

Supporting information for Multimode vibronic spectra of the Holstein molecular crystal model

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(Dated: February 12, 2010)

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I. THE BROWNIAN OSCILLATOR MODEL

The MBO Hamiltonian is given by [1–5]

$$H = |g\rangle H_g \langle g| + |e\rangle H_e \langle e| + H', \quad (1)$$

where

$$H_g = \sum_j \left[\frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 q_j^2 \right], \quad (2)$$

$$H_e = \hbar\omega_{eg}^0 + \sum_j \left[\frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 (q_j + d_j)^2 \right], \quad (3)$$

and

$$H' = \sum_n \left[\frac{P_n^2}{2m_n} + \frac{1}{2} m_n \omega_n^2 \left(Q_n - \sum_j \frac{c_{nj} q_j}{m_n \omega_n^2} \right)^2 \right]. \quad (4)$$

Here p_j (P_n), q_j (Q_n), m_j (m_n), and ω_j (ω_n) are the momentum, the coordinate, the mass, and the angular frequency of the j th (n th) nuclear mode of the primary (bath) oscillators, respectively. d_j represents the displacement for the j th nuclear mode in the excited electronic state. $\hbar\omega_{eg}^0$ is the energy separation of the purely electronic levels. H' describes the bath modes and their coupling to the primary oscillators with a coupling strength c_{nj} . The cross terms in $q_j Q_n$ are responsible for damping. By defining the energy gap coordinate operator U as:

$$U = H_e - H_g - \hbar\omega_{eg}^0. \quad (5)$$

We can write the correlation function for the j th mode from the parameters of the Hamiltonian:

$$C_j(t) = -\frac{1}{2\hbar^2} [\langle U(t)U(0)\rho_g \rangle - \langle U(0)U(t)\rho_g \rangle], \quad (6)$$

where $U(t)$ is the operator U in the interaction representation and ρ_g is the equilibrium ground-state vibrational density matrix:

$$\rho_g = \frac{|g\rangle\langle g| \exp(-\beta \hat{H}_g)}{\text{Tr} [\exp(-\beta \hat{H}_g)]} \quad (7)$$

with $\beta = 1/k_B T$.

In the present study, we adopt a simple form of the BO model with the bath modes is assumed to be a constant (i.e., $\gamma_j(\omega) = \text{constant}$, called Markovian or Ohmic limit) to

compute PL spectra. For this simple case, the spectral density function reads [3]

$$\tilde{C}_j''(\omega) = \frac{2\lambda_j\omega_j^2\omega\gamma_j}{\omega^2\gamma_j^2 + (\omega_j^2 - \omega^2)^2}, \quad (8)$$

where the real part of the self-energy, $\Sigma_l(\omega)$, is set to zero.

The spectral response function $g(t)$ can be expressed in terms of the frequency-domain correlation function $C_j''(\omega)$

$$g(t) = -\frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \frac{\sum_j \tilde{C}_j''(\omega)}{\omega^2} [1 + \coth(\beta\hbar\omega/2)] (e^{-i\omega t} + i\omega t - 1). \quad (9)$$

Finally, the linear absorption and the relaxed fluorescence line shape can be then obtained from the spectral response function $g(t)$:

$$\sigma_{abs}(\omega) = \frac{1}{\pi} \text{Re} \int_0^{\infty} dt \exp [i(\omega - \omega_{eg}^0 - \lambda)t - g(t)] \quad (10)$$

$$I_{PL}(\omega) = \frac{1}{\pi} \text{Re} \int_0^{\infty} dt \exp [i(\omega - \omega_{eg}^0 + \lambda)t - g^*(t)] \quad (11)$$

Without the coupling to the bath phonons, the Huang-Rhys theory [6] gives a Poisson distribution for phonon side peaks in the absorption spectrum at zero temperature:

$$\sigma_{abs}(\omega) = \exp(-S_j) \sum_{n=0}^{\infty} \frac{S_j^n}{n!} \delta(\omega - \omega_{eg} - n\omega_j) \quad (12)$$

S here is the intensity ratio between the first and zeroth phonon lines, and can also be identified with the average number of phonons emitted. For larger S , the Poisson distribution morphs into a Gaussian centered at S . Upon broadening due to bath dissipation and thermal effects, the well-resolved phonon peaks will acquire widths that increase with n . The width of the individual phonon peaks also increase with the temperature, linearly if the bath is Markovian [7].

II. LIMITING CASES

If there is only one Einstein phonon mode that is coupled to the exciton, no quadratic term included, and no transfer integral J considered, the Hamiltonian of the system at zero temperature recovers the form from the independent boson model:

$$\hat{H} = E_0 a^\dagger a + g a^\dagger a (b^\dagger + b) + \omega_0 b^\dagger b \quad (13)$$

As the bath phonons are assumed to be dispersionless, for the 0K case, the phonon occupation factors are zero, thus the Green's function has the form

$$G(t) = -i\theta(t)\exp[-itE_0 - g(1 - i\omega_0t - e^{-i\omega_0t})] \quad (14)$$

The spectral function is the imaginary part of the retarded Green's function of frequency:

$$A(\omega) = -2\text{Im}(-i) \int_0^\infty dt e^{i\omega t} \exp[-itE_0 - g(1 - i\omega_0t - e^{-i\omega_0t})] \quad (15)$$

or

$$A(\omega) = 2\text{Re} \int_0^\infty dt \exp[it(\omega - E_0 + g\omega_0) - g + ge^{-i\omega_0t}] \quad (16)$$

By expanding the $ge^{-i\omega_0t}$ part of the exponent in a power series:

$$\exp(ge^{-i\omega_0t}) = \sum_l \frac{g^l}{l!} e^{-i\omega_0lt} \quad (17)$$

it is possible to evaluate the time integral, so that it contains terms such as:

$$\int_0^\infty dt \exp[it(\omega - E_0 + g\omega_0 - \omega_0l)] = \frac{i}{\omega - E_0 + g\omega_0 - \omega_0l + i\delta} \quad (18)$$

If the limit $\delta \rightarrow 0$ is taken,

$$\frac{i}{\omega - E_0 + g\omega_0 - \omega_0l + i\delta} = P \frac{i}{\omega - E_0 + g\omega_0 - \omega_0l} + \pi\delta(\omega - E_0 + g\omega_0 - \omega_0l) \quad (19)$$

The spectral functional can then be expressed as the real part of this time integral, which is a series of delta functions

$$A(\omega) = 2\pi e^{-g} \sum_{\lambda=0}^{\infty} \frac{g^\lambda}{\lambda!} \delta(\omega - E_0 + g\omega_0 - \omega_0\lambda) \quad (20)$$

This spectral function provides a Poisson distribution of delta peaks with equal spacing of ω_0 , which is equivalent to the well-known Huang-Rhys theory[6].

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