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The origin of absorptive features in the two-dimensional electronic spectra of rhodopsin†

Marwa H. Farag, Thomas L. C. Jansen and Jasper Knoester

In rhodopsin, the absorption of a photon causes the isomerization of the 11-cis isomer of the retinal chromophore to its all-trans isomer. This isomerization is known to occur through a conical intersection (CI) and the internal conversion through the CI is known to be vibrationally coherent. Recently measured two-dimensional electronic spectra (2DES) showed dramatic absorptive spectral features at early waiting times associated with the transition through the CI. The common two-state two-mode model Hamiltonian was unable to elucidate the origin of these features. To rationalize the source of these features, we employ a three-state three-mode model Hamiltonian where the hydrogen out-of-plane (HOOP) mode and a higher-lying electronic state are included. The 2DES of the retinal chromophore in rhodopsin are calculated and compared with the experiment. Our analysis shows that the source of the observed features in the measured 2DES is the excited state absorption to a higher-lying electronic state and not the HOOP mode.

1 Introduction

The primary photochemical event in vision is the ultrafast isomerization of the 11-cis retinal chromophore in rhodopsin (Rh). After excitation with a 500 nm photon, it undergoes an ultrafast 11-cis to all-trans isomerization. The photoisomerization process is known to be very efficient with a quantum yield of 0.67 and is completed within 200 fs. This ultrafast cis-to-trans isomerization occurs through a conical intersection (CI), as has been confirmed by recent ultrafast transient absorption spectroscopy and previous theoretical works. The internal conversion through a CI is known to be vibrationally coherent and, thus, the coherent vibrational dynamics play a crucial role in driving the photoisomerization in Rh. Visual Rh can be used for the design of bio-electronic devices and optical memories. For such applications, it is crucial to understand the atomic motions that drive the chemical reaction in Rh. Previous experimental and theoretical studies have led to the conclusion that in Rh, the delocalized torsional mode, the C=C ethylene stretch mode, and the hydrogen wagging mode are essential for the isomerization mechanism. More recently, transient absorption experiment revealed the nuclear motions that drive the transition of the 11-cis isomer to the primary photoproduct in Rh. The authors of ref. 11 reported photoisomerization dynamics on a sub-50 fs timescale and concluded that a localized torsional mode represents the reaction coordinate in Rh rather than a delocalized torsional mode. The experiment in ref. 11 was performed using resonant ultrashort pulses (11 fs pulses in the blue (450–495 nm)–green (495–570 nm) region). This spectral bandwidth allowed for the observation of the evolution modes coupled to the electronic states and probing up to the in-phase ethylenic stretch vibrational mode during the isomerization. This is different from the experiment in ref. 2 where Rh was excited by a pump pulse with 10 fs duration centered at 520 nm and then, probed by frequency resolved <20 fs pulses at the visible (500–720 nm) and near-infrared (820–1020 nm) wavelength. The probe pulse in the experiment of ref. 2 is, therefore, not short enough to reveal the evolution of the nuclear motions during the isomerization and only the electronic dynamics during the isomerization of Rh was probed. Stock and coworkers have proposed a minimal model that includes two states (S0 and S1) and two modes (the ethylene stretch mode and the delocalized torsional mode) and used this model to conduct an exact time-dependent wave-packet calculation for the retinal chromophore in Rh. This minimal model has been shown to qualitatively reproduce the measured pump–probe spectra in Rh. However, it was unable to reproduce the absorptive features observed at short waiting times in the recently measured two-dimensional electronic spectra (2DES) in Rh. Apparently, to account for the multidimensional nature of the non-adiabatic photoisomerization process in Rh, a more sophisticated model should be employed.

Participation of the hydrogen out-of-plane (HOOP) mode during the isomerization in Rh has been studied extensively,
both experimentally and theoretically. From computational studies, using ab initio multi-configurational quantum chemistry, it is expected that the photoproduct generation is controlled by the HOOP mode.\textsuperscript{25,26,32} From experiment, using 10-fluoro, 12-fluoro, and 14-fluoro analogues of Rh, it was observed that the rotation of the C\textsubscript{12}=H bond of the retinal chromophore in Rh plays a major role in the efficient photoisomerization process.\textsuperscript{33} Further experiments using femtosecond stimulated Raman spectroscopy (FSRS) demonstrated that the excited state decay through the CI is mediated by the fast HOOP motion and that the HOOP mode facilitates the internal conversion during the isomerization.\textsuperscript{21} A simulation of the time-dependent FSRS\textsuperscript{21} revealed that the HOOP mode relaxes on the photoproduct potential energy surface with a 140 fs time constant.\textsuperscript{34} Moreover, recent experiments using ultrafast transient absorption spectroscopy indicated that the HOOP mode is one of the major coupling modes of the system.\textsuperscript{22}

Recently, two-dimensional photon echo experiments were used to reveal the vibrational coherences of Rh during the isomerization.\textsuperscript{24} The measured spectra show two different kinds of absorptive features, one at early waiting times (20–35 fs) associated with the transition through the CI and the others at delay times starting at 65 fs and persisting for all remaining waiting times measured. The calculations of the two-dimensional photon echo using the common two-state two-mode model developed by Stock and co-workers\textsuperscript{27,31,36,37,44} did not reproduce the measured spectra.\textsuperscript{24} Therefore, we modified the frequently used parameters (Huang–Rhys factor and the frequency of the torsional mode) of the two-state two-mode model Hamiltonian\textsuperscript{27,31} to achieve acceptable agreement with the experiment in ref. 24 on which we are co-authors. The modified Hamiltonian allowed the authors to reproduce the measured spectra at delay times from 65 fs and beyond. The absorptive features could be assigned to the absorption of the trans photoprodut. With the modified model, however, it was not possible to reproduce the spectra at the early waiting time\textsuperscript{24} and speculated that the absorptive features in this time range could be attributed to the HOOP mode which was absent in the applied theoretical model.\textsuperscript{24} So far, independent theoretical evidence is missing that the HOOP mode should be included to properly simulate the 2DES of the retinal chromophore in Rh, and thus, to fully understand the photoisomerization reaction. A recent computational study using a hybrid QM/MM approach based on a multi-configurational method investigated the excited-state manifolds of the retinal chromophore in Rh and has predicted that the transition from the first excited state to other higher lying excited states is possible and is expected.\textsuperscript{39} Unlike other systems such as bacteriorhodopsin,\textsuperscript{6,40,41} the higher excited states in Rh are not involved in the isomerization mechanism,\textsuperscript{2,21,42,43} but are expected to give rise to induced-absorption peaks in the spectral window observed in the measured two-dimensional electronic spectra (2DES) of ref. 24. This strongly suggests that an improved model Hamiltonian should, in addition to the HOOP mode, also include this bright excited state. The aim of this work is to build on the model in ref. 24 and employ a model for Rh going beyond the commonly considered two-state two-mode models\textsuperscript{24,31,36,37,44} and use it to simulate the 2DES at early waiting times to uncover the origin of the spectral features observed in the measured 2DES of the retinal chromophore in Rh at early times (20–35 fs), before the photoproduct formation.\textsuperscript{24}

This paper is organized as follows. First, we present the model Hamiltonian that is employed throughout the paper to simulate the 2DES. Next, the electronic state population and the cis-trans isomerization probability are investigated for the model Hamiltonian employed; afterwards, the expectation values for the coordinates of the normal modes are analyzed; then, the 2DES are investigated and compared with the available experiments. Finally, we summarize and conclude.

2 Model and methods

Previous experiments using resonance Raman (RR) analyzed the initial dynamics and the vibrational normal modes that govern the photoisomerization in the retinal chromophore of Rh.\textsuperscript{10} The RR spectrum exhibits a number of vibrational normal modes (28 normal modes) that are active (i.e., they experience shifts in their equilibrium geometry upon electronic excitation). Strictly speaking, the retinal chromophore in Rh lacks symmetry and belongs to the \textit{C\textsubscript{1}} point group. Previous studies approximated the point group in the planar 11\textit{cis} retinal chromophore in Rh by \textit{C\textsubscript{2v}} and the all-trans retinal by \textit{C\textsubscript{2h}}.\textsuperscript{10,21} The symmetry classification \textit{(C\textsubscript{2v} or C\textsubscript{2h})} is approximate to the symmetry group of the polyene that has common spectroscopic features with Rh.\textsuperscript{6} Based on the measured RR spectra, we modify the existing model Hamiltonian by Domcke\textsuperscript{45} and Stock.\textsuperscript{27,37} Two different novel model Hamiltonians are constructed from the modulated Hamiltonian. Model-I, where symmetry is not taken into account, and model-II, where symmetry is considered. In both models, we define a three-state model involving three vibrational modes: the in-phase C=C ethylenic stretch mode with coordinate \textit{q\textsubscript{cis}}, the HOOP wagging motion of the 11 and 12 hydrogen with coordinate \textit{q\textsubscript{ci}}, and the reaction coordinate defined by the localized C\textsubscript{11}=C\textsubscript{12} torsional mode with coordinate \textit{\theta}. These modes are illustrated in Fig. 1.

![Fig. 1. The 11-cis retinal chromophore in rhodopsin with illustration of the three vibrational modes.](image-url)
We begin by introducing model-I. Adopting dimensionless normal coordinates and neglecting the anharmonic mode-mode coupling, our model-I Hamiltonian ($\hbar = 1$) in the diabatic representation reads

$$\hat{H} = \sum_{n=0}^{2} \langle S_n | (\hat{T} + \hat{V}_{nm}) | S_n \rangle + \langle (| S_0 \rangle \hat{\lambda}_c | S_1 \rangle + | S_1 \rangle \hat{\lambda}_c | S_0 \rangle \rangle$$

(1a)

$$\hat{T} = -\frac{1}{2\hbar} \frac{\partial^2}{\partial t^2} - \frac{\omega_c}{2} \frac{\partial^2}{\partial q_c^2} - \frac{\omega_t}{2} \frac{\partial^2}{\partial q_t^2}$$

(1b)

$$\hat{V}_{00} = \frac{1}{2}W_0(1 - \cos \hat{\theta}) + \frac{1}{2} \omega_c q_c^2 + \frac{1}{2} \omega_t q_t^2$$

(1c)

$$\hat{V}_{11} = E_1 = \frac{1}{2}W_1(1 - \cos \hat{\theta}) + \frac{1}{2} \omega_c q_c^2 + \frac{1}{2} \omega_t q_t^2 + \beta \hat{q}_c + \gamma \hat{q}_t$$

(1d)

$$\hat{V}_{22} = E_2 = \frac{1}{2}W_2(1 - \cos \hat{\theta}) + \frac{1}{2} \omega_c q_c^2 + \frac{1}{2} \omega_t q_t^2 + \gamma \hat{q}_c + \zeta \hat{q}_t$$

(1e)

where $| S_0 \rangle$, $| S_1 \rangle$, and $| S_2 \rangle$ are the diabatic electronic ground state, the first excited singlet state, and the second excited singlet state, respectively. Here, $| S_2 \rangle$ is introduced in the simplest way to represent the third electronic state in the model and it is decoupled from the $| S_0 \rangle$ and $| S_1 \rangle$ states. Other states may exist between $| S_0 \rangle$ and $| S_2 \rangle$ that are not visible in the spectroscopic window of interest. We should mention that the simulation of the 2DES (see below) is quite time consuming prohibiting attempting to fit the experimental spectra including more states involving additional free parameters. The presence of other (dark) electronic states may potentially influence the spectra and dynamics. A previous theoretical study, investigating the excited electronic states of the retinal chromophore of Rh, predicted that the $S_1 \rightarrow S_0$ transition is bright.\(^{39}\) Thus, in the present work, $| S_2 \rangle$ state is likely corresponding to that $| S_4 \rangle$ electronic state. $\omega_c$ and $\omega_t$ are the frequencies of the HOOP mode and the ethylenic stretch mode, respectively. $W_0$, $W_1$, and $W_2$ characterize the variation of the PES along the reaction coordinate. The parameters $W_0$ and $W_1$ are chosen to reproduce the photon-energy storage, the net change in energy ($\Delta E$) in going from the reactant (cis) to the product (trans), observed in Rh, which amounts to about $\sim 30$ kcal mol$^{-1}$.\(^{46,47}\) $l$ is the moment of inertia for the torsional mode and it is determined by taking into account the localized torsional mode frequency $\omega_R = 570$ cm$^{-1}$ ref. 10, 11 and 24 ($\omega_R = \sqrt{W_0/2l}$) as suggested by the measured 2DES in ref. 24. $E_1$ and $E_2$ are the vertical excitation energies from $| S_0 \rangle$ to the states $| S_1 \rangle$ and $| S_2 \rangle$, respectively. $\beta$, $\kappa$, $\gamma$, and $\zeta$ are the gradients of the first and the second excited state potential, which determine the displacement of the excited state potential well. The dimensionless displacement between the minima of the ground- and excited-state harmonic well is given by $\left(\frac{\Xi/\omega_l}{2}\right)^2$, where $\Xi$ is $\beta$, $\kappa$, $\gamma$, or $\zeta$ and $l$ is t or c. The gradient $\hat{\beta}$ and $\hat{\kappa}$ parameters are chosen such that the $S_1$ gradient for the HOOP mode and the C=C ethylenic stretch are consistent with the RR spectra\(^{10}\) (i.e., the Franck–Condor displacement are 0.57, 0.88 for the HOOP mode and the ethylenic stretch modes, respectively). $\lambda$ is the interstate coupling constant which mixes the diabatic electronic states $S_0$ and $S_1$. The value of lambda was defined as in previous theoretical works.\(^{24,31}\) Here, we assume that the HOOP mode couple the two-electronic states $S_0$ and $S_1$;\(^{22}\) The parameters for the $S_2$ electronic state, on the other hand, were not fixed a priori because no values are available from experiment or theory. The parameters for the $S_0$, thus, were chosen to reproduce the measured 2DES\(^{24}\) best. The parameters of model-I are listed in Table 1.

In model-II, we assume that the CI in Rh is symmetry allowed. In this model, the C=C ethylenic stretch is totally symmetric and the HOOP mode is classified to be non-totally symmetric. Moreover, we assume that the electronic wavefunctions for $S_0$ and $S_1$ transform according to different irreducible representation of the symmetry group. Then, the gradient $\hat{\beta}$ will be negligible and $\lambda$ is non-zero only along the HOOP mode. The parameters of this model are the same as those in model-I (see Table 1) except that $\beta$ is zero. The corresponding adiabatic PES of the model are shown schematically in Fig. 2. The adiabatic PES in Fig. 2 are the eigenstates obtained from the diabatic Hamiltonian. Here, Fig. 2(a) can be qualitatively compared with the excited state manifolds along the minimum energy path (MEP) of the retinal isomerization in ref. 39. In our model, the system reaches the CI when $\hat{\theta} = \pi/2$ in agreement with PES obtained in ref. 39.

Following the same procedure as in ref. 24 and 48, the wavefunction of the system $\Psi(\hat{\theta}, \hat{q}_c, \hat{q}_t, t)$ is numerically integrated to solve the time-dependent Schrödinger equation and the propagated wavefunction is described using the Discrete Variable Representation (DVR).\(^{49}\) We employ the fast Fourier transform DVR with 200 grid points to describe the torsional mode $\hat{\theta}$ and two harmonic oscillator DVRs with 21 grid points each to describe the ethylenic stretch mode as well as the HOOP mode. The equation of motion is solved by a fourth-order Runge–Kutta integrator and a time step $\Delta t = 0.01$ fs is employed.

**Table 1. The parameters of the model-I Hamiltonian for the retinal chromophore in Rh**

<table>
<thead>
<tr>
<th>Normal mode</th>
<th>Parameter</th>
<th>Value (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Torsional mode $\theta$</td>
<td>$l$</td>
<td>$28.06 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$W_0$</td>
<td>$3.50$</td>
</tr>
<tr>
<td></td>
<td>$W_1$</td>
<td>$1.06$</td>
</tr>
<tr>
<td></td>
<td>$W_2$</td>
<td>$2.00$</td>
</tr>
<tr>
<td></td>
<td>$E_1$</td>
<td>$2.45$</td>
</tr>
<tr>
<td></td>
<td>$E_2$</td>
<td>$4.61$</td>
</tr>
<tr>
<td>HOOP mode $q_c$</td>
<td>$\omega_c$</td>
<td>$12.03 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$\beta$</td>
<td>$0.07$</td>
</tr>
<tr>
<td></td>
<td>$\lambda$</td>
<td>$0.19$</td>
</tr>
<tr>
<td></td>
<td>$\gamma$</td>
<td>$0.15$</td>
</tr>
<tr>
<td>C=C mode $q_t$</td>
<td>$\omega_t$</td>
<td>$19.20 \times 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>$\kappa$</td>
<td>$0.17$</td>
</tr>
<tr>
<td></td>
<td>$\zeta$</td>
<td>$0.10$</td>
</tr>
</tbody>
</table>
The wavefunction $\Psi_0(0, q_c, q_t, t_0)$ is initially prepared in the ground state using the relaxation method.\textsuperscript{50} Unlike the Landau–Zener approach,\textsuperscript{51–53} our model is a fully quantum mechanical and the equation of motion is solved numerically. Here, no approximations are needed when the wavefunction approach the CI from the initially excited state and depart it to return to the ground state. For the optical excitation, a vertical transition from the initial ground state to the first excited state is assumed

\[ \Psi(0, q_c, q_t, t_0) = \hat{\mu}_{01} \Psi_0(0, q_c, q_t, t_0) \]

where $\mu_{01}$ is the electronic dipole moment operator, which allows a vertical excitation of the initial wavepacket from the ground state to the first excited state PES. The transition dipole moment operator for the excitation from the first-to-second excited state is $\mu_{21} = 1.41 \mu_{01}$ and the vertical transition is given by

\[ \Psi(0, q_c, q_t, t) = \hat{\mu}_{01} \Psi(0, q_c, q_t, t) \]

Here, the 1.41 scaling factor is added to scale the intensity of the excited state absorption contribution to the 2DES spectra and this value was adjusted to approximately reproduce the measured spectra in ref. 24 and it is comparable in magnitude to the $S_1$ + $S_2$ transition dipole reported in ref. 39.

To characterize the isomerization dynamics, we calculate the population of the electronic state in the adiabatic representation\textsuperscript{45}

\[ P_{k}(t) = \langle \Psi(0, q_c, q_t, t)|S_k^{ad}\rangle \langle S_k^{ad}|\Psi(0, q_c, q_t, t)\rangle, \quad k = 0, 1 \]

and the probabilities of finding the system in either the cis $\left(\frac{-\pi}{2} \leq \theta \leq \frac{\pi}{2}\right)$ or the trans $\left(\frac{\pi}{2} < \theta < \frac{3\pi}{2}\right)$ conformation

\[ P_{cis}(t) = \int_{-\pi/2}^{\pi/2} d\theta \int dq_c \int dq_t \sum_{k=0,1} \left|\langle S_k^{ad}\rangle|\Psi(\theta, q_c, q_t, t)\rangle\right|^2 \]

and $P_{trans}(t) = 1 - P_{cis}(t)$. $|S_k^{ad}\rangle$ represents the $k$ adiabatic electronic state.

To investigate the vibrational coherences during the isomerization process, we consider the expectation values of the position operator that provide information about the nuclear coherences of the system. The expectation value for the coordinates $q_c$ and $q_t$ is defined as\textsuperscript{45}

\[ \langle \hat{q}_i \rangle = \langle \Psi(0, q_c, q_t, t)|\hat{q}_i|\Psi(0, q_c, q_t, t)\rangle \]

and analogous for $\hat{q}_c$.

Different contributions to the 2DES spectra are illustrated in Fig. 3. At early delay times, i.e., in the Franck–Condon region, the 2DES consist of the ground-state bleach (GB), stimulated emission (SE), and the excited-state absorption (EA) signals. After the system passes through the CI (see Fig. 2), there is an internal conversion of electronic population from the first excited-state to the ground-state PES. As a consequence, the SE and EA are vanishing and the 2DES have contributions that come from the GB and photo-induced absorption (PA) signals. The latter arise due to the formation of the trans photoproduct in the ground-state PES. In the calculations, all these contributions are accounted for. The full computational details for the 2DES are presented elsewhere.\textsuperscript{24,46} The simulations of the 2DES are performed in the impulsive limit (i.e., assuming delta function shape laser pulses) and are given by the sum of the rephasing (R) and non-rephasing (NR) contributions to the
The eight Feynman diagrams for the third-order nonlinear spectroscopy. GB denotes the ground-state bleach, SE is the stimulated emission, PA represents the photo-induced absorption and EA refers to the excited state absorption. The dashed vertical lines in the PA diagrams indicate the internal conversion from the first excited-state to the ground-state potential energy surface that may occur for longer waiting times. The diagrams are labeled R₁ through R₈.

Fig. 3

spectra⁵⁶,⁵⁷ after the Fourier transform with respect to the coherence times \( t_1 \) and \( t_3 \),

\[
R_R(\omega_1, t_2, \omega_3) = \int_0^\infty \int_0^\infty \sum_{n=1}^4 R_n(t_1, t_2, t_3) e^{-(t_1-t_n)^2/2t^2} \times e^{-(t_1-t_n)/4} e^{-\omega_1/4} e^{\omega_2/4} dt_1 dt_3 \tag{7}
\]

where \( R_n(t_1,t_2,t_3) \) is the response function in the time domain and the numbers \( n \) running through the contributions in the double-sided Feynman diagrams in Fig. 3. The inhomogeneous \( (Γ = 1112 \text{ cm}^{-1}) \) and homogeneous \( (A = 667 \text{ cm}^{-1}) \) broadening parameters account for the effect of the environment. These parameters are chosen to reproduce the lineshape of the measured 2DES in ref. 24.

The simulations of the 2DES are performed using the response function approach, where the light matter interaction is included through time-dependent perturbation theory. We further assume the impulsive limit.⁵⁸ In the experiment, the 2DES were measured with resonant 11 fs pulses in the blue-green region for all excitations with sufficient spectral bandwidth to allow for the observation of vibronic effects up to and including the in-phase ethylenic stretch frequency.

3 Results and discussion

We first present our results for the time evolution of the electronic state population and the cis–trans probability during the photoisomerization in our three-state three-mode model Hamiltonian. Fig. 4 presents the population of the adiabatic ground and the adiabatic first excited state for both model-I and model-II after excitation to the \( S_1 \) state. As one can see, they are very similar.

During the first 25 fs, the system is exclusively on the first excited-state PES. At 30 fs, the population of the adiabatic first excited state begins to decrease and at \( ≈ 70 \text{ fs} \), 80% of the adiabatic excited state population is transformed to the adiabatic ground state. By analyzing the probability of finding the system either in the cis or trans configuration (see Fig. 4), it is apparent that at 30 fs, the probability of the cis isomer in the first adiabatic excited state starts to decrease, while the population of the trans conformer in the adiabatic ground state begins to increase. These results indicate that during the first 20 fs, the wavepacket is in the Franck–Condon region; at 30 fs, it reaches the \( C_s \) and at 70 fs the isomerization is completed. This fast isomerization in the retinal chromophore is attributed to the localized torsional mode, which is defined as the reaction coordinate.¹¹,²⁴ The results in Fig. 4 are, thus, in agreement with experimental studies¹¹,²⁴ and previous theoretical work using the two-state two-mode model Hamiltonian.²⁴ Thus, the HOOP mode does not significantly change these early time dynamics. Here, the analysis shows that the normal mode oscillations are concealed and difficult to extract from the time-dependent population.

Next, we analyze the time evolution of the vibrational coherences for the ethylenic stretch and the HOOP mode during the isomerization process, see Fig. 5. The expectation values for these coordinates are computed in the adiabatic ground and the adiabatic first excited states. For the ethylenic stretch mode, in both model-I and model-II, the expectation values of the \( \hat{q}_l \) oscillate periodically in the adiabatic excited state \( |S_1\rangle \), during the first 40 fs. After 40 fs, there is a change of the electronic state due to the radiationless electronic decay (see Fig. 4) and we find that the coherent vibrational motion of the ethylenic stretch mode continues to oscillate in the

\[
P_nR(\omega_1, t_2, \omega_3) = \int_0^\infty \int_0^\infty \sum_{n=1}^8 R_n(t_1, t_2, t_3) e^{-(t_1-t_n)^2/2t^2} \times e^{-(t_1-t_n)/4} e^{\omega_1/4} e^{\omega_3/4} dt_1 dt_3 \tag{8}
\]
adiabatic ground state $|S_0\rangle$. For the HOOP mode, however, the coordinate $\hat{q}_c$ only in model-I oscillates periodically in the adiabatic excited state $|S_1\rangle$ and the adiabatic ground state $|S_0\rangle$ as in the ethylenic stretch mode. The expectation values of the HOOP mode $\hat{q}_c$ in model-II vanishes as expected due to the symmetry. The data obtained for model-I in Fig. 5 are thus in agreement with previous experimental works.\textsuperscript{10,21,22} We fit the coherent oscillation in Fig. 5 to the sinusoid function $A\sin(Bt + \phi) + P$ and the fitted parameters are presented in Table 2. We find that the vibrational frequencies in the adiabatic ground and excited states are different. This difference arises from the interstate coupling $(\lambda)$ between the surfaces.\textsuperscript{48}

The linear absorption spectrum obtained with the present model is presented in Fig. 6. The Franck–Condon progression is more clearly resolved at this level of theory than in the experiment and previous calculation. This is due to the absence of the other 25 Franck–Condon active modes which were observed in the measured resonance Raman spectra and were added as a weakly coupled quantum bath to the total Hamiltonian in the previous theoretical study.\textsuperscript{24} The inclusion of these modes to the total Hamiltonian as a harmonic bath can be expected to broaden the peaks in the linear spectra and 2DES, but this is not expected to significantly affect the dynamics of the system nor the presence of absorptive features. In the current study, we neglect those additional bath modes to allow for a tractable computational speed.

Fig. 7 and 8 introduce the 2DES during the first 35 fs (i.e., before the isomerization). At $T = 15$ fs, the wavepacket of the system is in the Franck–Condon (FC) region and the spectra have a contribution from the GB, SE, and EA signals. At $T = 20–25$ fs, the wavepacket starts leaving the FC region and the contribution from the SE and EA contributions start to decrease. At $T = 30–35$ fs, the wavepacket evolves out of the FC region and through the CI before it arrives at the photoproduct PES and the contributions from the SE and EA spectra decrease due to lack of population in the first excited state. For analysis purposes, we compute the 2DES in the absence of the S$_2$ electronic state (i.e., neglecting the EA contribution) and in the presence of this state (i.e., including the EA contribution). Comparing the results of model-I and model-II with each other as well as with the measured 2DES (Fig. 4 in the supporting information of ref. 24) allows us to uncover the effect of the HOOP mode and the EA contribution on the total 2DES and reveal the origin of the spectral features observed in the measured 2DES of the retinal chromophore in Rh.\textsuperscript{24}

The calculated 2DES in the absence of the EA for model-I and model-II are presented in Fig. 7. Here, the 2DES have contributions that derive only from the GB and SE processes. The 2DES in model-I are similar to the 2DES in model-II. We notice that the 2DES exhibit well-resolved bleach peaks (red contours) with clear vibrational structure along the diagonal line and cross peaks both above and below the diagonal line. These peaks are dominated by the in-phase ethylenic stretch mode.

### Table 2

<table>
<thead>
<tr>
<th>State</th>
<th>Time region</th>
<th>Model-I $C=\equiv C$</th>
<th>HOOP $C=\equiv C$</th>
<th>Model-II $C=\equiv C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_1$</td>
<td>0–40 fs</td>
<td>1544 (21.6)</td>
<td>1062 (31.4)</td>
<td>1573 (21.2)</td>
</tr>
<tr>
<td>$S_0$</td>
<td>75–110 fs</td>
<td>1509 (22.1)</td>
<td>796 (41.9)</td>
<td>1530 (21.8)</td>
</tr>
</tbody>
</table>
In model-I, we do not see any significant additional structure due to the presence of the HOOP mode compared to model-II. In model-II, the HOOP mode is a non-totally symmetric mode; as a consequence, the coherence vanishes by symmetry as discussed above. The concealing of the HOOP mode in model-I is likely due to the overlap between the peaks that arise from the coherence of the ethylenic stretch and the HOOP modes and the anharmonic character of the HOOP mode in the vicinity of the CI.22,59 Thus, it is difficult to distinguish between these two coherences in the total 2DES. By comparing the 2DES in Fig. 7 with the calculated 2DES in ref. 24, we find that the 2DES in Fig. 7 are comparable to the calculated 2DES from the two-state two-mode model (see Fig. S1, ESI†). This demonstrates that the HOOP mode does not significantly affect the 2DES. In the experiment,24 the measured 2DES show that the positive peaks, which correspond to the GB and SE, are sharply defined and in addition, several negative peaks are prominent. The calculated 2DES for the two-state three-mode model in Fig. 7 do not exhibit these absorptive features. These results show that the observed features in the measured 2DES cannot be attributed to the HOOP mode as was previously suggested.24

The 2DES calculated including the EA contribution are shown in Fig. 8. We only show the 2DES for model-II and similar results are expected for model-I. Here, the 2DES have contributions that result predominantly from the GB and SE processes (red contours) and the EA process (blue contours). There is an absorptive contribution (blue contours) at ~17 500 cm⁻¹, similar to the one observed in the experiment. This peak shows a clear vibronic progression that contains contributions from both the HOOP and the ethylenic stretch modes. Further analysis shows that the 2DES do not change significantly when varying the Huang–Rhys factor of the HOOP and the ethylenic stretch modes on the S₂ PES.
The calculated 2DES spectra for our new three-state three-mode model are in good qualitative agreement with the experimental spectra of ref. 24. The remaining discrepancy between the calculated and the measured 2DES could be due to the contributions from other higher excited states, the present approximation for the linebroadening, and from neglecting effects of finite pulse durations. These effects may deform the experimental spectra and eliminate spectral contributions involving transitions with energies outside the laser bandwidth. The 2DES in Fig. 8 confirm that the spectral features that were experimentally observed in the 2DES at early waiting times are due to the contribution of the EA spectra, i.e., the third electronic level, to the total 2DES.

In experiment, the spectral linewidths are broader than in the present simulations. For the linear absorption spectra, it was already shown that this can easily be accounted for by including the Raman active modes of the chromophore. The experimental 2DES exhibit surprisingly narrow features. This suggests that the bath coupling for the higher excited state, here denoted S3, is very similar to that of the S1 state resulting in narrowing of the EA features. To justify this theoretically, joint quantum/classical mechanics calculations are needed to determine both the coupling between the system and protein degrees of freedom and the magnitude of protein structure fluctuations similar to what have been done for other simpler systems. The present work demonstrates the need for high level ab initio calculation of the S1 and in particular the S2 state for determining a model that gives a quantitatively accurate description of the 2DES.

4 Conclusion

In summary, we modified the existing three-state three-mode model Hamiltonian for Rh and employed it to investigate the origin of the spectral features observed in the measured 2DES of Rh at early waiting times. Unlike previous studies employing a two-state two-mode model, our model Hamiltonian includes a higher lying electronic excited state recently reported from ab initio calculations as well as the HOOP wagging motions that plays a crucial role in facilitating the internal conversion during the isomerization. The calculated 2DES showed that although the HOOP mode is coherently active, the origin of the absorptive spectral features that were observed in the recent experiment is the excited state absorption and not the HOOP mode as was previously suggested. We found that the HOOP mode does not significantly affect the 2DES, even though it is involved in the isomerization. The features observed from the higher electronic state are only observable in the Franck-Condon region and disappear as the system moves through the CI. The disappearance of the absorptive features is thus correlated with the arrival of the vibrational wave-packet at the CI. Our findings stress that caution must be taken when interpreting 2DES spectra solely in terms of coupled two-level systems, because higher electronic excited states may contribute to these complex spectra.

Conflicts of interest

There are no conflicts to declare.

References
