Inhomogeneous Broadening Induced Long-Lived Integrated Two-Color Coherence Photon Echo Signal

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1 Supporting Information

ABSTRACT: Recent observations of the long-lasting nonlinear signals in a variety of light-harvesting complexes have initiated an active debate on the origin of long-lived coherence in the biological systems. In this work we show that disorder of site energy can induce a long-lived electronic coherence between two chromophores in a strongly coupled dimer system, in addition to the ensemble dephasing effect. This phenomenon is physically explained as the correlated fluctuation of excitons with the equal delocalization on two sites, when the site-energy distributions overlap to give resonance. Using the integrated two-color coherence photon echo signal as an example, we show that the coherence in such a system exhibits a biexponential decay with a slow component with a lifetime of hundreds of femtoseconds and a rapid component with a lifetime of tens of femtoseconds. The current result provides a possible microscopic basis for the electronic coherence to be the origin of the long-lived coherence signals to be considered along with other recently proposed mechanisms.

1. INTRODUCTION

In nuclear magnetic resonance (NMR) experiments, the signal experiences a decay after an initial excitation pulse. This decay is induced by two physical mechanisms, the spin relaxation and the ensemble dephasing from the static disorder among different spins. The first case results in an irreversible loss of the magnetization, while the latter can be removed by the spin echo method with an inversion pulse. Similar echo methods have been applied with femtosecond laser technology to probe chromophore–solvent dynamics and ultrafast energy transfer by partially removing the ensemble dephasing caused by the static disorder, known as inhomogeneous broadening. For example, the recent development of two-dimensional electronic photon echo spectroscopy has enabled direct probing of the relevant energy transfer dynamics in the photosynthetic system. A remarkable long-lived coherence signal was reported as the beating of the off-diagonal peak in the Fenna–Matthews–Olson complex at 77 K. This observation was later confirmed in a variety of light-harvesting complexes. The intriguing physical question behind these observations is the origin of the long-lived signals in the “noisy” environments of biological systems.

The direct theoretical approach to understand these observations is via dynamical simulation, based on a typical Hamiltonian, estimated from other spectra, such as the linear absorption spectrum. The reliability of the typical dynamics relies on it being representative of the statistical average behavior of the dynamics of the whole ensemble system. For a condensed phase system, such as light-harvesting pigment–protein complexes, the difference of site energy among individual units may be large and is generally assumed to obscure the actual individual behavior of a single system through the ensemble averaging effect. In terms of the two-dimensional Fourier transformed (2DFT) coherence signal, the lifetime of the coherence is dramatically reduced by disorder of site energy. Mathematically, the most probable value is representative, only if it is close to the mean value of a statistical distributions, e.g., a Gaussian distribution. The excitonic coherence related signal from an ensemble generally involves the disorder of the exciton energy gap, which is a nonlinear function of the site energies. For a strongly coupled system with a large amount of disorder, the distribution of the exciton energy gap is dramatically distorted from a Gaussian shape to a bimodal structure, which, in turn, induces a complex effect on the coherence signal.

In this article, we investigate the impact of disorder on the nonlinear signal related to excitonic coherence in a strongly coupled dimer system, such as the bacteriopheophytin–bacteriochlorophyll pair in the bacterial reaction center. Beside the ensemble dephasing, we show the emergence of a long-lived electronic coherence signal due to the inhomogeneous broadening. The amplitude of such a signal depends on the overlap of the site-energy distributions of the individual chromophores in the dimers. The result provides a possible basis for the electronic coherence to be the origin of the observed long-lived coherence signal for dimer systems with...
strong electronic coupling, compared to the site energy fluctuations. We illustrate the mechanism via the integrated two-color coherence photon echo (2CCPE) signal\textsuperscript{10,18} which directly probes the interexciton coherence by arranging the pulses with different frequencies to be “resonant” with different excitons. Such a mechanism for long-lived coherence generation will need to be included along with other proposed origins such as electronic coupling\textsuperscript{19–21} and vibronic effects\textsuperscript{22–28} etc.

2. MODEL

We consider a dimer, consisting of two chromophores A and B. The Hamiltonian of the dimer is given by

\begin{equation}
H = H_A + H_B + J|A\rangle\langle B| + |B\rangle\langle A|
\end{equation}

where \(H_i = \varepsilon_i + \sum_\omega \omega_i(|i\rangle\langle i| + 1/2) + |i\rangle\langle i|d^\dagger d+i\rangle\langle i|\) is the Hamiltonian of chromophore \(i = A, B\) with the corresponding environmental degree of freedoms (DoF) \(i\) = a, b. The electronic degrees of freedom can be diagonalized with the following transformations

\begin{equation}
|+\rangle = \cos \theta |A\rangle + \sin \theta |B\rangle
\end{equation}

\begin{equation}
|\rangle = \sin \theta |A\rangle - \cos \theta |B\rangle
\end{equation}

where \(\theta = 1/2 \arctan[2f/(\varepsilon_A - \varepsilon_B)]\) is the mixing angle. The corresponding exciton energies read \(\varepsilon_{\pm} = [\varepsilon_A + \varepsilon_B \pm ((\varepsilon_A - \varepsilon_B)^2 + 4f^2)^{1/2}]/2\). In pigment–protein complexes, the slow motions of the protein environment result in a static site-energy distribution, which is called inhomogeneous broadening or static disorder. We assume independent Gaussian disorder \(\varepsilon_i \in N(\varepsilon_0, \sigma)\) for the chromophore \(i = A, B\) with the central frequency \(\varepsilon_0\) and the distribution width \(\sigma\). The static disorder is an important factor in reducing the electronic coherence between the ground state and the excited state through ensemble dephasing. For example, an average over a Gaussian distribution of \(\omega \in N(0, \sigma = 50 \text{ cm}^{-1})\) results in a Gaussian decay, with lifetime around 100 fs, to an infinite long-lived oscillation \(\exp(\omega t)\). The photon echo method is experimentally utilized to overcome this ensemble dephasing and reveal the relevant environmental dynamical fluctuations\textsuperscript{5.6}. In the integrated two-color coherence photon echo experiment, the first two pulses with delay \(t_1\) excite the system into a coherence state \(|+\rangle\langle-|\), which evolves for \(t_2\) before the third pulse stimulates the output signal. Supporting Information is included to describe the 2CCPE method. In contrast to two-dimensional electronic spectroscopy, the signal is integrated over the echo time \(t_2\)\textsuperscript{10} resulting in loss of frequency resolution.

In the 2CCPE measurement, the dynamics of the coherence is recorded by the signal evolution over waiting time \(t_2\). This evolution is related to the exciton energy gap \(\Delta = \varepsilon_{+} - \varepsilon_{-}\) through the phase factor \(\exp[-i\Delta t_2]\). For the ensemble system, the exciton energy gap has a distribution due to the site energy disorder on the two chromophores. The distribution of exciton energy gap \(\Delta\) is described by the function

\begin{equation}
p(\Delta) = \frac{1}{\pi \sigma \sqrt{\Delta^2 - 4f^2}} \left[ e^{-(\Delta_0^2 + 4f^2)/2\sigma^2} + e^{-(\Delta_0^2 + 4f^2)/2\sigma^2} \right]
\end{equation}

where \(\sigma = (\sigma_A^2 + \sigma_B^2)^{1/2}\) and \(\delta_0 = \varepsilon_A - \varepsilon_B\) is the mean site energy difference. In Figure 1, we show the distribution of the exciton energy gap with different disorder amplitudes \(\sigma(\sigma_B) = 40, 60, 100, \text{ and } 130 \text{ cm}^{-1}\) with the mean exciton energy gap \(\Delta_0 = (\sigma_0^2 + 4f^2)^{1/2} = 680 \text{ cm}^{-1}\) and electronic coupling, \(J = 280 \text{ cm}^{-1}\). These parameters for the dimer are based on observations of the purple bacterial reaction center\textsuperscript{10,18} (bRC). However, the bRC is far more complicated than a dimer. For example, the asymmetry between two branches will bring interference\textsuperscript{29} and the inclusion of the special pair will result in a complex exciton level structure. The full model of bRC will thus inevitably complicate the physical mechanism of the disorder-induced long-lived coherence presented. Therefore, for clarity, we present a simplified dimer model with parameters estimated from bRC in the current discussion. For relatively small disorder amplitude, e.g., \(\sigma(\sigma_B) = 40 \text{ and } 60 \text{ cm}^{-1}\), the distribution of exciton energy gap is similar to a Gaussian function and becomes broader as the site disorder amplitude increases. This increase of the distribution width, in turn, results in a decrease of the coherence lifetime. With further increase of disorder amplitudes, \(\sigma(\sigma_B) = 100 \text{ and } 130 \text{ cm}^{-1}\), the shape of the distribution is dramatically distorted from a Gaussian distribution, illustrated in Figure 1. A singular peak emerges at the site-energy resonance, \(\varepsilon_A = \varepsilon_B\) on the tail of the exciton energy gap distribution. In this resonance region, the exciton energy gap is twice the electronic coupling, \(\Delta = 2f = 560 \text{ cm}^{-1}\). The sharp peak in the distribution of \(p(\Delta)\) gives rise to the reduction of the ensemble dephasing, as compared to the typical dynamics for a system with an exciton energy gap at \(\Delta = \Delta_0\).

Of course in a real system, the coherence lifetime is also influenced by the amplitude of the dynamical fluctuations, known as homogeneous broadening. In a typical experiment, pulses with different frequencies are arranged to excite the corresponding excitons. The resultant spectrum in the 2CCPE studies directly shows the time-domain dynamics of the excitons, rather than the individual sites. For these excitons, their environments are composed of contributions from the two chromophores. The composite environment is described by the joint line broadening functions\textsuperscript{10,16} and \(g_{+}(t) = \cos^4 \theta g^4(t) + \sin^4 \theta g^4(t), g_{-}(t) = \sin^2 \theta g^2(t) + \cos^2 \theta g^2(t)\), in the response function formalism\textsuperscript{33}. In the resonance region, the mixing angle is \(\theta = \pi/4\) and both excitons \(|\pm\rangle\) delocalize equally over the two sites. The two excitons experience the same environmental fluctuations, namely, \(g_{+}(t) = g_{-}(t)\), which results in a longer lifetime decay for the coherence between the excitons \(|+\rangle\) and \(|\rangle\rangle\).\textsuperscript{9} For one special case \(g_A(t) = g_B(t)\), the dynamic fluctuation is reduced to 50% of the initial amplitude when \(\theta = \pi/4\).
Without losing generality, we assume the homogeneous line broadening functions are the same for both sites to clearly demonstrate the mechanism in the following discussion.

3. RESULTS AND DISCUSSION

Combining the effect of the narrow peak in the tail of the exciton energy gap distribution with the longer lifetime of the excitonic coherence around this peak, we predict a slow decay component in the photon echo signal, in addition to the rapid decay predicted by a dynamic simulation with a typical Hamiltonian. For long waiting time \( t_2 \), the signal from the dimers in the resonance region dominates the decay pattern, while the signal from the bulk of the distribution has decayed. In Figure 2a, we present simulated 2CCPE signals with different inhomogeneous broadenings 0, 60, 100, and 130 cm\(^{-1}\) at a delay time \( t_1 = 30\) fs. The corresponding distributions of the site energies are presented in the three insets of the figure, and the linear absorption spectra are presented in Figure 2b.

We assume that each chromophore couples to an independent bath characterized by a continuous spectral density function, which is described by the Drude-Lorentz spectral density

\[
J(\omega) = \frac{2\omega_0\omega}{\omega_0^2 + \omega^2}
\]

For clarity, we choose the same cutoff frequency for the baths, \( \omega_0 = 50\) cm\(^{-1}\), and reorganization energy \( \lambda = 50\) cm\(^{-1}\) for both chromophores A and B in the following discussion. The disorders are integrated by the 128-point Gaussian-Hermite method, which has been shown to be reliable for simulation of disorders are integrated by the 128-point Gaussian-Hermite method. We assume independent baths with the same cutoff frequency \( \omega_0 = 50\) cm\(^{-1}\) and a reorganization energy \( \lambda = 50\) cm\(^{-1}\) for both chromophores A and B. The insets show the site-energy distributions, with the resonance region (gray shadowed area).

Figure 2. (a) Integrated two-color coherence photon echo signal with the time delay \( t_1 = 30\) fs and (b) the linear absorption spectra at 77 K. The simulation is performed on dimers with an exciton energy gap \( \Delta_0 = 680\) cm\(^{-1}\) and a coupling constant \( J = 280\) cm\(^{-1}\). The signals are evaluated for different static disorders of 0, 60, 100, and 130 cm\(^{-1}\), respectively, which are integrated through the 128-point Gauss-Hermite method. We assume independent baths with the same cutoff frequency \( \omega_0 = 50\) cm\(^{-1}\) and a reorganization energy \( \lambda = 50\) cm\(^{-1}\) for both chromophores A and B. The insets show the site-energy distributions, with the resonance region (gray shadowed area).

The physical basis of both this model and the one described in this paper is identical. Which model (or both) applies will depend on the variation in the electronic coupling strength and the extent of the inhomogeneous broadening. Since the 2CCPE is homodyne detected, a beating pattern with the frequency of the exciton energy gap is not observed. However, the nuclear DoF interference\(^8\) and the asymmetry of two branches\(^9\) may provide an oscillating modulation of the decay signal.\(^{10}\) This effect is beyond the main scope of the paper and will be discussed elsewhere.

Recently, a considerable number of theoretical studies\(^{22-28}\) have focused on the possible mixing the nuclear vibrational coherence signal with the excitonic coherence signal. To disentangle the various possible contributions, one needs to characterize the behavior of the excitonic coherence signal fully and then add the additional complexity of the vibration coupling. In the following discussion, we will present characterization of the excitonic coherence signal of a strongly coupled dimer, by showing the dependence of the lifetimes and amplitudes on the amplitudes of disorder, the amplitudes of the dynamical fluctuation, and the environment temperature.

To characterize the properties of the biexponential decay in the 2CCPE signal of Figure 2, we present the dependence of the long and short lifetimes and their corresponding amplitudes on the static disorder \( (\sigma_{A(B)}) \) in Figure 3. The error bars result from the intrinsic uncertainty of fitting a multiple exponential decay. For relatively small disorder \((<100\) cm\(^{-1}\)) , the lifetime of rapid decay component decreases with increase in disorder, illustrated in Figure 3a. In this region, the distribution of the exciton energy gap still resembles a Gaussian distribution (see Figure 1) and provides only the ensemble dephasing effect. The corresponding amplitude is near 100%, which means one exponential decay can be used to accurately fit the signal profile. The lifetime of the rapid decay stops decreasing, after a slow decay component emerges at a disorder of 115 cm\(^{-1}\) with an amplitude about 1%. The increase of the short lifetime is understood as the effective reduction of the ensemble dephasing, when more dimers are in the resonant region. This increase of dimers in the resonance region results in a lifetime around 700 fs. Experimentally, such two distinct lifetimes in the coherence decay have been detected in the 2DFT spectrum on LHCl,\(^9\) a system with 14 monomers. In that work, the two times scales of coherence decay were discussed via a model including the mixing angle changes as a result of different coupling strengths between chromophores.\(^9\)
broader resonance peak. Thus, the lifetime of the slow component decreases as the amplitude of the disorder increases, as shown in Figure 3b. However, the amplitude of the slow component is proportional to the area of the resonance region in the energy gap distribution. We show an increase of amplitude from 1% at $\sigma_{A(0)} = 115 \text{ cm}^{-1}$ to 10% at 135 cm$^{-1}$.

To evaluate the impact of dynamic fluctuations on the lifetime, we show the dependence of the lifetimes and the corresponding amplitudes on the strength of the environmental fluctuation through the reorganization energy, $\lambda$, at 77 K in Figure 4. Both the lifetimes of the slow and rapid coherence components decrease, as expected, with an increase in the fluctuation amplitude. For the rapid component, the lifetime, at reorganization energy $\lambda = 140 \text{ cm}^{-1}$, reaches 20 fs. For the slow component, the lifetime is about 400 fs with $\lambda = 140 \text{ cm}^{-1}$. As illustrated in Figure 2, the amplitudes of the slow and rapid decay are primarily determined by the overlap of the site-energy distributions. Therefore, the amplitudes of the decay components, presented in Figure 4b, are independent of the fluctuation amplitude. In the current simulation of 2CCPE signals, we assign a time-independent mixing angle $\theta$ for the dimer with one parameter set ($\langle \epsilon_d, \epsilon_a \rangle$). However, the dynamical fluctuation of environmental DoF provides an effective modulation of the site energy, which results in a time-dependent mixing $\theta(t)$. For a small reorganization ($\lambda \ll 2J$), the mixing angle does not change dramatically with the fluctuation of the sites energies. Therefore, all the discussions above are valid. However, this approximation fails when the dynamic fluctuation is on the similar amplitude of the coupling ($\lambda \approx 2J$), known as the intermediate region.33

The amplitude of the dynamic fluctuation is also related to the temperature. Table 1 presents the temperature dependence of the two lifetimes with the small ($\lambda = 50 \text{ cm}^{-1}$) and large reorganization energy ($\lambda = 140 \text{ cm}^{-1}$). For both cases, we observe a reduction of the lifetimes for both slow and rapid decay components. With small fluctuation ($\lambda = 50 \text{ cm}^{-1}$), the lifetime of the slow decay component drops to 360 fs at room temperature (300 K), compared with 680 fs at 77 K. However, the biexponential decay is retained with a lifetime for the rapid decay of 25.4 fs. For large fluctuation ($\lambda = 140 \text{ cm}^{-1}$), we show a similar reduction of the short lifetime to 9.6 fs and the long lifetime to 152 fs. This decrease of the lifetime is caused by the increasing fluctuation amplitudes of electronic energy on the pigment with the increase of temperature.30

4. CONCLUSION

In conclusion, we have presented a residual long-lived coherence signal in integrated two-color coherence photon echo experiments on a strongly coupled dimer system resulting from inhomogeneous broadening (static disorder). The physical mechanism is understood as the correlated fluctuation of excitons in the resonance region. This mechanism provides an extension of the physical origin for the correlated fluctuation of excitons34,35 in a strongly coupled dimer, in addition to that arising directly from the coupling over the mean donor–acceptor energy gap.9,13 We show that the inhomogeneous broadening leads to a biexponential decay of coherence with one short lifetime (tens of femtoseconds) and long lifetime (hundreds of femtoseconds). We also investigate the dependence of the lifetimes and amplitudes of both decays on the amplitude of the disorder, the amplitude of the dynamical fluctuation, and the environment temperature.

In analyzing real data, the considerations presented here are just one of the factors to be considered. As we sharpen our understanding of coherence phenomena in photosynthetic light harvesting complexes, a full understanding will require inclusion of variation of the site energy,9,36–38 coupling strength,9 the inhomogeneous broadening described here, and the role of

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**Table 1. Lifetimes at 77 K and Room Temperature, 300 K, with Different Reorganization Energies $\lambda = 50$ and $140 \text{ cm}^{-1}$**

<table>
<thead>
<tr>
<th>Reorganization Energy (cm$^{-1}$)</th>
<th>77 K</th>
<th>300 K</th>
<th>77 K</th>
<th>300 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>679.9</td>
<td>360.1</td>
<td>46.3</td>
<td>25.4</td>
</tr>
<tr>
<td>140</td>
<td>412.6</td>
<td>151.9</td>
<td>28.2</td>
<td>9.6</td>
</tr>
</tbody>
</table>

*The inhomogeneous broadening is $\sigma_{A(0)} = 130 \text{ cm}^{-1}$. The simulation is performed on dimers with an exciton energy gap $\Delta_0 = 680 \text{ cm}^{-1}$ and a coupling constant $J = 280 \text{ cm}^{-1}$. 

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**Figure 3.** Lifetimes (a) and amplitudes (b) of the two coherence decay components as a function of inhomogeneous broadening at 77 K with delay time $\tau_t = 30 \text{ fs}$. The simulation is performed on dimers with an exciton energy gap $\Delta_0 = 680 \text{ cm}^{-1}$ and a coupling constant $J = 280 \text{ cm}^{-1}$. The reorganization energy is $\lambda = 50 \text{ cm}^{-1}$.

**Figure 4.** Lifetimes (a) and amplitudes (b) of the two decay components as functions of the reorganization energy at 77 K with the delay time $\tau_t = 30 \text{ fs}$. The simulation is performed on dimers with an exciton energy gap $\Delta_0 = 680 \text{ cm}^{-1}$ and a coupling constant $J = 280 \text{ cm}^{-1}$. The inhomogeneous broadening is chosen as $\sigma_{A(0)} = 130 \text{ cm}^{-1}$ to allow a significant amount of the slow decay component.
vibrionic and vibrational effects\textsuperscript{22–28} in determining the observed spectroscopic signals and their evolution.

**ASSOCIATED CONTENT**

* Supporting Information

The definition and properties of the coherent state. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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