**1. Equations of Motion**

**The Hamiltonian**

The basic model of a carotenoid is the 4-state (S0, S1, S2, Sn) displaced oscillator model. We assume that transitions between these states are optically coupled to a small number of vibrational normal modes, . In practice we have two strongly-coupled high frequency modes () corresponding to symmetric C=C and C-C stretching. The remaining vibrational modes (plus other environmental degrees of freedom) are assumed to constitute the classical bath which is represented as an infinite set of harmonic oscillators (indexed by ). Initially we treat the strongly-coupled modes classically and can express our Hamiltonian in the basis of pure electronic states with eigenvalues, ,

The first line of Eqn. (1) characterizes each electronic (system) state as an orthogonal set of harmonic potential energy surfaces (PES) which represent the optically-coupled high frequency modes. is the pure electronic energy (i.e. the minima of the set of PES) while , , and are the coordinate, momentum, mass and frequency of the th oscillator respectively. represents the displacement of oscillator in state from its position in state . The second line characterizes the infinite set of oscillators that comprise the bath. The third line characterizes how fluctuations in the coordinates of the bath oscillators, , are coupled to fluctuations in the coordinates of the system oscillators. The couplings are assumed to be linear in both and and have some characteristic coupling strengths, . The fourth and final term characterizes how fluctuations in the coordinates of the bath oscillators couple different electronic states. It is assumed to be linear in with characteristic coupling strengths, . This model makes several implicit assumptions. Firstly, we assume that the system oscillators are the same on each electronic state but for some displacement. In effect we are neglecting Duschinsky rotations. Secondly, the linearity assumed in the system-bath interaction means that the bath only effects the dynamics of the system via fluctuations (). This means that effects such as interconversion through a conical intersection are neglected.

This description is incomplete as it treats the system oscillators classically. Quantizing these oscillator transforms our systems states into a manifold of vibronic levels,

where counts our system modes ( for this model), is the vibrational quantum number for mode , and is the ket for the th oscillator on the th electronic state. In the short-hand notation, , the index is a tuple of the vibrational quantum numbers of each oscillator, . We now understand our system dynamics in terms of transitions between vibronic states within and between electronic states, characterized by the vibronic Hamiltonian,

The first term is the system Hamiltonian,

Where,

is the vibrational contribution to the energy of a particular electronic state (the vibrational manifold is identical for all electronic states). is the bath Hamiltonian which is, as before,

As before, we split the system-bath interaction into two parts.

characterizes bath-induced transitions between vibrational levels within the same electronic state, termed *vibrational relaxation*. The index denotes a tuple that differs from by the addition of a single phonon to the th mode. The form of arises from the harmonic approximation in which the transitions that are permitted are between adjacent states belong to the same mode. Overtone transitions and anharmonic couplings between modes are neglected.

characterize the bath-induced interconversion between vibrational manifolds on different electronic states. Here simply denotes a different set of vibrational quantum numbers to and

are the Frank-Condon factors for transitions between different levels of the same mode on different electronic states. Transitions are only allowed between adjacent electronic states.

**The populations**

The dynamics of this system are given by the time-evolution of the diagonal elements of the reduced density matrix (the populations). The equations of motion are derived by treating the system-bath interaction as a second-order perturbation and invoking both the secular and Markov approximations. The time-evolution of the coherences are independent of the populations in the secular approximation and are not relevant to the problem. The equations of motion of the populations are,

where is the population of the vibronic level . The first term contains the vibrational relaxation,

where and are the rate constants for transfer of population to the upper or lower adjacent vibrational state on mode . These are given by the Fourier transform of the bath correlation function, evaluated at the frequency of the oscillator,

where the subscript is used because the fluctuations responsible for vibrational relaxation and IC may have different correlation functions. We intuitively express these in terms of the ***spectral density***,

**Note, in the literature an opposite sign convention with representing the downward rate and vice versa. Although this previous convention is in line with the sign of the frequency in Eqn. (12) it is counter-intuitive when considering the direction of energy transfer.** Before we describe the spectral densities we will consider the other terms in Eqn. (9). The interconversion dynamics are given by,

Here the and as before. The first line describes the flow of population between state and the state above it, . Therefore, the rate characterizes the upward transition **from** **to**  and the rate characterizes the downward transition **from** **to** . The second line characterizes population flow between and the state below it, . Therefore, is the rate of the downward transition **from** **to**  and is the rate of the upward transition **from** **to**

To define the rate constants we define the transition frequency between different vibronic states,

where,

is the purely electronic energy gap between electronic states and

is the energy gap between vibrational states on the same electronic state. This is assumed to be identical for each electronic state. The ***uphill*** IC rate constants are given by,

while the ***downhill*** rate is,

The last term is due to the optical pumping and will be discussed in a subsection below.

**Franck-Condon Overlap**

Due to the symmetry inherent in a system of identical, but mutually-displaced, oscillators the FC overlap factors depend entirely on the relative displacements between equivalent modes on different electronic states, . The relationship is given by,

Computationally, it is better to obtain these quantities recursively. We start with the nuclear overlap of the purely electronic transition,

Then one calculates,

and

The rest are then calculated with,

and

**Spectral Densities**

Although we have previously used highly-structured spectral densities to model the steady-state spectroscopy of carotenoids this would be something of an over-parameterization here. We are going to assume a standard over-damped oscillator (ODO) spectral density,

The damping rate is assumed to be identical for all processes and takes the value or based on previous modelling. Therefore, the two processes of vibrational relaxation () and interconversion () are differentiated by their respective reorganization energies. For vibrational relaxation the reorganization energy is specific to a given electronic state but assumed to be the same for all optically coupled modes,

For interconversion the reorganization is specific to a given pair of electronic states but is again assumed to be the same for all modes,

**The Pumping Term**

The pumping term simply induces excitation of the system. This could involve narrow or broadband optical excitation or transfer of energy from a neighbouring chromophore. Here we are attempting to model a simple *pump-probe* experiment, in which the excited state is populated with a short, narrow coherent laser pulse. How we treat this depends on how we treat the ground state of the molecule and on the assumed frequency selectivity of the pulse.

*(a) Absolute ground state with a highly selective pulse*

For room temperature it is reasonable to assume that the system starts in the lowest vibrational state on the electronic ground state,

Secondly, if the natural frequencies of the optically-coupled modes are much larger than the frequency width of the pulse then it is reasonable to assume that we can resonantly select a single vibronic state. For carotenoids we often assume that this is . We can therefore treat the pumping term in a purely phenomenological way.

We assume that the pulse entirely depopulates the ground state and transfers it to the selected excited vibronic state.

where is the temporal envelope of the pulse, is the arrival time and is the pulse width. We employ a normalized ***squared hyperbolic secant*** function,

Where the normalization ensures that ground state is entirely emptied over the full duration of the pulse,

The complementary term for the selected state is, ,

*(b) Thermal ground state with a highly selective pulse*

If we are interested in temperature effects then we must consider the thermally-populated ground state,

where the partition function is given by the canonical ensemble,

This introduces significant complexity. Due to the symmetry of the displaced oscillator model there will be several transitions selected by the pulse. For example, if we tune the laser pulse to select the purely electronic energy gap, then according to Eqn. (14) we will also select all gaps . More generally,

where is the vibrational tuple,

and is some positive integer. The problem, however, arises from the fact that these iso-energetic transition will not generally have the same amplitudes due to different FC overlaps. We therefore propose a pumping term of the form,

where is simply a delta-function filter that ensures that a particular vibronic transition is in resonance with the pulse centre frequency, . Correspondingly the ground state term is,

is a constant determined (in part) by the intensity of the laser, oscillator strength of the electronic transition, and a myriad of other things. Its purpose is to ensure that the ground state vibronic manifold is completely emptied by the pulse and it will be treated as a free parameter.

*(c) Thermal ground state with a broad pulse*

Eqns. (34) and (35) can be trivially extended to account for a pulse with some distribution of frequencies. We simply replace the delta-filter with a normalized Gaussian function,

where is the pulse width.