Spectroscopic signatures of excited state dynamics in organic materials
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Mapping the evolution of spatial coherence through time-resolved fluorescence

Quantum coherence is expected to have a positive effect on the transfer efficiency of excitation energy through photosynthetic aggregates and conjugated polymers, but its significance to the functioning of these molecular assemblies remains largely unknown. In this chapter, we propose a new experimental means to monitor the coherence between distant molecular sites on a timescale relevant to energy transfer. Through numerical calculations, we demonstrate that the range of such spatial coherence continually scales as the 0-0 to 0-1 vibronic peak ratio in time-resolved fluorescence spectroscopy. As such, this observable allows one to monitor the coherent evolution of an excited state, displaying the large coherence length following optical excitation, and the subsequent dephasing over time.

7.1 Introduction

Quantum coherence is a hotly debated topic in the context of electronic energy transfer through light-harvesting complexes, conjugated polymers, and organic bulk heterojunction solar cells, as it involves versatile wavelike motion of the electronic excitation as opposed to slow diffusive hopping. Beating signals observed in two-dimensional spectroscopy of photosynthetic systems have been attributed to robust coherences among quantum eigenstates, suggesting that coherent transport of the excitation holds a firm connection with the remarkable efficiency reached in natural light harvesting. Nevertheless, perhaps more than inter-eigenstate coherences, the spatial coherence of a quantum excitation is of direct relevance to energy transfer. Spatial coherence determines the degree of electronic correlation between molecular sites underlying a delocalized excited state. Recently, such correlation over distances has been shown theoretically to modulate transfer efficiency, and its control is an attractive prospect for man-made devices.

In this chapter we propose the possibility to directly monitor the evolution of spatial coherence by means of time-resolved fluorescence. The proposed method relies on the vibronic progression due to coupling of the electronic excitation to a single high-frequency vibration. This is a ubiquitous phenomenon in organic materials, with as a notable example the 1400 cm$^{-1}$ symmetric vinyl-stretching
mode common to conjugated molecules. In a typical spectroscopic experiment, an incoming light field interacts coherently with macroscopic fractions of a molecular assembly, preparing excitations with considerable coherence lengths. Such a sizable coherence field will subsequently decline as a result of static and dynamic fluctuations in the environment. As we will demonstrate, the 0-0 to 0-1 vibronic peak ratio in the fluorescence spectrum continually tracks the coherence length for the case of a J-aggregate. Moreover, the peak ratio accurately indicates the early decay of spatial coherence for both J- and H-aggregates.

The impact of the exciton coherence length on the optical response was already long-known in the form of enhanced radiative decay in J-aggregates \cite{171,201} light-harvesting complexes \cite{202,203} and polyacine thin films \cite{204,205}. Spatial coherence was also found to affect the separation between bleach and induced absorption features in pump-probe \cite{206} and two-dimensional spectroscopy \cite{176} of J-aggregates. However, only quite recently a robust method was proposed to quantitatively determine the degree of spatial coherence through experiment: in Ref. \cite{207} it was recognized that the 0-0 to 0-1 fluorescence peak ratio provides a direct measure of the coherence length, $N_{coh}$. Nevertheless, the evinced applicability of this method was restricted to thermalized molecules under steady-state conditions, for which the peak ratio indicates coherence averaged over the band-bottom emitting states. As such, it does not yield insight in the excitations or the dynamics relevant to energy transfer. In this chapter, we show as a proof of principle that the peak ratio serves equally well as a coherence measure at ultrafast timescales, where it instead indicates $N_{coh}$ of a coherently prepared wavepacket of eigenstates.

### 7.2 Results and discussion

Over the last decades, technological advances drastically improved the time-resolution in up-conversion spontaneous emission experiments, allowing one to resolve fluorescence spectra down to 50 fs \cite{208}. In this time regime, fluorescence should be regarded merely as a class of nonlinear spectroscopy \cite{76}. The underlying third-order response function is the result of four light-matter interactions, separated in time by intervals $t_1$, $t_2$ and $t_3$,

$$R(t_3,t_2,t_1) = \text{Tr} (\mu \rho^{(3)}(t_3,t_2,t_1)), \quad (7.1)$$

where the trace is taken over the dipole operator $\mu$ acting on the molecular density matrix $\rho^{(3)}$ after 3 interactions have taken place. The first two interactions correspond to optical excitation of the molecular assembly. Assuming this process to take place instantaneously, so that $t_1 = 0$, one can neglect resonant Raman scattering contributions \cite{76}. Furthermore, each fluorescence band can then be described by a single Feynman diagram as is illustrated in Fig. 7.1 for the 0-0 and
Figure 7.1: Feynman diagrams describing spontaneous emission for the 0-1 (left) and 0-0 band (right). Solid arrows depict an optical excitation at $t = 0$ (see text). The time axis on the left includes a schematic representation of the gate pulse (green envelope), during which the emitted signal (dashed arrows) is detected. As illustrated above, the 0-0 pathway couples a collective excitation to the collective vacuum state $|G, 0\rangle$. The resulting signal benefits from interferences between transitions at spatially correlated sites $n$ and $m$. In contrast, the 0-1 signal results from a transition terminating at a single vibrational quantum localized at site $n$ (denoted $|g_n, 1\rangle$), rendering such interferences impossible.

0-1 transitions. The spontaneous emission signal at time $t^*$ is given by

$$S(t^*, \omega) \sim \text{Re} \int_0^\infty dt_3 \int_0^\infty dt_2 R(t_3, t_2, 0) E_G(t_2 - t^*) E_G(t_2 + t_3 - t^*) e^{i\omega t_3},$$

with the field $E_G$ representing the amplitude of the time-gate pulse used to acquire the emitted signal.

To quantify the delocalization of excitations, several measures have been introduced, including inverse participation ratios and degrees of entanglement. In this chapter, we conform to the measure employed in Ref. 207 which is based on the electronic autocorrelation function, generalized to include vibronic basis states whose electronic ($e_n$) and vibrational ($\nu$) components are jointly denoted
as $|e_n, \nu\rangle$. Accordingly, the coherence field operator is given by

$$C(r) = \sum_n B_n^\dagger B_{n+r}, \quad (7.3)$$

where $r$ is the distance between correlated molecular sites. The operator $B_n^\dagger \equiv |e_n, 0\rangle \langle G, 0|$ creates an electronic excitation at site $n$, while leaving the vibrational mode in the vacuum state ($0$). For an excited state $\rho^{(2)}(t_2, t_1)$, resulting from two light interactions, the time-dependent coherence field is then defined as

$$C(t, r) = \text{Tr}\left( \sum_n B_n^\dagger B_{n+r} \rho^{(2)}(t_2, t_1) \right). \quad (7.4)$$

The coherence length (in units of the inter-chromophore distance) is derived from this field through

$$N_{\text{coh}}(t) = \frac{1}{|C(t, 0)|} \sum_r |C(t, r)|. \quad (7.5)$$

The absolute value in the summand of $N_{\text{coh}}$ corrects for sign changes from site to site that typically occur for band-bottom states in H-aggregates. Note that for a completely localized excitation (single-chromophore limit), the coherence field is delta peaked at $r = 0$, yielding a length of $N_{\text{coh}} = 1$.

In order to compare the fluorescence peak ratio with $N_{\text{coh}}$ at different times, calculations are performed in the vibronic exciton model. Accordingly, the molecular aggregate under consideration is described by the Holstein Hamiltonian, given by

$$H(t) = \sum_n \epsilon_n(t)|e_n\rangle\langle e_n| + \sum_{n,m\neq n} J_{n,m} |e_n\rangle\langle e_m|$$

$$+ \omega_0 \sum_n b_n^\dagger b_n + \omega_0 \sum_n |e_n\rangle\langle e_n| \left[ \lambda (b_n^\dagger + b_n) + \lambda^2 \right]. \quad (7.6)$$

Here, $|e_n\rangle$ denotes the purely-electronic basis state in which molecular site $n$ is excited while the others reside in the ground state, and $b_n^\dagger$ is the vibrational annihilation (creation) operator. In our model, electronic excitation transfer ($J_{n,m}$), the effect of static and dynamic fluctuations in the environment (through $n$- and $t$-dependent site energies $\epsilon$) and coupling to the vibrational mode $\omega_0$ are all treated nonperturbatively. Vibronic coupling is manifested as a spatial shift of the vibrational potential, quantified by the Huang-Rhys factor $\lambda^2$. In the following, $\nu$ will be used to indicate vibrational wavefunctions in the unshifted (electronic ground state) potential, whereas $\tilde{\nu}$ (including a tilde) refers to the shifted potential.

*Note that the coherence length $N_{\text{coh}}$ employed in this chapter was referred to as coherence number in Ref. 207, where the “coherence length” was instead defined as $L_{\text{coh}} \equiv N_{\text{coh}} - 1$. 
Results presented in this chapter are based on linear J- and H-aggregates consisting of $N = 10$ chromophores. Electronic interactions are limited to nearest-neighbors, with a strength $J = +50$ cm$^{-1}$ and $-50$ cm$^{-1}$ for the case of an H- and a J-aggregate, respectively. Periodic boundary conditions are imposed ($J_{N,1} = J$), mimicking the situation of a ring-shaped complex or an extended chain. Vibronic coupling is included using $\omega_0 = 2000$ cm$^{-1}$ and $\lambda^2 = 1$. The electronic transition energies $\epsilon_n(t)$ are fluctuating as a function of time due to the dynamical environment. This is accounted for by employing the over-damped Brownian oscillator model, using a width of 50 cm$^{-1}$ and a correlation time of 200 fs. In doing so, the site fluctuations are treated mutually uncorrelated, and each average site energy is set to 15 000 cm$^{-1}$. Feedback of the quantum excitation on the fluctuating coordinates is accounted for through a surface-hopping algorithm [10], resulting in a thermalization of the quantum system to a temperature which is fixed at 77 K (details can be found in Sec. 7.4, as well as in chapter 3). Results are averaged.

Figure 7.2: Vibronic exciton bands for J- (left) and H-aggregates (right). The bandwidth ($W$) is assumed to be small as compared to the vibrational quantum $\omega_0$. The vacuum state is denoted $|G, 0\rangle$, whereas $|G, 1\rangle$ represents the total of (degenerate) purely-vibrational states $|g_n, \nu = 1\rangle$ ($n = 1, ..., N$). For the case of an H-aggregate, optical excitation into the lowest-energy vibronic band populates mostly the symmetric states residing at the band-top (collectively denoted as $|\Psi_i\rangle$). Subsequently, nonadiabatic coupling induces population relaxation to antisymmetric low-energy eigenstates. For J-aggregates, both the initially populated states and the thermally relaxed states reside at the band-bottom.
over 5000 disorder trajectories. In order to ensure convergence of results, the Holstein Hamiltonian is evaluated in the two-particle approximation.

Our choice of parameters resembles a typical low-temperature experiment for which the eigenstates are organized in narrow, well-separated vibronic bands, as is illustrated in Fig. 7.2. In calculating the fluorescence spectra and coherence field, the aggregate is assumed to be optically prepared in the lowest-energy band. Accordingly, the corresponding initial quantum excitation satisfies $|\Psi_i\rangle = N^{-1/2} \sum_n |e_n, \tilde{0}\rangle$, where the local basis state $|e_n, \tilde{0}\rangle$ represents a vibronic excitation at site $n$ involving $\tilde{\nu} = 0$ quanta in the shifted vibrational well, and with all other chromophores electronically and vibrationally unexcited. Preparation of $|\Psi_i\rangle$ requires an excitation pulse having a width less than $\sim 2000 \text{ cm}^{-1}$, and a flat top covering the exciton bandwidth of $\sim 100 \text{ cm}^{-1}$. The corresponding pulse duration of about 5 fs is neglected in the simulation scheme, where the excitation event is assumed to take place instantaneously (see Fig. 7.1). The subsequent quantum dynamics is evaluated using a novel propagation scheme, described in chapter 3, which relies on the Numerical Integration of the Schrödinger Equation method.

The time-gate pulse is described using a Gaussian lineshape with a standard deviation of 20 fs, centered at $t^*$. Such a short pulse allows us to resolve spectra down to 40 fs. The downside is that the gate acts as the primary source of spectral line broadening. Still, the vibronic bands come out well-separated, and taking the peak ratio $I_{0-0}(t^*)/I_{0-1}(t^*)$ is simply done by integrating the peak profiles (a fitting procedure usually works quite well for more congested cases).

Shown in Fig. 7.3, top panels, are simulated fluorescence spectra for the case of a J- (black) and H-aggregate (red) at different times $t^*$ up to 400 fs. From these results, it is obvious that the 0-0 peak drops considerably in intensity over the first few hundreds of femtoseconds. This already suggests that the principal peak benefits from enhanced constructive interference due to the coherent excitation at early times. In marked contrast, the 0-1 sideband remains fairly static over the entire time interval. In Ref. 207 it was shown for steady-state fluorescence of J-aggregates, that the coherence length is accurately reproduced by the 0-0 to 0-1 peak ratio multiplied with the Huang-Rhys factor. We will proceed with demonstrating that this scaling relation holds equally well for both J- and H-aggregates at ultrafast times, that is,

$$N_{coh}(t^*) \approx \lambda^2 \frac{I_{0-0}(t^*)}{I_{0-1}(t^*)}.$$  \hspace{1cm} (7.7)

To this end, Fig. 7.3 (bottom left) compares the calculated coherence length (solid curves) with the peak ratio (markers) at 40 fs intervals. Both are in excellent agreement.

\hspace{0.5cm}†To obtain the line strengths from the spectral areas, one needs to deconvolute the cubic frequency dependence.
agreement up to 200 fs. Moreover, for the case of a J-aggregate, $N_{\text{coh}}$ remains equal to the peak ratio throughout the entire time range.

In the introductory paragraph, a distinction was made between inter-eigenstate coherences and spatial coherence, or $N_{\text{coh}}$. Interestingly, the latter receives contributions from coherences between (adiabatic) eigenstates as well as from coherences *intrinsic* to eigenstates. Technically speaking, these correspond to the diagonal and off-diagonal contributions of the density matrix $\rho^{(2)}$ (in the eigen-basis) to Eq. 7.4. In Fig. 7.4 these contributions to $N_{\text{coh}}$ and the peak ratio are differentiated. It is evident that, both for the J- and H-aggregate case, the major part of the early spatial coherence stems from off-diagonal entries, and that the decay of $N_{\text{coh}}$ is mostly caused by dephasing of these matrix elements.

Regarding $N_{\text{coh}}$ and the peak ratio, the J- and H-aggregates behave perfectly the same for the first 150 fs, which is not unexpected since both cases commence
with the same initial excitation $|\Psi_i\rangle$. As illustrated in Fig. 7.2, this symmetric wavefunction is predominantly composed of the band-top eigenstates for the H-aggregate case. When time evolves, nonadiabatic coupling induces thermal equilibration in the form of population relaxation towards lower energies. Gradual population of the anti-symmetric band-bottom states leads to an additional quenching of the 0-0 emission strength, causing the fluorescence ratio to eventually shrink below the single-chromophore value (see Fig. 7.3, bottom left). This mechanism is reflected in the corresponding coherence field shown in Fig. 7.3 (bottom right) which evolves into a sign-alternating profile, and acts as the main source of discrepancy between $N_{coh}$ and the peak ratio (as is clear by comparing the diagonal contributions in Fig. 7.4). These findings are entirely consistent with earlier reports on steady-state fluorescence of H-aggregates: the emission from the antisymmetric eigenstates suffers from coherent suppression, rather than enhancement. The situation is quite different for J-aggregates, where the initially populated symmetric eigenstates reside at the bottom of the band. Consequently, no significant population transfer occurs, and spontaneous emission from the symmetric band-bottom excitation retains its connection to $N_{coh}$ over time.

Fluorescence at longer time scales, or under steady-state conditions, is conventionally calculated through Fermi’s Golden Rule, which neglects off-diagonal

![Figure 7.4: Calculated fluorescence (markers) and spatial coherence (solid curves) for an $N = 10$ J-aggregate (left panel) and H-aggregate (right panel). Red plots represent the total fluorescence ratio (markers) and coherence length (solid curve), whereas the blue plots indicate the contribution from diagonal elements of the system density matrix in the eigenbasis. For the coherence length, the contributions from diagonal and off-diagonal elements are represented by the blue and red areas, respectively.](image-url)
contributions from $\rho^{(2)}$. Fig. 7.4 underlines the importance of properly including inter-eigenstate coherences by employing the third-order response in the ultrafast regime. Furthermore, the corresponding Feynman diagrams help clarifying the origin of the principal peak’s coherent enhancement. As shown in Fig. 7.1, the emission event involves both a ket and a bra interaction. For the 0-0 transition, which connects a delocalized excited state to the vacuum state, these two interactions can take place at different molecular sites, $n$ and $m$. Coherent enhancement occurs when all such site pairs constructively interfere to the total emitted signal. On the other hand, the 0-1 transition couples to a local purely-vibrational state, $|g_n, 1\rangle$, and hence both the ket and bra interactions should happen at site $n$. Alternatively, if the delocalized quantum excitation is considered as a particle that “moves” along the aggregate chain, the probability for the local 0-1 process to happen is $1/N$. In contrast, the 0-0 transition is a delocal event yielding a probability of unity in the limit of maximal spatial coherence.

The Feynman diagrams pertaining to time-resolved fluorescence are easily identified with those of a stimulated emission process. Consequently, the coherence length can in principle also be obtained by taking the peak ratio from the stimulated emission contribution to pump-probe measurements, or alternatively through integrating the stimulated emission signal over the excitation energy in coherent two-dimensional spectroscopy. However, in both cases the necessary presence of vibronic coupling will give rise to strong overlapping ground state bleach contributions that can not be straightforwardly disentangled from the total signal (see chapters 4, 5, and 6, as well as Refs. 142, 143, 165, and 144). In that sense, the spontaneous emission of a photon allows the selective isolation of the coherent fingerprint of a quantum excitation in the singly-excited manifold.

Our results strongly indicate that the correspondence between the coherence length and the 0-0 to 0-1 peak ratio is a universal property, common to J-aggregates, that holds both for steady-state conditions and at ultrafast timescales. No significant dependence on the choice of parameters was found in our calculations. Nevertheless, the applicability of Eq. 7.7 demands that the Huang-Rhys factor should be large enough for a resolvable vibronic progression, and the vibronic bandwidth should be small enough compared to the vibrational quantum to be able to selectively excite the lowest-energy band. Exemplary cases in this respect are recent studies by Heeger and coworkers, suggesting that the charge-separation event in several polymer:fullerene blends benefits from the broad coherence field existing for about 200 fs, as well as a presumed long-lived coherence measured by Holcman et al. for an organic molecular chain, isolated under extremely pure conditions. According to our findings, time-resolved fluorescence has the potential to reinforce such claims with direct experimental evidence. In-
terestingly, conjugated polymers exhibit optoelectronic behavior very similar to J-aggregates\(^{216}\) and hence our findings have the potential to help elucidating the mechanism behind coherent intrachain energy migration observed for such systems.\(^{53}\)

### 7.3 Conclusion

To summarize, we have proposed a relation between the degree of spatial coherence and the 0-0 to 0-1 vibronic peak ratio in time-resolved fluorescence spectroscopy. This relation occurs as a robust property of J-aggregates, but is also shown to apply for H-aggregates at early times after excitation. Our findings suggest the possibility of monitoring the spatial coherence in time, and propose fluorescence measurements as an attractive complement of two-dimensional spectroscopy to study quantum coherence effects.

### 7.4 Appendix: Numerical methods

Calculations in the vibronic exciton model are based on the Holstein Hamiltonian (see Eq. 7.6). In a slightly modified form, explicitly limiting the electronic interactions to nearest neighbors, this Hamiltonian reads

\[
H(t) = \sum_n (\epsilon + D_x(t)) |e_n\rangle\langle e_n| + J \sum_n (|e_n\rangle\langle e_{n+1}| + |e_n\rangle\langle e_{n-1}|) \\
\omega_0 \sum_n b_n^\dagger b_n + \omega_0 \sum_n |e_n\rangle\langle e_n| (\lambda (b_n^\dagger + b_n) + \lambda^2).
\]

The corresponding parameters are recapitulated in Tab. 7.1. Note that the electronic transition energies are now subdivided into a static (average) contribution \(\epsilon\), and a fluctuating contribution \(D_x(t)\). The latter is treated in the classical approximation, as will be discussed below.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
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<tr>
<td>Av. electronic transition energy</td>
<td>(\epsilon)</td>
<td>15 000 cm(^{-1})</td>
</tr>
<tr>
<td>Electronic coupling</td>
<td>(J)</td>
<td>(\pm 50) cm(^{-1})</td>
</tr>
<tr>
<td>Vibrational quantum</td>
<td>(\omega)</td>
<td>2000 cm(^{-1})</td>
</tr>
<tr>
<td>Huang-Rhys factor</td>
<td>(\lambda^2)</td>
<td>1</td>
</tr>
<tr>
<td>Coupling to classical environment</td>
<td>(D)</td>
<td>3125 cm(^{-1})nm(^{-1})</td>
</tr>
</tbody>
</table>

**Table 7.1:** Parameters used for the quantum calculations.
Vibronic coupling through $\lambda$ results in a spatial shift of the vibrational potential upon electronic excitation. In our calculations, the high-frequency vibrational mode $\omega_0$ is represented in the shifted basis (denoted $\tilde{\nu}$) for the electronically-excited manifold, whereas the unshifted basis (denoted $\nu$ without a tilde) is used for (electronic) ground-state vibrational excitations. The Holstein Hamiltonian is evaluated using the two-particle approximation. Accordingly, the electronically-excited manifold is spanned by the basis states
\begin{equation}
|e_n, \tilde{\nu}\rangle, |e_n, \tilde{\nu}; g_m, \nu\rangle.
\end{equation}
The first state represents a vibronic excitation at site $n$ involving $\tilde{\nu} \geq 0$ vibrational quanta in the corresponding shifted potential, while all other sites are both electronically and vibrationally unexcited. For the second state, such a vibron is accompanied by a single purely-vibrational excitation $\nu \geq 1$ on site $m$. In the same vein, the electronic ground state manifold is described using the states
\begin{equation}
|g_n, \nu\rangle, |g_n, \nu; g_m, \nu'\rangle, \quad \nu, \nu' \geq 1,
\end{equation}
and the vacuum state $|G, 0\rangle$. In all cases, the basis set is limited by truncating the total of vibrational quanta such that $\tilde{\nu} + \nu < 3$ and $\nu + \nu' < 3$.

In our calculations, the molecular aggregate is assumed to initiate in the vacuum state, which is valid provided that $k_B T \ll \omega_0$. Interaction with the excitation pulse at time $t = 0$ results in the aggregate being optically prepared in the lowest-energy vibronic band. The corresponding interaction Hamiltonian can be formulated as
\begin{equation}
H_i = \sum_n \left(|e_n, \tilde{0}\rangle\langle G, 0| + |G, 0\rangle\langle e_n, \tilde{0}|\right).
\end{equation}
The wavefunction of the initial excitation is thus given by
\begin{equation}
|\Psi(t = 0)\rangle = |\Psi_i\rangle = H_i |G, 0\rangle.
\end{equation}
(Note that in the above, a prefactor $\langle \tilde{0}|0\rangle$ accounting for the overlap between the $\tilde{\nu} = 0$ and $\nu = 0$ vibrational wavefunctions is omitted. This constant factors out in both the coherence length and the fluorescence peak ratio.)

The subsequent dynamics of the quantum system is evaluated using the Numerical Integration of the Schrödinger Equation (NISE) method. Accordingly, the time is discretized using increments of $\Delta t$, and the wavefunction at time $k\Delta t$ is given by
\begin{equation}
|\Psi(k\Delta t)\rangle = U(k\Delta t, 0) |\Psi_i\rangle.
\end{equation}
with the propagator given by

\[ U(t + k\Delta t, t) = \prod_{l=0}^{k-1} \exp \left(-iH(t + l\Delta t)\Delta t \right). \]  

(7.14)

In our calculations, a time step \( \Delta t = 5 \) fs is used, while the mean \( \epsilon \) is (temporarily) subtracted from the Hamiltonian \( H \) in order to properly account for fast-fluctuating contributions.

As explained in Sec. 7.2, ultra-fast time-resolved fluorescence is a third-order nonlinear optical technique which derives from four interactions between the light field and the aggregate’s density matrix, separated in time by the intervals \( t_1, t_2 \) and \( t_3 \). The first two interactions bring the quantum system from the vacuum state to the initial excited state. The resulting "second-order" density matrix evolves in time according to

\[ \rho^{(2)}(t, t_1 = 0) = U(t, 0)|\Psi_i\rangle\langle\Psi_i|U(0, t), \]  

(7.15)

where the optical preparation event is assumed to have taken place instantaneously \((t_1 = 0)\). Substitution of this expression for \( \rho^{(2)} \) into Eq. 7.4 yields the coherence field at time \( t \).

The third and fourth light-matter interactions correspond to the emission of a photon, and the resulting optical response follows from the expectation value of the transition dipole operator acting on the third-order density matrix (see Eq. 7.1). The latter is given by

\[ \rho^{(3)}(t_3, t_2, t_1 = 0) = U(t_2 + t_3, 0)|\Psi_i\rangle\langle\Psi_i|U(0, t_2) \mu U(t_2, t_2 + t_3), \]  

(7.16)

with the transition dipole operator

\[ \mu = \sum_n (|e_n\rangle\langle g_n| + |g_n\rangle\langle e_n|). \]  

(7.17)

Here, we assume that all molecular transition dipoles have the same direction. The operator \( \mu \) acts solely on the electronic component of the basis states, leaving the vibrational state unchanged. Combining Eq. 7.16 with Eq. 7.1 results in the final expression for the third-order response underlying the time-resolved fluorescence spectrum,

\[ R(t_3, t_2, t_1 = 0) = \langle\Psi_i|U(0, t_2) \mu U(t_2, t_2 + t_3) \mu U(t_2 + t_3, 0)|\Psi_i\rangle. \]  

(7.18)

As formulated in Eq. 7.8, the effect of the dynamic environment on the quantum system is modeled by attributing a coordinate \( x_n \) to each chromophoric unit.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>$m$</td>
<td>1 u (atomic units)</td>
</tr>
<tr>
<td>Spring constant</td>
<td>$k$</td>
<td>2500 u ps$^2$</td>
</tr>
<tr>
<td>Damping constant</td>
<td>$\gamma$</td>
<td>50 ps$^{-1}$</td>
</tr>
<tr>
<td>Temperature</td>
<td>$T$</td>
<td>77 K</td>
</tr>
</tbody>
</table>

| Table 7.2: Parameters used for the classical dynamics. |

Such a coordinate is considered as a classical particle that describes stochastic harmonic oscillatory motion, and whose dynamics is governed by the Langevin equation

$$m\ddot{x}_n = -kx_n - m\gamma\dot{x}_n + F^T_n + F^Q_n,$$

where the time indices are dropped for the sake of clarity. In our modeling, Eq. 7.19 is solved using the same discrete time step as used in the quantum dynamics, $\Delta t = 5$ fs. The applied classical parameters, summarized in Tab. 7.2, roughly correspond to the overdamped limit, with an associated width of 50 cm$^{-1}$ and a correlation time of 200 fs. Beside the harmonic potential and damping terms, the right-hand side of Eq. 7.19 is added with two contributions. The first, $F^T_n$, accounts for the stochastic effect of temperature, and is randomly drawn from a normal distribution at each time step. In accordance with the fluctuation-dissipation theorem, the width of this distribution is taken to be $(2\gamma mk_B T / \Delta t)^{1/2}$ (Ref. 76).

The last term in Eq. 7.19 represents the feedback of the quantum system on the classical coordinates. This contribution is necessary to self-consistently model the mixed quantum-classical dynamics, and in particular allows to account for correct thermal relaxation of the diagonal elements (populations) of $\rho^{(2)}$. To this end, we have employed Tully’s fewest-switches surface-hopping (FSSH) algorithm, which is known to result into proper thermalization in most cases. See chapter 3 for a detailed account on the implementation of FSSH in the simulation of third-order spectroscopy, and the exact formulation of $F^Q_n$ in Eq. 7.19. In short, all diagonal and off-diagonal elements of $\rho^{(2)}$ in the eigenbasis of $H(t = 0)$ are propagated separately, while FSSH is applied exclusively to the diagonal elements. As such, a sum-over-states is performed at $t = 0$. Since $|\Psi_i\rangle$ is solely composed of eigenstates from the lowest-energy vibronic band, and regarding that interband mixing is small for the chosen parameters, this sum is limited to the $N$ lowest-energy eigenstates, where $N$ is the number of chromophores.