

Extreme Parametric Sensitivity in the Steady-State Photoisomerization of Two-Dimensional Model Rhodopsin

Chern Chuang* and Paul Brumer*



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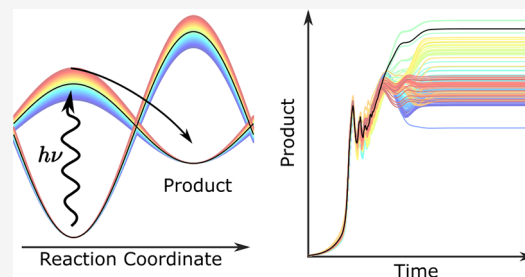


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ABSTRACT: We computationally studied the photoisomerization reaction of the retinal chromophore in rhodopsin using a two-state two-mode model coupled to thermal baths. Reaction quantum yields at the steady state (10 ps and beyond) were found to be considerably different than their transient values, suggesting a weak correlation between transient and steady-state dynamics in these systems. Significantly, the steady-state quantum yield was highly sensitive to minute changes in system parameters, while transient dynamics was nearly unaffected. Correlation of such sensitivity with standard level spacing statistics of the nonadiabatic vibronic system suggests a possible origin in quantum chaos. The significance of this observation of quantum yield parametric sensitivity in biological models of vision has profound conceptual and fundamental implications.



Retinal proteins are a family of important membrane proteins responsible for various photobiological functions in bacteria and higher life forms.^{1–3} Despite the variety of their functions and the host organisms, the general structure of the retinal proteins is consistent, i.e., seven transmembrane helices with a retinal chromophore bound to a lysine residue through a protonated Schiff base. Two systems are frequently studied: (1) rhodopsin that is found in animal retina, responsible for dim light vision, and (2) bacteriorhodopsin found in certain bacteria which functions as a light-driven proton pump. In particular, rhodopsin, with its retinal chromophore initially in an 11-*cis* conformation, undergoes photoisomerization to its all-*trans* counterpart within 200 fs upon pulsed laser excitation.^{4–6} This has been recently revised to 60 fs.⁷ The short reaction time is attributed to a conical intersection between the ground and excited states and has been suggested as being responsible for the high photoisomerization quantum yield (~67%).⁸ These observations have prompted the important question of the correlation between quantum coherence and biological function. Our view is clear: such coherences are induced by the laser pulses and are irrelevant to nature, which operates with incoherent light.^{9,10} Indeed, the natural vision process operates in the steady-state regime. Here, we report the observation of a dramatic dependence of the steady-state quantum yield (QY) on minute changes in system parameters. Our study is based on a two-state two-mode (2S2M) model coupled to thermal baths initially proposed by Stock et al.^{11,12} and later modified/extended to account for numerous experimental observations of bovine rhodopsin photoisomerization.^{7,13} The dependence of the biologically important steady-state QY on the system parameters is correlated with level spacing statistics, a well established measure for quantum chaos in molecular systems. This parametric sensitivity has profound implications for the

biology of vision, raising issues as to whether nature's parameters occupy a “Goldilocks” region for optimal function.

This Letter is arranged as follows. We first introduce the necessary background and details of the theoretical treatment, which is followed by a demonstration of the dramatic parametric sensitivity of the steady-state photoisomerization QY. We then discuss relationships to quantum chaos, the possibility of experimental measurement of such extreme sensitivity, and its implications on generic photochemistry in the condensed phase and biological light sensing.

Models and Method. The model for the retinal rhodopsin photoisomerization reaction is simulated numerically using the 2S2M model pioneered by Stock et al.^{11,12,14} This has been shown to be an adequate minimal model for studying the photoisomerization dynamics of retinal chromophores, describing the vibronic structure of a conical intersection.¹⁵ To account for the environmental effects associated with the protein pocket, the 2S2M system is further coupled to two sets of harmonic bath modes, and the system dynamics is simulated using second-order quantum master equations.

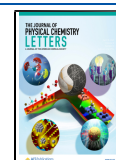
A general system–bath Hamiltonian can be written as

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

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Here, the system (2S2M) Hamiltonian is composed of two diabatic electronic states $|0\rangle$ and $|1\rangle$, a reaction coordinate (coupling mode) ϕ , and a tuning mode x .

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

where $T = -(1/(2m))(\partial^2/\partial\phi^2) + (\omega/2)(\partial^2/\partial x^2)$ is the kinetic energy operator. All parameters, updated in 2017, are obtained from ref 7 and given in Table 1. We define the range $\phi \in [-\pi/2, \pi/2]$ to be the *cis*-conformer, and the range $\phi \in [\pi/2, 3\pi/2]$ to be the *trans*-conformer. The eigenstates of H_s can be expressed in the direct product space of the electronic diabatic states $\{|0\rangle, |1\rangle\}$, the tuning mode x , and the reaction coordinate ϕ .¹¹ The adiabatic potential energy surfaces are plotted in Figure 1a. We note that the protein pocket of rhodopsin is such that the retinal chromophore is pretwisted and chiral, which eq 2 does not account for.¹⁶

Table 1. List of Parameters, Adopted from Ref 7

parameter	value (eV)
m^{-1}	2.80×10^{-3}
E_0	0
E_1	2.58
V_0	3.56
V_1	1.19
w	0.19
κ	0.19
λ	0.19

A generic property of such a Hamiltonian is that the low-energy part of its eigenstates is localized in either the *cis*- or the *trans*-wells, while higher-energy states are more delocalized over the reaction coordinate ϕ .¹⁷ To better demonstrate this character, of relevance later below, we define the following quantity

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

where $|k\rangle$ is the k th eigenfunction of the system Hamiltonian H_s and $|\phi\rangle$ is the eigenfunction of the position operator in the reaction coordinate. This quantity is a non-negative real number with a maximal value of unity. It measures the “*trans*-ness” of the eigenfunctions: $l_k = 0$ (1) corresponds to $|k\rangle$ fully localized in the *cis*- (*trans*-) well. For intermediate values it indicates an averaged position of the eigenstate, localized or delocalized. Figure 1b shows the distribution of l_k and eigenstate energies $\epsilon_k = \langle k | H_s | k \rangle$. Contribution from the *trans* species occurs at most energies but becomes significant above ~ 1.4 eV.

System–Bath Coupling. To properly account for relaxation effects, the system is coupled to environmental degrees of freedom, 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 only on the system and the bath coordinates, respectively. The superscript b runs over all system–bath interactions involved. This form of system–bath interaction Hamiltonian is then treated with the standard Markovian–Redfield approximation that leads to a quantum master equation, which in the system eigenbasis reads

$$\frac{\partial}{\partial t} \rho_{ij} = -i\omega_{ij} \rho_{ij} + \sum_b \sum_{kl} \mathcal{R}_{ij,kl}^{(b)} \rho_{kl} \quad (5)$$

$$\mathcal{R}_{ij,kl}^{(b)} = -\delta_{jl} \sum_r \Gamma_{irr}^{(b)} + \Gamma_{ljk}^{(b)} + (\Gamma_{ljk}^{(b)})^* - \delta_{ik} \sum_r (\Gamma_{lrr}^{(b)})^* \quad (6)$$

where ω_{ij} is the energy difference between the system eigenstates i and j , and $\hbar = 1$. The damping tensors $\Gamma_{ijkl}^{(b)}$ are given by

$$\Gamma_{ijkl}^{(b)} = S_{ij}^{(b)} S_{kl}^{(b)} J^{(b)}(\omega_{kl}) \bar{n}_{BE}(\omega_{kl}, \beta) \quad (7)$$

where $S_{ij}^{(b)} = \langle i | \hat{S}^{(b)} | j \rangle$ and $\bar{n}_{BE}(\omega, \beta) = 1/(e^{\beta\omega} - 1)$ is the Bose–Einstein distribution at inverse temperature $\beta = 1/k_B T$ with the Boltzmann constant k_B .

The computational cost of propagating the Redfield master equation (eq 6) can be formidable given that one typically needs up to a thousand lowest-energy eigenstates, enough to converge the Franck–Condon transition from the ground to excited state. Significantly, this is made more difficult by the fact that we need to examine the long time steady-state properties, which requires

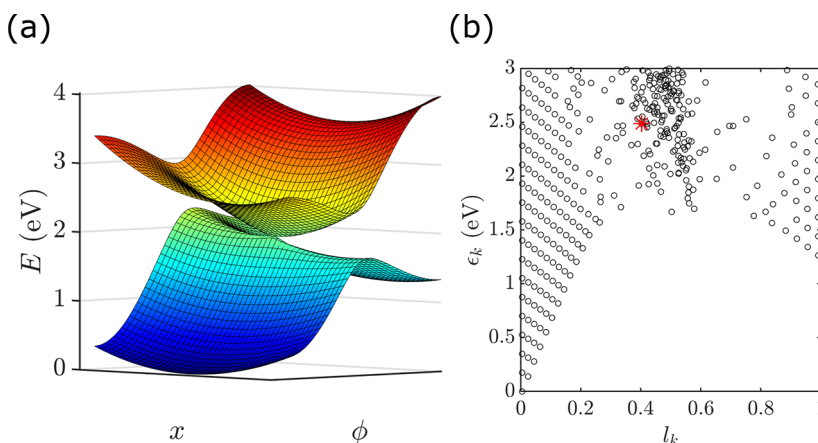


Figure 1. (a) Adiabatic potential energy surfaces of the 2S2M model. (b) The distribution of the system eigenstates with their energies as the vertical coordinates and l_k , defined in eq 3 as the horizontal coordinates. The state that contributes most to the Franck–Condon state is marked with an asterisk. See text for detailed description.

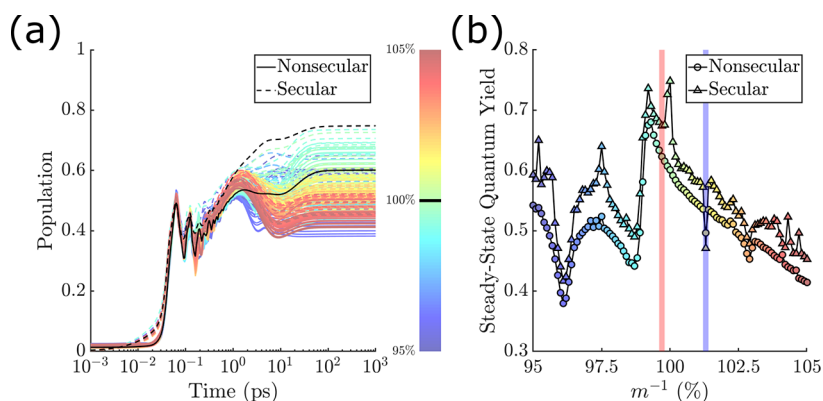


Figure 2. (a) Time-dependent *trans*-photoproduct population. The full nonsecular dynamics is shown as solid lines, and those of the Bloch-secular are shown with dashed lines. The data corresponding to the original set of parameters given in Table 1 are shown in black. Data with varied m^{-1} are color coded as indicated by the color bar. (b) QY recorded at 10 ns. The blue and red shaded area correspond to the connectivity graphs shown in Figure 4, discussed later below. The bath parameters are adopted from ref 14.

propagating the dynamics up to a nanosecond and beyond. To this end, one can invoke the Bloch-secular approximation which decouples the population dynamics from that of the coherences.¹⁴ We compare the results from the full nonsecular treatment to those of the secular approximation in the next section (for issues of secular versus nonsecular master equations, see ref 18).

The phonon bath is described within the harmonic approximation, $H_{\text{ph}} = \sum_k \omega_k b_k^\dagger b_k$, where the system–phonon interaction can be further separated into two components:

$$H_{\text{s-ph}} = H_{\text{s-x}} + H_{\text{s-}\phi} \quad (8)$$

$$H_{\text{s-x}} = |1\rangle\langle 1| \cdot \sum_k g_{k,x} (b_{k,x}^\dagger + b_{k,x}) \quad (9)$$

$$H_{\text{s-}\phi} = |1\rangle\langle 1| (1 - \cos \phi) \cdot \sum_k g_{k,\phi} (b_{k,\phi}^\dagger + b_{k,\phi}) \quad (10)$$

where $g_{k,x}$ and $g_{k,\phi}$ are the coupling strengths of the phonon mode k . It is customary to represent the summation over the phonon coupling strengths g_k as a continuous spectra density $J(\omega)$, taken here in accord with the work of Stock et al.,^{12,14} to be an Ohmic bath with exponential cutoff, $J(\omega) = \eta \omega e^{-\omega/\omega_c}$. Couplings to these baths represent the fluctuations and dissipation of the system dynamics along the modes x and ϕ .

In the simulation of the retinal photoisomerization, it is customary to choose the initial condition of the dynamics to be the Franck–Condon state from the ground state located in the *cis*-well.^{7,11,19} On the other hand, the dynamics initiated from a state similar to the Franck–Condon state but with all coherence in the energy eigenbasis removed, termed the Franck–Condon mixed state, mimics the effect of an incoherent light source such as sunlight.¹⁷ We focus on the dynamics initiated with the Franck–Condon states and compare the effect of incoherent Franck–Condon mixed initial state in the Supporting Information. Similar parametric sensitivity was also observed in the nonequilibrium steady-state case, where the retinal system is simultaneously connected to a photon bath describing the incoherent sunlight and a phonon bath describing the protein environment (see the Supporting Information).

Variation of System Parameters. As noted above, the main result of this work is our observation of the extreme sensitivity of the steady-state photoisomerization QY to parameter variation. To demonstrate the extreme sensitivity,

consider the results of varying two representative parameters, as manifest in the computed steady-state QY. First, we vary the inverse mass m^{-1} in the kinetic energy term of the reaction coordinate. In the 2S2M model, m^{-1} determines the characteristic frequency of the reaction coordinate in the harmonic regime, $\omega_\phi = \sqrt{k/m}$ and $k = V_0/2$. It is worth noting that in the original model of Hahn and Stock¹¹ $m^{-1} = 4.84 \cdot 10^{-4}$ (eV), nearly 6-fold smaller than the value recently suggested by Johnson et al.,⁷ introduced to reflect the shortening of the rise time of the *trans*-photoproduct observed in pump–probe and 2D photon echo measurements with better temporal resolution. Here we consider $\pm 5\%$ variation of m^{-1} about the value proposed by Johnson et al. Note that this corresponds to a small change, i.e. $\pm 2.5\%$, of the harmonic frequency along the reaction coordinate.

We have also examined the effect of varying the optical gap between the two diabatic electronic states, namely, the parameter E_1 . It is estimated that the inhomogeneous contribution to the broad absorption band of retinal rhodopsin is $\sim 1000 \text{ cm}^{-1}$,²⁰ $\sim 5\%$ of the optical gap, which is the range over which we vary the optical gap. To avoid the complication associated with changing the energy storage ($E_1 - V_1$) and the optical gap of the *trans*-product ($V_0 - E_1 + V_1$) when varying E_1 , we simultaneously change V_1 to keep $E_1 - V_1$ constant.

Variation of m^{-1} . Figure 2a shows the time-dependent *trans*-ground-state population of the photoisomerization dynamics, which gives the “time-dependent quantum yield”, defined as the population of diabatic electronic state |1⟩ in the *trans*-region ($\pi/2 \leq \phi < 3\pi/2$). The dynamics of the original model with parameters given in Table 1 is shown in black, and those with modified m^{-1} parameters are color-coded. The bath temperature is kept at 0 K to avoid the complication of thermally activated isomerization. Test computations with the bath at room temperature were also carried out to ensure that the parameter dependences reported below remained qualitatively unchanged.

Note first that there are signs of coherent beatings at times less than 1 ps, reflecting the fact that the population is oscillating between the reactant and the product wells, as the population in the *cis*-well mirrors that of the *trans*- (data not shown). The photoproduct appears on the time scale of 100 fs alongside the beatings, in general agreement with ultrafast pulsed laser experiments,^{4–7} signaling coherent wavepacket dynamics along the direction of the reaction coordinate ϕ . While the beatings disappear on the picosecond time scale, the QY

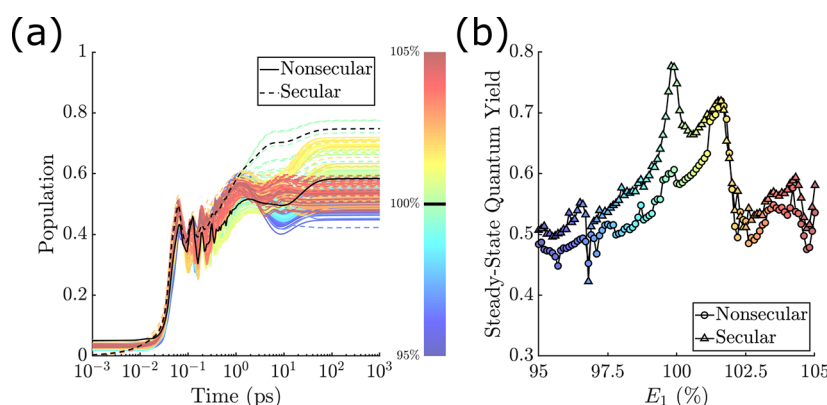


Figure 3. As in Figure 2, but with E_1 changed instead of m^{-1} .

continues to fluctuate on a far longer time scale, up to 100 ps. This is consistent with the experimental observations of a closely related system, the photoisomerization of bacteriorhodopsin, which shows a similar time-dependent photoproduct signal (up to hundreds of picoseconds) after the pump pulse.²¹ Computationally, the photoproduct signal has a nonmonotonic time dependence, a steep rise on the time scale of 1 ps, followed by a smooth decay until 20 ps, reaching its stationary value at longer times.

Here we are varying the particular system parameter m^{-1} within the range of $\pm 5\%$ with respect to the original value. The transient dynamics, up to ~ 0.5 ps, show limited m^{-1} dependence. However, most significantly, the QY at longer times (and hence not observable in transient dynamics reported in most pulsed laser experiments) depends very sensitively on m^{-1} , spanning a wide range between 35% and 75%. This is clearly seen in the QY recorded at 10 ns as a function of m^{-1} shown in Figure 2b. Note also that Figure 2 shows both secular and nonsecular simulations. In general, these two sets of results agree qualitatively with QY sensitive to the value of m^{-1} . However, it is clear that the steady-state QY depends on the level of treatment for the system–bath interaction.

Variation of The Optical Gap. To corroborate the above result and ensure that the parameter m^{-1} is not particularly special with regard to the sensitivity of steady-state QY, we also examined the system dependence on the value of the optical gap. This quantity is known to be inhomogeneously broadened in natural systems and easier to measure in concert with the photoisomerization reaction itself. In our case, this amounts to changing the parameter E_1 in the 2S2M model as described in Models and Method. The results are shown in Figure 3 and are similar to those found in variation of m^{-1} , i.e., large variations in QY as a function of small changes in the optical gap.

We also examined other parameters, such as ω (the frequency of the harmonic, second mode in the 2S2M model) and λ (the magnitude of the nonadiabatic coupling, similar to that studied in ref 22), and, moreover, two-state-one-mode and two-state-two-mode models with avoided crossings instead of a conical intersection (parameters given in ref 14). In light of recent computational study,^{13,23} we simulated and found similar parametric sensitivity in a two-state-three-mode model as well. In addition to the above-mentioned nonadiabatic, two-surface models, we consider a single-surface double well (1S2M) model as well that is more suitable for describing the adiabatic regime (strong nonadiabatic coupling) of the isomerization reaction. Details are provided in the Supporting Information. In all cases similar extreme sensitivities of steady-state QY are

found with respect to variations of system parameters. This suggests that the phenomenon may be an inherent property of the multidimensional vibronic/vibrational systems.^{24,25}

System Eigenstate Statistics and Relaxation Pathways. We conjecture that the parametric sensitivity of the steady-state QY results from the sensitivity of chaotic system dynamics that moves between the two wells and eventually settles into the product well by relaxation induced by the system–bath coupling. As mentioned above, previous studies on similar systems in the quantum chaos literature focus mainly on the statistical properties of their eigenstates²⁴ or short-time trajectory-based simulations in the absence of thermal relaxation.^{26,27} The system part in the current study, eq 2, falls under the same category of nonadiabatic vibronic Hamiltonians.^{22,24} It is thus expected, if the open system character is not significant, that similar quantum chaos characteristics would exist in this system as well. Figure 1b shows the distribution of eigenstates according to their energies and l_k , a measure of the average position along the reaction coordinate. It is clear that in the low-energy and deeply *cis/trans* regions ($l_k \rightarrow 0$ or $l_k \rightarrow 1$), the distribution of eigenstates forms a regular grid point lattice. This implies that these states can be written as direct products of the eigenstates of the two modes, $|k\rangle \propto |n_\phi\rangle \otimes |n_x\rangle$, where n_ϕ and n_x are the quantum numbers of the respective modes. On the other hand, for states with higher energies and l_k closer to 0.5, the grid pattern disappears and the characters of the two diabatic electronic states and the two modes mix.

The nearest-neighbor spacing distribution (NNSD) of energy eigenstates is a commonly utilized measure to characterize the possible chaotic nature of an isolated system.^{22,26} Specifically, level repulsion tends to imply chaos, most clearly manifest in a Wigner distribution of adjacent energy level spacings. Here, the procedure described by Haller et al. is used to account for the smoothly varying part of the density of states.²⁶ The “unfolded” energy levels are defined as

$$\tilde{\epsilon}_{i+1} = \tilde{\epsilon}_i + (2k + 1) \frac{\epsilon_{i+1} - \epsilon_i}{\epsilon_{j_2+1} - \epsilon_{j_1}} \quad (11)$$

where ϵ_i are the energies of the eigenstates of H_s with the state index i that runs from 1 to n ; k is a small positive integer defining the locality of the unfolding; $j_1 = \max(1, i - k)$ and $j_2 = \min(n - 1, i + k)$. NNSD is the distribution function of $S = \tilde{\epsilon}_{i+1} - \tilde{\epsilon}_i$. A nonmonotonic NNSD signals quantum chaotic behavior. Most notably, by assuming linear repulsion between adjacent levels one arrives at the Wigner distribution for chaotic systems:

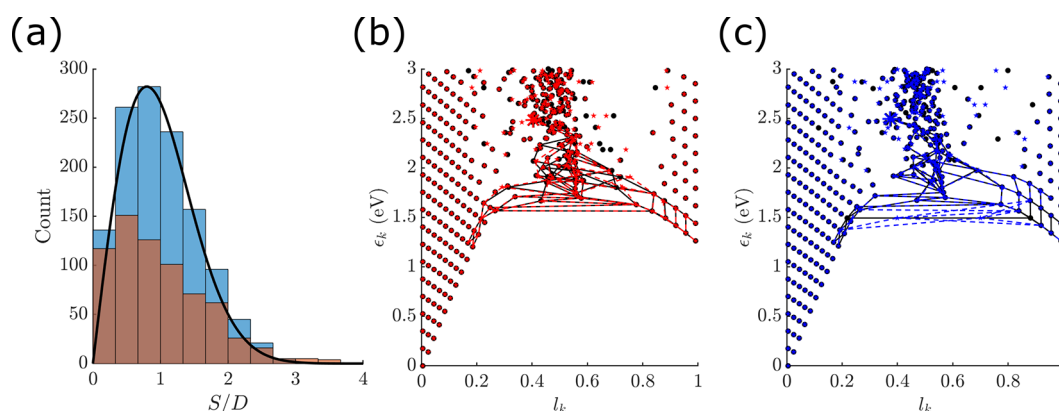


Figure 4. (a) Nearest-neighbor energy level spacing distribution of the model system studied, using parameters in Table 1. The blue bars (higher) are the 1240 eigenstates taken from the energy range of 4–6.4 eV, and the brown bars (lower) are the 686 eigenstates with energy below 4 eV. The local mean spacing parameter is set to $k = 2$. The average spacing of the unfolded levels is $D = 1.00$ meV. The curve is the Wigner distribution, given in eq 12. [The adoption of the higher energy range in panel a is for the purpose of emphasizing the contribution from the chaotic regime. In all other instances in the Letter the photoisomerization dynamics is well-converged by including energy eigenstates below 3 eV.] (b) The connectivity tree graph of the systems with m^{-1} values 99.70% and 99.80% of that in Table 1 (red shaded region in Figure 2b), rooted at the brightest state (asterisk). (c) Tree graph of the systems with m^{-1} 101.3% and 101.4% of that in Table 1 (blue shaded region in Figure 2b).

$$P_w(S) = \frac{\pi S}{2D^2} e^{-\pi S^2/4D^2} \quad (12)$$

where D is the mean of the distribution.

The NNSD for our system is shown in Figure 4a. It is clear that the distribution is nonmonotonic and near Wignerian and hence chaotic. This is especially true for the higher-energy part of the eigenspectrum (blue), in comparison to the lower-energy counterpart (brown).

Quantum chaos in the context of vibronic eigenspectrum of small molecules/ions in the gas phase has been well-established. However, the situation is less clear with systems, such as ours, coupled to a dissipative environment. As one insightful route, we analyze the relaxation pathways from the brightest state (the eigenstate contributing the most to the Franck–Condon state) by examining the Bloch–secular rate matrix elements among the eigenstates.

In Figure 4b,c we show the tree graphs representing the connectivity matrix²⁸ of the relaxation pathways among system energy eigenstates calculated using two pairs of m^{-1} values differed by only 0.1%, corresponding to the red and blue shaded regions shown in Figure 2b, while keeping all other parameters fixed. Each graph shows the eigenstate distributions (as in Figure 1b) of the two system Hamiltonians with slightly different m^{-1} values, using different markers (black filled circles and colored stars). As shown in Figure 2b, the red region corresponds to a parameter regime that shows smooth changes of steady-state QY with changing m^{-1} values, whereas the blue region shows dramatic changes. To simplify the graphs we only connect each higher-energy state i to the two lower-energy states j with the largest scattering rates $\sum_b \mathcal{R}_{ji}^{(b)}$ in eq 6. The connectivity graphs are rooted at the brightest state of the corresponding systems, defining tree graphs of degree two.

In both pairs of the tree graphs it can be seen that very small changes in m^{-1} leaves the approximated direct product structure for states close to the *cis*- ($l_k \approx 0$) and the *trans*-wells ($l_k \approx 1$) nearly unaffected. That is, a 0.1% change of m^{-1} corresponds to a $\sqrt{10^{-3}} \approx 3\%$ change in the harmonic frequency along the reaction coordinate (the vertical spacing between the lowest and the second-lowest symbols), generally not perceivable by the

naked eye. By contrast, a significant portion of the states with l_k close to 0.5 shows a noticeable horizontal shift, signifying the existence of level repulsion discussed above. In addition, a change in the eigenstate structure induces a dramatic change in the steady-state QY only if the shifted states are involved in the dominant relaxation pathways. This is so in the case shown in Figure 4c in contrast to that in Figure 4b, in agreement with the respective behavior of the steady-state QY shown in Figure 2b. These observations complement the parametric sensitivity of long-time dynamics displayed in Figures 2 and 3, supporting the view that isolated system chaos propagates through the relaxation dynamics in the open system.

Possible Experimental Verification. We note the recent work from Schnedermann et al., where rhodopsins reconstituted with isotope-substituted retinal chromophores show similar short-time dynamics but very different steady-state QY.²⁹ This observation supports the view that a shorter rise time (the time it takes for the first peak of photoproduct signal to appear) corresponds to faster reaction but not necessarily to higher reaction QY. That is, there is a disconnect between transient and steady-state behavior. However, changes with isotope substitution are not directly comparable to the sensitivity of steady-state QY seen in Figures 2 and 3. First, the isotope labelings in these experiments constitute much stronger perturbations to the system than those studied here. Second, the experimental observations are typically, if not exclusively, made on large ensembles of molecules. Within the ensemble, one expects significant inhomogeneity among the parameters, which would wash out the kind of parametric sensitivity observed in our computations.

For the real retinal system in an opsin protein pocket, the experimental situation is expected to be much more complicated than we have modeled above. Indeed, the established methods of measuring steady-state QY typically involve macroscopic amounts of the sample being photoisomerized (for example, loss of $\sim 10\%$ of the optical density of the reactant over the course of a few minutes^{30,31}). This being the case, and as noted above, it is likely that the sensitivity observed here is washed out by the sheer number of retinal molecules in a sample ($\sim 10^{20}$), each possessing a different conformation. Hence, experimental confirmation of the sensitivity of QY will require measurements

of small ensembles or even of single molecules. Provided that such sensitivity can be verified experimentally for retinal systems, it may well be the case that one can find similar phenomena in other light-induced condensed phase curve-crossing systems.

Open Theoretical Challenges. Additional investigation is needed to clarify the relationship between quantum chaos and parametric sensitivity of metastable state populations in an open system under environmental dissipation. Whereas we continue to examine a number of possible measures of quantum chaos for open systems proposed in the literature, such as the Loschmidt echoes and the ratio of eigenvalue differences of the Liouville operator,^{32–36} results thus far are inconclusive. (These results are available upon reasonable request.) For example, they suggest a need for a criterion that applies to open systems whose isolated system component displays both integrable and chaotic energy level regions. Further, it is worth noting that our treatment of system–bath interactions is restricted to a Markovian and perturbative (fast bath) limit, with other environmental effects included as static disorder (slow bath). In doing so, we do not detect QY sensitivity to the parameters of the system–bath coupling term or to the bath itself. In the future it would be interesting to examine nonperturbative system–bath effects using more sophisticated methods that also account for the intermediate regime in which the system and the bath time scales overlap.^{19,37}

Furthermore, while admittedly premature, it is not difficult to suggest a connection between this result and its possible significant biological implications. That is, does a biological light-sensing apparatus benefit from the high sensitivity of the underlying curve-crossing mechanism to parameter variation? Do the system parameters have to be in a specific (“Goldilocks”) regime of parameter space? Has natural selection tuned these parameters? These and related questions warrant further study. The key here is the highly significant possibility of quantum chaotic contributions and parametric sensitivity in biological processes and its role in tuning biological function.

In conclusion, the photoisomerization dynamics of retinal chromophore in rhodopsin was studied using a two-state-two-mode model coupled to dissipative phonon baths. Assuming the Franck–Condon state as the initial state, the photoproduct (*trans*-conformer) populations first show a rapid rise with strong oscillatory features (quantum beats) on the 100 fs time scale. The oscillations then fade out and are replaced by a smooth time-dependent profile leading to the stationary values on longer time scales. Time-dependent behavior of this type agrees with available experimental observations of the closely related system bacteriorhodopsin, suggesting that simple pictures that correlate short time transient spectral features with steady-state quantum yield are suspect.

Most significantly, we find that the steady-state quantum yield is highly sensitive to slight changes in system parameters, while the transient dynamics remains almost unaffected. Such sensitivity is also observed by changing numerous other parameters of the model system, suggesting that it is an inherent feature of the nonadiabatic vibronic system studied. Further, possible experimental measurements of such sensitivity are discussed. The implications of these results are profound in biological light-sensing systems and possibly in condensed phase photochemistry.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpclett.1c00577>.

Parametric sensitivity of steady-state photoisomerization observed with incoherent initial conditions and incoherent excitations; parametric sensitivity and nonsensitivity in single surface models (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Chern Chuang – Chemical Physics Theory Group, Department of Chemistry, and Center for Quantum Information and Quantum Control, University of Toronto, Toronto, Ontario M5S 3H6, Canada; orcid.org/0000-0002-9450-4087; Email: chern.chuang@utoronto.ca

Paul Brumer – Chemical Physics Theory Group, Department of Chemistry, and Center for Quantum Information and Quantum Control, University of Toronto, Toronto, Ontario M5S 3H6, Canada; orcid.org/0000-0002-4763-2393; Email: Paul.Brumer@utoronto.ca

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acs.jpclett.1c00577>

Notes

The authors declare no competing financial interest.

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