Supplementary information to the "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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Derivation of the β-Car model equations of motion

Time dependence of the Davydov D_2 trial wavefunction

$$
\begin{aligned}
|\Psi(t)\rangle = \sum_n^N \alpha_n(t) & \underbrace{|n\rangle \times |\tilde{\lambda}_1(t), \tilde{\lambda}_2(t), \ldots, \tilde{\lambda}_K(t)\rangle}_{\text{molecule state}} \\
& \times \underbrace{|\lambda_1(t), \lambda_2(t), \ldots, \lambda_P(t)\rangle}_{\text{solvent phonon state}}, \qquad (1)
\end{aligned}
$$

for a general system made up of N electronic states, is given in terms of its dynamical parameters $\alpha_n(t)$, $\tilde{\lambda}_k(t)$, $\lambda_p(t)$. To deduce their equations of motion, we apply the Euler-Lagrange equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial \mathcal{L}(t)}{\partial \dot{\eta}_i^\star(t)}\right) - \frac{\partial \mathcal{L}(t)}{\partial \eta_i^\star(t)} = 0, \qquad (2)$$

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

$$\mathcal{L}(t) = \frac{\mathrm{i}}{2}\left(\langle\Psi|\frac{\mathrm{d}}{\mathrm{d}t}\Psi\rangle - \langle\frac{\mathrm{d}}{\mathrm{d}t}\Psi|\Psi\rangle\right) - \langle\Psi|\hat{H}|\Psi\rangle, \qquad (3)$$

is the Lagrangian of the model given in terms of the Hamiltonian $\hat{H} = \sum_n \hat{H}^{(n)} + \hat{H}_{\mathrm{B}} + \hat{H}_{\text{S-B}}$ where

$$
\begin{aligned}
\hat{H}^{(n)} = & \left(\varepsilon_n + \Lambda_n^{\mathrm{vib}} + \sum_k \frac{\omega_{nk}}{2}\left(\left(\hat{p}_k^{(n)}\right)^2 + \left(\hat{x}_k^{(n)}\right)^2\right)\right)|n\rangle\langle n| \\
& - \sum_k \omega_{nk}\tilde{d}_k^{(ng)}\hat{x}_k^{(n)}|n\rangle\langle n|, \qquad (4)
\end{aligned}
$$

is the system Hamiltonian of the nth electronic state, while

$$\hat{H}_{\mathrm{B}} = \sum_p \frac{w_p}{2}\left(\hat{\rho}_p^2 + \hat{\chi}_p^2\right), \qquad (5)$$

$$\hat{H}_{\text{S-B}} = -\sum_n \sum_p w_p f_{np}\hat{\chi}_p|n\rangle\langle n|, \qquad (6)$$

are the phonon bath and electron–phonon coupling Hamiltonians, respectively.

It is first required to calculate the model Lagrangian, defined in Eq. (3), and it is equal to

$$
\begin{aligned}
\mathcal{L} = & \frac{\mathrm{i}}{2}\sum_n \left(\alpha_n^\star \dot{\alpha}_n - \alpha_n \dot{\alpha}_n^\star\right) \\
& + \frac{\mathrm{i}}{2}\sum_n |\alpha_n|^2 \left(\sum_q \left(\tilde{\lambda}_q^\star \dot{\tilde{\lambda}}_q - \tilde{\lambda}_q \dot{\tilde{\lambda}}_q^\star\right) + \sum_p \left(\lambda_p^\star \dot{\lambda}_p - \lambda_p \dot{\lambda}_p^\star\right)\right) \qquad (7) \\
& - \sum_n |\alpha_n|^2 \left(\varepsilon_n + \Lambda_n^{\mathrm{vib}}\right) \\
& - \sum_n |\alpha_n|^2 \sum_k \frac{\omega_{nk}}{2}\frac{1}{2}\sum_b \left(\beta_{nk,b}^2 + \beta_{nk,b}^{-2}\right) a_{kb}^{(ng)2} \\
& - \sum_n |\alpha_n|^2 \sum_k \frac{\omega_{nk}}{2}\frac{1}{2}\sum_{a,b} \beta_{nk,a}\beta_{nk,b} a_{ka}^{(ng)} a_{kb}^{(ng)} \left(\tilde{\lambda}_a^\star + \tilde{\lambda}_a\right)\left(\tilde{\lambda}_b^\star + \tilde{\lambda}_b\right) \\
& + \sum_n |\alpha_n|^2 \sum_k \frac{\omega_{nk}}{2}\frac{1}{2}\sum_{a,b} \beta_{nk,a}^{-1}\beta_{nk,b}^{-1} a_{ka}^{(ng)} a_{kb}^{(ng)} \left(\tilde{\lambda}_a^\star - \tilde{\lambda}_a\right)\left(\tilde{\lambda}_b^\star - \tilde{\lambda}_b\right) \\
& + \sum_n |\alpha_n|^2 \sum_k \omega_{nk} d_k^{(ng)} \sum_b \beta_{nk,b} a_{kb}^{(ng)} \frac{1}{\sqrt{2}}\left(\tilde{\lambda}_b^\star + \tilde{\lambda}_b\right) \\
& - \sum_p w_p \left(|\lambda_p|^2 + \frac{1}{2}\right) + \sum_n |\alpha_n|^2 \sum_p w_p \frac{f_{np}}{\sqrt{2}} \left(\lambda_p^\star + \lambda_p\right). \qquad (8)
\end{aligned}
$$

Applying variation to the $\alpha_n^\star(t)$, i.e., by computing the $\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial \mathcal{L}(t)}{\partial \dot{\alpha}_n^\star(t)}\right) - \frac{\partial \mathcal{L}(t)}{\partial \alpha_n^\star(t)} = 0$, we get the first equation of motion

$$
\begin{aligned}
\dot{\alpha}_n = & + \frac{\mathrm{i}}{2}\alpha_n \sum_q \left(\tilde{\lambda}_q^\star \dot{\tilde{\lambda}}_q - \tilde{\lambda}_q \dot{\tilde{\lambda}}_q^\star\right) + \frac{\mathrm{i}}{2}\alpha_n \sum_p \left(\lambda_p^\star \dot{\lambda}_p - \lambda_p \dot{\lambda}_p^\star\right) \\
& - \mathrm{i}\alpha_n \left(\varepsilon_n + \Lambda_n^{\mathrm{vib}}\right) \\
& - \mathrm{i}\alpha_n \sum_k \frac{\omega_{nk}}{2}\frac{1}{2}\sum_b \left(\beta_{nk,b}^2 + \beta_{nk,b}^{-2}\right) a_{kb}^{(ng)2} \\
& - \mathrm{i}\alpha_n \sum_k \frac{\omega_{nk}}{2}\frac{1}{2}\sum_{a,b} \beta_{nk,a}\beta_{nk,b} a_{ka}^{(ng)} a_{kb}^{(ng)} \left(\tilde{\lambda}_a^\star + \tilde{\lambda}_a\right)\left(\tilde{\lambda}_b^\star + \tilde{\lambda}_b\right) \\
& + \mathrm{i}\alpha_n \sum_k \frac{\omega_{nk}}{2}\frac{1}{2}\sum_{a,b} \beta_{nk,a}^{-1}\beta_{nk,b}^{-1} a_{ka}^{(ng)} a_{kb}^{(ng)} \left(\tilde{\lambda}_a^\star - \tilde{\lambda}_a\right)\left(\tilde{\lambda}_b^\star - \tilde{\lambda}_b\right) \\
& + \mathrm{i}\alpha_n \sum_k \omega_{nk} d_k^{(ng)} \sum_b \beta_{nk,b} a_{kb}^{(ng)} \frac{1}{\sqrt{2}}\left(\tilde{\lambda}_b^\star + \tilde{\lambda}_b\right) \\
& + \mathrm{i}\alpha_n \sum_p w_p \frac{f_{np}}{\sqrt{2}} \left(\lambda_p^\star + \lambda_p\right), \qquad (9)
\end{aligned}
$$

while further variation of $\tilde{\lambda}_h^\star(t)$ and $\lambda_p^\star(t)$ parameters yields

$$\begin{aligned}
\dot{\tilde{\lambda}}_h =& -\frac{1}{2}\sum_n \left(\dot{\alpha}_n\alpha_n^\star + \alpha_n\dot{\alpha}_n^\star\right)\tilde{\lambda}_h \\
&- \mathrm{i}\sum_n |\alpha_n|^2 \sum_k \frac{\omega_{nk}}{2}\sum_b \beta_{nk,h}\beta_{nk,b}a_{kh}^{(ng)}a_{kb}^{(ng)}\left(\tilde{\lambda}_b^\star + \tilde{\lambda}_b\right) \qquad (10)\\
&+ \mathrm{i}\sum_n |\alpha_n|^2 \sum_k \frac{\omega_{nk}}{2}\sum_b \beta_{nk,a}^{-1}\beta_{nk,b}^{-1}a_{ka}^{(ng)}a_{kb}^{(ng)}\left(\tilde{\lambda}_b^\star - \tilde{\lambda}_b\right)\\
&+ \mathrm{i}\sum_n |\alpha_n|^2 \sum_k \omega_{nk}d_k^{(ng)}\beta_{nk,h}a_{kh}^{(ng)}\frac{1}{\sqrt{2}}, \qquad (11)
\end{aligned}$$

and

$$\dot{\lambda}_p = -\frac{1}{2}\sum_n \left(\dot{\alpha}_n\alpha_n^\star + \alpha_n\dot{\alpha}_n^\star\right)\lambda_p - \mathrm{i}w_p\left(\lambda_p - \sum_n |\alpha_n|^2\frac{f_{np}}{\sqrt{2}}\right). \qquad (12)$$

As seen here, variation of the parameter complex conjugates results in equations of motion involving their non-conjugate counterparts. The resulting system of differential equations can be further simplified by constructing terms

$$\begin{aligned}
\tilde{\lambda}_q^\star\dot{\tilde{\lambda}}_q - \tilde{\lambda}_q\dot{\tilde{\lambda}}_q^\star =& -\mathrm{i}\left(\tilde{\lambda}_q^\star + \tilde{\lambda}_q\right)\sum_m |\alpha_m|^2\sum_k \frac{\omega_{mk}}{2}\sum_b \beta_{mk,q}\beta_{mk,b}a_{kq}^{(mg)}a_{kb}^{(mg)}\left(\tilde{\lambda}_b^\star + \tilde{\lambda}_b\right)\\
&+ \mathrm{i}\left(\tilde{\lambda}_q^\star - \tilde{\lambda}_q\right)\sum_m |\alpha_m|^2\sum_k \frac{\omega_{mk}}{2}\sum_b \beta_{mk,q}^{-1}\beta_{mk,b}^{-1}a_{kq}^{(mg)}a_{kb}^{(mg)}\left(\tilde{\lambda}_b^\star - \tilde{\lambda}_b\right)\\
&+ \mathrm{i}\left(\tilde{\lambda}_q^\star + \tilde{\lambda}_q\right)\sum_m |\alpha_m|^2\sum_k \omega_{mk}d_k^{(mg)}\beta_{mk,q}a_{kq}^{(mg)}\frac{1}{\sqrt{2}}, \qquad (13)
\end{aligned}$$

$$\lambda_p^\star\dot{\lambda}_p - \lambda_p\dot{\lambda}_p^\star = -2\mathrm{i}w_p\lambda_p^\star\lambda_p + \mathrm{i}w_p\left(\lambda_p^\star + \lambda_p\right)\sum_m |\alpha_m|^2\frac{f_{mp}}{\sqrt{2}}, \qquad (14)$$

from Eq. (11) and (12) and inserting them into Eq. (9). Also, terms $\propto \sum_n\left(\dot{\alpha}_n\alpha_n^\star + \alpha_n\dot{\alpha}_n^\star\right)$ in Eq. (11) and (12) can be set to zero by noticing that it is simply the time derivative of the Davydov D_2 wavefunction norm $\frac{\mathrm{d}}{\mathrm{d}t}\langle\Psi(t)|\Psi(t)\rangle = \sum_n\left(\dot{\alpha}_n\alpha_n^\star + \alpha_n\dot{\alpha}_n^\star\right) = 0$. By defining the coordinate and momentum operator expectation values as

$$x_k^{(n)} \equiv \langle\tilde{\boldsymbol{\lambda}}(t)|\hat{x}_k^{(n)}|\tilde{\boldsymbol{\lambda}}(t)\rangle = \sum_j \beta_{nk,j}a_{kj}^{(ng)}\frac{1}{\sqrt{2}}\left(\tilde{\lambda}_j^\star + \tilde{\lambda}_j\right) = \sum_j \beta_{nk,j}a_{kj}^{(ng)}\sqrt{2}\mathrm{Re}\tilde{\lambda}_j\ , \qquad (15)$$

$$p_k^{(n)} \equiv \langle\tilde{\boldsymbol{\lambda}}(t)|\hat{p}_k^{(n)}|\tilde{\boldsymbol{\lambda}}(t)\rangle = \sum_j \beta_{nk,j}^{-1}a_{kj}^{(ng)}\mathrm{i}\frac{1}{\sqrt{2}}\left(\tilde{\lambda}_j^\star - \tilde{\lambda}_j\right) = \sum_j \beta_{nk,j}^{-1}a_{kj}^{(ng)}\sqrt{2}\mathrm{Im}\tilde{\lambda}_j\ , \qquad (16)$$

the resulting system of equations can be put in a shorthand form

$$
\begin{aligned}
\dot{\alpha}_n =& -\mathrm{i}\alpha_n \left(\varepsilon_n + \Lambda_n^{\mathrm{vib}}\right) \\
& -\mathrm{i}\alpha_n \sum_h \frac{\omega_{nh}}{2}\frac{1}{2}\sum_b \left(\beta_{nh,b}^2 + \beta_{nh,b}^{-2}\right) a_{hb}^{(ng)2} \\
& -\mathrm{i}\alpha_n \sum_h \left[\frac{\omega_{nh}}{2}\left(x_h^{(n)2} + p_h^{(n)2}\right) - \sum_m |\alpha_m|^2 \frac{\omega_{mh}}{2}\left(x_h^{(m)2} + p_h^{(m)2}\right)\right] \\
& +\mathrm{i}\alpha_n \sum_h \left[\omega_{nh} d_h^{(ng)} x_h^{(n)} - \frac{1}{2}\sum_m |\alpha_m|^2 \omega_{mh} d_h^{(mg)} x_h^{(m)}\right] \\
& +\mathrm{i}\alpha_n \sum_p w_p \left(\frac{f_{np}}{\sqrt{2}} - \frac{1}{2}\sum_m |\alpha_m|^2 \frac{f_{mp}}{\sqrt{2}}\right)\left(\lambda_p^\star + \lambda_p\right) \\
& +\mathrm{i}\alpha_n \sum_p w_p |\lambda_p|^2 ,
\end{aligned}
\tag{17}
$$

$$
\dot{\tilde{\lambda}}_h = -\mathrm{i}\sum_n |\alpha_n|^2 \sum_k \frac{\omega_{nk}}{\sqrt{2}} \beta_{nk,h} a_{kh}^{(ng)} \left(x_k^{(n)} - d_k^{(ng)} + \mathrm{i}p_k^{(n)}\right), \tag{18}
$$

$$
\dot{\lambda}_p = -\mathrm{i}w_p \left(\lambda_p - \sum_n |\alpha_n|^2 \frac{f_{np}}{\sqrt{2}}\right). \tag{19}
$$

If an absolute value of electronic state energies are not of importance, in numerical simulation one can further dismiss the last term in Eq. (17), because it shifts all electronic state energies by a constant amount.

Equations of motion for the β-Car model excited state $|S_2\rangle = |e\rangle$ are recovered by setting index $n = e$ in Eq. (17). The ground state $|S_0\rangle = |g\rangle$ equations are obtained by setting $n = g$ in Eq. (17) as well as using the fact that the ground state is used as a reference point for which following are true: $\varepsilon_g = 0$, $\beta_{gh,b} = \delta_{h,b}$, $a_{hb}^{(gg)} = \delta_{h,b}$, $d_h^{(gg)} = 0$, $f_{np} = 0$.