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Review

Mechanisms of energy dissipation and ultrafast primary events in photostable systems: H-bond, excess electron, biological photoreceptors

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ABSTRACT

The fundamental property of biological systems is photostability. Without photostability no life would be possible. Molecular structures responsible for harvesting of the solar energy must be photostable and resistant to photo-induced chemical changes or must find a way for a recovery. To answer the questions about the photostability we have to understand mechanisms of relaxation and energy dissipation upon an optical excitation. There is a common agreement that such channels are provided by some special features of the potential energy surfaces including the conical intersections. The mechanism that leads to decrease in the energy gap between the excited-state potential and the ground state energy surfaces is related to the coupling between the excited state (electronic or vibrational) and the intramolecular and intermolecular vibrational modes. When the potential energy surfaces approach each other nonadiabatic transitions are facilitated by their close proximity and the rate of radiationless transitions increases. The mechanism seems to be universal both for simple species such as H-bond systems, solvated electrons, and biologically important photoreceptor proteins such as bacteriorhodopsin. In order to study energy dissipation and dynamical alterations in the structure, a system is triggered with laser and monitored with excellent time-resolution. Ultrafast spectroscopies have played an important role in the study of a number of biological processes and have provided unique information about primary events and the mechanism of energy relaxation. Biological activity of molecules is frequently initiated by elementary chemical reactions such as energy and electron transfer, *cis–trans* isomerizations, or proton transfer. Many of these reactions are usually very fast and efficient and occur on picosecond and femtosecond timescales. This paper reviews recent progress of understanding light-energy collection and dissipation, with a special emphasis on the role of the vibronic coupling in H-bonded systems, solvated electrons and light-initiated biological photoreceptors. We will concentrate on the spectroscopic methods based on the linear and nonlinear responses such as the time resolved coherent anti-Stokes Raman spectroscopy (CARS) and the pump-probe transient femtosecond absorption spectroscopy. Detailed understanding the paths of energy dissipation will reveal mechanisms that mediate light-induced signal transduction as well as the role of photoreceptors in photostability protection and reparation mechanisms in living cells.

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1. Introduction

Upon absorbing a photon of excitation light a molecule is promoted to higher energy states. From the excited states the molecule is then able to "relax" back to the ground state through radiative (fluorescence or phosphorescence) or non-radiative (heat) pathways according to the mechanisms depicted by a Jablonski diagram [1]. All molecules with quantum yields below 1 are accompanied by energy loss (energy dissipation) due to loss some vibrational energy to the surrounding environment (bath) or due to photochemical reactions (including bleaching and quenching). If radiative energy relaxation with a high quantum yield of fluorescence and relatively long excited-state lifetimes occurs, there is a great chance that profound chemical rearrangements occur leading to dangerous photoreactions in living cells reducing photostability protection. In contrast, when very fast nonradiative processes with particularly short excited-state lifetimes take place, the fluorescence is quenched efficiently, the energy of the photons is quickly dissipated into small quanta of heat before more profound chemical or structural rearrangements occur. This pathway of ultrafast nonradiative decay occurs in many H-bonded biological systems including DNA bases [2–4] and will be briefly discussed in Section 3.1.

The second pathway to avoid photochemical reactions in biological systems, in case when the energy of photons is sufficient to ionize molecules, is a fast relaxation of an excess electron followed by a recombination to the ground electronic state. An electron attachment to molecules, microsolvation of radical clusters and many other reactions with an excess electron involvement play an important role in biological systems [5]. The relevance of this mechanism for biological systems is briefly discussed in Section 3.2.

The third way to defend against the harmful energy of photons is the photocycle reaction observed in bacteriorhodopsin. In this pathway of energy dissipation a photoreceptor undergoes chemical rearrangements, but due to periodic nature of the events full recovery takes place.

These three paths illustrate how biological systems acclimate effectively to maintain photostability. Common feature of them is the capability for a fast recovery from the excited state to the ground state due to the energy dissipation by a mechanism of vibronic coupling. We have shown that the vibronic coupling is very effective in H-bonded systems [6,7], for an excess electron [8,9], and bacteriorhodopsin [10,11] and determines most of features in static and time resolved spectra including the band width, intensity, band shape and the frequency shift.

To explain briefly the idea of the vibronic coupling let us recall that energy dissipation upon an optical excitation is facilitated by the close proximity of potential energy surfaces. The rate for transitions depends on the energy gap ΔE. When the potential energy surfaces approach each other the Born–Oppenheimer (BO) approximation breaks down. It denotes that the motion of electrons and nuclei cannot be separated any longer, and as a result the Schrödinger equation cannot be separated into an electronic and nuclear part. The total wave function cannot be written as a product of electronic and nuclear wave functions for a given electronic state. When the electronic states approach each other, more than one of electronic states should be included to describe the total wave function. The strength of the coupling between the different electronic states is inversely proportional to the energy difference between them. Thus, the smaller the difference the larger the coupling. If $\Delta E = 0$ the coupling constant goes to infinity. When the coupling becomes infinite we observe the singularity in the potential energy landscape which is called the conical intersection. Two adiabatic potential energy surfaces cross (Fig. 1). Thus, the interstate coupling facilitates fast radiationless transitions between the surfaces. The coupling is often called the vibronic coupling because the coupling between different electronic states results in the coupling between electronic states and vibrational modes. When nonadiabatic terms of the coupling are relatively small we can still work in BO approximation. In this case, the coupling of electronic states can be included by assuming that the frequency of the electronic transition $\omega_{01}(Q)$ depends on the vibrational coordinate Q

$$\omega_{01}(Q) = \omega_{01}^{0} + bQ$$

where b describes the strength of the coupling and characterizes the relative displacement of the minima of the potential energy curves $E_0(Q)$ and $E_1(Q)$. The mechanism of the vibronic coupling is illustrated in Fig. 1.

We have applied the model of the vibronic coupling to calculate the absorption coefficient in the linear and nonlinear regime, which correspond to the signals obtained by the stationary absorption spectroscopy and the transient absorption by the pump-probe spectroscopy, respectively. For the linear regime the intensity $I(\omega)$ is given by

$$I(\omega) = (2\pi)^{-1}\left[1 - \exp\left(-\frac{\hbar\omega}{kT}\right)\right]\int_{-\infty}^{+\infty} dt e^{i\omega t}\langle M_{01}^{+}(0)M_{10}(t)\rangle \qquad (1)$$

where M_{01} is the matrix element of the dipole moment operator between the ground and the first excited electronic state. To calculate $I(\omega)$ we have to know the time evolution of the dipole moment operator $M_{10}(t)$. The symbol $\langle M_{01}(0)M_{10}(t)\rangle$ denotes averaging over bath.

For nonlinear regime the intensity of the hole burning profile is given by [12]

$$\begin{aligned} S_{HB}(\omega_1\omega_2\tau) = {} & \left(\frac{1}{\hbar}\right)^3 2\omega_2\int_0^\infty 2\omega_1\int_0^\infty dt_1\int_0^\infty dt_3 \\ & \times [e^{i(\omega_2 t_3 + i\omega_1 t_1)}\chi(t_3+t_1)[R_1^H(t_3,\tau,t_1) + R_4^H(t_3,\tau,t_1)]] \\ & + e^{(i\omega_2 t_3 - i\omega_1 t_1)}\chi(t_3-t_1)[R_2^H(t_3,\tau,t_1) + R_3^H(t_3,\tau,t_1)] \end{aligned} \qquad (2)$$

where ω_1 and ω_2 are the frequencies of the pump and probe pulses, respectively whereas τ is the time delay between the pump and the probe pulses. The inhomogeneous broadening contributes through the factor χ. The details are presented in Ref. [12]. We have applied the theoretical model of the vibronic coupling to explain the spectroscopic properties of H-bonded systems [6,7], solvated electron [8,9,13–15], bacteriorhodopsin and its retinal modified analogs [10,11].

2. Materials

Native BR is grown from a cell line of *Halobacterium salinarum*. The purple membrane typically has an absorbance ratio of 1.5 (protein absorbance (280 nm)/retinal absorbance (570 nm)) and is used without further purification. Artificial BR pigments containing modified-retinal chromophores (i.e., BR5.12, BR6.11 and BR6.9) are prepared by first isolating the bacterio-opsin protein using a bleaching procedure, and then reconstituting the protein with the modified-retinal chromophore [16].

3. Molecular mechanisms of energy dissipation in photostable systems

3.1. H-bonded systems

H-bonds are used to stabilize and determine the structure of large macromolecules like proteins and nucleic acids. They are involved in the mechanism of enzyme catalysis. Their