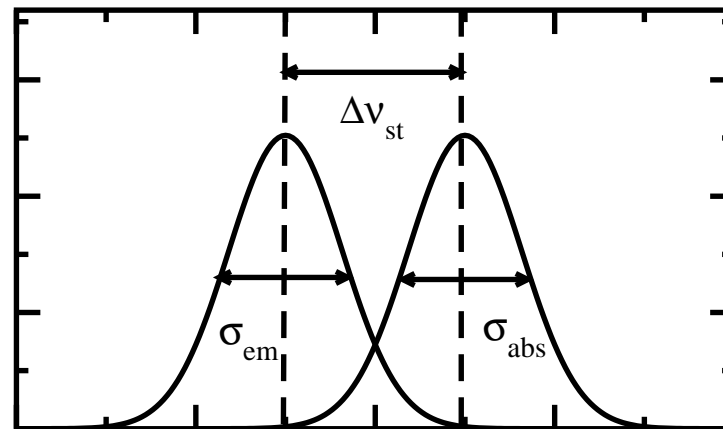
$$FC_i(\nu) = \int FC_{i,\text{gas}}(\nu - x)FC_{i,\text{solvent}}(x)dx$$

What do we expect to see? Steady-state spectra.

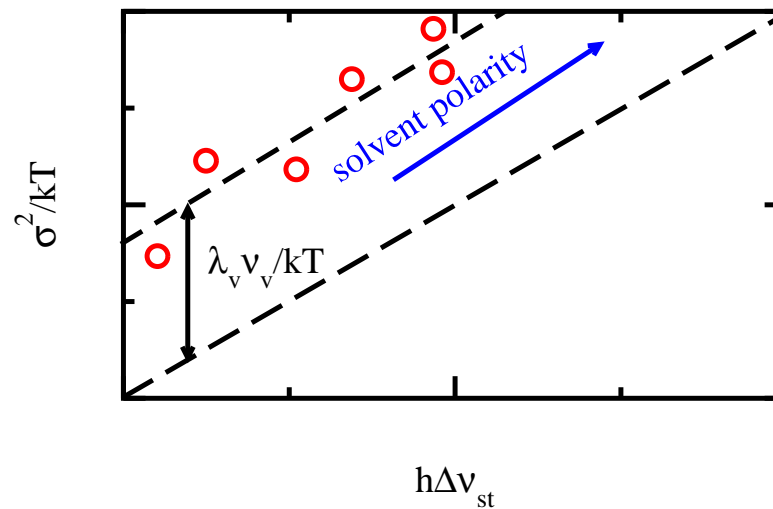
Solvent component of the band:



$$\frac{\sigma_{\text{abs}}^2}{k_B T} = \frac{\sigma_{\text{em}}^2}{k_B T} = h\Delta\nu_{\text{st}}$$

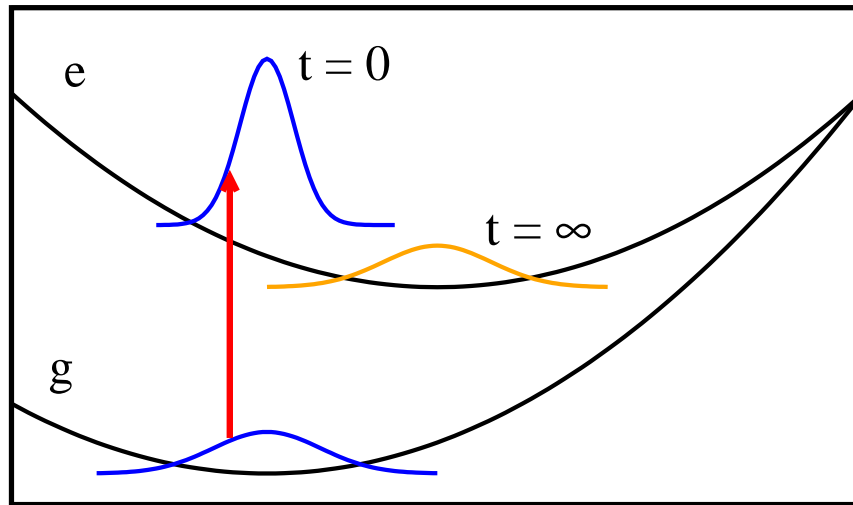


Total width vs the total Stokes shift:



Time-Resolved Spectra

Time-resolved excitation:



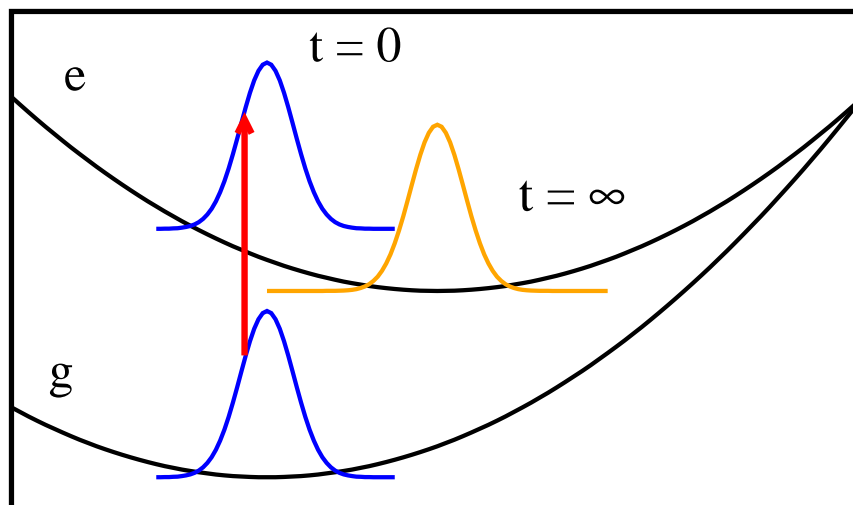
Linear response:

$$S_{\Omega,i}(t) = \frac{\langle \Omega(t) \rangle_i - \langle \Omega(\infty) \rangle_i}{\langle \Omega(0) \rangle_i - \langle \Omega(\infty) \rangle_i}$$

$$C_i(t) = \frac{\langle \delta\Omega(t)\delta\Omega(0) \rangle_i}{\langle \delta\Omega(0)^2 \rangle_i}$$

$$S_{\Omega,i}(t) = C_i(t)$$

TRF broad-band excitation:



$$\lambda_i(t) = \lambda = \text{Const}$$

Marcus-Hush Theory of Electron Transfer

Two-parameters model:

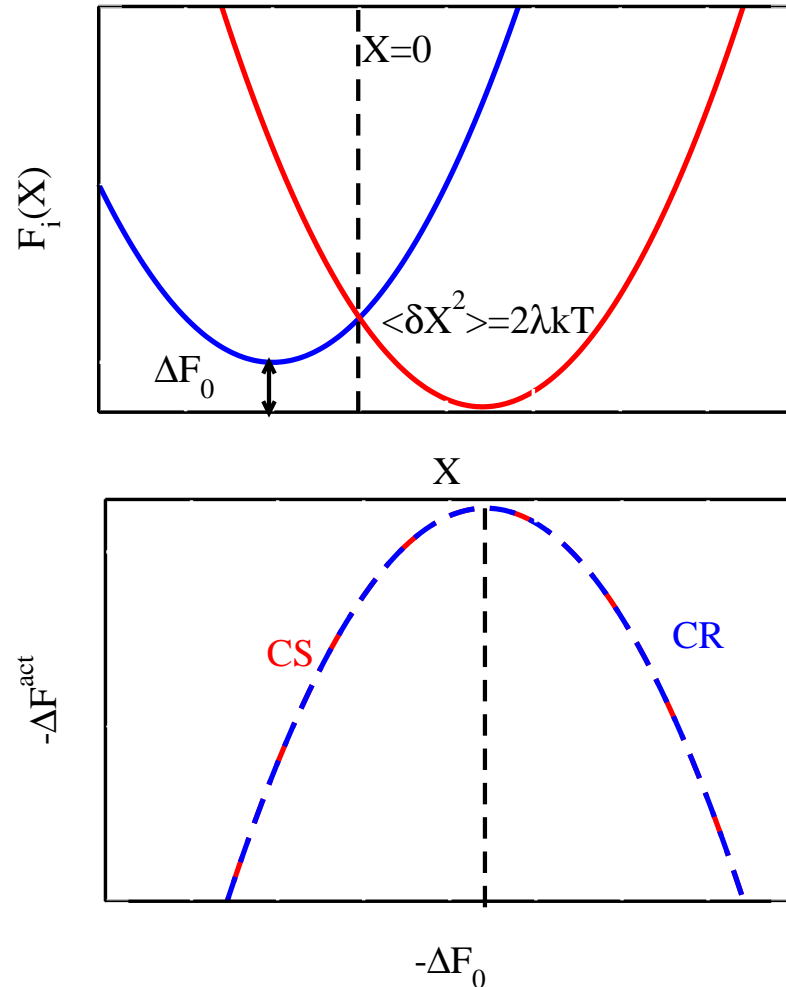
$$\Delta F^{\text{act}} = \frac{(\lambda + \Delta F_0)^2}{4\lambda}$$

λ is the reorganization energy

ΔF_0 is the driving force.

$$FC_i(X) = e^{-\beta F_i(X)}$$

Energy gap law is the **same** for charge separation (CS) and charge recombination (CR)



The Approximation of Fixed Charges

Transition $i = 1 \rightarrow i = 2$:

$$\begin{array}{ccc} H^{(i)} & \xlongequal{\hspace{1cm}} & H_0^{(i)} - \frac{1}{2} \sum_j e_j^{(i)} \phi_j^{\text{solv}} \\ & \xrightarrow{\hspace{1cm}} & H_0^{(i)} - \mathbf{m}_{0i} \cdot \mathbf{R} \\ & \boxed{\text{dipolar solute}} & \\ & & \downarrow \\ & & \boxed{\text{solute dipole moment}} \end{array}$$

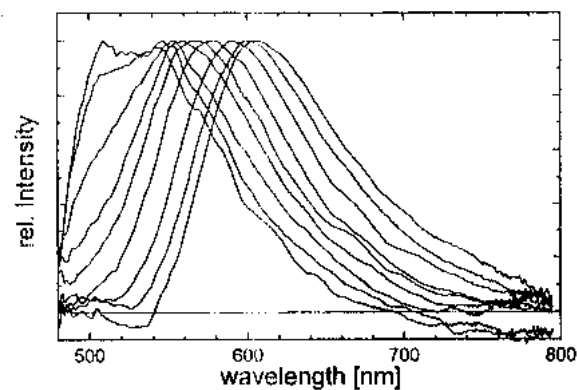
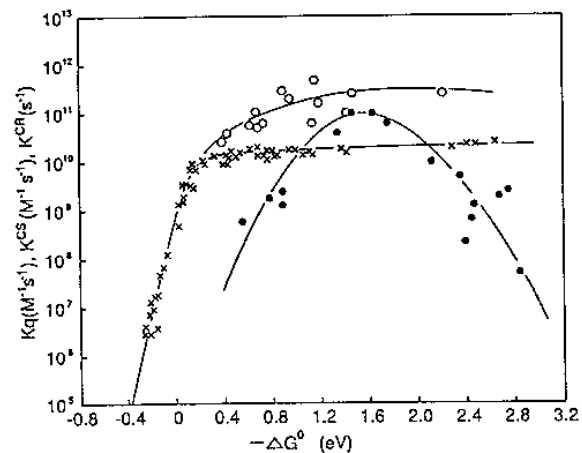
\mathbf{R} is the reaction field of the **nuclear subsystem** of the solvent.

Marcus-Hush picture is adequate when electronic transition changes (partial) charges of the donor-acceptor complex (optical chromophore)

Deviations from the Gaussian (Marcus-Hush) Picture

Experimental Evidence:

- Asymmetry between CS and CR energy gap laws
- Asymmetry between steady-state absorption and emission lines
- Change in the time-resolved optical width



Polarizable Solute

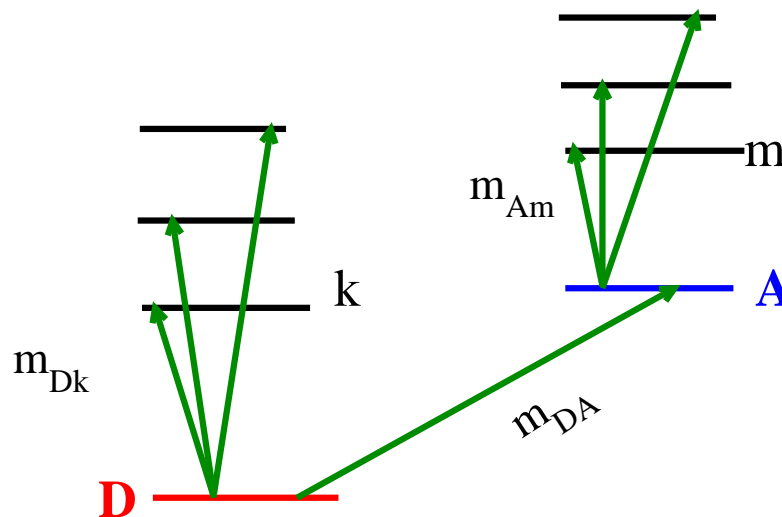
$$H^{(i)} \quad \equiv \quad H_0^{(i)} - \frac{1}{2} \sum_j e_j^{(i)} \phi_j^{\text{solv}} - \boxed{W_{\text{pol}}^{(i)}}$$

$$\xrightarrow{\text{dipolar solute}} \quad H_0^{(i)} - \mathbf{m}_{0i} \cdot \mathbf{R}_p - \boxed{\frac{1}{2} \alpha_{0i} \mathbf{R}_p^2}$$

↓
 α_i is the solute dipolar polarizability

Two sources of “polarizability”:

- D-A coupling through m_{DA}
- Coupling of D and A states to other electronic states



Q-Model

Hamiltonian:

$$H_i = H_0^{(i)} - \mathbf{m}_{0i} \cdot \mathbf{R}_p - \frac{1}{2} \alpha_{0i} \mathbf{R}_p^2$$

Free energy surfaces:

$$F_i(X) = F_{0i} + \left(\sqrt{|\alpha_i| \left| X - \Delta F_0 + \frac{\alpha_1^2 \lambda_1}{\alpha_2} \right|} - |\alpha_i| \sqrt{\lambda_i} \right)^2$$

$\alpha_2 = 1 + \alpha_1$, α_1 is the non-parabolicity parameter

$$\alpha_1 = \left(\sqrt[3]{\lambda_1/\lambda_2} - 1 \right)^{-1}$$

When $\alpha_1 \rightarrow \infty$, the parabolic surfaces are obtained

$$F_i(X) = F_{0i} + \frac{(X - \Delta F_0 \mp \lambda)^2}{4\lambda}, \quad \lambda_1 = \lambda_2 = \lambda$$

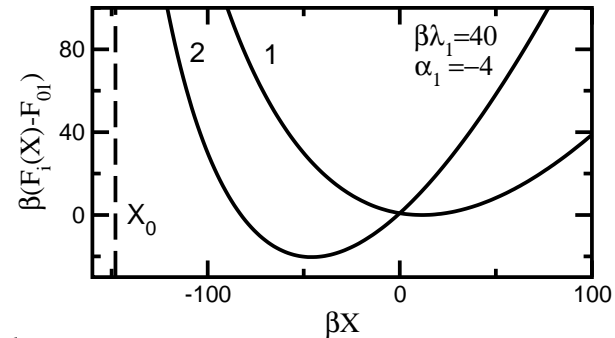
Q-Model: Properties

Energy conservation:

$$F_2(X) = F_1(X) + X$$

Connection to spectroscopic observables:

$$\lambda_i = \beta h^2 \langle \delta \nu^2 \rangle_i / 2 \quad \alpha_1 = -\frac{h \Delta \nu_{st} + \lambda_2}{\lambda_2 - \lambda_1}$$



Marcus-Hush term

Correction from non-parabolicity

$$\Delta F_0 = h \frac{\nu_{\text{abs}} + \nu_{\text{em}}}{2} - \frac{\lambda_1}{2} \frac{\alpha_1}{(1 + \alpha_1)^2}$$

Consistency condition:

$$\gamma = \frac{\sigma_{\text{abs}}^2}{\sigma_{\text{em}}^2} \times \left(\frac{\sigma_{\text{em}}^2 - 2kTh\Delta\nu_{\text{st}}}{\sigma_{\text{abs}}^2 - 2kTh\Delta\nu_{\text{st}}} \right)^3 \equiv 1$$

Reorganization Energy of Polarizable Chromophores

nuclear polarization response, $\mu_p = a_p m_0^2$

$$\lambda_i = a_p (f_i/f_{ei}) [\Delta\tilde{m}_0 + 2a_p \Delta\tilde{\alpha}_0 m_{0i}]^2$$

dipole moment change

polarizability change

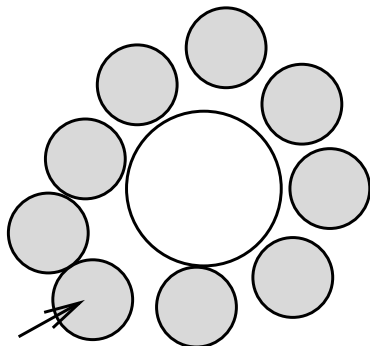
$$\Delta\tilde{\alpha}_0 = f_{e2}\alpha_{02} - f_{e1}\alpha_{01}, \quad \Delta\tilde{m}_0 = f_{e2}m_{02} - f_{e1}m_{01}$$

$$f_{ei} = [1 - 2a_e \alpha_{0i}]^{-1} \quad f_i = [1 - 2a_p \alpha_{0i}]^{-1}$$

a_e is the response of induced polarization, $\mu_e = a_e m_0^2$

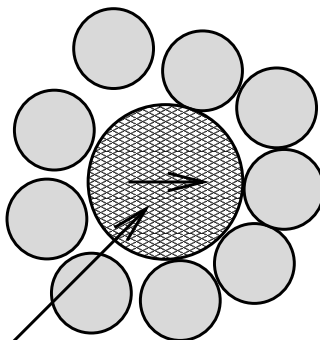
MC Simulations of Transitions in Polarizable Chromophores

CS transition



dipole moment m
polarizability α
diameter σ

CR transition



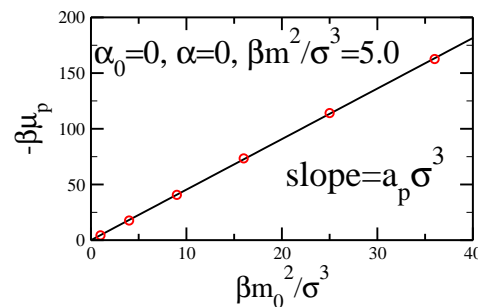
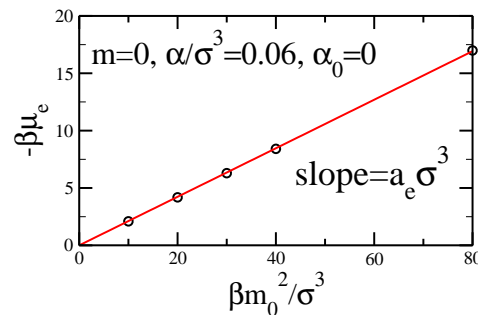
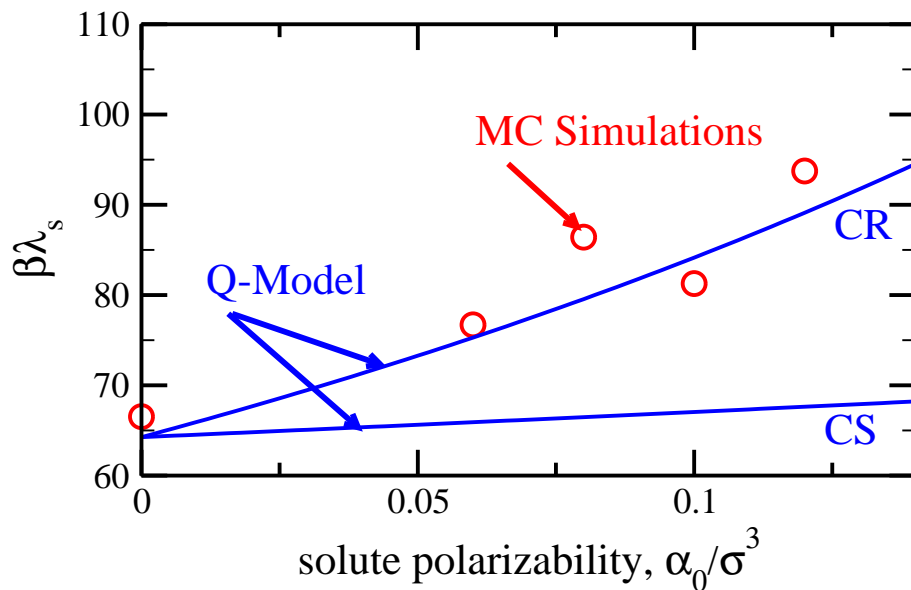
dipole moment m_0
polarizability α_0

Energy gap:

$$\Delta E = \Delta E_0 - \mathbf{m}_0 \cdot \mathbf{R}_p - \frac{1}{2} \alpha_0 \mathbf{R}_p^2$$

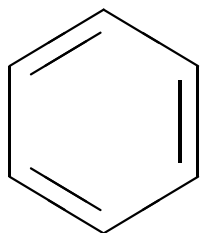
Reorganization energy:

$$\lambda_i = \beta \langle [\delta(\Delta E)]^2 \rangle_i / 2$$



Umbrella Sampling Simulations of ET Free Energy Surfaces

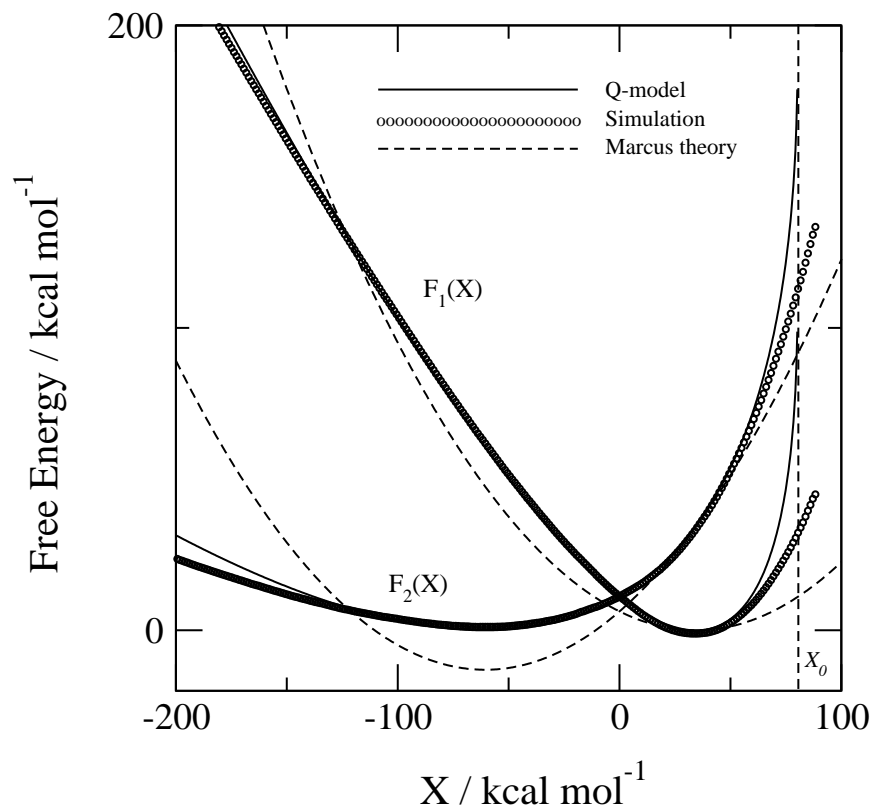
Solute:



$$m_{01} = 3.6D, \alpha_{01} = 4.43 \text{ \AA}^3$$

$$m_{02} = 9.8D, \alpha_{02} = 8.86 \text{ \AA}^3$$

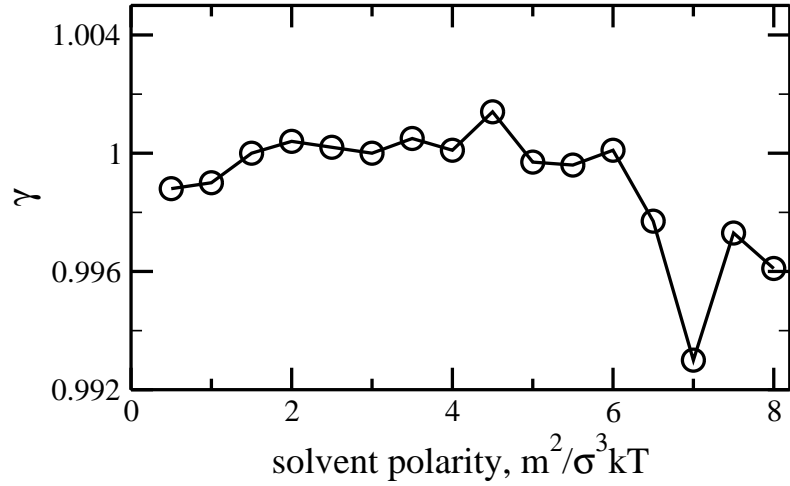
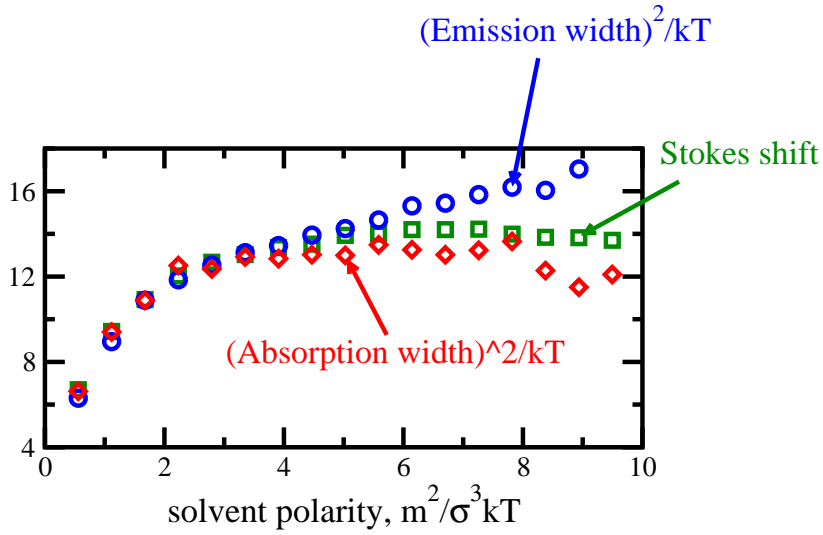
Solvent: polarizable water.



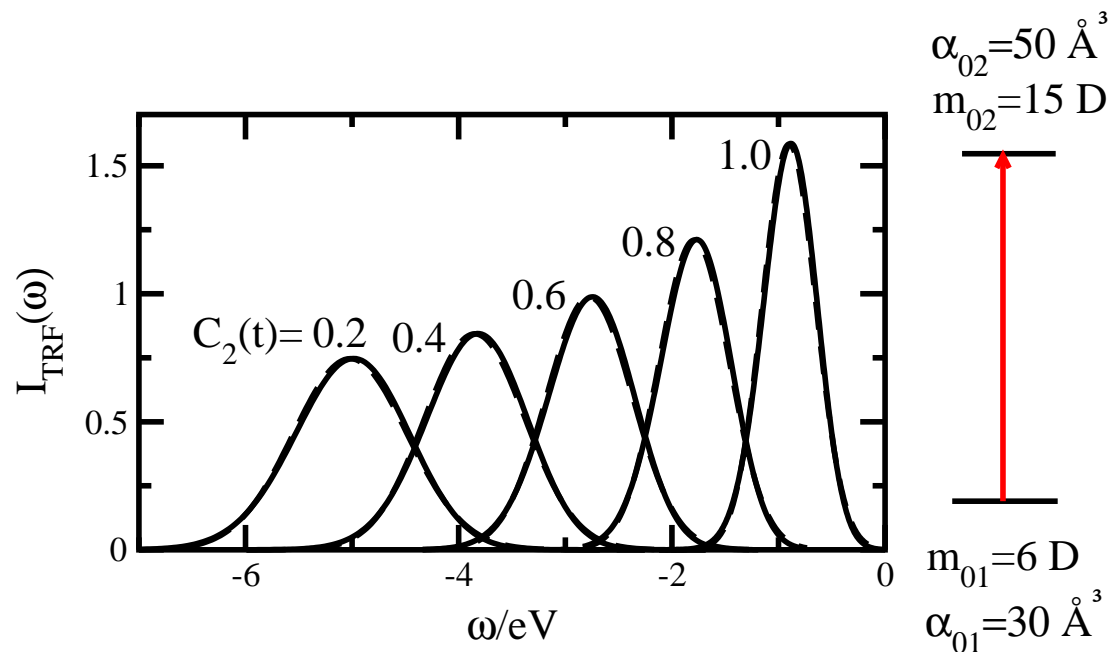
Small, Matyushov, Voth, JACS, in review.

γ-parameter in Nonlinear Dipole Solvation

$$\gamma = \frac{\sigma_{\text{abs}}^2}{\sigma_{\text{em}}^2} \times \left(\frac{\sigma_{\text{em}}^2 - 2kT\Delta\nu_{\text{st}}}{\sigma_{\text{abs}}^2 - 2kTh\Delta\nu_{\text{st}}} \right)^3$$



TRF band-shape



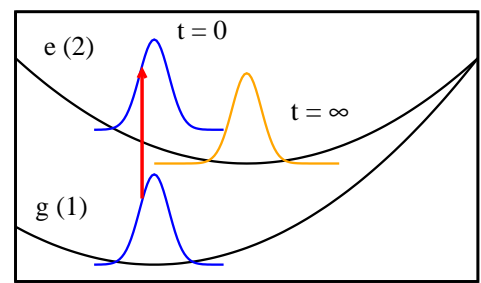
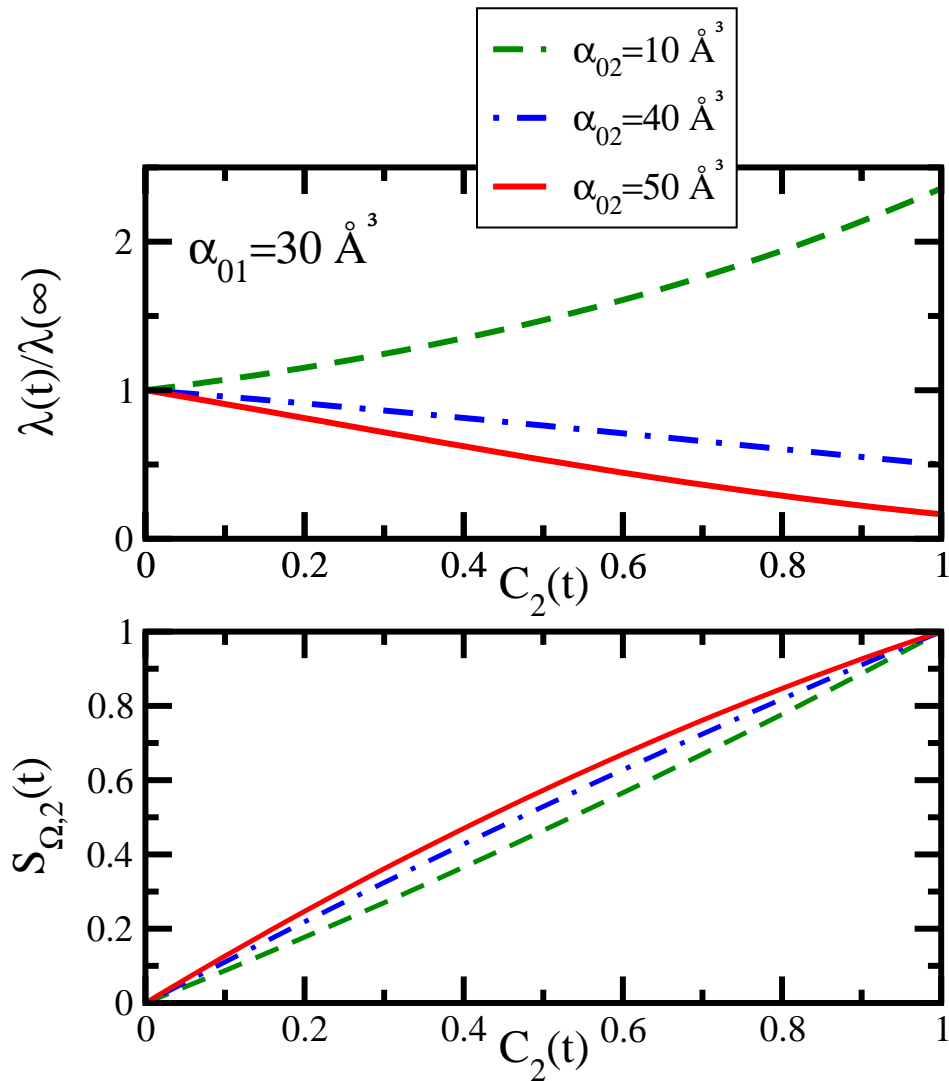
$$I_{\text{TRF}}(\omega, t) \propto e^{-\beta|\alpha(t)||\omega - \Omega_0|} I_1 \left(2\beta \sqrt{|\alpha(t)|^3 \lambda(t) |\omega - \Omega_0|} \right),$$

$$\lambda(t) = a_p \Delta \tilde{m}_0^2 f(t) \left[1 - \frac{\Omega_p(t)}{\Omega_0} \right]$$

limiting frequency

solvent-induced spectral shift

Time-Resolved Correlation Functions

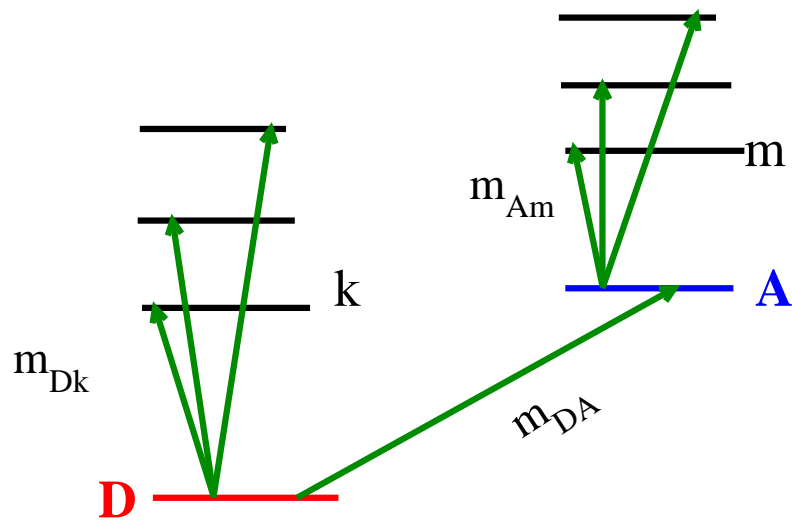
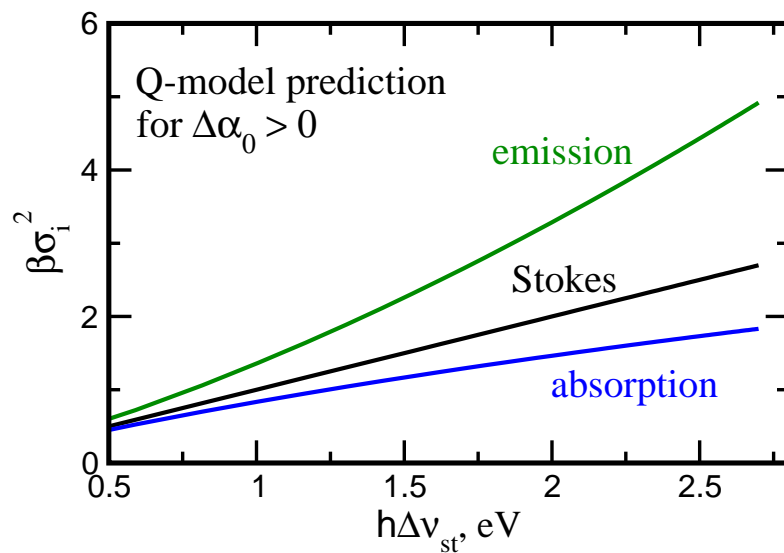
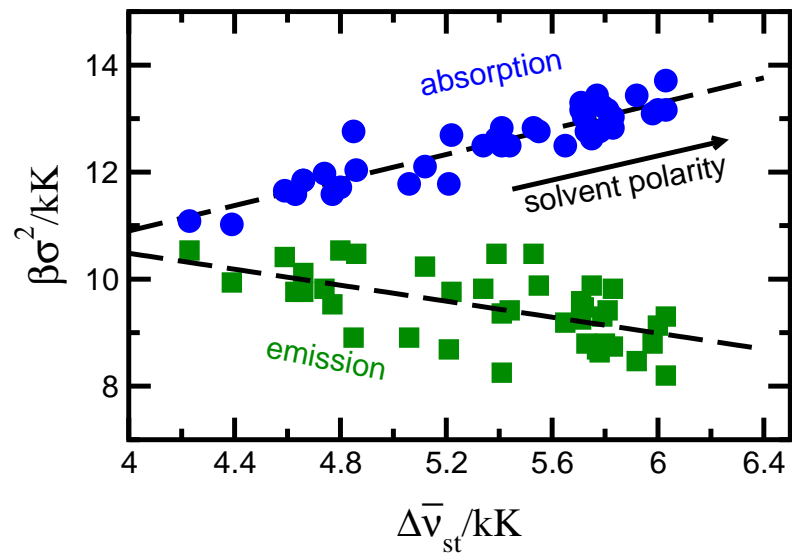
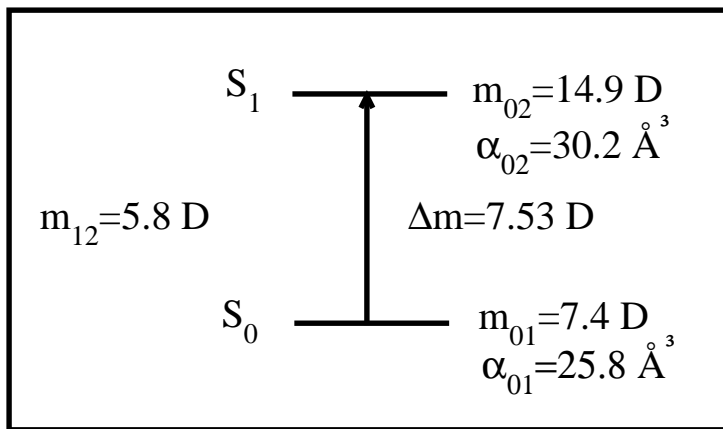


$$S_{\Omega,2}(t) = \frac{\langle \Omega(t) \rangle_2 - \langle \Omega(\infty) \rangle_2}{\langle \Omega(0) \rangle_2 - \langle \Omega(\infty) \rangle_2}$$

$$C_2(t) = \frac{\langle \delta\Omega(t)\delta\Omega(0) \rangle_2}{\langle \delta\Omega(0)^2 \rangle_2}$$

$S_{\Omega}(t)$ is NOT a good probe of nonlinear dynamics

Coumarin-153



Hybrid Model

- Coupling between the D and A states is explicitly considered
- Coupling to all other states is accounted through the dipolar polarizability

$$\bar{\alpha}_0 = \alpha_0 - 2 \frac{|m_{12}|^2}{\Delta E_{DA}}$$

Solute-solvent coupling:

$$\begin{pmatrix} -\mathbf{m}_{01} \cdot \mathbf{R}_p - \frac{1}{2} \bar{\alpha}_{01} \mathbf{R}_p^2 & -\mathbf{m}_{12} \cdot \mathbf{R}_p \\ -\mathbf{m}_{12} \cdot \mathbf{R}_p & -\mathbf{m}_{02} \cdot \mathbf{R}_p - \frac{1}{2} \bar{\alpha}_{02} \mathbf{R}_p^2 \end{pmatrix}$$

non-Condon coupling

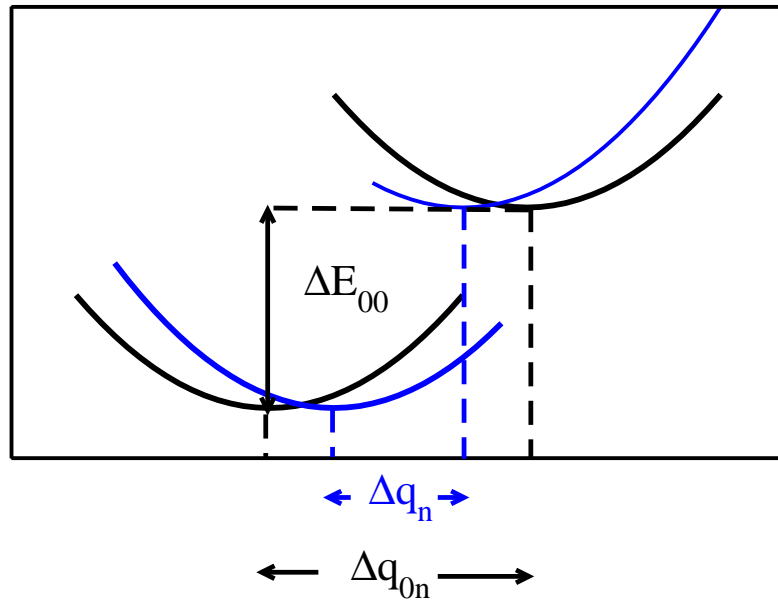
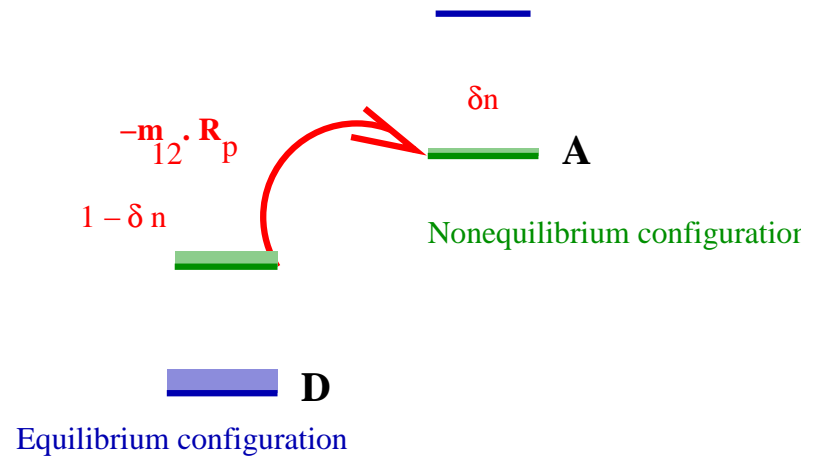
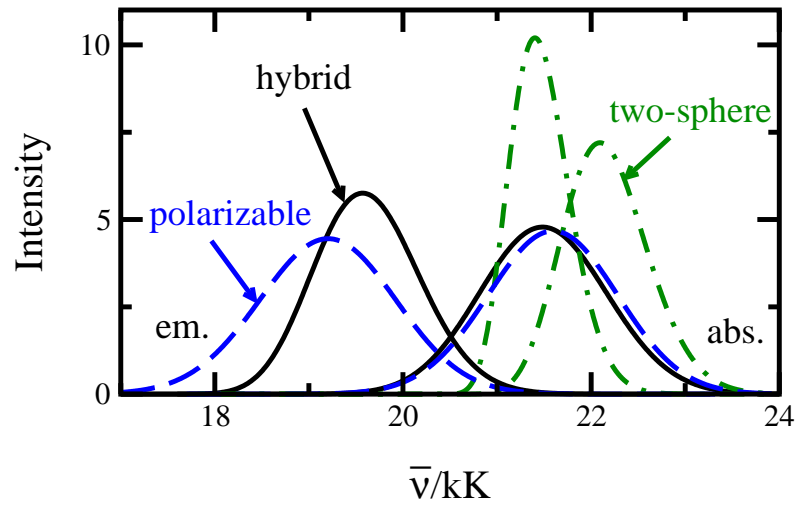
$-\mathbf{m}_{12} \cdot \mathbf{R}_p$

Electron-phonon coupling:

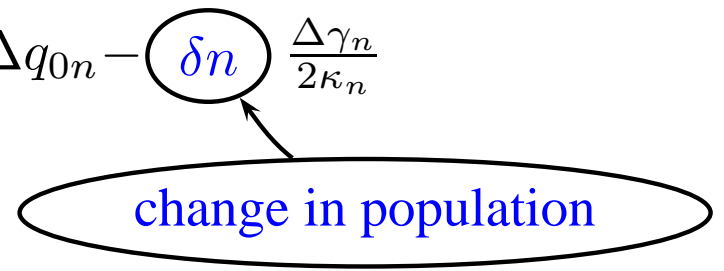
$$\begin{pmatrix} \sum_n \gamma_{1n} q_n n_1 & 0 \\ 0 & \sum_n \gamma_{2n} q_n n_2 \end{pmatrix}$$

electronic population

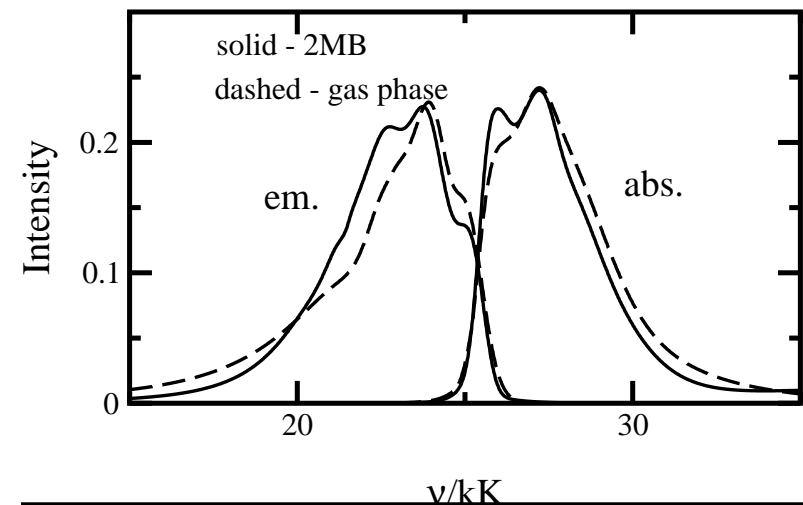
Model and Physical Picture



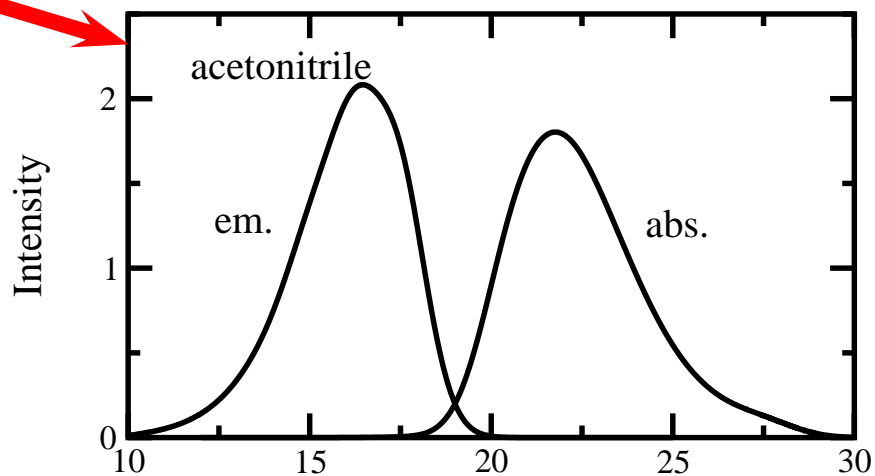
$$\Delta q_n = \Delta q_{0n} - \delta n \frac{\Delta \gamma_n}{2\kappa_n}$$



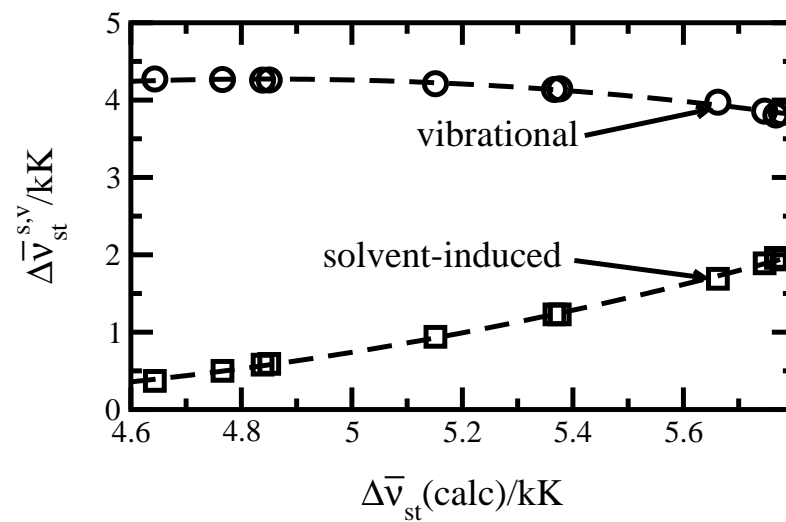
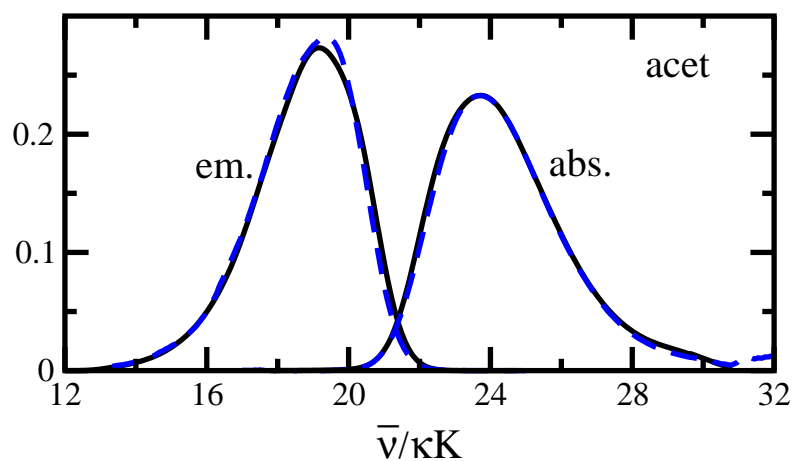
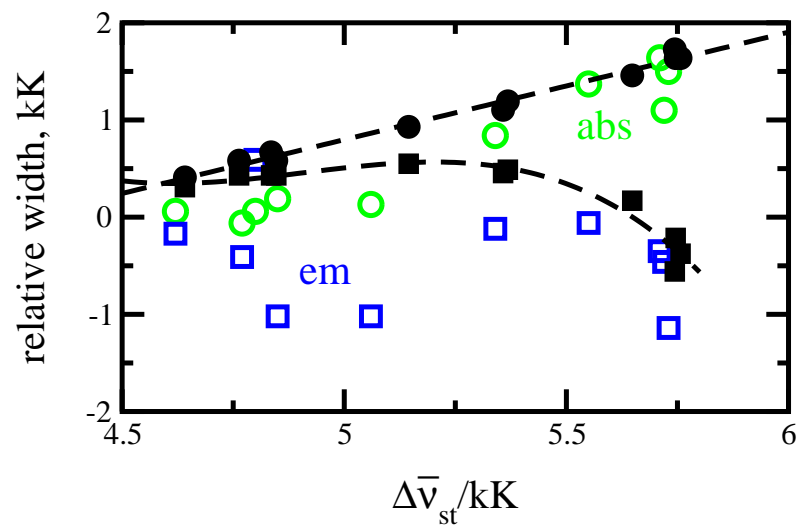
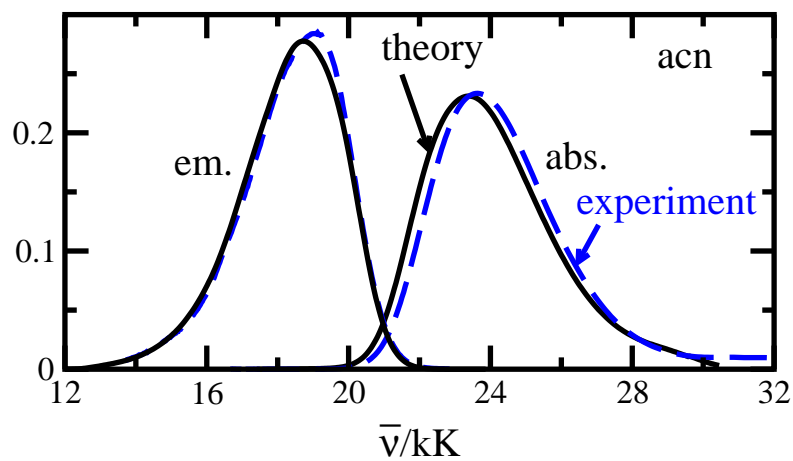
Calculation Procedure



$$\text{FCWD}(\bar{\nu}) = \int_{-\infty}^{\infty} dx \left\langle (\delta n(\mathbf{R}_p))^{-1} \delta(\bar{\nu} - x - \Delta E[\mathbf{R}_p]) \text{FCWD}^{\text{ref}}(\bar{\nu}^{\text{ref}} + x/\delta n(\mathbf{R}_p)) \right\rangle$$



Coumarin-153 band-shapes



Spectral intensity and the Franck-Condon factor

Lax, Kubo-Toyozawa, Davydov, 50's. Spectral intensity:

$$I_{\text{abs/em}}(\nu) \propto |m_{12}|^2 FCWD(\text{diagonal matrix elements}),$$

\mathbf{m}_{12} is the transition dipole arising from the interaction with the external electric field of the radiation

$$-\mathbf{m}_{12} \cdot \mathbf{E}_0(t)$$

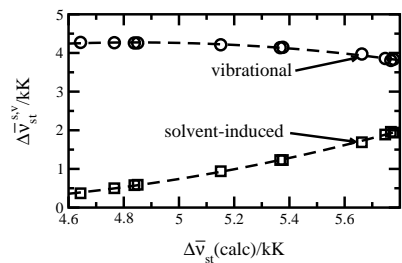
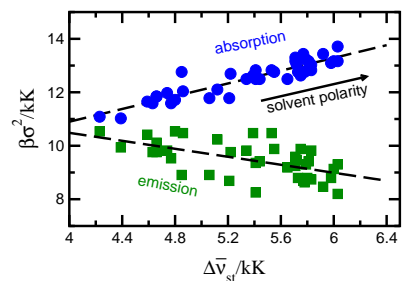
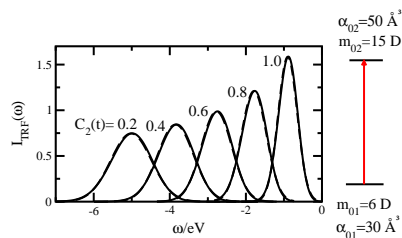
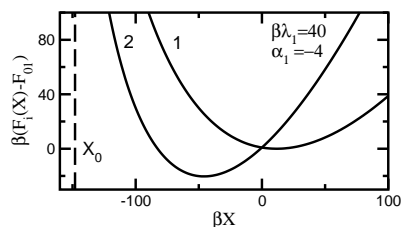
In a polar medium,

$$-\mathbf{m}_{12} \cdot \mathbf{R}$$

\mathbf{R} is the solvent local field.

$$I_{\text{abs/em}}(\nu) \propto |m_{12}|^2 FCWD(m_{12})$$

Conclusions



- The 3-parameter Q-model allows more flexibility in describing electronic transitions in condensed phases. Simulations show that the theory describes very accurately model systems.
- The time-resolved generalization of the Q-model gives the time-dependent spectral band-shape.
- The hybrid model including direct D-A coupling + polarizability reproduces experimental band-shapes of steady-state spectra.
- The solvent-vibrational coupling may be effective through the dynamic redistribution of the electronic density between the donor and acceptor states.

Collaboration:

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Anatoly Milischuk

Shikha Gupta

\$ PRF + Res. Corp.