

Simulation of Ab Initio Optical Absorption Spectrum of β -Carotene with Fully Resolved S_0 and S_2 Vibrational Normal Modes

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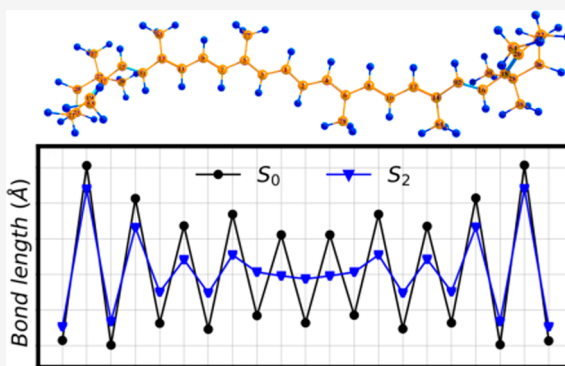


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ABSTRACT: The electronic absorption spectrum of β -carotene (β -Car) is studied using quantum chemistry and quantum dynamics simulations. Vibrational normal modes were computed in optimized geometries of the electronic ground state S_0 and the optically bright excited S_2 state using the time-dependent density functional theory. By expressing the S_2 -state normal modes in terms of the ground-state modes, we find that no one-to-one correspondence between the ground- and excited-state vibrational modes exists. Using the ab initio results, we simulated the β -Car absorption spectrum with all 282 vibrational modes in a model solvent at 300 K using the time-dependent Dirac–Frenkel variational principle and are able to qualitatively reproduce the full absorption line shape. By comparing the 282-mode model with the prominent 2-mode model, widely used to interpret carotenoid experiments, we find that the full 282-mode model better describes the high-frequency progression of carotenoid absorption spectra; hence, vibrational modes become highly mixed during the $S_0 \rightarrow S_2$ optical excitation. The obtained results suggest that electronic energy dissipation is mediated by numerous vibrational modes.



INTRODUCTION

Pigment molecules in nature form the basis of life on earth by enabling organisms to utilize the solar energy. Carotenoids form a unique class of pigments with a conjugated polyene chain, responsible for light absorption in a green-blue color region. Over 700 carotenoid molecules are found in nature. They primarily play a role as coloring materials, which underlie a vital and complex signaling process.^{1,2} In photosynthesis, carotenoids are essential in solar energy harvesting and in photoprotection from oxygen damage. The latter emerge on the microscopic level, when light illumination is high, by the formation of energy trapping states.^{3,4} This trapping has been related to quenching of the chlorophyll excited states by the carotenoid singlet state^{5,6} or by the excitonic interaction between chlorophyll and the carotenoid, which is controlled by carotenoid conformations.^{7,8} Carotenoids become thus responsible for the regulation of excitation energy fluxes in photosynthesis in volatile conditions of daylight irradiation. One of the possible mechanisms of such behavior involves a limited conformational rearrangement of the protein scaffold that could act as a molecular switch to activate or deactivate the quenching mechanism.⁹ A strong correlation between carotenoid and local environment deformations is necessary for such mechanism to exist.

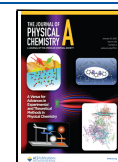
However, the primary deformations leading to carotenoid flexibility are the molecular vibrations. They are usually induced during photon absorption (and emission) and following excitation relaxation processes. Probing excitation

and vibration-mediated relaxation processes in carotenoids, necessary for understanding the fundamental physical processes involved in their functioning, is possible by performing time-resolved optical spectroscopy experiments. It is well established that carotenoids demonstrate a complex structure of electronic excited states^{10,11} with at least three electronic states necessary to fully capture the excitation longtime dynamics. Direct optical excitation induces electronic $S_0 \rightarrow S_2$ transition, where S_0 is the electronic ground state and S_2 is the first optically accessible (bright) electronic state, and the optically dark electronic state S_1 lies between S_0 and S_2 . Additional intramolecular charge-transfer (CT) states have been proposed in peridinin in agreement with the experimental results.^{12,13} Quantum chemical calculations using the time-dependent density functional theory with the Tamm–Dancoff approximation^{14–16} demonstrate the presence of the CT state in the same energy range. The energy of the CT state has been shown to decrease dramatically in solvents of increasing polarity, while the energy of the dark S_1 state remains comparatively constant.¹⁷ Several other types of electronic

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excited states have been suggested; however, their existence and involvement in the relaxation process are still debatable.¹⁸ Specific spectral features have been assigned to S_1 and CT states, and these may play an important role in de-excitation processes.^{9,13,19}

Vibrational heating and cooling are involved in the relaxation process via electronic-vibrational (vibronic) coupling.²⁰ Indeed, strong vibronic coupling is rooted in broad electronic absorption spectra, more specifically, in a strong vibronic shoulder for a range of different carotenoids as observed experimentally.²¹ This feature is often associated with two vibrational modes: C–C symmetric and asymmetric stretching vibrations with the cumulative Huang–Rhys factor larger than 1. These modes are known to be active in Raman spectra, and their frequencies scale linearly with the conjugation length in carotenoids.¹¹ While molecular vibrations affect the symmetry properties of the molecules, they do not affect the oscillator strength of the dark state.²² Such empirical effective 2-mode model has been extensively used for spectroscopy simulations.^{20,23–27} However, the two vibrational modes do not capture the high-energy vibrational wing, and it is not clear whether the two modes are sufficient to accurately describe the more complex ultrafast internal conversion and energy-transfer processes.

In this paper, we present quantum chemistry and quantum dynamics description of vibrational manifold of β -Car in its electronic states S_0 and S_2 . We find that numerous vibrational modes become highly mixed during the $S_0 \rightarrow S_2$ optical excitation, resulting in a complex S_2 state wave packet. We are able to reveal the full absorption spectrum, including the high-energy vibrational shoulder. Simulations thus suggest that pathways responsible for the ultrafast electronic excitation relaxation and internal conversion are mediated by numerous vibrational modes, resulting in a rapid and efficient electronic energy dissipation.

THEORETICAL METHODS

Quantum chemical analysis starts from the complete molecular Hamiltonian including both electronic and vibrational degrees of freedom (DOFs).^{28,29} Using the Born–Oppenheimer approximation, the full Schrödinger equation is split into separate equations for electronic and nuclear DOFs. The stationary Schrödinger equation for electrons then parametrically depends on the nuclear coordinates

$$\hat{H}_{\text{el}}(\mathbf{R})\Phi_m(\mathbf{R}) = E_m(\mathbf{R})\Phi_m(\mathbf{R}) \quad (1)$$

where \hat{H}_{el} includes the electron kinetic energy, electronic interaction with nuclei, electron–electron interactions, and internuclear interaction energy, $\mathbf{R} \equiv R_1, R_2, \dots$ labels nuclei coordinates. The eigenvalues $E_m(\mathbf{R})$ and the corresponding eigenstates $\Phi_m(\mathbf{R})$, which parametrically depend on nuclei configuration, characterize the electronic system.

Electronic energy minimum of the electronic ground state denotes the reference point—the equilibrium molecular structure. If the nuclear configuration deviates from the minimum, the electronic energy is increased; hence, the electronic energy can be treated as the potential energy for nuclei DOFs. For small deviations from the energy minimum, we use the harmonic approximation, where the potential energy operator is expanded up to quadratic terms. Therefore, the potential energy for nuclei displacements in the electronic

state n can be written as (using Einstein summation convention for repeating indices)

$$U_n(u) \approx \frac{1}{2} \mathcal{H}_{ij}^{(n)} u_i u_j \quad (2)$$

where we introduce mass-weighted Cartesian coordinates $u_i = \sqrt{M_i}(R_i - R_{i0}^{(n)})$, as the shifts of nuclei from their equilibrium positions, and

$$\mathcal{H}_{ij}^{(n)} = \frac{1}{\sqrt{M_i M_j}} \left. \frac{\partial^2 E_n(\mathbf{R})}{\partial R_i \partial R_j} \right|_{\min} \quad (3)$$

is the Hessian matrix with derivatives taken at the global minimum of the state n . The Schrödinger equation for the nuclear wave functions with respect to the specific electronic state n is

$$(\hat{T} + \hat{U}_n(u))\chi_{n\alpha}(u) = \varepsilon_{n\alpha}\chi_{n\alpha}(u) \quad (4)$$

where α is the vibrational quantum-state index with energy $\varepsilon_{n\alpha}$ and wave function $\chi_{n\alpha}$. The vibrational Schrödinger equation splits into an independent set of equations in the normal coordinate representation; we denote these coordinates by Q_k . Normal modes are obtained by diagonalizing the Hessian matrix for each electronic state n . Solving the eigenstate equation

$$\mathcal{H}_{ij}^{(n)} L_{jk}^{(n)} = \omega_{nk}^2 L_{ik}^{(n)} \quad (5)$$

yields normal mode frequencies ω_{nk} where k labels normal modes. The Hessian eigenvectors $L_{ik}^{(n)}$ relate the normal modes k and nuclei displacements u_i . Placing eigenvectors in columns, we form the matrix $L^{(n)}$, whose rank is $M = 3N - 6$ (six of the modes are physically irrelevant as three of them correspond to the uniform translation of the whole molecule along the Cartesian axes, while the other three are uniform rotations about these axes, they are excluded), and it is used to transform mass-weighted Cartesian internal coordinates u_i into normal coordinates $Q_k^{(n)} = (L^{(n)})_{ki}^{-1} u_i$.

Complete description of the vibronic molecular states, when the electronic and vibrational states are known, is given by the state vectors $|\mathbf{n}\alpha\rangle$, where $\alpha_n \equiv (\alpha_{n1}, \alpha_{n2}, \dots, \alpha_{nK})$ is the M -dimensional vector denoting the vibrational states of all vibrational modes in the electronic state n . As the normal modes are harmonic, the vibrational Hamiltonian in the electronic state n is given by

$$\hat{H}^{(n)} = \frac{1}{2} \sum_k ((\hat{P}_k^{(n)})^2 + \omega_{nk}^2 (\hat{Q}_k^{(n)})^2) |\mathbf{n}\rangle \langle \mathbf{n}| \quad (6)$$

The absorption spectrum of a vibronic system involves all possible optical transitions from the vibronic ground state $|\mathbf{g}\beta\rangle$ to the excited states $|\mathbf{l}\alpha\rangle$. Starting from the linear response theory, the absorption spectrum is given by the Fourier transform of the linear response function

$$S(\omega) = \frac{\omega}{nc} \text{Re} \int_0^\infty dt e^{i\omega t} F(t) \quad (7)$$

where n is the refraction index and c is the speed of light,^{28,30} and

$$F(t) = \langle \mathbf{g}\alpha | e^{i\hat{H}_s t} \hat{\mathbf{P}} e^{-i\hat{H}_s t} | \mathbf{l}\alpha \rangle \quad (8)$$

is the dipole operator correlation function. In the Born approximation, the polarization operator $\hat{\mathbf{P}}$ acts only on

electronic DOFs; hence, $\hat{\mathbf{P}} = \boldsymbol{\mu}_{\text{eg}}^{(\text{el})}(|e\rangle\langle g| + |g\rangle\langle e|)$ and $\boldsymbol{\mu}_{\text{eg}}^{(\text{el})}$ is the electronic transition dipole. The matrix elements of the polarization operator are given by

$$\langle e\alpha|\hat{\mathbf{P}}|g\beta\rangle = \boldsymbol{\mu}_{\text{eg}}^{(\text{el})} \int d^N \mathbf{u} \prod_{j,k} \chi_{e\alpha_j}^*(\mathbf{u}) \chi_{g\beta_k}(\mathbf{u}) \quad (9)$$

The multi-dimensional integral corresponds to the vibrational overlaps between the vibrational wave function in different electronic states. The integral computation is not trivial because the sets of normal modes in different electronic states are not orthogonal, and transformation of one set of normal modes into another is necessary.^{31–33}

Differences of the set of normal modes in different electronic states are characterized as follows. In the electronic state n , the deviation of atomic Cartesian coordinates R_i from the equilibrium position $R_{i0}^{(n)}$ may be expressed via the normal modes via the relation

$$\sqrt{M_i}(R_i - R_{i0}^{(n)}) = L_{ij}^{(n)} Q_j^{(n)} \quad (10)$$

and allows us to relate the relative mass-weighted atom shifts $D_i^{(mn)} \equiv \sqrt{M_i}(R_{i0}^{(m)} - R_{i0}^{(n)})$ between the equilibrium positions in electronic states m and n as

$$D_i^{(mn)} = L_{ij}^{(n)} Q_j^{(n)} - L_{ij}^{(m)} Q_j^{(m)} \quad (11)$$

then the normal mode coordinates in state m can be expressed in terms of state n normal mode coordinates as

$$Q_i^{(m)} = a_{ij}^{(mn)} Q_j^{(n)} - d_i^{(mn)} \quad (12)$$

where the expansion coefficient of the i th normal mode in the m th state in terms of j th mode in the n th state is

$$a_{ij}^{(mn)} \equiv (L^{(m)})_{ik}^{-1} L_{kj}^{(n)} \quad (13)$$

and the i th normal mode potential displacement in the m th state, with respect to the position in the n th state, is

$$d_i^{(mn)} \equiv (L^{(m)})_{ik}^{-1} D_k^{(mn)} \quad (14)$$

These are the two quantities that relate the normal modes in different electronic states. Likewise, the normal mode momentum is also expanded in terms of the $a_{kj}^{(\text{eg})}$ coefficients (and zero displacement)

$$P_i^{(m)} \equiv a_{ij}^{(mn)} P_j^{(n)} \quad (15)$$

Further on, we consider two electronic states: the ground state $|g\rangle$ and the electronic excited state $|e\rangle$. Instead of evaluating propagators in eq 8 by computing the multi-dimensional vibrational overlaps in eq 9, we choose to specify a vibronic state basis using the coherent-state representation and propagate it following the time-dependent Dirac–Frenkel variational principle.

We begin with writing dimensionless Hamiltonian by introducing the dimensionless momentum $\hat{p}_k^{(n)} \equiv \sqrt{\omega_{nk}}^{-1} \hat{P}_k^{(n)}$ and coordinate $\hat{q}_k^{(n)} \equiv \sqrt{\omega_{nk}} \hat{Q}_k^{(n)}$ operators for states $n = g, e$. After inserting them in eq 6, the electronic ground-state Hamiltonian is

$$\hat{H}^{(g)} = \sum_k \frac{\omega_{gk}}{2} ((\hat{p}_k^{(g)})^2 + (\hat{x}_k^{(g)})^2) |g\rangle\langle g| \quad (16)$$

and the electronic excited-state $|e\rangle$ Hamiltonian is

$$\begin{aligned} \hat{H}^{(e)} = & \left(\varepsilon_e + \Lambda_e^{\text{vib}} + \sum_k \frac{\omega_{ek}}{2} ((\hat{p}_k^{(e)})^2 + (\hat{x}_k^{(e)})^2) \right) |e\rangle \\ & - \sum_k \omega_{ek} \tilde{d}_k^{(\text{eg})} \hat{x}_k^{(e)} |e\rangle\langle e| \quad (17) \end{aligned}$$

where $\tilde{d}_k^{(\text{eg})} \equiv \sqrt{\omega_{ek}} d_k^{(\text{eg})}$ is the dimensionless displacement and $\Lambda_e^{\text{vib}} \equiv \frac{1}{2} \sum_k \omega_{ek} (\tilde{d}_k^{(\text{eg})})^2$ is the total vibrational reorganization energy. The resulting operators in eqs 16 and 17 read

$$\hat{x}_k^{(n)} \equiv \beta_{nk,j} a_{kj}^{(\text{ng})} \hat{q}_j^{(g)} \quad (18)$$

$$\hat{p}_k^{(n)} \equiv \beta_{nk,j}^{-1} a_{kj}^{(\text{ng})} \hat{p}_j^{(g)} \quad (19)$$

where $\beta_{nk,j} \equiv \sqrt{\omega_{nk}/\omega_{gj}}$. Equations 18 and 19 describe the dimensionless coordinate and momentum of the k th normal mode about its equilibrium point in the n th electronic state. Terms $\beta_{nk,j}$ appear due to the normal mode mixing and different vibrational frequencies in states g and e . We also add ε_e as the purely electronic excitation energy and set $\varepsilon_g = 0$ cm⁻¹. The total system Hamiltonian is the sum over all electronic state terms $\hat{H}_S = \hat{H}^{(g)} + \hat{H}^{(e)}$.

Solvent effects will be simulated by considering energy fluctuations of the molecular environment. Thermal fluctuations are induced by a set of quantum harmonic oscillators of a given temperature, and we will refer to this subsystem as the phonon bath. The phonon bath Hamiltonian is

$$\hat{H}_B = \sum_p \frac{w_p}{2} (\hat{p}_p^2 + \hat{x}_p^2) \quad (20)$$

where w_p is the frequency of the p th phonon mode, while \hat{p}_p and \hat{x}_p are the momentum and the coordinate operators, respectively. The interaction between the system electronic states and the phonon bath is included using the displaced oscillator model,²⁹ with the system–bath interaction Hamiltonian

$$\hat{H}_{S-B} = - \sum_p w_p f_{ep} \hat{x}_p |e\rangle\langle e| \quad (21)$$

where f_{ep} is the electron–phonon coupling strength of the p th phonon mode to the electronic state e . The electronic ground state is taken as the reference point, so it is not affected by bath fluctuations $f_{gp} = 0$. Notice that the system–bath coupling has the same form as the last term in eq 17. The electronic state energy modulation by the intramolecular and intermolecular vibrations is treated equivalently. Likewise, we get additional contribution to the reorganization energy $\Lambda_e^{\text{ph}} = \frac{1}{2} \sum_p w_p f_{ep}^2$. Usually, all excited electronic states are described as having the same coupling strength to the bath, thus changing all states' energies by the same amount. For simplicity, we absorb Λ_e^{ph} into the definition of the excited-state energy ε_e ; however, Λ_e^{ph} is still used to define the electron–phonon coupling strengths f_{ep} . The full model Hamiltonian is the sum of terms

$$\hat{H} = \hat{H}_S + \hat{H}_B + \hat{H}_{S-B} \quad (22)$$

The fluctuation characteristics of the phonon bath can be represented by the spectral density function

$$C_e''(\omega) = \frac{\pi}{2} \sum_p f_{ep}^2 w_p^2 [\delta(\omega - w_p) - \delta(\omega + w_p)] \quad (23)$$

where $\delta(\omega)$ is the Dirac delta function. Integration of eq 23 over the complete frequency range defines the phonon bath reorganization energy in the n th electronic state

$$\Lambda_e^{\text{ph}} = \frac{1}{\pi} \int_0^\infty \frac{C_e''(\omega)}{\omega} d\omega = \frac{1}{2} \sum_p w_p f_{ep}^2 \quad (24)$$

Many theories have been proposed to evaluate the linear response function and the necessary polarization operator matrix elements (eqs 8 and 9), notably, the foundational theory by Yan and Mukamel,³⁴ Franck–Condon approaches,^{35–37} and the theories that include non-Condon effects.^{38–41}

We chose to compute the linear response function by propagating the Davydov D_2 trial wave function originating from the molecular chain soliton theory.^{42,43} For N electronic states, we can write an arbitrary state of the system as a superposition—the Davydov D_2 wave function is

$$|\Psi(t)\rangle = \sum_n \alpha_n(t) |n\rangle \times \underbrace{|\tilde{\lambda}_1(t), \tilde{\lambda}_2(t), \dots, \tilde{\lambda}_K(t)\rangle}_{\text{molecule state}} \times \underbrace{|\lambda_1(t), \lambda_2(t), \dots, \lambda_p(t)\rangle}_{\text{solvent phonon state}} \quad (25)$$

It utilizes the coherent-state representation for all vibrational modes. For the shifted harmonic oscillator model, the coherent states result in an exact dynamics.⁴⁴ $\alpha_n(t)$ is the amplitude of electronic state $|n\rangle$, in our case $n = g, e$. Vibrational and phonon bath modes are represented using coherent states $|\hat{\lambda}(t)\rangle = \exp(\lambda(t)\hat{b}^\dagger - \lambda^*(t)\hat{b})|0\rangle$, defined with respect to the electronic ground-state vibrational modes, where $\lambda(t)$ is the coherent-state parameter and $|0\rangle$ is the vacuum state of a quantum harmonic oscillator. \hat{b}_i^\dagger and \hat{b}_i are the corresponding bosonic creation and annihilation operators. Only the electronic ground-state normal modes are represented by the coherent states, and modes of the excited state are expanded in terms of the ground-state coherent states. Davydov-type wave functions have been extensively used to model a single molecule, as well as their aggregate dynamics,^{45–49} linear and nonlinear spectra.^{50–54}

Time evolution of the Davydov D_2 wave function is obtained by applying the Euler–Lagrange equation

$$\frac{d}{dt} \left(\frac{\partial \mathcal{L}(t)}{\partial \dot{\eta}_i^*(t)} \right) - \frac{\partial \mathcal{L}(t)}{\partial \eta_i^*(t)} = 0 \quad (26)$$

to each of the time-dependent parameter $\eta_i = \alpha_n \tilde{\lambda}_k \lambda_p$, where

$$\mathcal{L}(t) = \frac{i}{2} \left(\langle \Psi | \frac{d}{dt} \Psi \rangle - \langle \frac{d}{dt} \Psi | \Psi \rangle \right) - \langle \Psi | \hat{H} | \Psi \rangle \quad (27)$$

is the Lagrangian of the model given in terms of the Hamiltonian \hat{H} . For convenience, we omit explicitly writing time dependence. The Euler–Lagrange equation yields a system of coupled differential equations for the α_n , $\tilde{\lambda}_k$, and λ_p parameters of the Davydov D_2 wave function, see the Supporting Information for the full derivation. Equations describing model dynamics while the system is in the excited state $|e\rangle$ are

$$\frac{d}{dt} \alpha_e = -i \alpha_e \left(\varepsilon_e + \Lambda_e^{\text{vib}} + \sum_{k,j} \frac{\omega_{ek}^2 + \omega_{gj}^2}{4\omega_{gj}} (a_{kj}^{(eg)})^2 \right) + i \alpha_e \left(\sum_k \frac{\omega_{ek}}{2} d_k^{(eg)} x_k^{(e)} + \sum_q w_q \frac{f_{eq}}{\sqrt{2}} \text{Re } \tilde{\lambda}_q \right) \quad (28)$$

$$\frac{d}{dt} \tilde{\lambda}_k = -i \sum_j \frac{\omega_{kj}}{\sqrt{2}} \beta_{ej,k} a_{jk}^{(eg)} (x_j^{(e)} - d_j^{(eg)} + i p_j^{(e)}) \quad (29)$$

$$\frac{d}{dt} \lambda_q = -i w_q \left(\lambda_q - \frac{f_{eq}}{\sqrt{2}} \right) \quad (30)$$

where $x_k^{(e)} = \beta_{ek,j} a_{kj}^{(eg)} \sqrt{2} \text{Re } \tilde{\lambda}_j$ and $p_k^{(e)} = \beta_{ek,j}^{-1} a_{kj}^{(eg)} \sqrt{2} \text{Im } \tilde{\lambda}_j$ are the expectation values of operators in eqs 18 and 19. The resulting system of equations for the ground state $|g\rangle$ dynamics can be solved analytically: $\alpha_g(t) = \alpha_g(0) \exp\left(-\frac{i}{2} \sum_k \omega_{gk} t\right)$, $\tilde{\lambda}_k(t) = \tilde{\lambda}_k(0) \exp(-i\omega_{gk} t)$, $\lambda_q(t) = \lambda_q(0) \exp(-i w_q t)$. Separation of equations into the ground- and excited-state manifold is convenient for the computation of the optical observables using the response function theory. Terms due to the mixing of normal modes remain present in eqs 28 and 29. In the latter, evolution of the k th mode is influenced by the motion of all other j th modes. Equations 28–30 were solved numerically using the adaptive step size Runge–Kutta algorithm.

The temperature of the normal vibrational modes, as well as the phonon modes, is included by performing the Monte Carlo simulation to generate the thermal ensemble of the Davydov D_2 wave function trajectories. At the zero time, before optical excitation, in each trajectory, the initial coherent-state displacements $\tilde{\lambda}_q(0)$ and $\lambda_p(0)$ are sampled from the Glauber–Sudarshan distribution⁵⁵

$$\mathcal{P}(\lambda) = \mathcal{Z}^{-1} \exp(-|\lambda|^2 (e^{\omega/k_B T} - 1)) \quad (31)$$

where \mathcal{Z} is the partition function of a single coherent state $|\lambda\rangle$ with the corresponding frequency ω , k_B is the Boltzmann constant, and T is the model temperature. Observables averaged over the thermal ensemble will be denoted as $\langle \dots \rangle$. We found 500 trajectories to be sufficient to obtain the converged ensemble for the model of β -Car as described in the next section.

■ SIMULATION RESULTS

Normal Modes of β -Car in S_0 and S_2 Electronic States.

We consider a model of β -Car in thermal equilibrium with a solvent at 300 K. For the photon absorption process, β -Car is described by the electronic ground state $|S_0\rangle \equiv |g\rangle$ and the excited state $|S_2\rangle \equiv |e\rangle$. The optically dark excited state $|S_1\rangle$ does not directly participate in the electronic absorption process and is excluded.

The electronic Schrödinger equation of the β -Car molecule was solved using the density functional theory (DFT) method for the ground electronic state S_0 , and the time-dependent DFT (TD-DFT) method for the electronic excited state S_2 , from which atom equilibrium positions R_0^g , R_0^e are acquired. The GAMESS⁵⁶ and Gaussian-16 codes⁵⁷ were used.

The calculation methods were based on the experience from previous calculations of resonance RAMAN spectra of carotenoids, investigation of dependence between the position of the $S_0 \rightarrow S_2$ transition and the frequency of the $\nu 1$ Raman

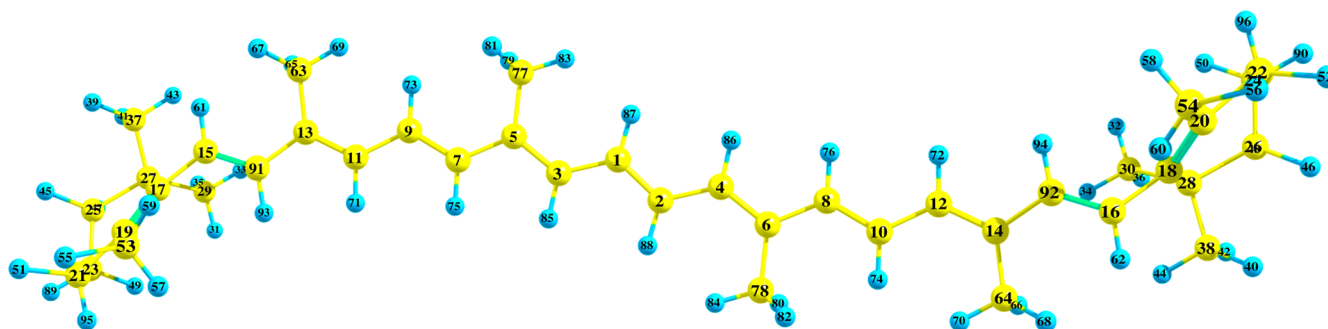


Figure 1. Structure and atom numbering of the C_{2v} symmetry carotene.

band.^{58,59} The most RAMAN intense band, ν_1 , located at around 1500 cm^{-1} , arises from the stretching of the C=C bonds. Previous calculations of the ν_1 Raman bands in the ground electronic state S_0 were performed for another carotenoid, lycopene, using the DFT method with B3LYP/6-31G, B3LYP/TZVP, B3LYP/6-31G(2df,p), BP86/6-31G(d), BPW91/6-31G(d), B3P86/6-31G(d), B3PW91/6-31G(d), and SVWN/6-31G(d) potentials.⁶⁰ It was shown that all methods based on DFT are able to perform calculation of vibrational frequencies with an overall root-mean-square error of $34\text{--}48\text{ cm}^{-1}$.⁶¹ Also, it was shown that the dependence of the Raman peak frequency shift, compared between that computed under vacuum and experimental, is linear over the whole spectra,⁵⁸ using the B3LYP/6-311G(d,p) method, and a scaling factor of 0.9613 has to be used.^{58,61} On the other hand, the energy of β -Car corresponding to the first optically allowed transition in the gas phase was reported to be between 2.85 and 2.93 eV.⁵⁹ This value is 0.62 eV higher than the excitation energy calculated using TD-DFT at the B3LYP/6-311G(d,p) level (2.224 eV).⁵⁸ Other methods give similar results: Tamm–Dancoff approximation (TDA) blyp/6-31G(d)—2.15 eV, TD b3lyp/cc-pvdz—2.19 eV, and TD b3lyp/cc-pvtz—2.21 eV.

Equilibrium structures of excited states, optimized using the TDA⁶² and TD-DFT^{63,64} with the BLYP functional, and the DZP basis set, in contrast to B3LYP, yields correct energetic order of the two lowest β -Car excited states, and it has been shown to reach an accuracy of 0.2 eV for the S_1 excitation energy in carotenoids.⁶⁵ However, later this has been explained by a fortuitous cancellation of errors caused by the neglect of double excitations in the ground and excited states.⁶⁶

We performed geometry optimization using various methods with TD-SCF, TDA-SCF basis sets and b3lyp/6-311G(d,p), blyp/6-31G(d), b3lyp/cc-pvdz, and b3lyp/cc-pvtz potentials. The Car molecule equilibrium structure and enumeration of atoms are shown in Figure 1, and the changes of the C–C bond lengths along the Car polyene chain in both electronic states calculated using the TD-SCF B3LYP/6-311G(d,p) method are shown in Figure 2. All the tested methods give similar alternation of the C–C bond lengths in the S_0 state, close to that shown in Figure 2. For the S_2 state, the situation is different—methods using the TDA-SCF basis set give alternation similar to the S_0 -state case. The largest alternation of the S_2 state polyene bond lengths was achieved using the TDA blyp/6-31G(d) method. All TD-SCF calculations provide almost 10 times smaller alternation of C–C bond lengths in the middle of the polyene chain, as compared to the TDA-DTF calculations, again, similar to the results shown in Figure 2.

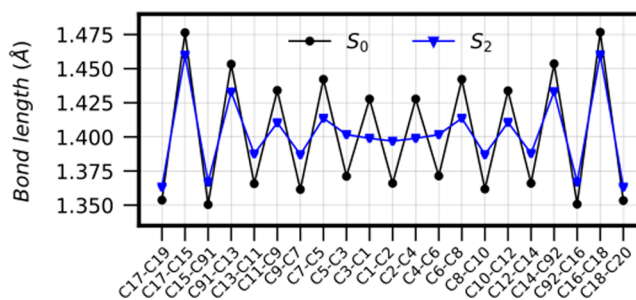


Figure 2. Polyene chain C–C bond lengths in the electronic ground state S_0 and the excited state S_2 calculated using the TD-SCF B3LYP/6-311G(d,p) method.

In order to evaluate the influence of the chosen method to the vibrational mode frequencies and their bands, we performed the calculation of vibrational spectra using TD-SCF and TDA-SCF methods with different basis sets and potentials (b3lyp/6-311G(d,p), blyp/6-31G(d), b3lyp/cc-pvdz, and b3lyp/cc-pvtz). In the S_0 state, the valence vibrational frequencies of the C–C bonds of the polyene chain scale equally and agree to within the range of 20 cm^{-1} . The same vibrational frequencies in the S_2 state also scale equally, with the exception of the TDA blyp/6-31G(d) method, as shown in Figure 3. All the tested methods agree

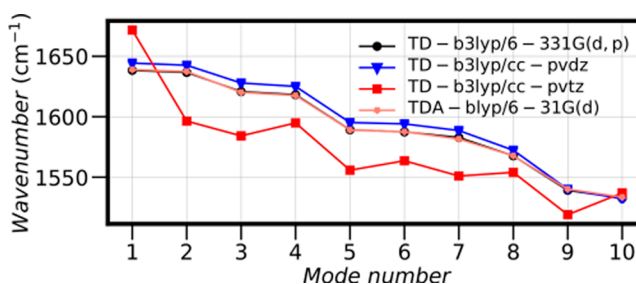


Figure 3. Polyene backbone C–C valence vibrational mode frequencies in the excited state S_2 calculated using various quantum chemistry methods.

on the C–C bond vibrational frequencies in the S_2 state within a range of 46 cm^{-1} . Previous ν_1 Raman band evaluation and correlation with $S_0 \rightarrow S_2$ excitation in the gas phase were performed under vacuum using the TD-SCF B3LYP/6-311G(d,p) method, and the results are in agreement with the experimental observations.^{58,59} Based on this knowledge, all further presented quantum chemistry calculations were performed under vacuum using the B3LYP/6-311G(d,p) method as in ref 59 and the scaling factor was not applied.

The changes in polyene chain geometry during $S_0 \rightarrow S_2$ electronic excitation causes changes in molecular electronic structure, normal mode frequencies, and vibrational mode coordinates. The C–H valence bond vibrations in all β -Car parts are in the region of 2970–3170 cm^{-1} for the ground state and in the region of 2960–3168 cm^{-1} for the excited state. The lower frequency region is characterized by the change of C=C bond lengths in polyene chain. Here, the S_0 normal mode frequencies lay in the region of 1558–1674 cm^{-1} and the corresponding region for the S_2 state is 1533–1636 cm^{-1} . Transition $S_0 \rightarrow S_2$ mainly induces differences in the polyene chain bond lengths between carbon atoms in both electronic states. As a consequence, the vibrational frequencies in the S_2 state become lower by 40–50 cm^{-1} .

Expressing normal mode coordinates in the electronic state S_2 by the normal coordinates of the ground electronic state S_0 , according to eq 12, allows us to investigate normal mode mixing upon $S_0 \rightarrow S_2$ electronic transition. In Figure 4, we plot

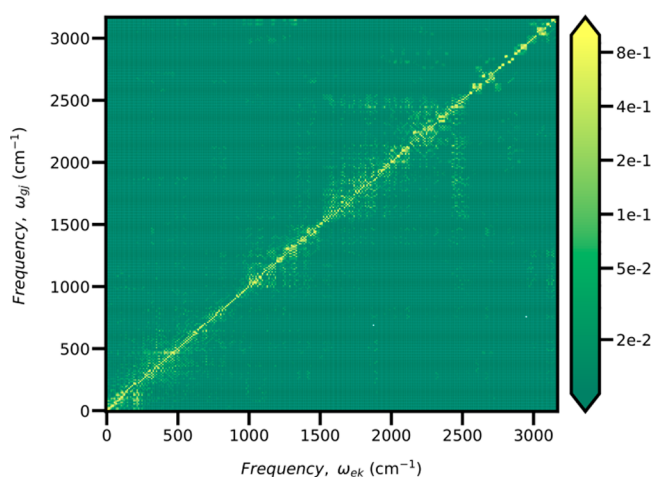


Figure 4. Expansion coefficient absolute value $|a_{kj}^{(eg)}|$ of the β -Car normal modes. The k th mode in the S_2 state is expanded in terms of the mode j th in the state S_0 calculated using the TD-SCF B3LYP/6-311G(d,p) method.

the expansion coefficient absolute value $|a_{kj}^{(eg)}|$, that is, the k th mode in the S_2 state is expanded in terms of the mode j th in the state S_0 . The largest expansion coefficients lay close to the main diagonal, implying that the majority of normal modes are non-negligibly mixed with similar frequency modes. However, certain modes show mixing with modes that has vastly different frequencies; for example, modes in a frequency region of $\approx 2500 \text{ cm}^{-1}$ are highly mixed with modes in a frequency range of 1500–2500 cm^{-1} . Strong mixing can also be clearly seen between modes in frequency regions of 0–250 cm^{-1} , 400–750 cm^{-1} , and 1000–1500 cm^{-1} . Such a broad frequency mixing range signifies a wide range of available vibrational relaxation pathways. At a first glance, expansion coefficients along the $\omega_{ei} = \omega_{gi}$ diagonal may look symmetric; however, they are not, even when absolute values are considered $|a_{kj}^{(eg)}| \neq |a_{jk}^{(eg)}|$. This demonstrates that there is no one-to-one correspondence between the β -Car normal modes in the electronic S_0 and S_2 states.

Additionally, we found that during transitions between S_0 and S_2 electronic states, the transition dipole weakly depends on the nuclear configuration. For transition $S_0 \rightarrow S_2$, the transition moment components are $\mu_{02} = (8.35, 0.71, 0.0)$ in a.u.

(21.28 Debye), while for the $S_2 \rightarrow S_0$, it is equal to $\mu_{20} = (9.45, 0.57, 0.0)$ in a.u. (24.06 Debye). The difference between the two transitions is minimal; thus, the non-Condon effects can be reasonably excluded from the calculations. The transition dipole moment is oriented with the z component being perpendicular to the plane of the polyene chain, while the x component is directed along the polyene chain.

Absorption Spectrum of the β -Carotene Model. The quantum chemistry results of the β -Car are now used to compute the absorption spectrum given by eq 7. Fourier transformation is performed on the linear response function averaged over the thermal ensemble, $\langle F(t) \rangle$, and the single trajectory of the ensemble linear response is defined in eq 8 and is equal to

$$F(t) = |\mu_{eg}^{(el)}|^2 e^{i/2 \sum_k \omega_{skt}} \alpha_g^*(0) \alpha_e(t) \times \exp \sum_k \left(e^{i\omega_{skt}} \tilde{\lambda}_k^*(0) \tilde{\lambda}_k(t) - \frac{1}{2} (|\tilde{\lambda}_k(0)|^2 + |\tilde{\lambda}_k(t)|^2) \right) \times \exp \sum_p \left(e^{i\omega_{pt}} \lambda_p^*(0) \lambda_p(t) - \frac{1}{2} (|\lambda_p(0)|^2 + |\lambda_p(t)|^2) \right) \quad (32)$$

It is expressed in terms of the dynamical parameters $\alpha_n(t)$, $\tilde{\lambda}_k(t)$, and $\lambda_p(t)$; therefore, it is enough to propagate the excited-state dynamics.

For the solvent, the phonon bath modes are defined by uniformly discretizing the spectral density function $C_e''(\omega)$ in the frequency domain in the range $[w_{\min} = 0.1, w_{\max} = 1250] \text{ cm}^{-1}$ with discretization step size $\Delta_w = 10 \text{ cm}^{-1}$. Then, the frequency of the p th bath mode is given by $w_p = w_{\min} + (p - 1)\Delta_w$. Form of the spectral density function was chosen to be the overdamped Brownian oscillator function $C_e''(\omega) = 2\Lambda_e^{\text{ph}} \omega \gamma / (\omega^2 + \gamma^2)$. The damping parameter $\gamma = 200 \text{ cm}^{-1}$ (167 fs) has been chosen based on the previous modeling of the β -Car⁶⁷ spectra. The amplitude of the spectral density function is set by normalizing the f_{ep} values according to the reorganization energy definition by eq 24. The bath reorganization energy of $\Lambda_e^{\text{ph}} = 100 \text{ cm}^{-1}$ has been chosen to qualitatively match the line widths of the experimental data.

The simulated absorption spectrum of the β -Car model with 282 normal modes at different temperatures is shown in Figure 5 along the experimental β -Car spectrum in diethylamine solvent at room temperature.²⁷ The absorption spectra have been normalized to their maximum value, as well as aligned on the 0–0 transition band for easier comparison. We find the 282-mode model spectrum to qualitatively reproduce the position and amplitudes of the first two absorption peaks; however, it greatly overestimates the amplitude of vibrational peak progression at 300 K temperature. Also, absorption of the high-frequency modes displays non-trivial dependence on the temperature. For majority of modes, the average thermal energy is much smaller than the energy gap between the vibrational mode energy levels, $k_B T \ll \omega$; thus, for non-mixed modes, dependence of absorption spectrum on temperature would be negligible. However, in Figure 5, we observe strong dependence of absorption on temperature due to the mode mixing; that is, thermally excited low-frequency vibrational modes contribute to the excitation of the high-frequency modes, which result in a wide high-frequency absorption shoulder.

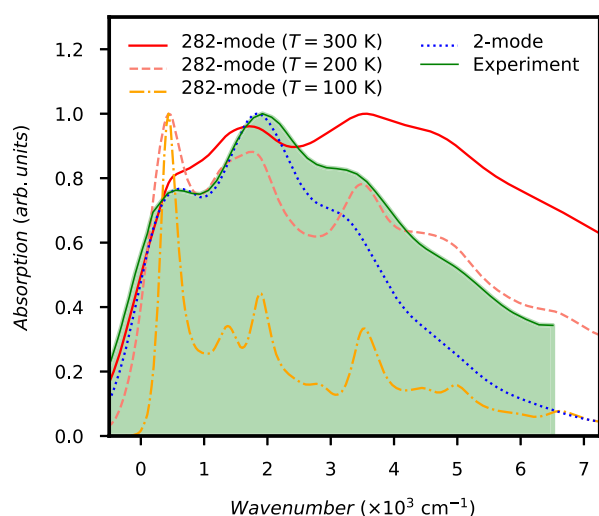


Figure 5. Absorption spectra of the β -Car model, based on the B3LYP/6-311G(d,p) method, at different temperatures along the experimental β -Car spectrum in diethylamine solvent at room temperature (shown as contoured green). The widely used two-mode model at 300 K temperature is also shown for comparison, and the model parameters are taken from ref 23. All spectra are normalized to their maximum value and aligned on their 0–0 transition band.

For comparison, we also computed the absorption spectrum of a widely used empirical two-mode β -Car model at 300 K temperature, which includes only the C=C and C–C stretching vibrational modes with no mixing between them. Typical model frequencies $\omega_{e,C=C} = 1522 \text{ cm}^{-1}$ and $\omega_{e,C-C} = 1157 \text{ cm}^{-1}$ and displacements $d_{C=C}^{(eg)} = 1.3$ and $d_{C-C}^{(eg)} = 0.9$ are taken from ref 23. To have correct line widths, the bath reorganization energy is now set to a much larger $\Lambda_e^{\text{ph}} = 800 \text{ cm}^{-1}$ to account for the lack of the rest β -Car modes. As shown in Figure 5, the two-mode model fits the first two peaks well but underestimates the amplitude of the higher frequency progression.

To further compare the 282-mode and the 2-mode models, we look at their stick absorption spectrum in Figure 6. The purely electronic transition energy is set to 0 cm^{-1} for both spectra. For visibility, the spectra have been convoluted with the $\tau = 1 \text{ ps}$ variance Gaussian function, and $\tau = 5 \text{ ps}$ is used for the spectra in the inset. The 2-mode model stick spectrum has a straightforward peak progression; that is, the spectrum is a sum of each of the two-mode peak progressions. The 282-mode model spectrum has a more complex structure. Even though each of the 282 modes has a small absorption peak, the combined spectrum produces frequency regions with non-negligible absorption intensity. These regions show a clear overlap with the absorption peaks of the two-mode model. The two-mode spectrum has peaks at 1522 and 1157 cm^{-1} frequencies, produced by the C=C and C–C stretching vibrational modes. The 282-mode spectrum has similar frequency regions, only this time, they are due to the absorption of a large number of mixed normal modes. These modes are responsible for the first two peaks seen in the Figure 5 spectra.

Looking further on in Figure 6, the 282-mode model has absorption in the 3000, 4500, and 6000 cm^{-1} frequency regions. These account for the high-frequency absorption tail seen in experiments. Due to the C=C and C–C mode

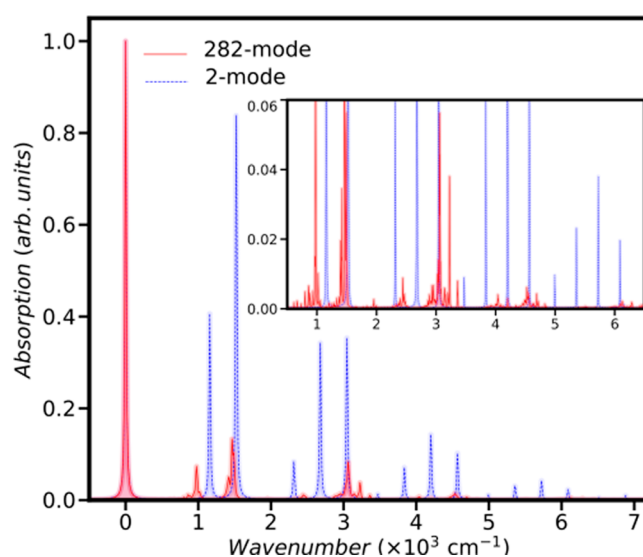


Figure 6. Stick absorption spectrum of the 282-mode model, computed using the B3LYP/6-311G(d,p) method, and the empirical 2-mode model. Purely electronic transition energy is set to 0 cm^{-1} for both spectra. For visibility, each spectrum has been convoluted with the $\tau = 1 \text{ ps}$ variance Gaussian function. The inset more closely shows low-amplitude sticks, and these have been convoluted with the $\tau = 5 \text{ ps}$ variance Gaussian function.

progression, the two-mode model has a peak at these frequencies as well; however, even though visually they look more intense than the 282-mode model peaks, Figure 5 simulations show it being the opposite. Again, the strong absorption is produced by the summation of a large number of weak intensity absorption peaks. Two harmonic modes simply cannot accurately describe absorption over such a wide range of frequencies; therefore, the high-frequency absorption of the two-mode model is lacking.

DISCUSSION

The vibrational modes of carotenoids have been extensively studied by Raman spectroscopy.^{68,69} The frequency of the most Raman-active vibration in the S_0 state is 1642.3 cm^{-1} , which changes to a weak Raman vibration of frequency 1584.08 cm^{-1} in the S_2 state. The C–C valence bond frequencies in the S_0 state lay in the region of $1018\text{--}1353 \text{ cm}^{-1}$, while it is in the region of $1156\text{--}1370 \text{ cm}^{-1}$ for the S_2 state. These frequencies are strongly mixed with the polyene chain C–H bond in-plane vibrations and the C–C valence vibrations of peripheral rings. The strongest Raman-active vibration in this region, for the S_0 state, is 1187.22 cm^{-1} , while the mode with the most similar vibrational form in the S_2 state has a frequency of 1219 cm^{-1} . The vibrations of lower frequencies are associated with the C–H vibrations outside of the polyene chain, deformations of the peripheral rings, changes of the polyene chain valence angles, dihedral angles, and the deformations of the whole molecule by twisting and waving. The frequencies of these vibrations change by no more than 10 cm^{-1} after the $S_0 \rightarrow S_2$ transition. The differences in the vibrational forms are not as strong for these modes as were in the case of the polyene chain C–C and C=C valence bond vibrations.

Recently, Balevičius Jr. and co-workers²⁰ have presented an in-depth excitation energy relaxation model in carotenoids by considering four relaxation processes. Simply put, the event of

photoexcitation instantaneously promotes the carotenoid molecules to a non-equilibrium state and launches the internal vibrational redistribution (IVR) cascade within the high-frequency optically active modes, resulting into a transient thermally “hot” state. Generally, it is assumed that the thermally hot carotenoid subsequently transfers the vibrational energy to the solvent molecules; that is, vibrational cooling (VC) takes place. The authors demonstrated how modeling the IVR and VC concurrently, and not subsequently, naturally explains the presence of the highly discussed transient absorption S^* signal⁷⁰ in terms of the vibrationally hot ground-state S_0 . The two-mode model was used; that is, only the C–C and C=C intramolecular modes were coupled to the thermal bath—their coupling strength remains speculative. Both the IVC and VC relaxation were modeled implicitly by prescribing process timescales. We have shown that the two-mode (not mixed) model is not sufficient in describing the photon absorption spectrum. In fact, upon photoexcitation, many vibrational modes become excited. No two distinctive modes could be isolated in the relevant frequency region. We observe grouping of vibrational modes in the 1000 and 1500 cm^{-1} frequency regions, as shown in Figure 6. The two-mode model yields progression of peaks with few strong features at 2700 and 4000–6000 cm^{-1} frequencies. Meanwhile, the 282-mode model has a large number of weak absorption features at these frequencies; however, it is the cumulative effect that combines them into the observed “progression”. This entropic factor actually simplifies the overall electronic excitation relaxation picture since each mode is weakly coupled to the electronic transition; therefore, the weak coupling regime could be used in the theoretical models of relaxation dynamics. Consequently, the two- or multiple-quanta vibrational excitations become improbable. Hence, only the entropic factor as a cumulative effect of all modes would have decisive impact on both the IVR and VC process timescales.

In nature, carotenoids participate in the energy conversion process together with other types of pigments. Carotenoids play an important role in light-harvesting complexes by transferring their excitation to chlorophylls on a femtosecond timescale. It is especially evident in the peridinin–chlorophyll–protein, in which the dominant energy transfer occurs from the peridinin S_2 to chlorophyll Q_y state via an ultrafast coherent mechanism. The coherent superposition of the two states functions in a way as to drive the population to the final acceptor state,⁷¹ providing an important piece of evidence in the quest of connecting coherent phenomena and biological functions.⁷² This process is highly sensitive to structural perturbations of the peridinin polyene backbone, which has a profound effect on the overall lifetime of the complex.⁷³ We have found that β -Car also undergoes polyene backbone changes, mainly in its C–C bond lengths.

Also, it has been suggested that the ultrafast population transfer from the carotenoid state S_2 to the bacteriochlorophyll (BChl) state Q_x occurs due to the vibronic coupling of the carotenoid electron-vibrational DOFs to the BChl.⁷⁴ The energy flow pathway opened up by the resonance of the energy gap between the carotenoid vibrational levels, and the BChl $|g\rangle_{\text{BChl}} \rightarrow |Q_x\rangle$ transition is the primary reason for its ultrafast nature. We, hence, suggest that by going beyond the two-mode model and taking into account more carotenoid vibrational modes, in turn, more vibrational levels, the probability of resonance between the carotenoid and BChl would greatly increase, changing the overall population-transfer rate.

In conclusion, we have presented a β -Car model with a fully explicit treatment of all its 282 vibrational normal modes, which were computed using the quantum chemical methods. Additionally, we described how to treat the β -Car excited-state dynamics when in contact with solvent at finite temperature. We found β -Car to change the bond lengths between the polyene chain atoms during the $S_0 \rightarrow S_2$ electronic transition and that there is no one-to-one correspondence between the ground- and excited-state vibrational modes; that is, modes on different electronic states are highly mixed and should not be treated as being the same. The model absorption spectrum qualitatively matches the experimental data, and it better describes the high-frequency progression of the carotenoid spectrum than the typical two-mode carotenoid model.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpca.1c06115>.

Derivation of the Davydov D_2 ansatz equations of motion for the β -carotene model using the Dirac–Frenkel variational method (PDF)

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Notes

The authors declare no competing financial interest.

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