



Photoexcited state dynamics of carotenoids

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Carotenoid excited states

Carotenoids are a family of linear polyenes found in light harvesting complexes of plants and algae.

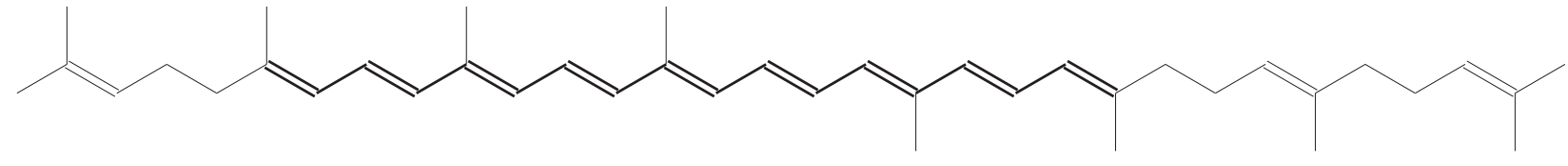


Figure 1: Chemical formula of neurosporene, a carotenoid with 18 π -conjugated carbon atoms in the π -conjugated polyene backbone.

The quasi one-dimensional geometry of carotenoids gives rise to enhanced electron-electron and electron-nuclear interactions. As a consequence, the optically dark $2^1A_g^-$ state (S_1) can fall below the optically excited $1^1B_u^+$ state (S_2).

Singlet fission

Singlet fission is a process by which a photoexcited state dissociates into two uncorrelated triplets. In carotenoids, singlet fission proceeds via a correlated singlet triplet-pair state.

$$1^1B_u^+ \rightleftharpoons {}^1(TT) \rightleftharpoons T_1 + T_1. \quad (1)$$

Aim of the project

We seek to investigate the carotenoid internal conversion (first step of Eq. (1)) via dynamical simulations based on density matrix renormalization group techniques.¹⁻³ Two internal conversion (IC) pathways are investigated.⁴

Model : UV-Peierls Hamiltonian

$$\begin{aligned} \hat{H} &= \hat{H}_{UVP} + \hat{H}_\epsilon \\ \hat{H}_{UVP} &= \hat{H}_{UV} + \hat{H}_{e-n} + \hat{H}_{elastic} \\ \hat{H}_{UV} &= -t \sum_{n,\sigma} \left(\hat{c}_{n,\sigma}^\dagger \hat{c}_{n+1,\sigma} + \hat{c}_{n+1,\sigma}^\dagger \hat{c}_{n,\sigma} \right) \\ &\quad + U \sum_n \left(\hat{N}_{n\uparrow} - \frac{1}{2} \right) \left(\hat{N}_{n\downarrow} - \frac{1}{2} \right) \\ &\quad + V \sum_n \left(\hat{N}_n - 1 \right) \left(\hat{N}_{n+1} - 1 \right) \\ \hat{H}_{e-n} &= -\alpha \sum_{n,\sigma} (u_{n+1} - u_n) \left(\hat{c}_{n,\sigma}^\dagger \hat{c}_{n+1,\sigma} + \hat{c}_{n+1,\sigma}^\dagger \hat{c}_{n,\sigma} \right) \\ \hat{H}_{elastic} &= \frac{K}{2} \sum_n (u_{n+1} - u_n)^2 \\ \hat{H}_\epsilon &= \sum_n \epsilon_n \left(\hat{N}_n - 1 \right) \end{aligned}$$

$t = 2.4$ eV is the electron hopping integral for a uniform chain, U is the on-site Coulomb interaction, V is the nearest neighbour Coulomb repulsion, $\alpha = 4.593$ eV \AA^{-1} is the electron-nuclear coupling parameter, and $K = 46$ eV \AA^{-2} is the nuclear spring constant. ϵ_n is the on-site energy of site n found by mapping on to π -electron Mulliken charges found via density functional theory.

Symmetry breaking, adiabatic and diabatic states

\hat{H}_ϵ breaks particle-hole symmetry and facilitates internal conversion from the $1^1B_u^+$ state to triplet-pair states.

diabatic states : $\hat{H}_{UVP} |\Phi_i\rangle = E_{\Phi_i} |\Phi_i\rangle$, $\Phi_i \in \{1^1A_g^-, 2^1A_g^-, 1^1B_u^+, \dots\}$
 adiabatic states : $\hat{H} |S_i\rangle = E_i |S_i\rangle$, $i \in \{0, 1, 2, \dots\}$

Dynamical simulation scheme

Electronic wavefunction evolves under the time dependent Schrödinger equation, $\delta t \rightarrow 0$.

$$|\Psi(t + \delta t)\rangle = e^{-i\hat{H}\delta t/\hbar} |\Psi(t)\rangle$$

Since $\hat{H} = \sum_i \hat{H}_{i,i+1}$, $e^{-i\hat{H}\delta t/\hbar}$ can be decomposed via a Suzuki-Trotter decomposition.^{5,6}

$$e^{-i\hat{H}\delta t/\hbar} = e^{-i\hat{H}_{1,2}\delta t/2\hbar} \dots e^{-i\hat{H}_{N-1,N}\delta t/2\hbar} \times e^{-i\hat{H}_{N-1,N}\delta t/2\hbar} \dots e^{-i\hat{H}_{1,2}\delta t/2\hbar} + O(\delta t^3)$$

Time evolution operator is propagated using adaptive time-dependent density matrix renormalization group. Nuclear propagated classically via Ehrenfest equations of motion.

$$f_i = - \left\langle \frac{\partial \hat{H}}{\partial u_i} \right\rangle, \quad f_i - \gamma p_i = \frac{dp_i}{dt}, \quad \frac{du_i}{dt} = \frac{p_i}{M}$$

f_i , p_i , u_i are force, momentum, and displacement of site i respectively. M is the nuclear mass. $\gamma = 1.52 \times 10^{14} \text{ s}^{-1}$ facilitates linear damping.

Theoretical transient spectra calculation

Transient absorption spectrum from the S_i state at time t is calculated using Lanczos-DMRG.^{7,8}

$$I_\mu(t, \omega) = \frac{1}{\pi} \sum_n |\langle n | \hat{\mu} | S_i(t) \rangle|^2 \delta(E_i + \omega - E_n),$$

Internal conversion via the $1^1B_u^-$ state

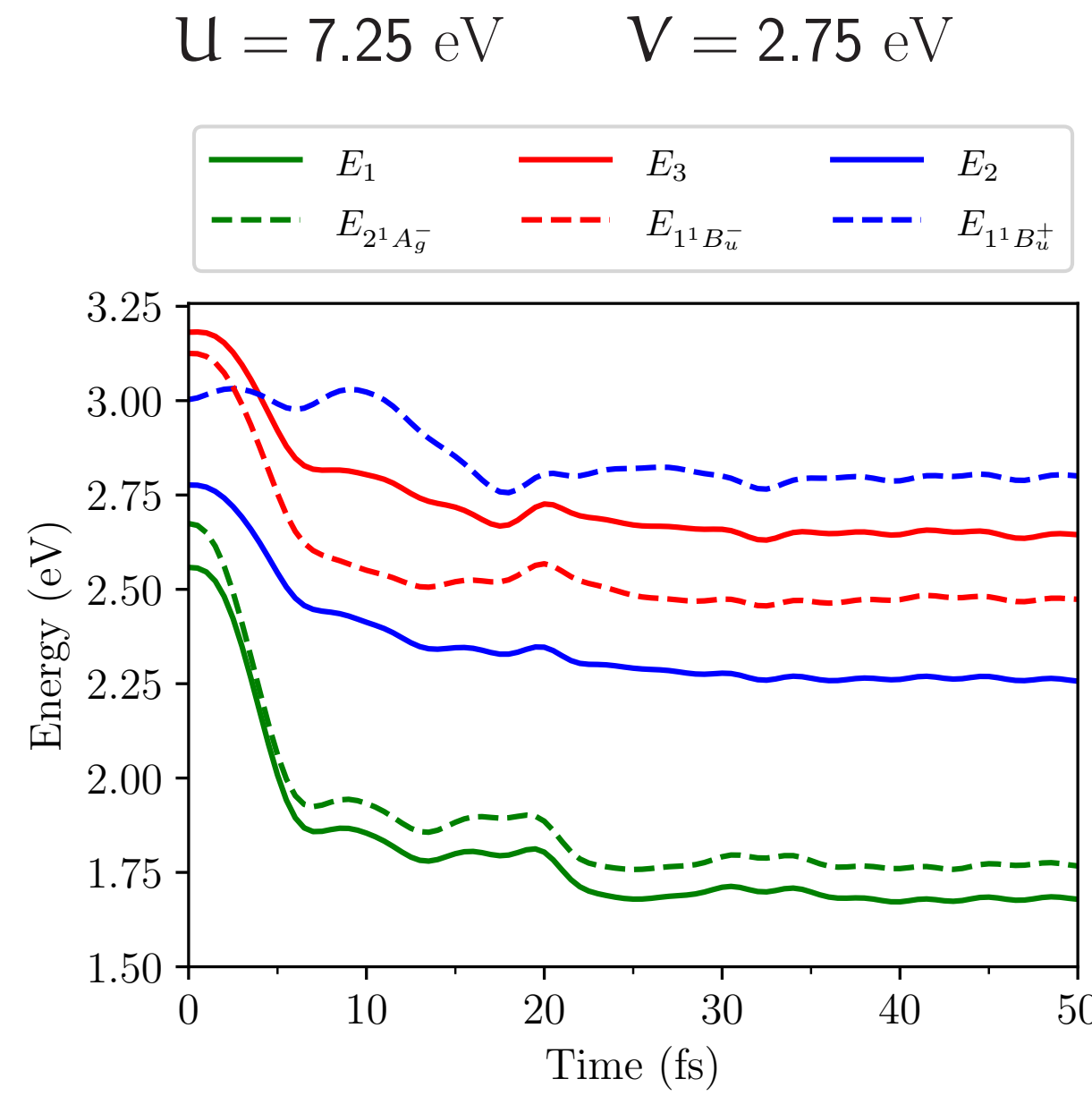


Figure 2: Excitation energies of the diabatic singlet $2^1A_g^-$, $1^1B_u^+$, and $1^1B_u^-$ states, and adiabatic singlet states S_1 , S_2 , and S_3 of neurosporene as a function of time. $1^1B_u^+$ and $1^1B_u^-$ states exhibit a diabatic crossover within 5 fs.

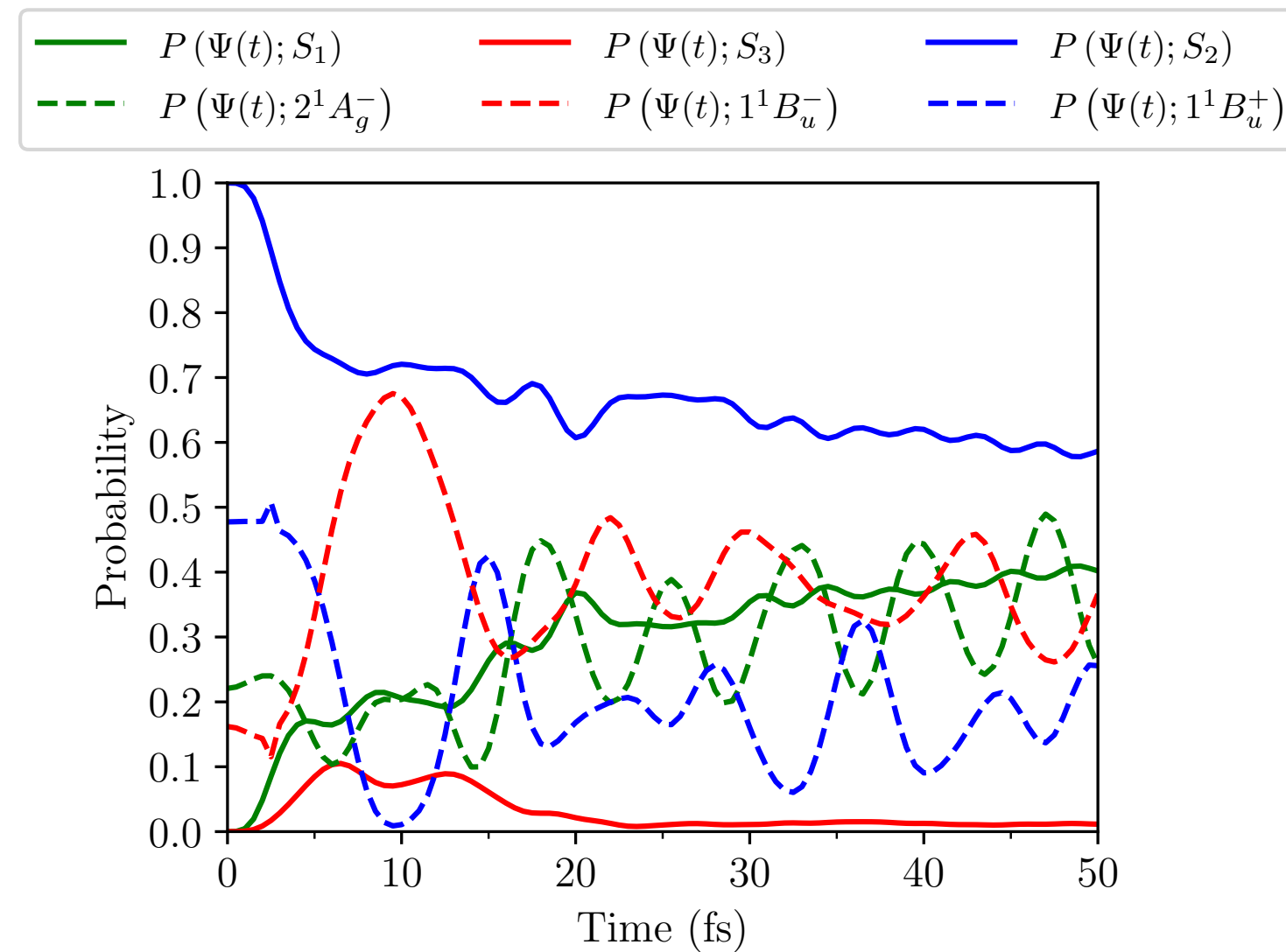


Figure 3: Probabilities that the system described by $\Psi(t)$ occupies the adiabatic excited singlet states S_1 , S_2 , and S_3 , and diabatic states $2^1A_g^-$, $1^1B_u^+$, and $1^1B_u^-$.

Rapid $1^1B_u^+ \rightarrow 1^1B_u^-$ IC within 10 fs via an adiabatic transition is followed by slow nonadiabatic IC to the $2^1A_g^-$ state. A total triplet-pair yield of 70% is predicted after 50 fs.

Direct $1^1B_u^+ \rightarrow 2^1A_g^-$ internal conversion

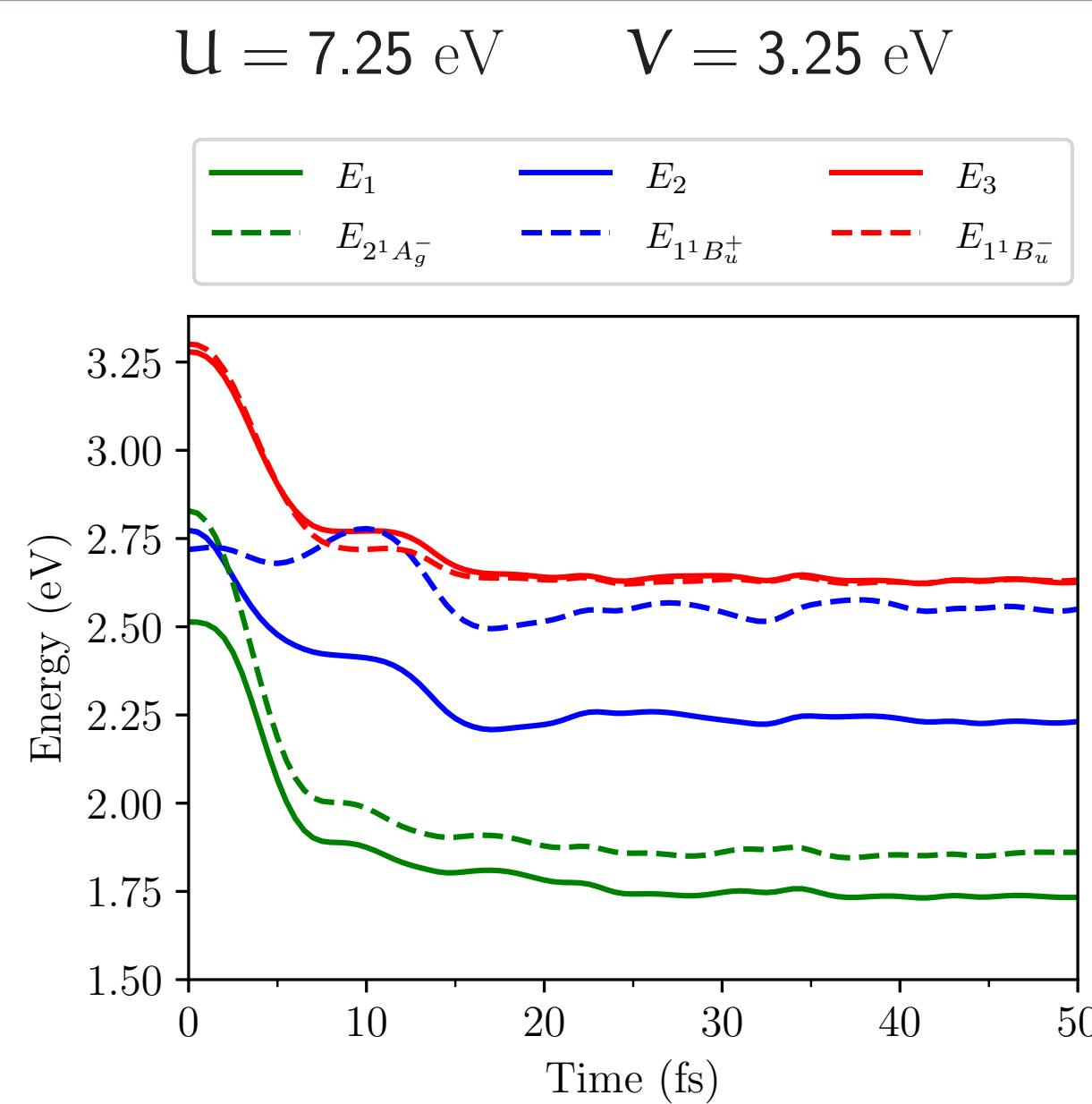


Figure 4: Excitation energies of the diabatic singlet $1^1B_u^+$, $2^1A_g^-$, and $1^1B_u^-$ states, and adiabatic singlet states S_1 , S_2 , and S_3 of neurosporene as a function of time. $1^1B_u^+$ and $2^1A_g^-$ states exhibit a diabatic crossover within 3 fs.

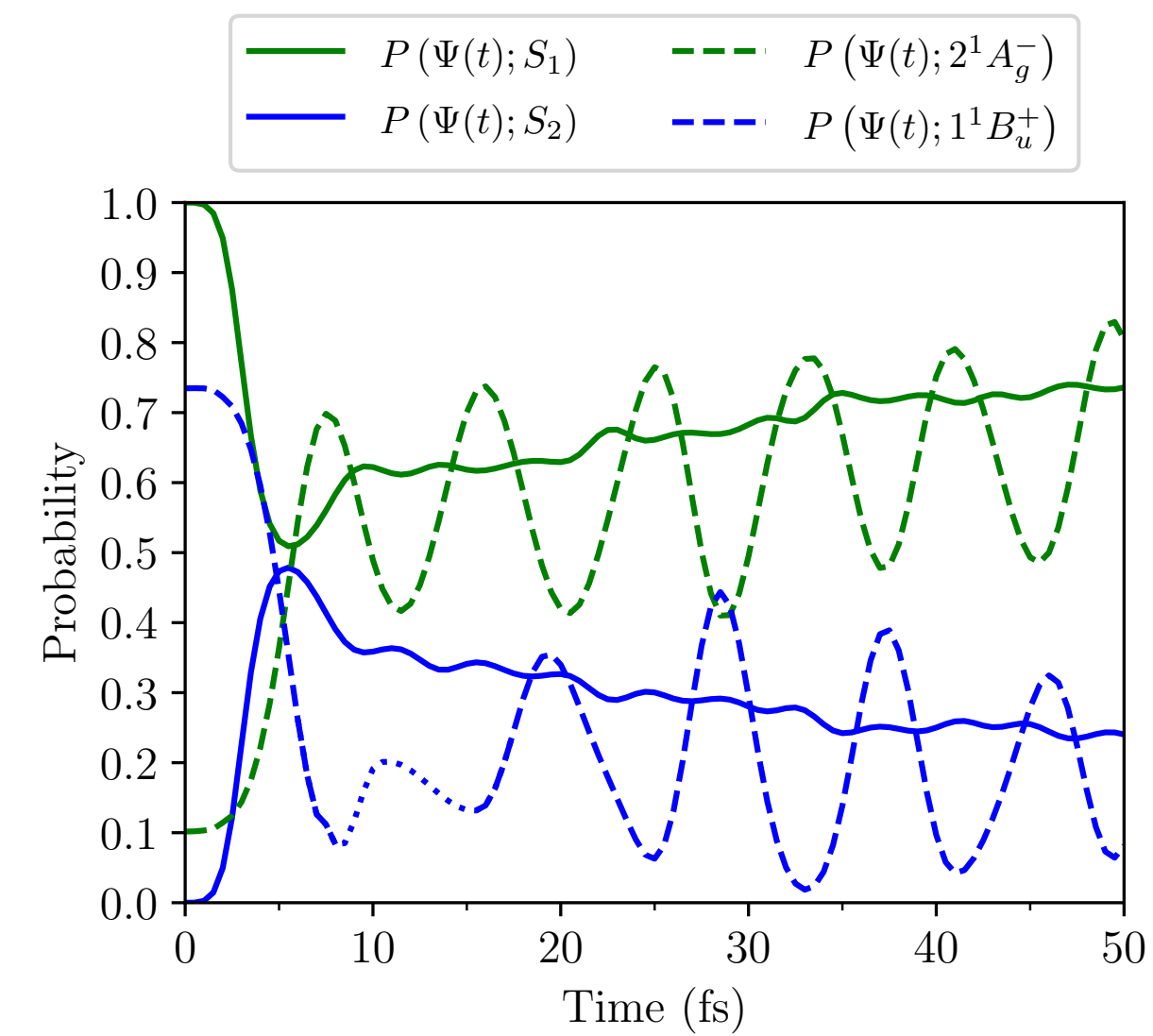


Figure 5: Probabilities that the system described by $\Psi(t)$ occupies the adiabatic excited singlet states S_1 and S_2 , and diabatic states $1^1B_u^+$ and $2^1A_g^-$.

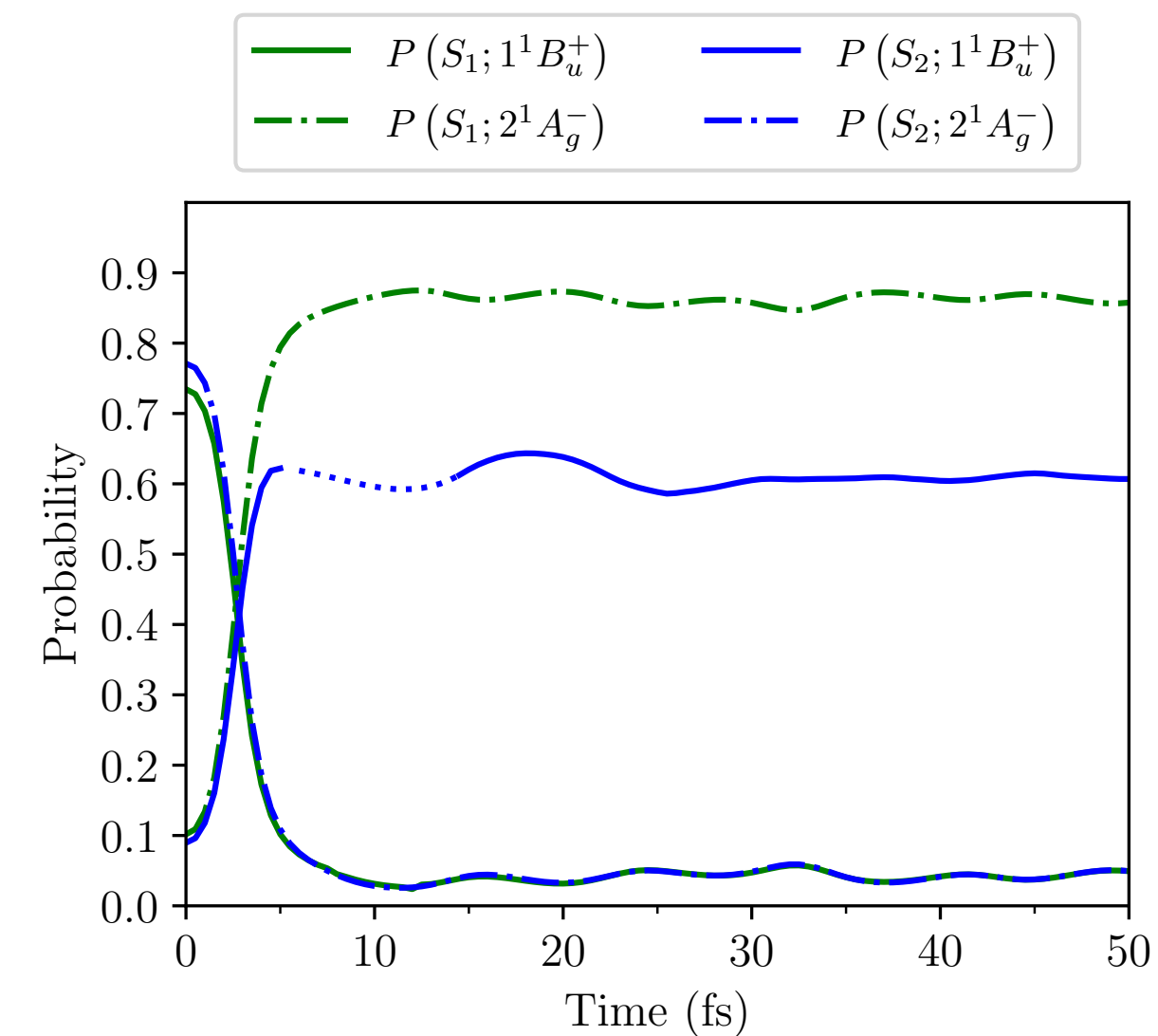


Figure 6: Probabilities that the adiabatic states, S_1 and S_2 , occupy the diabatic states, $2^1A_g^-$ and $1^1B_u^+$. At time $t = 0$, S_1 is the primary photoexcited state, which predominately occupies the exciton state, $1^1B_u^+$. Within 50 fs, S_1 predominately occupies the triplet-pair state $2^1A_g^-$.

We observe rapid internal conversion to the $2^1A_g^-$ state via an adiabatic transition within 10 fs. A $2^1A_g^-$ yield of 60% is predicted after 50 fs.

Landau-Zener type transition

We study the direct $1^1B_u^+ \rightarrow 2^1A_g^-$ IC as a function of the particle-hole symmetry breaking term, by linearly scaling \hat{H}_ϵ by a factor ζ .

$$U = 7.25 \text{ eV} \quad V = 3.25 \text{ eV}$$

Classical $2^1A_g^-$ probability measures the adiabaticity of IC:

$$P_{\text{classical}}(2^1A_g^-) = P(S_1; 2^1A_g^-)P(\Psi(t); S_1) + P(S_2; 2^1A_g^-)P(\Psi(t); S_2)$$

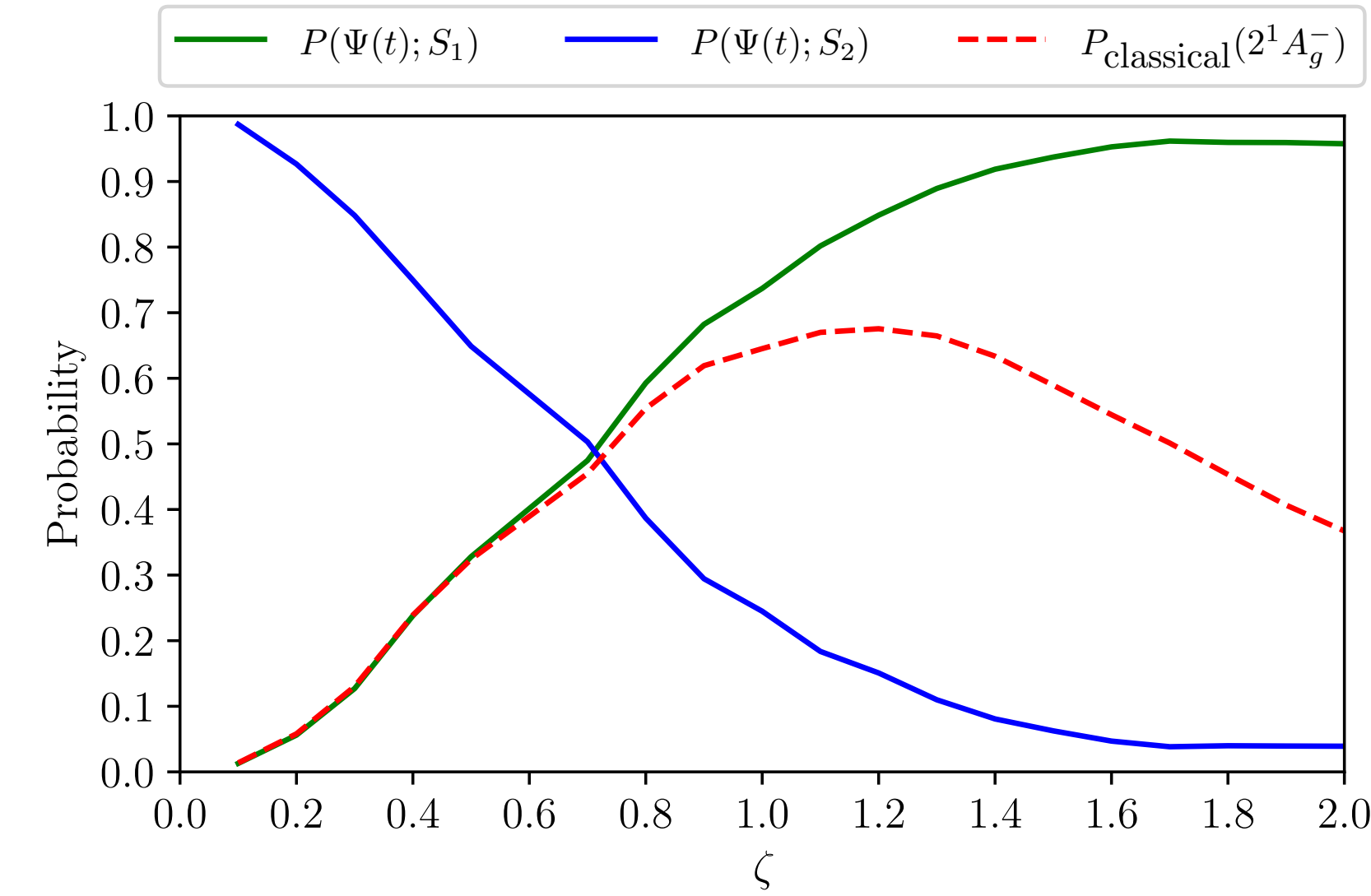


Figure 7: Probabilities at $t = 50$ fs that the system described by $\Psi(t)$ occupies the adiabatic excited singlet states S_1 and S_2 , and $P_{\text{classical}}(2^1A_g^-)$ as a function of ζ .

As $\zeta \rightarrow 0$, $\Psi(t)$ evolves nonadiabatically from S_1 to S_2 while remaining on the diabatic $1^1B_u^+$ state. At large ζ , $\Psi(t)$ evolves adiabatically on the S_1 surface from the $1^1B_u^+$ state to the $2^1A_g^-$ state.

Transient absorption spectra of direct IC

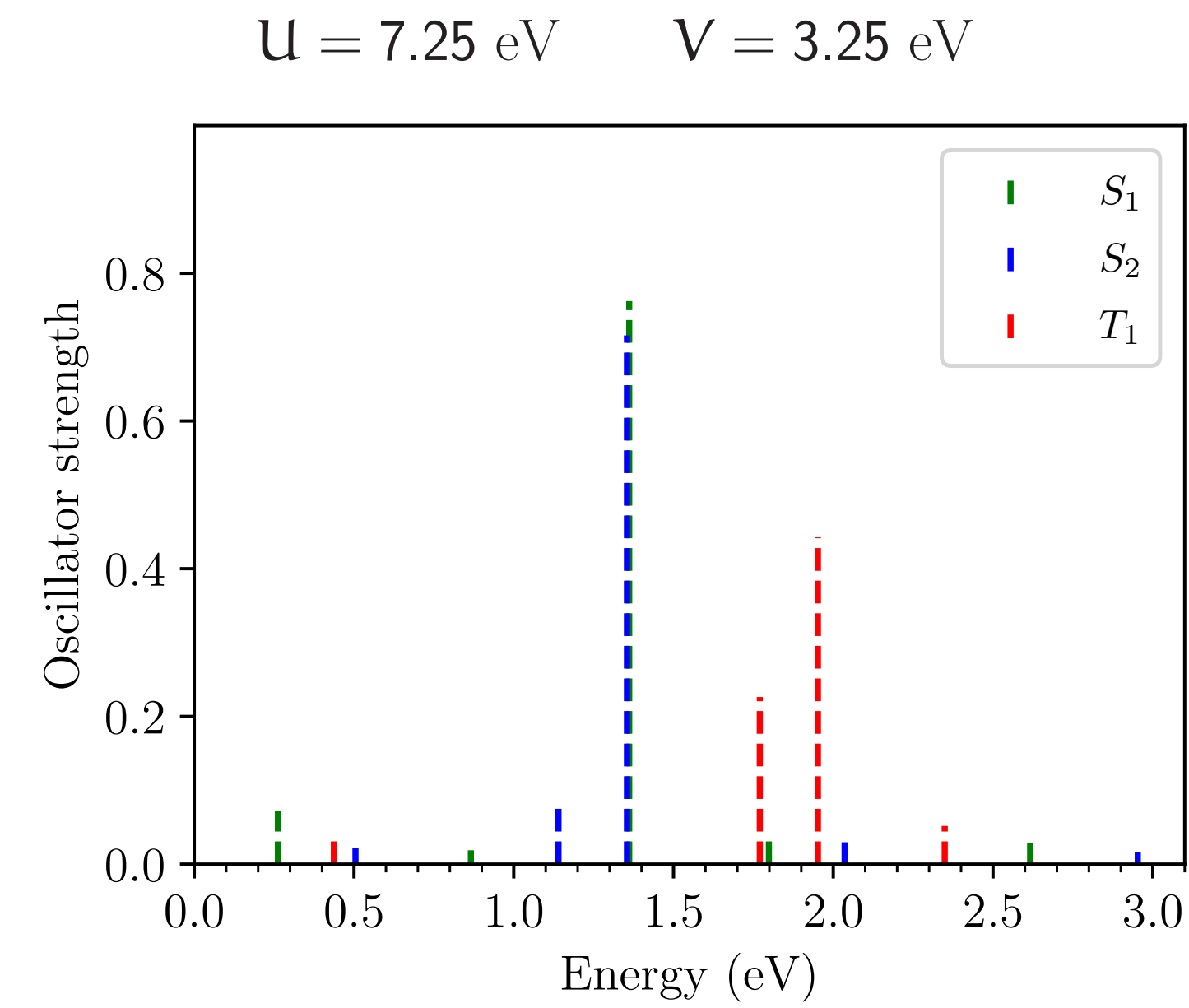


Figure 8: Transient absorption spectra at $t = 0$ from the S_1 , S_2 , and T_1 states of neurosporene.

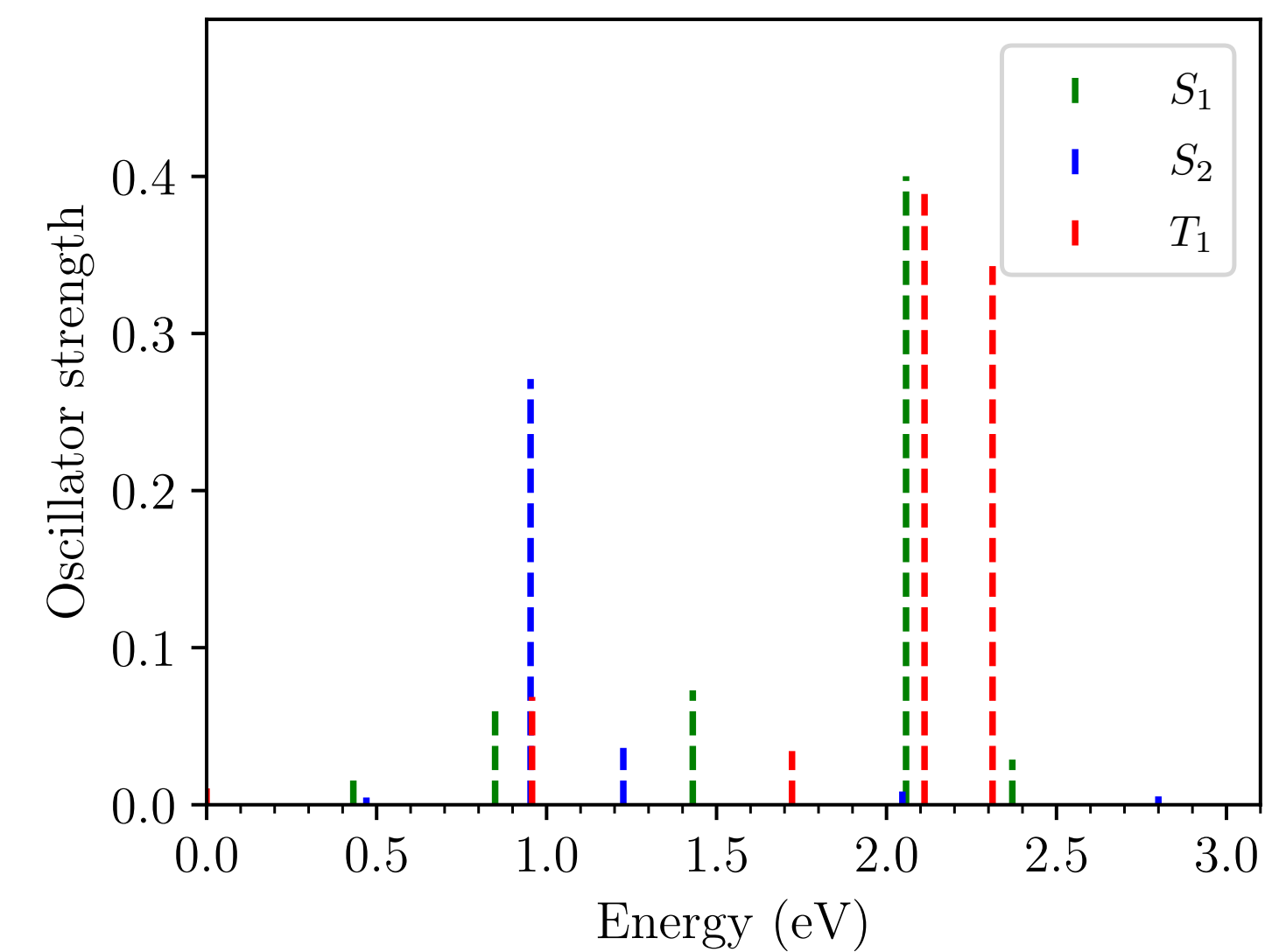


Figure 9: Transient absorption spectra at $t = 20$ from the S_1 , S_2 , and T_1 states of neurosporene. Singlet states are weighted by $P(\Psi(t); S_i)$.

Absorption from the $2^1A_g^-$ state is blue shifted from ~ 1.4 eV at $t = 0$ (S_2) to ~ 2.0 eV at $t = 20$ fs due to large nuclear reorganization energy of the $2^1A_g^-$ state.

Absorption from the $2^1A_g^-$ is below the absorptions from T_1 at all times, indicating transition from the charge-transfer component of the $2^1A_g^-$ state and not from the triplet-pair component. This is verified via an exciton wavefunction calculation.²

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