Femtosecond secondary emission arising from the nonadiabatic photoisomerization in rhodopsin

Susanne Hahn, Gerhard Stock *

Theoretical Quantum Dynamics, Faculty of Physics, University Freiburg, D-79104 Freiburg, Germany

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Abstract

A microscopic quantum-mechanical model of the femtosecond photodynamics and the associated secondary emission of rhodopsin is presented. The formulation consists of a two-state two-mode model describing the nonadiabatic photoisomerization of retinal, a harmonic multi-mode ansatz accounting for the remaining Raman-active modes, and a low-frequency bath accounting for the coupling of retinal to the protein environment. The interaction between the various subsystems of the model is described in a mean-field approximation. Explicit simulations of absorption, resonance Raman and fluorescence spectra of rhodopsin are presented and compared to available experimental data. The model assumptions and the validity of the approximations involved are discussed in some detail. Furthermore, it is studied to what extent the secondary emission spectra reflect the photochemical reaction of the molecular system. It is shown that standard continuous-wave techniques such as absorption, resonance Raman and fluorescence spectra may yield only little direct information on the photoreaction. Considering the time- and frequency-resolved fluorescence spectrum, on the other hand, the time evolution of the excited-state wave function can be monitored, thereby providing a real-time measurement of the nonadiabatic photoreaction. Moreover, the proposed model of rhodopsin reveals recurrences of time-resolved emission which are shown to reflect coherent vibrational motion on coupled potential-energy surfaces. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Following resonant photoexcitation, a molecular system exhibits spontaneous secondary emission which consists of coherent resonance Raman scattering as well as of incoherent fluorescence. These contributions reveal different aspects on the photoprocess under consideration [1–3]: the Stokes shift of the fluorescence band yields valuable information on the excited-state dynamics of the system, while the intensity of the resonance Raman fundamentals is a direct measure for the local gradient of the excited-state potential energy surface (PES) in the Franck–Condon region. Numerous resonance Raman and fluorescence studies have been devoted to the investigation of the photoinduced cis–trans isomerization in polyenes [4]. It is commonly believed that the twisting of a C=C double bond leads to a degeneracy of electronic states, thus resulting in a conical intersection of the corresponding PESs [5,6]. Due to this “photochemical funnel,” ultrafast internal conversion processes may arise, which lead to radiationless relaxation of the system from the
electronic excited state back to the ground state [7–9]. First attempts to extend ab initio molecular-dynamics simulations to include excited-state processes have revealed a complex interplay between this electronic relaxation, the cis–trans large-amplitude motion, and the vibrational relaxation dynamics of the system [10–17].

A well-established procedure to simulate continuous wave (cw) absorption and emission spectra of molecular systems is to employ a harmonic model that contains the Raman-active modes of the molecule [2,3]. All remaining dynamical aspects of the system are then taken into account through phenomenological broadening factors. Although being a valuable tool to fit experimental data, in many cases, this approach cannot lead to a true microscopic understanding of the underlying dynamical processes. This is because, the method completely neglects the nonseparable nature of the multi-mode vibronic problem as well as the strong anharmonicity of the reaction coordinate. In a first attempt to account for the multidimensional nature of nonadiabatic photoisomerization processes, Domcke and coworkers have proposed a model Hamiltonian which include the vibronic coupling of the lowest singlet states \(S_0, S_1\), a large-amplitude torsional mode, as well as one or two accepting modes for the radiationless transition [18,19]. Exact time-dependent wave-packet calculations have been reported including up to four nuclear degrees of freedom, showing that the model is suitable to reveal basic features of photoisomerization and internal-conversion processes.

Employing this ansatz, we have recently proposed a simple quantum-mechanical model of the photoisomerization of retinal in rhodopsin [20]. Due to its importance for the first step in vision, there has been considerable effort to understand this photoreaction [21,22]. In particular, resonance Raman spectra [23–25], fluorescence measurements [26,27], various time-resolved investigations [28–31], as well as a number of theoretical works [32–41] have been reported. The effective two-state two-mode model suggested in Ref. [20] has been found to qualitatively reproduce available femtosecond experiments on rhodopsin. In particular, the onset of the photoproduct absorption band within 200 fs as well as the prominent 60 cm\(^{-1}\) beating of the time-resolved pump-probe signals [29] could be explained in terms of multidimensional wave-packet motion on nonadiabatically coupled PESs. Furthermore, the model is able to account for the high quantum yield of the isomerization, thus indicating that the high reaction efficiency observed for rhodopsin is indeed facilitated by the femtosecond dynamics of retinal.

The goal of this work is to investigate how ultrafast nonadiabatic isomerization is reflected in the secondary emission of the molecular system. To this end, the two-mode model of rhodopsin is extended via a mean-field ansatz to include all Raman-active modes of retinal. In a second step, we furthermore include a bath of low-frequency vibrational modes accounting for the coupling of retinal to the protein environment. Within this extended model, we undertake explicit simulations of cw absorption, resonance Raman and fluorescence spectra as well as of time-resolved fluorescence spectra. We discuss the main effects of nonadiabatic isomerization on the secondary emission, the validity of the dynamical approximations employed, as well as the applicability of the suggested model to reproduce the experimental spectra on rhodopsin.

2. Theory

2.1. Model system

Let us first introduce the vibronic-coupling model of the photoisomerization of retinal in rhodopsin proposed in Ref. [20]. Adopting a diabatic electronic representation with basis states \(|\psi_0\rangle, |\psi_1\rangle\), the model Hamiltonian reads

\[
H_M = \sum_{n,m=0,1} |\psi_n\rangle (T\delta_{nm} + V_{nm}) |\psi_m\rangle,
\]

where \(T\) denotes the kinetic energy and \(V_{nm}\) are the elements of the diabatic potential matrix. The model contains two nuclear degrees of freedom: A large-amplitude coordinate along which the molecule undergoes isomerization (the “reaction mode” \(\phi\)) and a vibronically active mode which may couple the two electronic states (the “coupling
mode" $q$). Assuming dimensionless coordinates and setting $\hbar = 1$, the diabatic matrix elements of Eq. (1) are given as

$$T = \frac{1}{2m} \frac{\partial^2}{\partial \phi^2} + \frac{\omega}{2} \frac{\partial^2}{\partial q^2},$$

$$V_{nn} = V_{n}^R(\phi) + \frac{1}{2} \omega q^2 + \delta_{1n} k q,$$

$$V_{01} = V_{10} = \lambda q,$$

where $m$ is the effective mass of the reaction coordinate, while $\omega$ and $\lambda$ denote the frequency and the interstate coupling of the coupling mode, respectively. Exploiting quantum-chemical calculations [17,35,36,38,39] and resonance Raman experiments [23–25], it is assumed that the coupling coordinate mainly reflects the ethylenic stretch mode of the polyene chain. Due to the low symmetry of retinal, this coordinate also exhibits a nonvanishing excited-state gradient $\kappa$.

The chemical aspects of the model are reflected by the reaction-mode potentials

$$V_{01}^R(\phi) = \frac{1}{2} W_0 (1 - \cos \phi),$$

$$V_{10}^R(\phi) = E_1 - \frac{1}{2} W_1 (1 - \cos \phi),$$

which are drawn in Fig. 1(a). Note that the excited-state potential $V_{10}^R(\phi)$ is inverted, i.e., the upper diabatic electronic state for $\phi = 0$ (cis configuration) becomes the lower one for $\phi = \pi$ (trans configuration). The corresponding adiabatic PESs of the model system exhibit a conical intersection, which has been shown to trigger irreversible isomerization and internal-conversion dynamics on a femtosecond time scale [18,19]. The isomerization potentials (5) are parameterized such that the experimentally measured energy relations of the photoreaction are reproduced, that is, the energy storage of the photoreaction ($\Delta E = 32$ kcal mol$^{-1}$) and the center wavelengths of the cis and trans absorption bands $\lambda_{cis} = 500$ nm and $\lambda_{trans} = 570$ nm [20]. The effective mass $m$ pertaining to the motion along $\phi$ can be obtained by requiring that isomerization takes place within 200 fs as observed in time-resolved experiments. It should be stressed that the thus defined reaction coordinate does not necessarily correspond to a specific internal coordinate of retinal (e.g., the $C_11 - C_{12}$ torsional mode) but collectively accounts for the energy relations of the reaction. The effect of the protein environment is thereby included in the parameters $m$, $E_1$, $W_0$, $W_1$ of the model. The parameters of the model are in eV: $m^{-1} = 4.84 \times 10^{-4}$, $E_1 = 2.48$, $W_0 = 3.6$, $W_1 = 1.09$, $\omega = 0.19$, $\kappa = 0.1$, and $\lambda = 0.19$.

The two-mode two-state model described above has been found to qualitatively reproduce femtosecond transient transmittance experiments on rhodopsin [29]. It is noted, however, that experimental resonance Raman spectra of rhodopsin [23–25] exhibit a number of vibrational modes that are not included in the model. While these modes may not directly be involved in the photochemical reaction monitored in the time-resolved experiments, they obviously contribute to the Raman spectra and therefore, also to the fluorescence emission. Hence, these Condon-active vibrational modes need to be included in an appropriate theory of secondary emission. To this end, we adopt the harmonic ansatz

$$H_B = \sum_{n=0,1} \left| \psi_n \right> \left< \psi_n \right| \sum_j \frac{1}{2} \omega_j (p_j^2 + x_j^2) + \delta_{1n} c_j x_j,$$

where the frequencies $\omega_j$ and excited-state gradients $c_j$ are chosen to reproduce the resonance Raman excitations observed in experiment. Since, about twenty Raman-active modes of retinal should be considered and because of the nonseparability of the vibronic-coupling Hamiltonian $H_M$, it is clear that the resulting total problem $H = H_M + H_B$ cannot be treated quantum-mechanically exactly. Therefore, we pursue the following strategy. The isomerization Hamiltonian $H_M$ is meant to account for the strongest interactions in the system which predominantly determine the initial nonadiabatic photochemical reaction. The dynamics of these degrees of freedom is

\[ \text{This assumes that the collective modes of the model essentially correspond to normal modes. In general, however, a single collective vibrational mode may give rise to a number of Raman excitations which result from the projections of the collective mode onto the normal modes of the system.} \]
therefore treated exactly, while the effects due to weakly coupled vibrational modes of the Hamiltonian $H_B$ may be taken into account in an approximate manner via a time-dependent Hartree

(or time-dependent self-consistent-field) ansatz [42–45].

Following recent work on the approximate description of secondary emission spectra [46], we
employ a “single-configuration” Hartree ansatz for the time-dependent wave function

$$\Psi(s, x, t) = e^{i\eta(t)}\chi(s, t)\phi(x, t),$$  \hspace{1cm} (7)

where $\eta(t)$ is an overall phase factor, while $s = \{\psi_n, \varphi, q\}$ and $x = \{x_j\}$, denote the degrees of freedom of the two subsystems $H_M$ and $H_B$, respectively. As discussed below, this short-time approximation should be sufficient to correctly reproduce the initial time evolution of the model determining the absorption and Raman spectra of rhodopsin. Furthermore, it has been demonstrated that this simple ansatz affords at least a qualitative modeling of electronic dephasing effects [46,47]. Inserting Eq. (7) into the time-dependent Schrödinger equation for the total Hamiltonian $H = H_M + H_B$, we obtain the well-known self-consistent-field equations [42–44]

$$i\dot{\chi}(t) = (\phi | H | \phi)\chi(t),$$  \hspace{1cm} (8)

$$i\dot{\phi}(t) = (\chi | H | \phi)\phi(t).$$  \hspace{1cm} (9)

Since the Hamiltonian $H_B$ is assumed to be harmonic, Eq. (9) describes the time evolution of a set of driven harmonic oscillators. Without invoking a further approximation, the corresponding wave function may therefore be written in terms of Gaussian wave packets

$$\phi(x, t) = \prod_j \pi^{-1/4} \exp \left\{-\frac{1}{2}[x_j - x(t)]^2 \right\}$$

$$+ ip_j(t)[x_j - x(t)] + i\gamma(t) \right\},$$  \hspace{1cm} (10)

which are completely described by the classical trajectory $x(t) = \{x_j(t)\}$, the corresponding momentum $p(t)$ and the classical action integral $\gamma(t)$ [43,44,48]. The numerical effort for the single-configuration Hartree description therefore scales linearly with the number of vibrational modes of $H_B$.

It should be stressed, however, that the time evolution of the wave function $\chi(s, t)$ cannot be described in terms of Gaussian wave packets. Although the Hamiltonian $H_M$ in Eq. (1) appears to be harmonic as well, the vibronic coupling renders the problem nonseparable. To solve Eq. (8), the wave function $\chi(s, t)$ is represented by a direct-product basis constructed from the two diabatic electronic states, 150 free-rotor states for the reaction coordinate, and 24 harmonic-oscillator states for the vibronically active coordinate. Further information on the dynamical description of multidimensional vibronic-coupling problems can be found in Refs. [8,9].

2.2. Calculation of spectra

In the time-dependent formalism, the linear cw absorption spectrum can be written as [49]

$$\sigma_\lambda(\omega) = 2\Re \omega_i \int_0^\infty dt \exp[i(\omega + \omega_\lambda)l]d(t)$$

$$\times \langle \Psi_0 | \mu_{01} e^{-iHt} \mu_{10} | \Psi_0 \rangle,$$  \hspace{1cm} (11)

where $\omega_1$ denotes the excitation frequency and $\mu_{10}$ represents the dipole operator of the electronic $|\psi_1\rangle \leftrightarrow |\psi_0\rangle$ transition. Throughout this work we neglect effects of finite temperature and assume that the system is initially in its electronic and vibrational ground state $|\Psi_0\rangle$ with energy $\epsilon_0$. Assuming, furthermore, that the optical transition is inhomogeneously broadened, the electronic depopulating function $d(t)$ can be written as

$$d(t) = e^{-t/\Gamma},$$  \hspace{1cm} (12)

where $\Gamma$ denotes the inhomogeneous line width. The time-dependent expression for the resonance Raman spectrum is given by [50]

$$\sigma_R(\omega_s, \omega_\lambda) = \omega_s \omega_\lambda \sum_f |A_f(\omega_\lambda)|^2$$

$$\times \delta(\epsilon_0 + \omega_\lambda - \omega_s - \epsilon_f),$$  \hspace{1cm} (13)

$$A_f(\omega_\lambda) = \int_0^\infty dt \exp[i(\omega_\lambda + \omega_s)l]d(t)\langle \Psi_f | \mu_{01} e^{-iHt} \mu_{10} | \Psi_0 \rangle.$$  \hspace{1cm} (14)

Here $\omega_s$ denotes the frequency of the spontaneous emission and $|\Psi_f\rangle$ is the final state of the system with energy $\epsilon_f$.

Let us next consider the calculation of the time-resolved fluorescence spectrum, which is experimentally measured via up-conversion techniques. To describe this experiment, we assume that at
time \( t = 0 \) the molecular system is prepared by an ultrashort pump pulse into a nonstationary state \( | \Psi_p \rangle \), whose time evolution is interrogated by a probe pulse at the delay time \( t_d \). Disregarding all details of the up-conversion process, we assume that the time-resolved fluorescence spectrum is equivalent to the stimulated-emission contribution of the transient transmittance spectrum (e.g., the discussion in Ref. [9]). The latter is proportional to

\[
I(t_d, \omega) = 2 \text{Im} E_2^\omega(t_d) P(\omega),
\]

where \( E_2(\omega) \) and \( P(\omega) \) denote the Fourier transform of the probe field \( E_2(t) \) and the nonlinear electronic polarization \( P(t) \), respectively. Assuming impulsive excitation by an ultrashort pump pulse, the nonlinear electronic polarization \( P(t) \) describing the emission process can be written as [51,52]

\[
P(t) = \int_{-\infty}^{t} \text{d}t_d E_2(t_d) P_s(t, t_d),
\]

\[
P^s(t, t_d) = i \text{d}(t - t_d) \langle \Psi_p(t_d) | \mu_{10} e^{iH(t-t_d)}
\]

\[
	imes (\mu_{01} + \mu_{10}) e^{-iH(t-t_d)} | \Psi_p(t_d) \rangle,
\]

where \( | \Psi_p(t_d) \rangle \) denotes the excited-state wave function prepared by the pump pulse. Note that \( P_s(t, t_d) \) can be interpreted as the nonlinear polarization for an impulsive (i.e., \( \delta \)-function) probe pulse. Combining Eqs. (15) and (17), we obtain for the corresponding impulsive emission spectrum

\[
I^s(t_d, \omega) = 2 \text{Im} \int_{0}^{\infty} \text{d}e^{i\omega t_d P^s(t + t_d, t_d)}.
\]

As has been discussed in detail elsewhere [9,51,52], \( I^s(t_d, \omega) \) represents an idealized time- and frequency-resolved emission spectrum, which is independent of laser-field properties and therefore, directly reflects the time evolution of the excited-state wave function. Furthermore, the frequency-integrated impulsive signal \( I^s(t_d) = \int \text{d}\omega I^s(t_d, \omega) \) is directly related to the time-dependent population probability of the optically excited electronic state [53]. Hence, the time evolution of \( I^s(t_d) \) directly monitors the nonadiabatic dynamics of the molecular system. Eqs. (16)–(18) represent the working equations used for the calculations presented below.

In the case of a cw probe field \( E_2(t) = e^{-i\omega t} \), we may relate the impulsive emission spectrum \( I^s(t_d, \omega) \) to the stationary fluorescence spectrum. In this case, the measured signal \( \sigma_F(\omega_s, \omega) \) is given by integrating Eq. (15) over all emission frequencies \( \omega \), thus yielding [46]

\[
\sigma_F(\omega_s, \omega) = \omega_s^3 \int_{-\infty}^{\infty} \text{d}t_d I^s(t_d, \omega).
\]

In accordance with physical intuition, Eq. (19) shows that the cw fluorescence spectrum may be obtained from the impulsive time-resolved fluorescence spectrum through an integration over all emission times.

We note in passing that the cw fluorescence spectrum is often approximated by the expression

\[
\sigma_F(\omega_s) = 2 \text{Re} \omega_s^3 \int_{0}^{\infty} \text{d}e^{i\omega t_d^d} P(\omega)
\]

\[
\times (\langle \Psi_1 | \mu_{10} e^{iH} \mu_{01} e^{-iH} | \Psi_1 \rangle).
\]

This ansatz assumes that the emission stems from a vibrationally relaxed excited electronic state \( | \Psi_1 \rangle \). As is discussed below, however, the fluorescence of rhodopsin reflects ultrafast nonstationary dynamics. The calculation of the fluorescence spectrum therefore requires a nonlinear formalism [e.g., Eqs. (16)–(19)] rather than the linear-response ansatz (20).

3. Computational results

To calculate absorption and emission spectra of rhodopsin, we employ a quantum-mechanical model description consisting of the two-mode two-state model \( H_M \) exhibiting nonadiabatic isomerization and a harmonic 23-mode model \( H_B \) of the remaining Raman-active vibrational modes of rhodopsin. As explained above, the dynamics of the vibronically coupled system \( H_M \) is coupled to the harmonic system \( H_B \) through a mean-field approximation. In order to account for the static effects of the protein environment, furthermore, a phenomenological inhomogeneous broadening (12) is assumed. Ab initio molecular-dynamics simulations of electronic spectra of organic chromophores in polar solvents have shown that the
averaging over numerous solvent geometries may result in quite large line-width broadening in the order of $\Gamma = 10^3 \text{ cm}^{-1} \ [54,55]$. To reproduce the width of the experimental electronic spectra of rhodopsin, a value of $\Gamma = 660 \text{ cm}^{-1}$ is assumed.

Let us first consider the cw absorption spectrum of rhodopsin. Fig. 2(a) compares the theoretical spectrum (full line) as obtained for the full 25-mode model and experimental data (dashed line) as adopted from Ref. [21]. While the calculation qualitatively matches the low-frequency side of the absorption band, it underestimates the width of the high-frequency part of the spectrum. As discussed in Ref. [21], the large asymmetry of the experimental spectrum is probably due to a higher-lying electronic state of rhodopsin which is centered around 23 000 cm$^{-1}$. This state is not included in the present model, i.e., the simulated spectrum solely reflects the absorption of the electronic “B” state of rhodopsin. To elucidate the various contributions to the large width of the absorption band, Fig. 2(b) compares the spectra obtained for the bare two-mode model, the inhomogeneously broadened two-mode model (dotted line) and the full 25-mode model of rhodopsin (full line). The discrete stick spectrum of the bare two-mode model is dense around the 0–0 transition at $\approx 20000 \text{ cm}^{-1}$ and exhibits a side maximum which results from the excitation of the vibronic mode $q$. The inhomogeneous broadening is seen to completely average out these fine structures and accounts for a large part of the overall width of the absorption band. Inclusion of the remaining 23 Condon-active modes results in further broadening and asymmetry of the spectrum.

We next discuss the resonance Raman spectrum of rhodopsin. Assuming an excitation wavelength of 488 nm, Fig. 3 compares the experimental spectrum as reported in Ref. [25] (upper panel) to the simulated spectrum (lower panel). As discussed in detail elsewhere [23–25], the experimental resonance Raman spectrum of rhodopsin mainly consists of a number of weak low-frequency peaks reflecting skeletal modes, an excitation of hydrogen out-of-plane modes at 970 cm$^{-1}$, various C–C stretch modes around $\approx 1200 \text{ cm}^{-1}$, and a prominent peak reflecting the ethylenic C=C stretch mode at 1550 cm$^{-1}$. In the simulation, the two shaded peaks reflect the isomerization mode and the coupling mode included in the vibronic-coupling Hamiltonian (1), while the remaining lines are due to the Condon-active modes included in the harmonic Hamiltonian (6). Since low-frequency skeletal modes are not adequately described by a harmonic ansatz, we have only included modes with frequencies larger than 500 cm$^{-1}$.

Let us first discuss the shaded peaks reflecting the two modes included in the isomerization Hamiltonian (1). The line at $\approx 500 \text{ cm}^{-1}$ corresponds to the isomerization mode $\varphi$, the line at $\approx 1470 \text{ cm}^{-1}$ corresponds to the coupling mode. Note that the unperturbed vibrational frequency of the coupling mode is 1532 cm$^{-1}$, i.e., one would expect that its fundamental line occurs at this point...
The significant frequency shift observed is a consequence of the strong vibronic interaction mediated by this mode. Furthermore, it is noted that in harmonic approximation the ground-state frequency of the isomerization mode is \( \omega_R = \sqrt{W_0/2m} = 238 \text{ cm}^{-1} \). The simulated peak at \( \approx 500 \text{ cm}^{-1} \) therefore corresponds to a double excitation of this mode. The missing fundamental line of this coordinate is an artifact of the symmetry of the isomerization potentials (5). Both inadequacies of the model could be easily corrected, e.g., by shifting the frequency \( \omega \) of the coupling mode and by relaxing the symmetry of Eq. (5).

The complete theoretical spectrum including the remaining Condon-active modes is seen to agree well with experimental data. This agreement does not come as a surprise, because the positions as well as the relative Raman intensities of these modes are a direct consequence of their frequencies and excited-state shifts, which have been adjusted to reproduce the experimental resonance Raman spectrum. ² It is noted, however, that the excited-state shifts employed are quite similar to the parameters obtained for an uncoupled harmonic model reported in Ref. [25]. The correct intensity ratios between these Raman lines and the Raman excitations obtained for the isomerization and coupling mode therefore indicate that the mean-field coupling between the two subsystems is a reasonable ansatz.

To complete the discussion of the resonance Raman spectrum, it is interesting to note that the most prominent low-frequency peak of the experimental spectrum is located around 250 cm\(^{-1}\), which is about equal to the frequency \( \omega_R \) of the fundamental line of the reaction coordinate. As \( \omega_R = \sqrt{W_0/2m} \), this frequency is solely determined by the parameters of the reaction mode, which were chosen in the model to satisfy the dynamics of the photoreaction, not to fit the resonance Raman spectrum. This result indicates that the experimentally observed Raman excitation at 250 cm\(^{-1}\) reflects large-amplitude motion important for the isomerization process. It should be stressed that, although the isomerization coordinate clearly represents the most important nuclear degree of freedom for the photoreaction, the resonance

² The frequencies \( \omega_j \) in (cm\(^{-1}\)) and dimensionless excited-state shifts \( c_j/\omega_j \) (in brackets) of the additionally included Condon-active modes of rhodopsin are: 792.8 (0.175), 842.8 (0.2), 866.2 (0.175), 882.4 (0.225), 970.3 (0.55), 976.0 (0.3), 997.0 (0.33), 1017.1 (0.45), 1089.6 (0.125), 1189.0 (0.175), 1214.7 (0.44), 1238.1 (0.5), 1267.9 (0.475), 1319.0 (0.238), 1359.0 (0.25), 1389.0 (0.25), 1428.4 (0.25), 1451.8 (0.225), 1486.2 (0.175), 1520.0 (0.25), 1572.8 (0.25), 1612.1 (0.225), 1629.2 (0.125), 1659.1 (0.225).
Raman spectrum exhibits only comparatively weak excitation of this mode.

Let us turn to the discussion of the fluorescence emission of rhodopsin as shown in Fig. 4. Following excitation at 473 nm, the experimental spectrum (dashed line) is centered at 15 500 cm\(^{-1}\), which corresponds to a Stokes shift of 4500 cm\(^{-1}\) [27]. To suppress background radiation, only the broad peak of the experimental emission band (dashed line) is displayed. Using Eqs. (16)–(19), we have calculated the fluorescence spectrum for the 25-mode (full line) and the two-mode (dotted line) model of rhodopsin, respectively. Both spectra exhibit a broad maximum which is followed by emission that extends to the far infrared, thus reflecting the decreasing electronic energy gap along the isomerization coordinate (cf. Fig. 1(a)). It is noted that far infrared emission has been found in numerous cis–trans photoisomerization systems, including rhodopsin [26,27,31], bacteriorhodopsin [56], and all-trans retinal [57]. While the width is comparable to experiment, the overall Stokes shift of the calculated spectra is too small. The fluorescence band of the two-mode model is hardly shifted at all, the fluorescence band of the 25-mode model is shifted by \(\approx 1000\) cm\(^{-1}\). The latter value reflects the reorganization energy \(E_R = \sum_j c_j^2/2\omega_j = 1200\) cm\(^{-1}\) of the additional Condon-active modes. Including only intramolecular vibrational modes of retinal, this simple model obviously misses an important aspect of the true photodynamics of rhodopsin (see discussion below).

Being integrated over all emission times (cf. Eq. (19)), the stationary fluorescence spectrum as shown in Fig. 4 merely yields time-averaged information. To obtain a more detailed picture of the fluorescence emission and the associated excited-state dynamics, it is therefore instructive to consider the time-resolved fluorescence spectrum. On the experimental side, two time-resolved measurements of the emission of rhodopsin have recently been reported. Using an excitation wavelength of 430 nm, fluorescence up-conversion experiments by Chosrowjan et al. observed a bi-exponential decay on a picosecond time scale [30]. Following resonant 500 nm excitation, pump-probe experiments by Haran et al. measured a red-shifted stimulated emission signal which decayed within \(\approx 100\) fs [31]. Since the former is off-resonant and the latter may be superposed by transient absorption, the time-evolution of the fluorescence of rhodopsin following resonant excitation is not yet clear. For this reason, we have restricted ourselves to the discussion of the impulsive emission spectrum defined in Eq. (18). As discussed above, this idealized time- and frequency-resolved signal is independent of laser-field properties and therefore reflects directly the excited-state dynamics of the system.

Fig. 5 shows the impulsive emission spectrum as obtained for (a) the 25-mode and (b) the two-mode model of rhodopsin. Both signals exhibit an ultrafast initial decay within 200 fs which is followed by prominent recurrences of the emission with a

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3 To approximate the initial excited wave function \(\Psi_P(t_d)\), a preparation by a Gaussian pump pulse of 20 fs duration has been assumed. Details on the calculations can be found in Ref. [46].

4 More precisely, at 430 nm the absorption of rhodopsin is presumably affected by a further excited electronic state [21]. Due to the moderate signal-to-noise ratio of the data reported in Ref. [30], moreover, it is not conclusive whether the signals are superimposed by oscillatory structures.
period of \( \approx 500 \) fs. As has been discussed in detail in Ref. [20], these recurrences reflect coherent wave-packet motion along the reaction-mode potential \( V^R_1(\phi) \). As illustrated in Fig. 1(a), the photoinduced wave packet thereby undergoes quasiperiodic motion on coupled adiabatic potential-energy surfaces. It has been suggested that this nonadiabatic wave-packet motion gives rise to the 60 cm\(^{-1} \) beating observed in femtosecond transient transmittance experiments [29]. Compared to the two-mode model, the recurrences of the 25-mode model are somewhat shifted in time and decay on a picosecond time scale. Similar to the stationary fluorescence, the emission of spectrum (a) is red-shifted to spectrum (b) by \( \approx 1000 \) cm\(^{-1} \).

4. Discussion

4.1. Interpretation of spectra in terms of excited-state wave-packet dynamics

It is instructive to discuss the results obtained above in terms of time-dependent wave-packet motion on adiabatic PESs. To this end, Fig. 1(a) shows a cut of the PESs along the reaction coordinate \( \phi \), assuming that \( q, x_j = 0 \). The photoreaction is initiated by a laser with frequency \( \omega_l \) which prepares a vibrational wave packet on the upper adiabatic PES. The wave packet follows the slope of the PES from the \( cis \) to the \( trans \) configuration until it bifurcates at the conical intersections at \( \phi = \pm \pi/2 \). It is clear from Fig. 1(a) that spontaneous emission can only arise during the time the wave packet is in the \( cis \) configuration. Furthermore, the figure indicates the possibility of quasiperiodic nonadiabatic wave-packet motion as is seen in the time-resolved fluorescence spectrum.

To illustrate the initial time evolution exhibited by the multidimensional model of rhodopsin, Fig. 1(b) shows a two-dimensional representation of the PESs consisting of the reaction coordinate \( \phi \) and the coordinate \( x = \{x_j\} \), which collectively represents all Condon-active modes. The coupling coordinate \( q \) is set to zero, i.e., the two-dimensional adiabatic PESs of the ground and excited electronic state intersect via a one-dimensional crossing seam. Apart from the optical transitions indicated by bold arrows, the figure also displays the minimum-energy path of the photoisomerization reaction. Starting out in the Franck–Condon region, the minimum-energy path follows the slope on the upper adiabatic PES. Since the descent is flat along \( \phi \) and steep along \( x \), the minimum-energy path first follows the direction of the Condon-active modes, before it continues along...
the isomerization coordinate. This indicates that the red-shifted maximum of the fluorescence spectrum is caused by the energy lowering of \( \sum c_j^2 / 2\omega_j \) due to the Condon-active modes.

It is interesting to compare this “static” picture of over-damped nuclear motion along the minimum-energy path with the true dynamical time evolution of the molecular system. Explicit calculations of the time-dependent excited-state wave function (data not shown) reveal that the wave packet is hardly ever found on the minimum-energy path. Following excitation to the Franck–Condon region, it rather performs several pronounced oscillations along the \( x \) coordinate on the upper adiabatic PES, before it disappears in the photochemical funnel of the intersecting PESs. Similar results have also been obtained in ab initio molecular-dynamics simulations of stilbene [11,12]. Due to the highly idealized topology of the PESs in our model, nevertheless, the wave packet follows the minimum-energy path at least in the average.

The analysis given above suggests that the femtosecond time evolution of retinal systems can be divided up in two stages: An initial phase that is dominated by high-frequency vibrational modes and occurs within tens of femtoseconds, and a subsequent phase in which the actual photochemical reaction may take place. As is well known from various ab initio studies [4,7,9,38,39], high-frequency vibrations such as the stretch modes of the C–C single and double bonds carry large Franck–Condon factors. These modes are therefore also responsible for large gradients of the excited-state PES in the Franck–Condon region, which in turn determine the time evolution during the first tens of femtoseconds. Experimental evidence for this picture of the ultrafast photoreponse of rhodopsins is provided by cw [2] and time-resolved [58] resonance Raman spectroscopy as well as by femtosecond transient transmittance experiments. Monitoring the femtosecond dynamics of the native system and of a \( C_{13} = C_{14} \) locked analog that cannot undergo photoisomerization, recent time-resolved experiments on bacteriorhodopsin have shown that within the first 100 fs the spectral evolution of the native and the locked system is essentially the same [59,60]. These experiments demonstrate that the initial excitation of high-frequency vibrational modes represents a generic aspect of organic photoreactions. It is an unresolved question yet, however, to what extent this motion is necessary to achieve isomerization and to access the conical intersection leading to the electronic ground state.

Let us now investigate the effects of the excited-state dynamics on the electronic spectra under consideration. Recalling that the total electronic dephasing time of the system is in the order of 10 fs and that absorption and Raman signals are determined during that time, it is clear that these spectra mainly reflect the initial wave-packet motion of the Condon-active modes. Since isomerization as well as electronic and vibrational relaxation has hardly started yet, cw absorption and resonance Raman spectra of systems with ultrafast electronic dephasing cannot yield much information on these processes. This is demonstrated, for example, by the finding that the Raman intensity of the reaction mode is rather weak, although this coordinate clearly represents the most important nuclear degree of freedom of the isomerization model. The fluorescence spectrum, on the other hand, in principle monitors the photoinduced wave-packet motion during the entire excited-state lifetime, which is typically much larger than the electronic dephasing time of the system. For this reason, the measured fluorescence quantum yield allows us to estimate the excited-state lifetime of the molecular system due to the nonadiabatic internal-conversion process. In many cases, however, the fluorescence spectrum yields only little additional information on the nonadiabatic photoreaction. For the model system under consideration, the Stokes shift of the emission maximum is a direct result of the Condon-active modes, which also show up in the resonance Raman spectrum. This analysis highlights the importance of femtosecond experiments for the interpretation of ultrafast photoreactions. As demonstrated in Figs. 1 and 5, the time- and frequency-resolved fluorescence spectrum directly monitors the time evolution of the excited-state wave function, thereby providing a real-time measurement of the nonadiabatic photoisomerization reaction.
4.2. Validity and limitations of the model

Let us next discuss possible deficiencies of the model description employed. While the 25-mode model is capable of reproducing the cw absorption and resonance Raman spectra of rhodopsin, it fails to account for the large Stokes shift of the fluorescence emission. Furthermore, the calculated time-resolved fluorescence persists on a time scale of several picoseconds, which seems to be at variance with the measured fluorescence quantum yield of $\gamma_f \approx 10^{-5}$ [26,27]. Assuming exponential kinetics and a radiative lifetime of 5 ns, this quantum yield corresponds to an excited-state lifetime $\tau_1$ in the order of 100 fs. It has to be kept in mind, however, that the calculated excited-state time evolution is by no means exponential but exhibits a rapid initial decay followed by recurrences. Furthermore, there are also experiments reporting a picosecond decay of the time-resolved fluorescence [30]. Nevertheless, from the available data on rhodopsin it seems reasonable to assume that the time-resolved fluorescence emission should decay within $\approx 1$ ps. This means that the model under consideration underestimates the overall electronic relaxation process in rhodopsin.

The first thing to check is the validity of the approximations employed in the dynamical calculations. As has been shown in Ref. [46], the approximate calculations of the fluorescence spectra through Eqs. (16)–(19) yields semiquantitative agreement with exact reference calculations. Hence, this approximation cannot account for the missing Stokes shift of the model description. Next, let us consider the validity of the time-dependent Hartree ansatz (7) employed to account for the additional Condon-active modes. Being a short-time approximation, the ansatz should reproduce the rapidly decaying correlation functions of the cw absorption and resonance Raman spectra. This is certainly true in the case of large inhomogeneous broadening giving rise to ultrafast electronic dephasing. For example, the inhomogeneous width $\Gamma = 660 \text{ cm}^{-1}$ employed in Eq. (12) results in a decay of these correlation functions on a 10 fs time scale. It is not that easy to check the applicability of the time-dependent Hartree ansatz to calculate the fluorescence spectrum, which in principle depends on the complete excited-state time evolution of the system. Test calculations have shown that the approximation may only qualitatively account for the long-time decay of the excited-state population [46]. This means that the fluorescence emission remaining after $\approx 2$ ps may be an artifact of the time-dependent Hartree ansatz. The missing Stokes shift, on the other hand, cannot be attributed to the Hartree approximation but is clearly a deficiency of the model itself. This is because the Stokes shift is essentially determined by the reorganization energy $E_R = \sum_j c_j^2/2\omega_j = 1200 \text{ cm}^{-1}$ of the Condon-active modes.

This brings us to the question to what extent the model itself is appropriate to describe the femtosecond dynamics rhodopsin. The assumptions employed in the model can be summarized as follows: (i) Only a single excited electronic state is involved in the reaction, (ii) the nonadiabatic photoisomerization process is described by a vibronic-coupling model involving two collective coordinates, (iii) the remaining Condon-active modes are modeled in harmonic approximation (6), and (iv) static effects of the protein environment are accounted for by a phenomenological broadening ansatz (12).

Although most ab initio calculations on models of retinal predict a single low-lying singlet state under isolated-molecule conditions [37–41], it is hard to rule out that further excited electronic states of retinal in rhodopsin are involved. As has been shown by multidimensional quantum-dynamical calculations [61], vibronic coupling of two low-lying singlet states may result in significant broadening of absorption and emission spectra as well as account for large Stokes shifts. Since there is no clear experimental or theoretical evidence that an additional electronic state is involved, the assumption of a single low-lying singlet state is considered as a working hypothesis.

The next main assumption, the construction of the model Hamiltonians (1) and (6), rests on some experience in the modeling of photoinduced relaxation dynamics associated with conical intersections [8,9], the results of extensive ab initio calculations on retinal and other cis–trans isomerizing systems [4–6,37–41], and on the fact that
the model is able to reproduce the complex time-
and frequency-resolved pump–probe spectra of
rhodopsin with a surprising accuracy [20]. Fur-
thermore, our strategy has been to keep the model
as simple as possible. Generalization of the model,
e.g., by including higher-order terms in the reac-
tion-coordinate potentials, may improve results
but also introduce additional parameters.

While we have adopted a microscopic descrip-
tion of the photoreaction of retinal, so far only
little attention has been paid to the interaction of
the retinal chromophore with the protein envi-
ronment. Although the environment enters the
theory via the parameterization of the reaction-
mode potentials (5) and a phenomenological
broadening term (12), no dynamical chromo-
phore–environment interaction has been consid-
ered. Ab initio molecular-dynamics simulations of
organic chromophores in polar solvents have
shown that excited-state energies of the solvated
chromophore can be significantly shifted com-
pared to isolated-molecule conditions [54,55].
Hence, the averaging over solvent conformations
does not only lead to a significant inhomogeneous
broadening of the spectra but may also result in a
large solvent-induced Stokes shift. Since the cis–
trans isomerization considered here involves
strong vibronic coupling of the ground and excited
electronic state, moreover, a shift of the electronic
gap directly affects the nonadiabatic relaxation of
the system. In particular, one expects that the re-
sulting increase of the overall level density give rise
to more efficient internal conversion into the
electronic ground state.

4.3. Microscopic description of the environment

The analysis suggests that an appropriate the-
etorical description of the femtosecond isomer-
ization in rhodopsin needs to account for the
interaction of retinal with the protein envi-
ronment in a microscopic manner. For example, one could
adopt a reduced density-matrix formulation for
retinal with bath correlation functions obtained
from a molecular-dynamics simulation of the
protein. Since that is beyond the scope of this
paper, we want to restrict ourselves to a simple
model calculation that aims to demonstrate the
main effects. To this end, we assume that the low-
frequency protein motion can also be modeled by
the harmonic ansatz (6). Frequencies \( \omega_i \) and cou-
pling constants \( c_j \) are chosen according to the
distribution for an Ohmic bath with the spectral
density

\[
J(\omega) = \sum_j c_j^2 \delta(\omega - \omega_j),
\]

where \( z \) denotes the overall chromophore–bath
coupling and the cut-off frequency \( \omega_c \) character-
izes the time-scale distribution of the bath. In
direct analogy to the theoretical formulation out-
lined above, the bath is represented by one hun-
dred vibrational modes which are coupled to the
chromophore via a time-dependent Hartree an-
satz. Choosing a relatively low cut-off frequency
\( \omega_c = 400 \text{ cm}^{-1} \) to account for the slow protein
motion, it is clear that at room temperature the
bath is thermally excited. Since this thermal aver-
aging represents a major computational effort in
the case of a quantum calculation with \( \approx 10^4 \)

basis states, however, we restrict ourselves in the fol-
lowing to the case of zero temperature. 5

We have calculated the absorption and emission
spectra for this simple model, which for further
reference will be called “spectroscopic model” of
the photoisomerization of retinal in rhodopsin.
Hereby, the overall chromophore–bath coupling
\( z = 16.3 \) has been chosen such that the model re-
produces the width of the experimental absorption
band of rhodopsin. The calculated absorption
spectrum thus obtained (data not shown) is very
similar to the case of the 23-mode model displayed
in Fig. 2(a). It should be pointed out, however,
that the spectroscopic model does not assume
any further phenomenological broadening and

5 Allowing for thermal excitation of the bath modes, the
spectra would show additional inhomogeneous broadening.
Readjusting the overall chromophore–environment coupling,
this effect is readily compensated to reproduce the width of the
experimental spectra. While details of the calculation such as
the exact position of the recurrences or the long-time decay of
the fluorescence may not be correct, it is nevertheless expected
that the model qualitatively accounts for the main effects of the
chromophore–environment interaction.
therefore affords a completely microscopic description of the photodynamics.

While the resonance Raman spectrum hardly changes compared to Fig. 3(b), the fluorescence emission of the spectroscopic model significantly differs from the fluorescence of the two- and 23-mode models shown in Fig. 5. As a representative example, Fig. 6 shows the impulsive time- and frequency-resolved fluorescence spectrum obtained for the spectroscopic model of rhodopsin. Again, the signal exhibits a rapid initial decay within ≈100 fs which is followed by recurrences of the emission. Compared to the case of the two- and 23-mode models shown in Fig. 5, however, the emission exhibits a much larger Stokes shift of about 4000 cm\(^{-1}\). Furthermore, overall emission decays faster due to the larger level density of the spectroscopic model. It is interesting to compare this calculation to recent femtosecond experiments on bacteriorhodopsin [60]. Recorded at 800 and 950 nm, the transient transmission observed is believed to reflect solely excited-state dynamics. The experiments showed that the onset of the 950 nm signal is delayed compared to the onset of the 800 nm signal, which can be readily explained by the dynamical redshift exhibited by the model calculation in Fig. 6. Furthermore, the experiment shows a similar transient beating of the emission signal.

5. Concluding remarks

We have outlined a microscopic model description of the femtosecond photodynamics and the associated secondary emission of rhodopsin. The formulation consists of a two-state two-mode model describing the nonadiabatic photoisomerization of retinal and of a harmonic multi-mode ansatz accounting for the remaining Raman-active modes. The coupling of the two subsystems is achieved via a mean-field approximation. The resulting model has been found to satisfactorily reproduce experimental absorption and resonance Raman spectra of rhodopsin. It failed, however, to account for the large Stokes shift and the ultrafast decay of the fluorescence emission observed for rhodopsin. For this reason, we have extended the model by including a bath of low-frequency vibrational modes that account for the coupling of retinal to the protein environment. It has been shown that the resulting formulation is able to explain the measured Stokes shift as well as the fluorescence quantum yield.

Employing these model descriptions, we have studied in some detail to what extent ultrafast nonadiabatic isomerization processes are reflected in the secondary emission of the molecular system. The information obtained by cw absorption and resonance Raman experiments is limited by ultrafast electronic dephasing processes due to intramolecular relaxation as well as inhomogeneous broadening. In the case of rhodopsin, for example, the total electronic dephasing time is in the order of 10 fs. Since isomerization as well as electronic and vibrational relaxation has hardly yet started, cw absorption and resonance Raman spectra of systems with ultrafast electronic dephasing cannot yield much information on these processes. In particular, it is difficult to find out to what extent the Condon-active modes observed in the resonance Raman spectrum participate in the photochemical process of interest. This is demonstrated, for example, by the finding that the Raman intensity of the reaction mode is rather weak, although this coordinate clearly represents the most important nuclear degree of freedom of the model.

The fluorescence spectrum, on the other hand, in principle monitors the photoreaction during the
entire excited-state lifetime, which is typically much larger than the electronic dephasing time of the system. Hereby, the Stokes shift of the emission reflects the variation of the electronic energy gap during the photoreaction, while the fluorescence quantum yield allows us to estimate the excited-state lifetime of the molecular system. Being averaged over all emission times, however, the stationary fluorescence spectrum may yield only little direct information on the nonadiabatic photoreaction under consideration. Therefore, much more is to be learned when the dynamical evolution of the fluorescence emission is measured. As demonstrated in Figs. 5 and 6, the time- and frequency-resolved fluorescence spectrum directly monitors the time evolution of the excited-state wave function, thereby providing a real-time measurement of the nonadiabatic photoreaction. In the case of rhodopsin, furthermore, the recurrences of time-resolved spectrum clearly reveal the motion of the vibrational wave packet along the reaction coordinate. It may be noted that the essential features of the photoreaction such as initial decay and recurrences of the excited-state population are already present in the simple effective two-state two-mode model proposed in Ref. [20].

The femtosecond photoisomerization of retinal in rhodopsin represents a paradigm of an ultrafast photochemical reaction in a biophysical system [21,22]. Therefore, it may be expected that methodology as well as results presented for this case will also apply to other complex photoreactive molecular systems.

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References