Explaining the observed long coherence effects by 2D photon echo experiments in photosynthetic EET : Two-Component Phonon Spectrum model

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We propose a simple stochastic model which successfully explains the long coherence effects observed in photosynthetic Excitation Energy Transport (EET) by 2D photon echo experiments of G. S. Engel et. al. (Nature, **446** 782, (2007)). Our Two-Component Phonon Spectrum (TCPS) model is based upon the division of phonon degrees of freedom into a systematic component which is treated through polaron transformation and a stochastic component which is treated through dynamical disorder. This model successfully explains the observed long coherence upto $\sim 600 fsec$ in EET experiments.

Key-word: 2-D photon echo spectroscopy; Quantum master equations; polaron transformation; Dynamical disorder; Novikov theorem

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I. THE PROBLEM

In the theoretical description of the Excitation Energy Transport (EET) in biological systems, two theories[1] are popular (1) Förster theory and (2) Second Born quantum master equation theory. The first one (Förster's theory) is applicable when the system (pigment)-bath (protein) coupling is very large as compared to the intra-system (pigment-pigment) coupling which leads to an incoherent exciton transfer. Thus in this theory the time evolution of the density matrix elements is studied using Pauli's master equation in which the excitonic transfer rates are calculated using Fermi Golden rule. In the opposite case when the pigment-pigment coupling is very strong as compared to the system-bath coupling, one treats the system-bath coupling as a perturbation to obtain the second Born quantum master equation for the reduced density matrix of the system. These two limiting cases define the two popular theories and are well studied.[1]

Recent experimental observations[2] show that EET in FMO complex (Fenna-Matthews-Olson) of Green Sulfur bacteria does not fall in the above two limiting cases. The reason for this is that in FMO-complex the magnitude of the system (BChl molecules)-bath (protein scaffold) coupling is of the same order as of the intra-system (BChl-BChl molecule) coupling. So one cannot apply the above mentioned limiting theories.

Also with the advent of 2-D photon echo spectroscopy it is observed[3,4] that the exciton dynamics is fully coherent i.e., during the time taken by the exciton to transfer from one site to another the off-diagonal elements of the density matrix are non-zero. This type of transfer is called the "coherent transfer". This coherent transfer time scale is of the order of $600 fsec$ in FMO experiments.[3,4]

Ishizaki and Fleming[5] have developed a theory to explain the long coherence effects in EET. They use the reduced hierarchy equation approach previously developed by Tanimura and Kubo.[6] Jang et al[7] have also given a theory of coherent energy transfer which goes beyond the two limiting cases discussed above. In this contribution we propose an alternative theory which is able to explain the experimental observation of G. S. Engel et al.[3]

II. TWO-COMPONENT PHONON SPECTRUM (TCPS) MODEL

A. The model

Here, we propose a Two Component Phonon Spectrum (TCPS) model. Typically phonon spectrum has the form, $J(\omega) \propto \omega^n e^{\omega/\omega_c}$. The cut-off frequency ω_c provides us with a natural way of dividing the phonon spectrum, since for the FMO problem the characteristic frequency of the exciton transfer $\omega_{sys} \equiv J/\hbar$ where J is the resonance coupling strength, is of the same order as ω_c. We divide the phonon spectrum into two parts, namely a stochastic component and a systematic component. The part of the phonon spectrum with frequency $\omega > \omega_c$, the phonons will show oscillations faster than the exciton transfer frequency and hence we assume that the contributions from such phonons can be replaced by a stochastic component. The other part of the phonon spectrum corresponding to $\omega < \omega_c$ will have a slower oscillations than the excitonic transfer and we treat this part as a systematic component.

The systematic component comprises of phonon dynamics with well defined phonon spectral density and it "dresses" the bare matrix elements of the system Hamiltonian. This component is treated through the polaron transformation. The second component is stochastic, and we assume that it randomly perturbs the site energies. With this picture in mind

we model the FMO problem as

$$H = H_s + H_b + H_{sb}$$
$$H_s = \epsilon_1|1\rangle\langle 1| + (\epsilon_2 + F(t))|2\rangle\langle 2| + J(|1\rangle\langle 2| + |2\rangle\langle 1|)$$

$$\langle F(t)\rangle = 0, \quad \langle F(t)F(\tau)\rangle = \eta\delta(t-\tau)$$

$$H_{sb} = \left(\sum_n \hbar\omega_n g_n(b_n + b_n^\dagger)\right)(|1\rangle\langle 1| - |2\rangle\langle 2|)$$
$$H_b = \sum_n \hbar\omega_n(b_n^\dagger b_n + 1/2) \tag{1}$$

Here H_s, H_b, and H_{sb} are the system, bath, and system-bath interaction Hamiltonians respectively. Our system is a two level system with site energies ϵ_1 and ϵ_2 with one site energy randomly perturbed by stochastic noise[8] which we take it to be a Gaussian White Noise (GWN). The interaction of the systematic component of the bath is given by H_{sb} which involves g_n which is the difference between the coupling strengths of the nth phonon mode with the two levels.

B. The solution

We use the polaron transformation[9] to deal with the systematic component. Starting with Liouvelle-von-Neumann equation ($\hbar = 1$),

$$i\frac{\partial\rho_{total}(t)}{\partial t} = [H_s + H_{sb} + H_b, \rho_{total}(t)], \tag{2}$$

we polaron transform[9] the above equation as $\tilde{\rho}_{total}(t) = e^G\rho_{total}(t)e^{-G}$, and $\tilde{H}_i = e^G H_i e^{-G}$ with $G = \left(\sum_n \hbar g_n(b_n + b_n^\dagger)\right)(|1\rangle\langle 1| - |2\rangle\langle 2|)$ to obtain the total Hamiltonian $\tilde{H} = \tilde{H}_s + \tilde{H}_{sb} + \tilde{H}_b$,

$$\tilde{H} = \left(\epsilon_1 - \sum_n \omega_n g_n^2\right)|1\rangle\langle 1| + \left(\epsilon_2 - \sum_n \omega_n g_n^2 + F(t)\right)|2\rangle\langle 2|$$
$$+J\Theta|1\rangle\langle 2| + J\Theta^\dagger|2\rangle\langle 1| + \sum_n \hbar\omega_n(b_n^\dagger b_n + 1/2). \tag{3}$$

Here

$$\Theta = e^{\sum_n g_n(b_n^\dagger - b_n)}. \tag{4}$$

The important point is that polaron transformation completely removes H_{sb} and it "dresses" the site energies as $\tilde{\epsilon}_1 \equiv \epsilon_1 - \sum_n \omega_n g_n^2$ etc. and J as $J\Theta$.

Liouvelle-von-Neumann equation takes the following form,

$$i\frac{\partial\tilde{\rho}_{total}(t)}{\partial t} = [\tilde{H}, \tilde{\rho}_{total}(t)], \tag{5}$$

In the subsequent analysis we perform two types of averaging:
(1) Averaging over the dynamical disorder which is denoted by $\langle ...\rangle$
. (2) Averaging over the systematic component of the bath which is denoted by $\overline{(...)} \equiv tr_b(...)$.

The calculation is performed in two steps:

Step I: Averaging over dynamical disorder:

$$i\frac{\partial\langle\tilde{\rho}(t)\rangle}{\partial t} = [\tilde{\epsilon}_1|1\rangle\langle 1| + \tilde{\epsilon}_2|2\rangle\langle 2|, \langle\tilde{\rho}(t)\rangle]$$
$$+\langle F(t)[|2\rangle\langle 2|, \tilde{\rho}(t)]\rangle$$
$$+J[\Theta|1\rangle\langle 2| + \Theta^\dagger|2\rangle\langle 1|, \langle\tilde{\rho}(t)\rangle] \tag{6}$$

Step II: Averaging over the systematic component:

$$i\frac{\partial\langle\overline{\tilde{\rho}}(t)\rangle}{\partial t} = [\tilde{\epsilon}_1|1\rangle\langle 1| + \tilde{\epsilon}_2|2\rangle\langle 2|, \langle\overline{\tilde{\rho}}(t)\rangle]$$
$$+\langle F(t)[|2\rangle\langle 2|, \overline{\tilde{\rho}}(t)]\rangle$$
$$+J[\overline{\Theta}|1\rangle\langle 2| + \Theta^\dagger|2\rangle\langle 1|, \langle\tilde{\rho}(t)\rangle] \tag{7}$$

Now we simplify the above averages term by term. We define the matrix elements of the system as $\rho_{ab}(t) \equiv \langle a|\langle\overline{\tilde{\rho}}(t)\rangle|b\rangle$, $a,\ b \in [1,2]$ i.e. by tracing out both the systematic and stochastic components.

Consider Term I on the RHS of Eq. (7)

$$i\left(\frac{\partial\rho_{11}(t)}{\partial t}\right)_I = \tilde{\epsilon}_1\rho_{11}(t) - \tilde{\epsilon}_1\rho_{11}(t) = 0 = i\left(\frac{\partial\rho_{22}(t)}{\partial t}\right)_I \tag{8}$$

$$i\left(\frac{\partial\rho_{12}(t)}{\partial t}\right)_I = (\tilde{\epsilon}_1 - \tilde{\epsilon}_2)\rho_{12}(t) = \Delta\rho_{12}(t) \tag{9}$$

Here $\Delta = \epsilon_1 - \epsilon_2$. The $\rho_{21}(t)$ is the complex conjugate of $\rho_{12}(t)$.

Consider Term II on the RHS of Eq. (7)

$$i\left(\frac{\partial\rho_{11}(t)}{\partial t}\right)_{II} = i\left(\frac{\partial\rho_{22}(t)}{\partial t}\right)_{II} = 0 \tag{10}$$

$$i\left(\frac{\partial\rho_{12}(t)}{\partial t}\right)_{II} = -\langle F(t)\rho_{12}(t)\rangle = -i\left(\frac{\partial\rho_{21}(t)}{\partial t}\right)_{II} \tag{11}$$

We note that $F(t)$ is a stochastic perturbation and $\rho_{12}(t)$ is a functional of $F(t)$. The problem now is to decouple the term $\langle F(t)\rho_{12}(t)\rangle$. Here, we use the result due to Novikov[10] for Gaussian random noises.

$$\langle F(t)\rho_{ab}(t)\rangle = \int_{-\infty}^{\infty} dt'\langle F(t)F(t')\rangle\left\langle\frac{\delta\rho_{ab}(t)}{\delta F(t')}\right\rangle \tag{12}$$

Here $\frac{\delta\rho_{ab}(t)}{\delta F(t')}$ is the functional derivative. Using the properties of stochastic noise and after some simplifications we get

$$\langle F(t)\rho_{12}(t)\rangle = i\eta\langle\rho_{12}(t)\rangle. \tag{13}$$

Consider Term III on the RHS of Eq. (7)

We assume that the bath is always in equilibrium, i.e., $\overline{\Theta\langle\tilde{\rho}(t)\rangle} = \overline{\Theta}\ \overline{\langle\tilde{\rho}(t)\rangle}$. This is similar to Born type approximation where the bath effects the system but the reverse is not true.

$$i\left(\frac{\partial\rho_{11}(t)}{\partial t}\right)_{III} = J\lambda(\rho_{21}(t) - \rho_{12}(t)) \tag{14}$$

$$i\left(\frac{\partial\rho_{12}(t)}{\partial t}\right)_{III} = J\lambda(\rho_{22}(t) - \rho_{11}(t)) \tag{15}$$

Where $\lambda \equiv \overline{\Theta} = tr_b(\rho_b\Theta) = e^{-2\sum_n g_n^2\coth(\hbar\beta\omega/2)}$.

Collecting all the terms we end up with the following system of equations

$$\frac{\partial\rho_{12}(t)}{\partial t} = -i\Delta\rho_{12}(t) - \eta\rho_{12}(t) - iJ\lambda(\rho_{22}(t) - \rho_{11}(t))$$
$$\frac{\partial\rho_{11}(t)}{\partial t} = -iJ\lambda(\rho_{21}(t) - \rho_{12}(t))$$
$$\rho_{11}(t) + \rho_{22}(t) = 1 \tag{16}$$

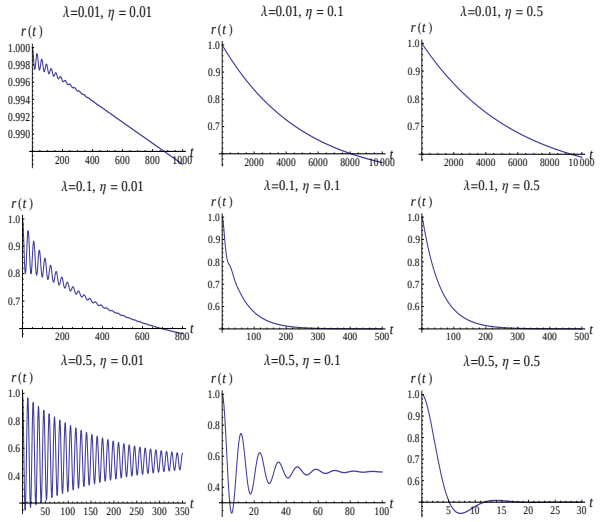

FIG. 1. The time evolution of population on site 1 i.e., $\rho_{11}(t) = r(t)$. Here $J = 0.5, \Delta = 0.2$ and the phonon coupling strength g_n decreases i.e., λ increases as we go down in the figure and the strength of dynamical disorder η increases as we go horizontally to right. The behaviour of $r(t)$ seems to be intuitively correct. As λ increases we see more oscillations and as η increases oscillations die out as expected.

Separating the real and imaginary parts $\rho_{12}(t) = x(t) + iy(t)$ and $\rho_{11}(t) = r(t)$ we have

$$\begin{aligned}\dot{x}(t) &= \Delta y(t) - \eta x(t)\\ \dot{y}(t) &= -\Delta x(t) - \eta y(t) - J\lambda(1 - 2r(t))\\ \dot{r}(t) &= -2J\lambda y(t)\end{aligned} \tag{17}$$

The above system of ODEs can be solved exactly with given initial conditions, however, the exact expression is very cumbersome. We give the analytic solution in the long time limit using Laplace transforms (see Appendix A) which clearly show that equilibrium value of $r(t \to \infty) = 1/2$..[11] The system of equations (17) is also solved for all times numerically (see figure 1). If we go vertically downwards in the figure, λ increases, i.e. the phonon coupling strength decreases and we see more oscillations, also if we go horizontally, then η increases (strength of the dynamical disorder) and oscillations die out as expected intuitively.

III. EXPLAINING THE EXPERIMENTAL OBSERVATIONS OF G. S. ENGEL ET. AL.

In this section we analyze the above model with experimentally known values of physical parameters and show that it explains the experimental observations of G. S. Engel et. al.[3]

A. Calculation of λ

First, we consider a continuum of systematically coupled phonons and the parameter λ for the phonon continuum is

$$\lambda = e^{-2\sum_n g_n^2 \coth(\hbar\beta\omega/2)} \tag{18}$$

We introduce the spectral density $J(\omega) = \sum_n \delta(\omega - \omega_n)\omega_n^2 g_n^2$. By inserting the integral over ω in the exponent and using the delta function one has

$$\lambda = e^{-2\int_0^\infty \frac{d\omega}{\omega^2} J(\omega)\coth(\beta\hbar\omega/2)} \tag{19}$$

We take the spectral density to be super-ohmic $J(\omega) = \frac{\xi}{3}(\frac{\omega^3}{\omega_c^2})e^{-\omega/\omega_c}$.[7] Here ξ is a dimensionless coupling constant, which we determine from the experimental information available. ω_c is the characteristic frequency of the bath which is $\sim 10^{13} Hz$ (for $\tau_c = \gamma^{-1} \sim 100 femto\ sec$) in the FMO problem.[5] At the temperatures $T = 77K$ of the experiment[3] the argument of the coth is a small quantity i.e., $\coth(x) \sim 1/x$. Thus the integral in the exponent of λ can be calculated as,[12]

$$\lambda = e^{-4\xi\frac{k_B T}{3\hbar\omega_c}} \tag{20}$$

Let us now calculate ξ from the experimental information. Let ϵ_{sb} be the bath re-organization energy which is given by

$$\epsilon_{sb} = \frac{\xi\hbar}{6\omega_c^2}\int_0^\infty d\omega\omega^2 e^{-\omega/\omega_c}\coth(\beta\hbar\omega/2) \simeq \frac{1}{3}\xi k_B T \tag{21}$$

Thus $\xi = 3\frac{\epsilon_{sb}}{k_B T}$ which is now given in terms of the known quantity ϵ_{sb} which is $\sim 100 cm^{-1}$ in the FMO problem. Collecting the above we have,

$$\lambda = e^{-4\frac{\epsilon_{sb}}{\hbar\omega_c}} \tag{22}$$

Thus our model parameter λ is now given in terms of the well known quantities in the FMO problem.

B. Line-shape analysis for η

We now determine the phenomenological parameter η in our model from the homogeneously broadened line shape. The absorption line shape $I(\omega)$ of the two level system (Eq. (1)) is given as

$$I(\omega) \propto \int_{-\infty}^{+\infty} dt e^{i\omega t} tr_{bath} tr_{system}((\mu(t)\mu(0))) \tag{23}$$

Where ω is the photon frequency and μ is the system's dipole operator. For $\hbar\omega >> k_B T$ we obtain $tr_{bath} tr_{system}((\mu(t)\mu(0))) = tr_{bath}\sum_{a,b=1,2,a\neq b}(\mu_{ab}(t)\mu_{ba}(0)) \propto \rho_{12} + \rho_{21}$.[13]

$$I(\omega) = 2Re\int_0^\infty dt e^{i\omega t}\rho_{12} \tag{24}$$

The initial conditions are $\rho_{11}(0) = 1$, $\rho_{22}(0) = \rho_{12}(0) = \rho_{21}(0) = 0$.

Our aim is to fit the model generated $I(\omega)$ with the real experimental observation and to extract our phenomenological parameters η which is the strength of the dynamical disorder. We will use this to simulate the quantum dynamics of the density matrix elements. One explains the experimental observations provided one observes oscillations in the populations and non-zero values of the off-diagonal elements of the simulated density matrix i.e., coherences of order $600 fsec$. The basic problem with linear absorption line shape is that its broadening is due to both homogeneous and in-homogeneous mechanisms. In our case the broadening is homogeneous due

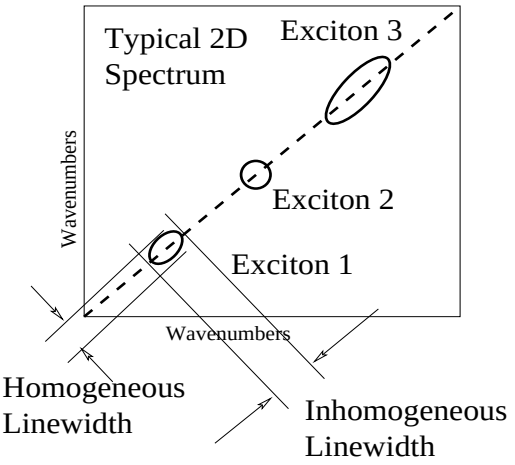

FIG. 2. Schematic line broadening information in 2-D photon echo spectrum shown without cross peaks. The linewidth due to homogeneous and in-homogeneous broadening are in orthogonal directions as shown.

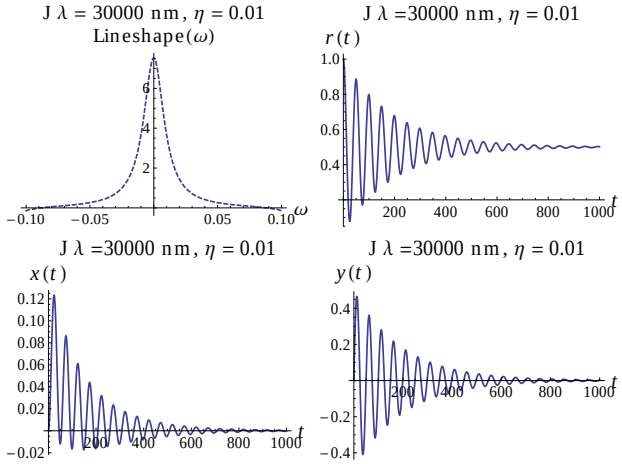

FIG. 3. Line shape function $I(\omega)$ for $\Delta = 100cm^{-1}, J = 100cm^{-1}$, $\eta = 0.01$, $\epsilon_{sb} = 100cm^{-1}$, $\omega_c = 2 \times \pi 10^{13} Hz$ (upper left). This value of η i.e., 0.01 give the correct value of homogeneous line-broadening $\delta\omega \simeq 2.87 \times 10^{13} Hz$. Other three graphs show the time dynamics of $r(t)$, $x(t)$, and $y(t)$ for the above parameters. Here time is measured in femto-seconds. Clearly one observe oscillations upto $600 fsec$.

to dynamical disorder and thus we need to subtract the in-homogeneous broadening due to static disorder. But thanks to the 2-D photon echo spectroscopy one has the important information about both homogeneous and in-homogeneous broadening. We want to measure Full Width at Half Maximum (FWHM) of the homogeneously broadened peak. We consider Fig 2 (a) of G. S. Engel et. al..[3] The homogeneous broadening is along the main diagonal (see figure 2 of this manuscript). From the scale given in terms of nano-meters of the figure 2(a) of G. S. Engel et. al.,[3] the FWHM is about $\simeq 10nm$ and the exciton peak occurs at 810 nm. This gives the frequency broadening $\delta\omega \simeq 2.87 \times 10^{13} Hz$. In what follows we take the experimental value of homogeneous broadening $\delta\omega$ from 2-D photon echo spectrum[3] and it is well known in FMO problem that site energy difference $\Delta \simeq 100cm^{-1}$. The resonance coupling $J \simeq 100cm^{-1}$. With this experimental information we plot the homogeneous broadened line shape such that its FWHM is equal to $10nm$ and this gives us our phenomenological parameter $\eta = 0.01$ (see the first graph of figure 3).

C. Long coherences

We now have all the required parameters in Eq. (17) from the experimental information, namely, $\eta = 0.01$, $J\lambda = 30,000nm$, and $\Delta = 100cm^{-1}$. With these values we plot the dynamics of the density matrix elements $r(t)$, $x(t)$, and $y(t)$ (see figure 3). We clearly see that the density matrix elements show oscillations upto $600 fsec$ thus corroborating the experimental observations of G. S. Engel et. al..[3]

IV. DISCUSSION

We have given a Two Component Phonon Spectrum (TCPS) model for the FMO problem which consists of a systematic phonon component and a stochastic component. We argue that the stochastic component comes from the high frequency phonons, $\omega > \omega_c$. For these phonons the phonon oscillations are much faster than the typical exciton transfer frequency $\omega_{sys} = J/\hbar$ which is of the order of $\omega_c \sim 10^{13} Hz$ for $J = 100\ cm^{-1}$ in the FMO problem. We expect and assume the contributions from these high frequency phonons to have a phase randomness. Hence this contribution can be effectively treated as noise. We stress that the theory given by us is phenomenological in nature. A rigorous theory justifying the origin of dynamical disorder from phase randomness for high frequency phonons has yet to be developed.

With the above model we have been able to explain the experimental observations reasonably well. Estimating the different parameters of the model from the experimental observations we are able to reproduce the coherence time of $600 Femto\ sec$.

Appendix A: Limiting solution of two-component phonon model

Laplace transform of the system Eq (17) takes the form

$$\begin{pmatrix} s & 0 & 2J\lambda \\ 0 & s+\eta & -\Delta \\ -2J\lambda & \Delta & s+\eta \end{pmatrix} \begin{pmatrix} \tilde{r}(s) \\ \tilde{x}(s) \\ \tilde{y}(s) \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ -\lambda J/s \end{pmatrix}$$

After inversion, in the long time limit one has

$$r(t) \simeq 1/2 + rational\ function(\lambda, J, \Delta, \eta) e^{-t\frac{4\eta\lambda^2 J^2}{\eta^2+4\lambda^2 J^2+\Delta^2}}$$

This takes the value 1/2 when $t >> t_{relax} = \frac{\eta^2+4\lambda^2 J^2+\Delta^2}{4\eta\lambda^2 J^2}$.

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[11]We know that $\frac{\rho_{11}}{\rho_{22}} = \frac{e^{-\epsilon_1/k_bT}}{e^{-\epsilon_2/k_bT}}$. Thus ρ_{11}/ρ_{22} will be 1 i.e., $r = 1/2$ only if the temperature T of the bath is infinite. This is the well known basic defect of the model of dynamical disorder.

[12]The contribution to the integral from $\omega > \omega_c$ (stochastic component) for the temperature of interest, $T = 77K$, is very small. Hence, we can extend the integral over ω to ∞ with negligible correction.

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