



Research paper

Is back-electron transfer process in Betaine-30 coherent?



Shahnawaz Rafiq, Gregory D. Scholes*

Frick Chemistry Laboratory, Princeton University, NJ 08542, United States

ARTICLE INFO

Article history:

Received 2 February 2017

In final form 8 March 2017

Available online 9 March 2017

Keywords:

Electron transfer

Coherent dynamics

Marcus inverted region

High frequency quantum vibrations

Incoherent transfer

Bixon-Jortner model

ABSTRACT

The possible role of coherent vibrational motion in ultrafast photo-induced electron transfer remains unclear despite considerable experimental and theoretical advances. We revisited this problem by tracking the back-electron transfer (bET) process in Betaine-30 with broadband pump-probe spectroscopy. Dephasing time constant of certain high-frequency vibrations as a function of solvent shows a trend similar to the ET rates. In the purview of Bixon-Jortner model, high-frequency quantum vibrations bridge the reactant-product energy gap by providing activationless vibronic channels. Such interaction reduces the effective coupling significantly and thereby the coherence effects are eliminated due to energy gap fluctuations, making the back-electron transfer incoherent.

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1. Introduction

Recent work has suggested that effects collectively called ‘coherences’ might be harnessed much more efficiently than previously imagined, even when electronic coupling is not such a dominant participant [1–7]. Fast charge separation in photosynthetic reaction centers [8,9], conjugated polymer-fullerene blends and molecular triads have been proposed to involve quantum coherence effects [10–13]. Most of these systems undergo ultrafast electron transfer before vibrational thermalization and hence under these circumstances, intramolecular vibrations can actively participate in driving the reaction [14–17]. Thereby, high frequency intramolecular vibrational motions can be exploited to facilitate efficient charge separation especially when vibrational levels bridge electronic gaps [18].

Betaine-30, also known as Reichardt’s dye, is a solvatochromic probe, which undergoes ultrafast back-electron transfer (bET) reaction after photoexcitation [19–23]. The locally excited (or Franck-Condon) state decays rapidly via a back-electron transfer process (Fig. 1). The bET rate constant ranges from sub-picoseconds to a few-picosecond timescale with a strong dependence on the solvent environment [24]. The rate of bET process is faster than predicted by conventional Marcus theory due to involvement of high frequency intramolecular modes in the charge transfer process in the Marcus inverted region [14,21,25–29]. Jortner and Bixon, for instance, summarize how vibrational levels multiply the number of reaction paths and some of these channels can have lower

activation energies than predicted from pure electronic states [14]. Here, in order to examine further the possible role of vibrations along the reaction coordinate, we used broadband pump probe spectroscopy with short pump/probe pulses of ca. 14 fs to generate and measure the response of vibrational wavepacket dynamics in the excited state during the timescale of the bET process. Two solvents were chosen; acetonitrile and methanol. The bET time constant in Betaine-30 is 1.2 ps and 3.1 ps in acetonitrile and methanol respectively [24].

In acetonitrile, early time transient spectra reveal the presence of excited state absorption (ESA) in the green spectral region with a maximum around 530 nm, also observed by Ernsting and coworkers [24]. The ground state bleach signal peaked around 650 nm at early time delays shifts towards blue due to obfuscation by the overlapping ESA signal, and decays during this timescale. The decay of the ESA and the bleach signal is in accordance with the depopulation of the excited state to the charge transfer ground state through internal conversion. In methanol, ESA covers all the probe spectral window. Ernsting and coworkers [24] have also proposed the existence of a dark state lying between the directly excited and the ground state. It has been found that stimulated emission, peaked at 750 nm is shifted from the absorption maximum by ca. $\sim 3000\text{ cm}^{-1}$, which indicates strong contribution from vibrational relaxation of high frequency intramolecular modes. In both these fast-relaxing solvents, the electron transfer rate is solvent controlled in accord with the Bixon-Jortner version of electron transfer theory. However, the predicted rates match the experimental values only after the consideration of averaged high-frequency accepting mode, when the electronic coupling matrix element is Franck-Condon dressed of the particular vibrational

* Corresponding author.

E-mail address: gscholes@princeton.edu (G.D. Scholes).

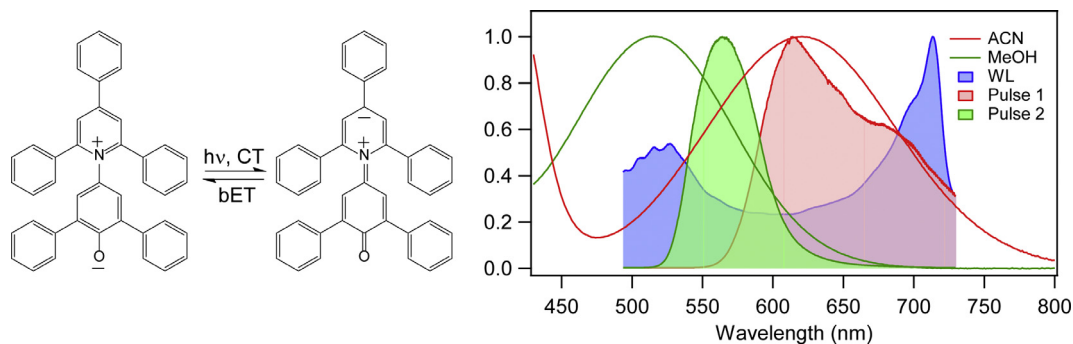


Fig. 1. Structures indicating photoinduced charge transfer and back-electron transfer process in Betaine-30. Absorption spectra of Betaine-30 in acetonitrile (red curve) and methanol (green curve) are normalized to unity. The pump pulse spectra used for Betaine-30 solution in acetonitrile and methanol are shown as shaded red and green semi-transparent curves filled to zero. White light spectrum is shown as blue semi-transparent curve. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

quantum [14]. Briefly, electron transfer rates match with the experimental values for both the Bixon-Jortner and Walker-Barbara models in fast-relaxing solvents. It is the slow relaxing solvents, when Bixon-Jortner model predicts slower electron transfer rates than the measured values [19,30].

In addition to high frequency quantum vibrations, low frequency modes can participate through anharmonic coupling to the high frequency modes to create a highly reactive potential energy landscape. As per this model of Ernstring and coworkers [24], photoexcitation of the charge transfer ground state promotes the molecules to the neutral Franck-Condon state, initiating relaxation of high frequency modes on a 10-fs timescale. Afterwards, simultaneous solvation and conformational rearrangement of the molecule in the excited state promotes back-electron transfer in the Marcus inverted region.

Owing to the extremely short time scale of the electron transfer process in the adiabatic limit (faster than longitudinal solvent relaxation in certain solvents), involvement of the intramolecular reaction coordinate besides the solvent coordinate becomes pertinent and coherent vibrational dynamics might play a role in the back-electron transfer. Our goal here is to delve into the coherent nuclear dynamics involved in the back-electron transfer process of Betaine-30 and explore possible implications for promoting the rapid electron transfer in the Marcus-inverted region. The temporal and spectral information of the nuclear wavepacket as a function of different timescales of bET is expected to reveal more information on the possible role of high frequency modes in coupling to the bET process.

2. Experimental section

Betaine-30 solution in acetonitrile and methanol was prepared with an optical density of ~ 0.25 at its absorption maximum of 621 nm in acetonitrile and 515 nm in methanol in a 1 mm glass cuvette. Two pump laser spectra were used due to large difference in the transition energies in two solutions. The normalized absorption spectra and the corresponding pump and probe pulse spectra employed for the two solutions are shown in Fig. 1.

For broad-band transient absorption spectroscopic measurements, the experimental setup is explained in detail elsewhere; [31] however, a brief description is provided here. Pulsed laser light (800 nm, 150 fs) from a Ti:sapphire seeded regenerative amplifier (Spectra-Physics, Spitfire) was used to pump a home-built nonlinear optical parametric amplifier (NOPA). The desired NOPA pulse spectrum was compressed into a folded grating compressor and a two-prism compressor, respectively. The two NOPA spectra; one extending from 560 to 730 nm and other extending

from 515 to 670 nm were compressed to ca. 14 fs and 15 fs full width at half maximum respectively as diagnosed with polarization-gated frequency resolved optical grating (PG-FROG) in a 1 mm path length methanol filled cuvette. The compressed output was split into three beams by a wedge beam splitter. Two beams reflected from the front and back surfaces of the wedge, having ca. 1% of total incident intensity, were used as reference and probe beams, respectively. The transmitted beam was used as a pump beam and had a translation stage in its path to control the arrival of pump pulses with respect to the probe pulses.

For the transient absorption measurements with a broader probe spectral range, a separate white light arm was put in place and before sending the generated white light continuum from 1 mm sapphire plate into the transient absorption setup, it was pre-compressed by inserting a pair of chirped mirrors in its path to remove the temporal chirp [32]. In general, the measurements can also be performed without putting chirped mirrors in the white light path, as it does not affect the temporal resolution of individual wavelengths. The normalized differential intensity (not the differential absorbance) of the probe as a function of its wavelength along the waiting time ($t_2^{max} = 3$ ps) is measured in the usual way. The positive-signed transient features represent GSB or SE and negative features indicate ESA. The main purpose of using white light continuum as a probe in addition to the replica of NOPA spectrum was to access the spectral region beyond the corresponding NOPA spectrum.

3. Results and discussion

Time resolved pump probe spectroscopy with broadband ultra-short pulses not only creates population in the electronic excited state, but also generates a superposition of vibrational states along all the accessible Franck-Condon active vibrational modes in the molecule [33–35]. Owing to the displaced nature of the excited state potential with respect to the ground state, this superposition of states—called a wavepacket oscillates along the minimum of the potential and manifests as ripples on top of population dynamics. To extract the oscillatory response of the wavepacket overlapped with the population dynamics, exponential fitting was performed at each probe wavelength and thereby slow varying electronic population contributions were removed, leaving behind residuals containing all the rapidly oscillating vibrational contributions, as has been implemented previously in our work [17,31,32]. The fitting is started at 50 fs to isolate the coherent artifact arising from pulse overlap effects. The residuals at each probe wavelength were Fourier transformed to convert the time-domain oscillatory signal into the frequency domain vibrational coherences.

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