

Steady State Photoisomerization Quantum Yield of Model Rhodopsin: Insights from Wavepacket Dynamics?

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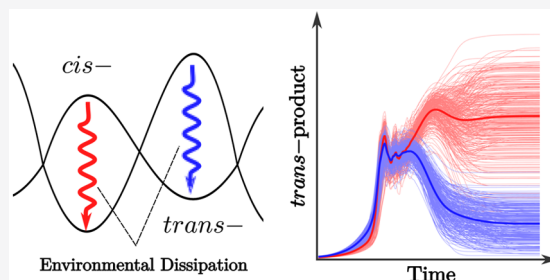
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ABSTRACT: We simulate the nonequilibrium steady state *cis*–*trans* photoisomerization of retinal chromophore in rhodopsin on the basis of a two-state, two-mode model coupled to a thermal environment. By analyzing the systematic trends within an inhomogeneously broadened ensemble of systems, we find that the steady state reaction quantum yield (QY) correlates strongly with the excess energy above the crossing point of the system, in agreement with the prediction of the short-time dynamical wavepacket picture. However, the nontrivial dependence of the QY on the system–environment interaction indicates that a pure dynamical picture is insufficient and that environment-induced partial internal energy redistribution takes place before the reaction concludes. These results imply that a proper treatment of the photoisomerization reaction, particularly its high QY, must account for the redistribution and dissipation of energy beyond the dynamical wavepacket motion that is typically employed in the literature and that is appropriate only in the transient regime.



Much of the detailed information regarding biologically significant light-induced processes (such as vision and photosynthesis) arises from modern laser experiments, in which ultrafast pulses are used to activate the first steps in photosynthesis, vision, skin response, etc. These experiments initiate dynamics on ever decreasing time scales, with current studies being on the scale of tens of femtoseconds or faster.^{1–6} The result is information on the nature of the system Hamiltonian and the system–environment interaction. However, natural light-induced processes, as we have repeatedly emphasized, take place under incoherent (e.g., sunlight) excitation where the molecules display responses totally different from those of pulsed laser excitation.^{7–12} Specifically, incoherent excitation leads to a nonequilibrium steady state (NESS), which is distinct from time evolving coherent evolution.

We focus here on the first steps in vision, the *cis*–*trans* isomerization of retinal, a process that occurs via a conical intersection between the lowest two electronic states.^{13–16} The analysis of ultrafast experimental results on such systems has yielded models and intuition based upon wave packet dynamics and upon an analogy to the Landau–Zener (LZ) model.^{3,17–20} The LZ formula provides a theoretical foundation that relates transient dynamics, specifically the velocity of the wavepacket in the vicinity of the crossing point, to the transition probability at infinite time after crossing. However, utilizing this short-time wavepacket picture to interpret condensed phase photochemical reactions involving conical intersections is extremely challenging. The high

dimensionality and strong dissipation afforded by the environment are expected to significantly alter this physical picture and, in the sense of evolutionary optimization, control the reaction dynamics.^{21–25} This includes the vibrational degrees of freedom (DOF) of the retinal residue other than the few key modes, including the torsional, hydrogen out-of-plane, and bond length alternation modes,^{26,27} as well as those belonging to the opsin protein pocket. More specifically, the rhodopsin protein pocket is known to critically affect both the static conformation of low-energy isomers and the dynamical processes relating them.^{15,28,29} These additional DOF introduce modifications into both the transient dynamics and, arguably more biologically relevant, the reaction quantum yield (QY) in the NESS. Consequently, establishing the connection between information retrieved in these two very different temporal regimes is crucial.

There has been a wealth of information about the photoisomerization of rhodopsin provided by short-time atomistic wavepacket simulations^{30–32} based on popular surface-hopping methods.^{33–35} These results are in general agreement with the corresponding transient nonlinear

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spectroscopic measurements. However, the connection between transient spectroscopic features, such as photoproduct rise time, and the NESS QY is less clear.³² Naively, a direct application of the LZ formula predicts a higher transition probability (QY) with a faster crossing speed: $P \propto e^{-A/\nu}$, where A is a constant proportional to the coupling between the two states and ν is the rate at which the energy gap closes, which can be interpreted as the component of the wavepacket velocity along the gap-closing direction. It has been argued that the correlation of the results from the two temporal regimes can be recovered in part by accounting for the phase relationship between key local vibrational modes.³⁶ However, a few fundamental questions remain. First, it is unclear how the influence on QY from the temporal phase relationships among the various DOF established by coherent excitation survives in the natural conditions of excitations by incoherent light.^{10,37} Second, in adopting such a coherent wavepacket picture, one assumes that the energy provided by the photoexcitation is conserved within these key modes before the reaction concludes. This is in sharp contrast to traditional rate theories in which energy flow among various system DOF is assumed to be fast and efficient.³⁸ Third, the vast Hilbert space for large molecules such as rhodopsin presents the possibility that the energy per mode is small while the overall energy is enough for the reaction to take place, rendering classical approximation invalid.³⁹

Here we address the specific question of the extent to which wavepacket-based intuition holds in the NESS that characterizes retinal isomerization in nature. We show that while the short-time wavepacket picture is capable of explaining some of our results in simulating rhodopsin photoisomerization under an open quantum system setup, the effect of energy exchange among various system DOF can be significant. As such, a dynamical, wavepacket-based physical picture is insufficient, and partial thermalization of the internal energy distribution is critical in determining the systematic trends of NESS QY.

MODEL AND METHOD

Consider first a general system-bath Hamiltonian that can be written as

$$H = H_s + H_b + H_{sb} \quad (1)$$

The system Hamiltonian H_s is composed of two diabatic electronic states, $|0\rangle$ and $|1\rangle$, a reaction coordinate ϕ , and a harmonic mode x :

$$H_s = \sum_{n,n'=0,1} \left\{ \hat{T} + E_n + (-1)^n \frac{V_n}{2} (1 - \cos \phi) + \frac{\omega x^2}{2} + \kappa x \delta_{n,1} + \lambda x (1 - \delta_{n,n'}) \right\} |n\rangle \langle n'| \quad (2)$$

where $\hat{T} = -\frac{1}{2m} \frac{\partial^2}{\partial \phi^2} - \frac{\omega}{2} \frac{\partial^2}{\partial x^2}$ is the kinetic energy operator. All of the parameters are taken from refs 20 and 40 and are summarized in Table 1. This is termed a two-state, two-mode (2S2M) model, and a schematic drawing of the diabatic states as functions of ϕ is shown in Figure 1a. By expressing the system Hamiltonian in the Fourier grid basis⁴¹ in the ϕ coordinate (220 grid points) and in the number basis for harmonic mode x (truncated at $N_x = 20$) and numerically diagonalizing it, we obtain its eigenvalues and eigenfunctions. As discussed in our previous report,⁴² a useful measure for

Table 1. Parameters^a

E_0	E_1	V_0	V_1	m^{-1}	ω
0	2.58	3.56	1.19	28.06×10^{-4}	0.19
κ	λ	η_ϕ	$\omega_{c,\phi}$	η_x	$\omega_{c,x}$
0.19	0.19	0.15	0.071^b	0.1	0.19

^a η_ϕ and η_x are dimensionless, and all other parameters are in electronvolts. ^bWhen the disorder in V_0 is sampled, the value of $\omega_{c,\phi} = \sqrt{V_0/2m}$ is calculated accordingly.

understanding the nature of the energy eigenfunctions of H_s is given by

$$l_k = \frac{1}{2\pi} \int_0^{2\pi} d\phi |\langle \phi | k \rangle|^2 \times \frac{1 - \cos \phi}{2} \quad (3)$$

where $|\phi\rangle$ is the position eigenfunction along reaction coordinate ϕ and $|k\rangle$ is the k th energy eigenfunction of H_s of energy ϵ_k . This quantity measures the “trans-ness” of the state in question. States completely localized in the *cis*-well correspond to $l_k = 0$, and those localized in the *trans*-well have $l_k = 1$. In Figure 1b, we plot all of the energy eigenstates of H_s under 3 eV using (l_k, ϵ_k) as coordinates. The brightest state (state with the largest amplitude composing the Franck–Condon state) is indicated by the red star, with its energy marked by the dashed line, and the solid line indicates the energy of the lowest-energy state for which $|l_k - 0.5| < 0.1$. The latter can be interpreted as the “point of no return” in the relaxation dynamics, similar to the curve crossing point of the LZ model. The photoproduct population is defined as that projected onto diabatic state $|1\rangle$ and within the range $\phi \in [\pi/2, 3\pi/2]$. We focus the discussion on this quantity, as its NESS value defines the photoisomerization QY.

It has been estimated that the inhomogeneous contribution to the absorption line width of rhodopsin is on the order of 1000 cm^{-1} .⁴³ In our simulations, we found that the absorption line width can be accounted for by introducing a Gaussian disorder of magnitude $\sigma = 2000 \text{ cm}^{-1}$ into parameter E_1 , the optical gap of the *cis*-conformer. The same disorder strength is also assumed for the *trans*-optical gap $V_0 - E_1 + V_1$. For the sake of simplicity, when changing the E_1 value, we simultaneously change V_1 the same amount to keep both the energy storage $(E_1 - V_1)$ and the *trans*-optical gap the same, while disorder in the *trans*-optical gap is independently applied to V_0 . The effect of this change in E_1 and V_0 will be discussed below.

System-bath coupling H_{sb} is approximated by the direct product form

$$H_{sb} = \sum_b \hat{S}^{(b)} \otimes \hat{B}^{(b)} \quad (4)$$

where $\hat{S}^{(b)}$ and $\hat{B}^{(b)}$ are operators that depend on only the system and the bath coordinates, respectively. The superscript b runs over all baths involved. The baths are described within the harmonic approximation $H_{ph} = \sum_k \omega_k b_k^\dagger b_k$ and comprise two components:

$$H_{s-ph} = H_{s-x} + H_{s-\phi} \quad (5)$$

$$H_{s-x} = S_x \times \sum_k g_{k,x} (b_{k,x}^\dagger + b_{k,x}) \quad (6)$$

$$H_{s-\phi} = S_\phi \times \sum_k g_{k,\phi} (b_{k,\phi}^\dagger + b_{k,\phi}) \quad (7)$$

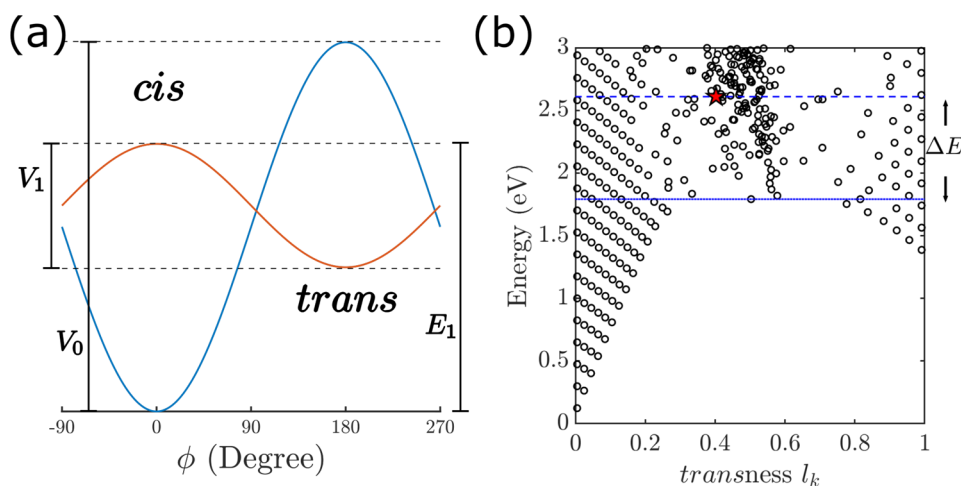


Figure 1. (a) Schematic drawing of the two diabatic surfaces as functions of reaction coordinate ϕ . (b) Energy eigenstate distribution (l_k, ϵ_k) of the system Hamiltonian (eq 2). ΔE is the energy difference between the Franck–Condon state and the lowest-energy eigenstate that is delocalized between the *cis*- and *trans*-wells (that is, where $l_k \approx 0.5$).

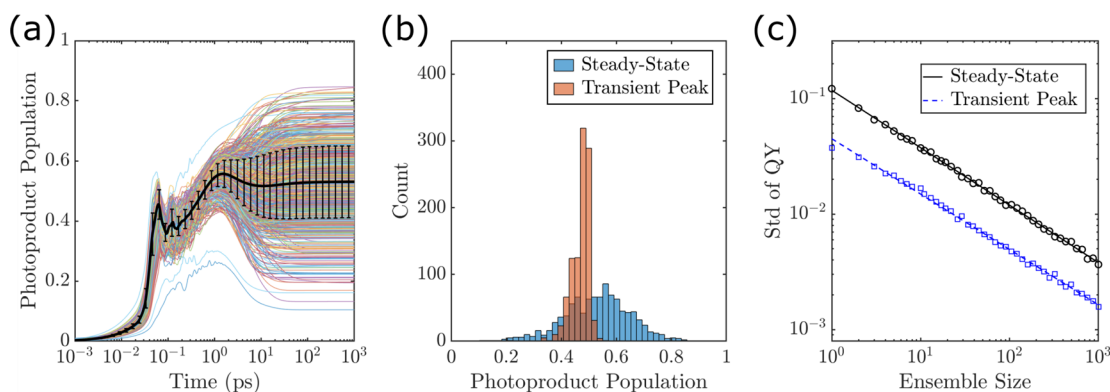


Figure 2. (a) One thousand time-dependent photoproduct population trajectories subject to a Gaussian-distributed E_1 parameter, representing the inhomogeneous broadening introduced by static disorder. The thick black line is the average, with the error bar indicating the standard deviation. (b) Histograms of the NESS (recorded at 1 ns, colored blue) and the transient peak photoproduct populations (brown), taken from the trajectories shown in Figure 1b. The latter is defined by the magnitude of the first peak of the photoproduct population for each trajectory. (c) Standard deviations of the NESS (black circles) and the transient peak photoproduct populations as functions of ensemble size N_E . The lines are $N_E^{-0.5}$ fits to the data points.

where $g_{k,x}$ and $g_{k,\phi}$ are the displacements of phonon mode k , $S_\phi = |1\rangle\langle 1| \times (1 - \cos \phi)$, and $S_x = |1\rangle\langle 1| \times x$. We follow Stock et al.^{40,43} and adopt an Ohmic bath with exponential cutoff $J_y(\omega) = \eta_y \omega e^{-\omega/\omega_c}$, where $y = x, \phi$, with the parameters listed in Table 1. It is worth noting that the ϕ bath in eq 7 couples primarily to the *cis*-well because of the $(1 - \cos \phi)$ factor, whose significance will be discussed below.

To help understand the effects of system–phonon interaction, we also consider two additional forms for $H_{s-\phi}$

$$H_{s-\phi'} = |1\rangle\langle 1| \times \mathbb{I}_\phi \times \sum_k g_{k,\phi} (b_{k,\phi}^\dagger + b_{k,\phi}) \quad (8)$$

$$H_{s-\phi''} = |1\rangle\langle 1| \times (1 + \cos \phi) \times \sum_k g_{k,\phi} (b_{k,\phi}^\dagger + b_{k,\phi}) \quad (9)$$

Here the ϕ dependence in $H_{s-\phi'}$ makes no distinction between the two wells, whereas $H_{s-\phi''}$ couples primarily to the *trans*-well.⁴³ In essence, the form of $H_{s-\phi} \propto S_\phi$ dictates how the phonon environment changes as a function of the reaction coordinate, as was carefully documented and discussed by Eyring et al.⁴⁴ Here such changes are approximated by a

position (ϕ, x) -dependent operator applied to the same collection of environmental modes, specified by the spectral density.

The effect of system–bath interaction is treated with the standard Markovian Redfield quantum master equation formalism,⁴⁵ where the system-reduced density matrix is subject to the following equation of motion in the system energy eigenbasis:

$$\frac{\partial}{\partial t} \rho_{ij} = -i\omega_{ij} \rho_{ij} + \sum_b \sum_{kl} \mathcal{R}_{ij,kl}^{(b)} \rho_{kl} \quad (10)$$

where ω_{ij} is the energy difference between system eigenstates i and j and we have taken $\hbar = 1$. Expressions for relaxation tensor $\mathcal{R}_{ij,kl}$ can be found in, e.g., ref 42. Assuming the initial state to be the Franck–Condon state from the overall ground state of $H_s(|g\rangle)$, that is $|FC\rangle = |1\rangle\langle 0|g\rangle$, corresponding to coherent excitation in the impulsive limit, the system-reduced density matrix is then propagated using eq 10. Furthermore, we adopt the Bloch-secular approximation that decouples the population dynamics from the coherence and greatly simplifies the numerical effort required. This is justified because we are

primarily interested in the long-time regime where this approximation introduces only minor deviations, as discussed in the literature.^{40,42}

Natural retinal photoisomerization occurs in an ensemble with, e.g., a variable optical gap. It is within such an ensemble that the short-time dynamical wavepacket picture has been utilized. In Figure 2a, we show the dynamics initiated at the Franck–Condon states of an ensemble of 1000 2S2M systems modeled by numerically solving eq 10. Within this ensemble, we sample a random optical gap parameter (E_1) drawn from a Gaussian distribution with a width of 2000 cm^{-1} , corresponding to 10% of the mean optical gap. The time-dependent mean and standard deviation of the dynamics are shown as a thick black line. The averaged dynamics shows a steep rise of photoproduct population on a time scale of <100 fs, followed by oscillatory features up to ~30 fs. Both of these features have been well documented in pulsed laser experiments, reflecting the coherent vibronic wavepacket motion as initiated therein.^{3,17,18,32,46} On the contrary, the mean photoproduct population continues to change after 1 ps and stabilizes to the steady state value of ~0.55% at around 100 ps for the current model, while its standard deviation increases significantly, up to ~10% at steady state. As we recently reported,⁴² this phenomenon indicates the extreme sensitivity of nonadiabatic dynamics to system parameters for a large family of theoretical models commonly employed to simulate various photochemical systems in the gas phase and condensed phase.^{47–50} It should be noted that the secular Redfield methodology adopted here obeys detail balance, so at infinite time after the initial excitation, the thermal state is always reached. Hereafter, we designate the photoproduct population at 1 ns as the reaction QY at NESS. We expect our results to remain qualitatively the same for a slow turn-on, incoherent photoexcitation scenario¹¹ that is relevant under natural biological conditions because those excitation conditions reach the same NESS.

In most retinal experimental setups, only the mean value of the quantum yield is reported. By contrast, here we show the standard deviation of the photoproduct population in Figure 2a and those of its short-time peak values and NESS counterparts in Figure 2b, providing far greater insight into the ensemble dependence. The effect of ensemble averaging is seen more directly in Figure 2c, which shows the dependence of the standard deviations of the NESS and the transient peak photoproduct populations on the number of independent trajectories over which they are averaged. The values in Figure 2b are understood as single-molecule trajectories in which systems with different parameters can be resolved individually. As such, they correspond to the left-most data point in Figure 2c, where $N_E = 1$. The data points at, for example, $N_E = 10$ are calculated by first averaging individual trajectories in groups of 10 and then taking the statistical measures with respect to the averaged trajectories.⁴ In essence, parametric sensitivity is attenuated upon averaging over a macroscopic number of molecules. (This is especially true for biological systems with inhomogeneity from slow and large-scale conformation changes inherent to their protein environment, as in rhodopsin.) As noted above, it is in the ensemble-averaged domain that the short-time dynamical wavepacket approaches have been advocated. They are not expected to *a priori* predict the extreme variation of QY from parameters evident in Figure 2a.

One can see that both the transient peak and the NESS values follow an $N_E^{-0.5}$ scaling, reflecting the Poisson statistics typically found in single-molecule/small ensemble measurements where individual events are uncorrelated.⁵¹ Also, the transient peak standard deviation is consistently smaller than the NESS counterpart by a factor of 2.7; i.e., the parametric sensitivity is much more significant at the NESS. The deviations become undetectable (<1%) for an ensemble size beyond ~100 for the current model, a lower bound for the ensemble size in which the short-time dynamical wavepacket perspective can be explored experimentally.

Here, however, we are primarily interested in the systematic features of NESS photoisomerization reaction QY subject to ensemble averaging, which concerns the majority of biological circumstances. In particular, our emphasis is on the effects of both the general structure of the system's vibronic topography and the influence of system–bath interaction (discussed below).

The short-time dynamical wavepacket perspective has been adopted to explain the excitation wavelength dependence of the photoisomerization QY of rhodopsin, where the QY was found to decrease when the excitation wavelength was red-shifted from the absorption peak.^{16,19} Does this particular feature extend to the NESS?

In simulating the NESS QY of the 2S2M model, we associate a higher crossing velocity with a larger excess energy ΔE , defined in Figure 1b, the energy difference between the Franck–Condon state and the lowest-energy state that delocalizes between the reactant and the product wells. The latter can be seen as the “point of no return” of the photoisomerization dynamics provided that the thermally activated contribution is negligible.^b Intuitively, a larger ΔE corresponds to a larger crossing velocity in the LZ model.^c Figure 3a examines the relationship between ΔE and the NESS

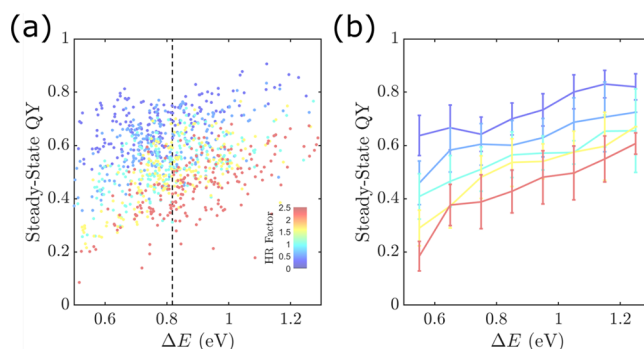


Figure 3. (a) Scatter plot of the NESS QY with respect to ΔE for a collection of 2S2M models with inhomogeneously broadened optical gaps and a varying κ parameter while holding all other parameters constant. The data points are grouped and color-coded according to their κ values. The dashed line indicates $\Delta E^{(0)} = 0.82$ eV, the value for the original model parameter set used in ref 20. (b) Data from panel a within a window averaged in steps of 0.1 eV in ΔE , where each group contains ≤ 50 data points. The error bars show the extent of one standard deviation.

reaction QY. Specifically, we plot the NESS QY against ΔE for a collection of 2S2M systems with a Gaussian-distributed optical gap, as described previously, keeping all other parameters the same but one (κ , the relative displacement of the κ mode). In particular, the data are divided into subgroups (color-coded) according to the magnitude of Huang–Rhys

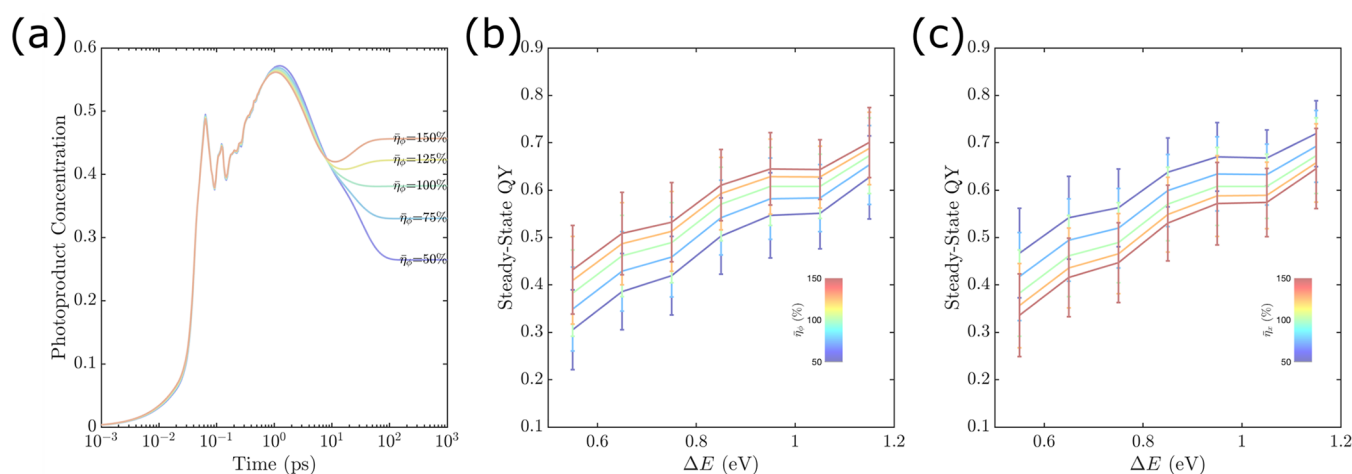


Figure 4. (a) Time-dependent photoproduct population of a sample system subject to different system–environment coupling magnitudes $\bar{\eta}_\phi$ while keeping all other parameters the same. The bottom (top) trajectory is $\bar{\eta}_\phi = 50\%$ ($\bar{\eta}_\phi = 150\%$), with a 25% increment for each successive trajectory. (b) Window-averaged data as functions of the relative coupling strength in $H_{s-\phi}$. The dependence on coupling strength prefactor $\bar{\eta}_\phi$ is color-coded. (c) Window-averaged data as functions of the relative coupling strength in H_{s-x} . The dependence on coupling strength prefactor $\bar{\eta}_x$ is color-coded.

factor $(\kappa/\omega)^2$. We also present the window-averaged data to the subgroups with an increasing ΔE in Figure 3b.

While the data points are scattered extensively, manifesting parametric sensitivity,⁴² we find a generic proportionality between the NESS QY and ΔE , supporting the short-time dynamical wavepacket perspective. In addition, with an increase in κ there is a trend toward a decreasing QY. This is also in accordance with the dynamical wavepacket picture, where the excess energy deposited into the second mode would be less conducive to the reaction QY. Experimentally, parameters such as ΔE and κ can be accessed by analyzing the vibrational spectra and by estimating the corresponding Franck–Condon factors.¹⁹

Would this perspective extend to larger systems? We note that there have been recent accounts of different vibronic effects by introducing and analyzing the dynamics along a third mode in the photoisomerization process.^{32,36} Specifically, it was found that the short-time QY is highly correlated with the relative phases of wavepacket motion along the three key local coordinates of the photoisomerization reaction: the reactive carbon and hydrogen torsional angles and the bond length alternation mode. While characterizing such dynamical effect on a higher-dimensional model such as a two-state, three-mode model²⁷ is an ongoing effort of the authors, we expect a trend similar to that shown in Figure 3. In this regard, a few other points are worth considering. First, while it is clear that wavepacket motion initiated at the Franck–Condon state remains coherent in the transient regime, and hence would be sensitive to the third mode, the reaction dynamics typically reaches the NESS limit in the 10 ps regime, where vibronic coherence is entirely lost. Hence, considerations regarding the dynamics of the three-mode case would likely be washed out. Second, as one can see in Figure 2a and extensively discussed previously,⁴² the NESS QY is only weakly correlated with short-time dynamics. Lastly, an LZ analysis is indeed less useful when comparing different systems such as those studied in ref 32 (deuteration of the retinal chromophore) and in ref 36 (different animal rhodopsins), where changes made to the systems are beyond perturbative. In such cases, the change in the vibronic topography is large so that exponential factor A in

the LZ expression $P \propto e^{-A/\nu}$ can change significantly, and the correlation between crossing speed ν and QY can be obscured. On the contrary, an LZ analysis of QY within an inhomogeneously broadened ensemble of the same system would reveal the connection between ν and QY more directly, as is done here and in ref 19.

It should be mentioned that there have been numerous efforts in augmenting the original 1D LZ theory to account for higher-dimensional systems and/or a dissipative environment, both analytically^{21,22,24} and numerically.^{23,25,35,52,53} In various situations, particularly when the additional DOF or the environment asserts a significant influence compared to the nonadiabatic coupling between the two states, it is known that the original LZ formula can be unreliable, such as the prediction of a nonmonotonic dependence on the crossing speed.^{24,25} It would be informative to apply or generalize these results and methods to the study of rhodopsin photoisomerization provided that the incoherent excitation and the NESS condition are accounted for.

The analysis presented above, while consistent with the short-time wavepacket perspective, is not the full physical picture required to understand our results. Figure 4 shows the dependence of the photoproduct population on the system–environment dissipation strength. Here we vary prefactor $\bar{\eta}_y$ of system–environment coupling term H_{s-y} in the form of $J_y(\omega) = \bar{\eta}_y(\eta_y \omega e^{-\omega/\omega_{cy}})$, where $y = \phi, x$. In Figure 4a, we show a set of sample trajectories calculated using the same system parameters with varying $\bar{\eta}_\phi$ while keeping all other parameters the same. It is clear that while the transient dynamics is nearly unaffected (≤ 10 ps), the long-time dynamics is sensitive to $\bar{\eta}_\phi$, a sensitivity that is completely missing in the short-time wavepacket dynamics picture.

For a more systematic study, in Figure 4b we show the window-averaged data (as introduced in Figure 3b) as functions of $\bar{\eta}_\phi$, as well as the dependence on $\bar{\eta}_x$ in Figure 4c. The results show that while in each set of data the reaction QY is generally proportional to ΔE consistent with the dynamical wavepacket picture, there is also a systematic increase in QY with an increase in $\bar{\eta}_\phi$ and a decrease in QY with an increase in $\bar{\eta}_x$. This suggests that the energy exchange

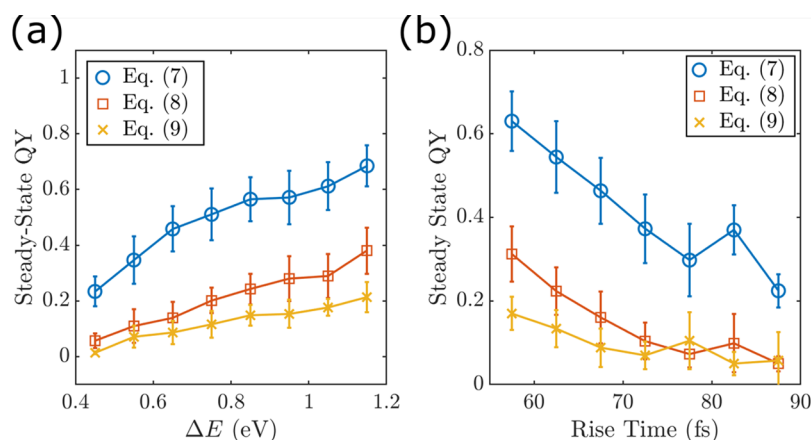


Figure 5. (a) Window-averaged data as in Figure 3b where the system part of the system–environment coupling S_ϕ is changed as in eqs 7–9. Specifically, eq 7 corresponds to stronger damping in the *trans*-region, eq 9 corresponds to stronger damping in the *cis*-region, and eq 8 is unbiased damping. (b) Same set of data in panel a plotted against the photoproduct rise time instead. The rise time is defined in conjunction with the transient peak photoproduct population shown in Figure 2, which is the time when the first peak in the photoproduct population is located.

between the two modes during the relaxation process, redistributing and dissipating the excess energy ΔE , is significant. Specifically, our results imply that with an increase in $\bar{\eta}_\phi$ a larger part of the excess energy is converted into the reaction coordinate, facilitating the conversion to the photoproduct, whereas the opposite is true for an increase in $\bar{\eta}_x$. By contrast, a dynamical wavepacket picture would expect a negligible exchange of energy among reactive and unreactive modes. That is, a wavepacket picture cannot explain these results; i.e., partial thermalization among the modes occurs during the photoisomerization process.

The effect of energy exchange also manifests in the functional form of system–environment coupling, especially its dependence on the reaction coordinate as in eqs 7–9. Some computational evidence is shown in Figure 5a. In all three cases, the NESS QY is found to be roughly proportional to excess energy ΔE , consistent with the dynamical wavepacket picture. However, the effect of partial thermalization is evident insofar as the NESS QY changes significantly with a change in S_ϕ .

Such partial thermalization is, as expected, most consequential beyond the transient regime. In Figure 5b, we compare the photoproduct rise time among the three different system–environment coupling models. While the rise time indeed correlates inversely with the NESS QY, again in agreement with the dynamical wavepacket picture, the strong correlation between the form of the system–environment coupling and the NESS QY indicates a deficiency in the simple wavepacket picture. In fact, using a simpler two-state, one-mode model for rhodopsin, and considering the reverse reaction, Hahn and Stock showed that nearly all initial state dependence is erased at the NESS.⁴³

Pulsed laser studies of light-induced biological processes provide deep insights into the nature of the Hamiltonian and its coupling to the environment, through transient dynamics induced by the pulsed excitation. Interpretations of these experiments, based on a short-time dynamical wavepacket picture, provide insight into the physics of the ongoing process. Here, we focused on the photoisomerization of rhodopsin, where interpretations of experiment have been closely linked to this dynamical perspective. In nature, however, this isomerization occurs in a nonequilibrium steady state (NESS) that is induced by incident incoherent (e.g., solar)

radiation and the phonon environment, as opposed to pulsed coherent light. The resultant molecular behavior is dramatically different. The key issue addressed here is the extent to which intuition gained from the wavepacket picture carries over to an understanding of the quantum yield (the primary quantity of interest) in the NESS. Features such as the positive correlation among the quantum yield, excess energy ΔE , and the inverse of the photoproduct rise time do persist in the NESS. However, aspects that consistently receive less attention in the literature such as the relative strength and the functional form of the system–environment couplings, among other qualitative and quantitative attributes of the system–environment interaction, are distinctly different in the NESS than in the short-time pulsed laser domain. In essence, interactions of the system with the environment, which can strongly affect the system QY, are manifest in the NESS and not in the transient dynamics. These conclusions are significant and are expected to carry over to other natural processes in which the light-induced NESS is operative.

In addition to these results, we note that current experiments, which naturally entail an ensemble average over system properties, do not reveal the extensive parametric sensitivity that we reported earlier, i.e., that the retinal QY depends strongly on system parameters. Here we have shown that the parametric sensitivity vanishes as $N_E^{-1/2}$, where N_E is the number of molecules in the ensemble. In addition to explaining why parametric sensitivity has not been observed, these results provide conditions under which experiments over smaller ensembles are expected to demonstrate this sensitivity.

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Notes

The authors declare no competing financial interest.

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ADDITIONAL NOTES

^aThe transient peak values of the standard deviation in Figure 2b are evaluated by averaging over the photoproduct population at the first peaks of individual trajectories. This is different from that shown in Figure 2c, where the standard deviation is taken at the same time stamp across all trajectories and, therefore, does not account for the out-of-sync effect among them.

^b ΔE is similar to the excess energy in ref 19. However, therein both the ground state and the excited state are treated as harmonic multidimensional surfaces.

^cWe note that this analogy is not exact as the system dynamics is studied with a quantum master equation, in which the system is generally described by a mixed state. The notion of wavepacket velocity is lost when the interstate coherence is destroyed by the couplings to the thermal environment.

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