

1. Анкетные данные

ФИО: Назаров Алексей Евгеньевич

Год рождения: 1994 г.

Образование:

Волгоградский государственный университет, 2016 г., бакалавр по направлению «Физика».

Волгоградский государственный университет, 2018 г., магистр по направлению «Физика».

2. Образовательный опыт до поступления в аспирантуру



РОССИЙСКАЯ ФЕДЕРАЦИЯ
Федеральное государственное автономное образовательное учреждение
высшего образования "Волгоградский государственный университет"
Волгоград

**ДИПЛОМ
МАГИСТРА
С ОТЛИЧИЕМ**

103418 1029023

ДОКУМЕНТ ОБ ОБРАЗОВАНИИ И О КВАЛИФИКАЦИИ

Регистрационный номер
ФКФм-004
Дата выдачи
05 июля 2018 года

Настоящий диплом свидетельствует о том, что
**Назаров
Алексей Евгеньевич**
освоил(а) программу магистратуры по направлению подготовки
03.04.02 Физика
и успешно прошел(ла) государственную итоговую аттестацию
Решением Государственной экзаменационной комиссии
присвоена квалификация
Магистр

Протокол № 4 от 25 июня 2018 г.

Председатель
Государственной
экзаменационной комиссии
Руководитель организации,
осуществляющей образовательную
деятельность



Завьялов Д. В.
Тараканов В. В.

РОССИЙСКАЯ
ФЕДЕРАЦИЯ



Федеральное
государственное
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учреждение высшего
образования
"Волгоградский
государственный
университет"
Волгоград

ПРИЛОЖЕНИЕ
к ДИПЛОМУ
магистра с отличием
103418 1033929

Регистрационный
номер

ФКФм-004

Дата выдачи

05 июля 2018 года

1. СВЕДЕНИЯ О ЛИЧНОСТИ ОБЛАДАТЕЛЯ ДИПЛОМА

Фамилия **Назаров**

Имя **Алексей**

Отчество **Евгеньевич**

Дата рождения **25 марта 1994 года**

Предшествующий документ об образовании или
об образовании и о квалификации

Диплом бакалавра, 2016 год

2. СВЕДЕНИЯ О КВАЛИФИКАЦИИ

Решением Государственной экзаменационной
комиссии присвоена квалификация

Магистр

03.04.02 Физика

Срок освоения программы магистратуры в очной форме
обучения

2 года

БЕЗ ДИПЛОМА НЕДЕЙСТВИТЕЛЬНО

3. СВЕДЕНИЯ О СОДЕРЖАНИИ И РЕЗУЛЬТАТАХ ОСВОЕНИЯ
ПРОГРАММЫ МАГИСТРАТУРЫ

Наименование дисциплин (модулей) программы, вид практики	Количество зачетных единиц/ академических часов	Оценка
Современные технологии программирования	2 з.е.	отлично
Философские вопросы естествознания	2 з.е.	зачтено
Компьютерное моделирование физико-химических процессов	3 з.е.	отлично
Физика неупорядоченных структур	2 з.е.	отлично
Иностранный язык в профессиональной сфере	2 з.е.	зачтено
Математические методы теоретической физики	3 з.е.	отлично
Алгоритмы дискретной математики	3 з.е.	зачтено
Компьютерная математика	3 з.е.	отлично
Современные проблемы физики	2 з.е.	отлично
Элементарные химические процессы	3 з.е.	отлично
Web-программирование	2 з.е.	отлично
Компьютерная графика	3 з.е.	отлично
История и методология физики	2 з.е.	зачтено
Компьютерное моделирование эволюционных уравнений	3 з.е.	отлично
Специальный физический практикум: Компьютерные методы моделирования физических явлений	4 з.е.	отлично
Вариационный принцип в теоретической физике	2 з.е.	зачтено
Методы обработки изображений	2 з.е.	зачтено
Механика сплошных сред	3 з.е.	отлично
Дополнительные главы высшей алгебры	3 з.е.	отлично
Молекулярная спектроскопия	3 з.е.	отлично
Физика плазмы	2 з.е.	отлично
Квантовые вычисления	3 з.е.	отлично
Практики	54 з.е.	х
в том числе:		
Учебная практика, педагогическая практика	6 з.е.	отлично
Производственная практика, научно-исследовательская практика	24 з.е.	отлично
Производственная практика, преддипломная практика	15 з.е.	отлично
Производственная практика, научно-исследовательская работа	9 з.е.	отлично
Государственная итоговая аттестация	9 з.е.	х
в том числе:		
Государственный экзамен	х	отлично
Выпускная квалификационная работа (магистерская работа) "Моделирование сверхбыстрой кинетики фотоиндуцированного переноса электрона"	х	отлично
Объем образовательной программы	120 з.е.	х
в том числе объем работы обучающихся во взаимодействии с преподавателем:	728 час.	х

Наименование дисциплины (модулей) программы, вид практики	Количество зачетных единиц/ академических часов	Оценка

4. КУРСОВЫЕ РАБОТЫ (ПРОЕКТЫ)	ОЦЕНКА

5. ДОПОЛНИТЕЛЬНЫЕ СВЕДЕНИЯ

Форма обучения: очная

Направленность (профиль) образовательной программы: "Компьютерная физика"

Руководитель организации,
осуществляющей образовательную
деятельность



Тараканов В. В.

БЕЗ АНТИСЛОНА НЕДЕЙСТВИТЕЛЬНО

Настоящее приложение содержит 4 страниц

3. Достижения в результате освоения основной образовательной программы подготовки научно-педагогических кадров в аспирантуре

Предполагаемая тема исследования: «Закономерности кинетики сверхбыстрого переноса заряда в донор-акцепторных парах в растворах».

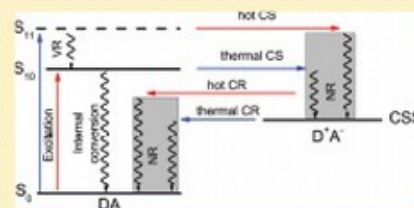
4. Достижения в научно-исследовательской деятельности

Effect of Intramolecular High-Frequency Vibrational Mode Excitation on Ultrafast Photoinduced Charge Transfer and Charge Recombination Kinetics

Alexey E. Nazarov, Vadim Yu. Barykov, and Anatoly I. Ivanov*

Volgograd State University, University Avenue 100, Volgograd 400062, Russia

ABSTRACT: A model of photoinduced ultrafast charge separation and ensuing charge recombination into the ground state has been developed. The model includes explicit description of the formation and evolution of nonequilibrium state of both the intramolecular vibrations and the surrounding medium. An effect of the high-frequency intramolecular vibrational mode excitation by a pumping pulse on ultrafast charge separation and charge recombination kinetics has been investigated. Simulations, in accord with experiment, have shown that the effect may be both positive (the vibrational mode excitation increases the charge-transfer rate constant) and negative (opposite trend). The effect on charge separation kinetics is predicted to be bigger than that on the charge recombination rate but nevertheless the last is large enough to be observable. The amplitude of both effects falls with decreasing vibrational relaxation time constant, but the effects are expected to be observable up to the time constants as short as 200 fs. Physical interpretation of the effects has been presented. Comparisons with the experimental data have shown that the simulations, in whole, provide results close to that obtained in the experiment. The reasons of the deviations have been discussed.



I. INTRODUCTION

Currently there is a growing interest in the study of the kinetics of electron transfer occurring from nonthermalized states. Typically, the kinetics of such reactions is rather complex, in contrast with thermal reactions, which are characterized by a single parameter—the rate constant.^{1–3} A quantitative description of processes proceeding from nonthermalized states requires the development of relevant theories. At the same time requirements for these theories are immeasurably higher because they have to reproduce complex kinetics, which cannot be reduced to a few rate constants. Nevertheless, the complexity of the kinetics of nonthermal processes provides us certain benefits because its quantitative description demands improvement of current theories, and their elaboration leads to a deeper understanding of the microscopic mechanisms of not only nonequilibrium but also equilibrium reactions.

Photoinduced charge transfer can proceed on a time scale comparable to the relaxation times of the nuclear subsystem of the reactants and the surrounding medium.^{4–8} In such ultrafast processes the chemical transformation effectively competes with the nuclear relaxation.^{9–15} One of the manifestations of this competition is the spectral effect (a dependence of the charge-transfer rate constant on the excitation pulse carrier frequency) that was observed in ultrafast charge recombination of excited donor–acceptor complexes in polar solvents.^{10,11,14} Supposing the charge recombination to proceed from a nonequilibrium state of the surrounding medium created by the pumping pulse and the relaxation of intramolecular high-frequency vibrational modes to occur at considerably shorter

time scales than both the medium relaxation and charge recombination, the spectral effect was rather well described in the framework of the stochastic multichannel point-transition model.¹⁴

The excitation of the intramolecular high-frequency modes by a pumping pulse is also expected to alter charge-transfer kinetics when the charge transfer proceeds on the time scale comparable to that of the intramolecular vibrational relaxation. Although there is a lot of experimental evidence of manifestations of the excited states of high-frequency vibrations in the charge-transfer dynamics,^{9,13,15,16–23} only recently first systematic investigation of the influence of the vibrational excited states on the charge-transfer dynamics has been reported.²⁴ These experiments have discovered that the excitation of high-frequency vibrational modes can considerably change not only the forward electron transfer rate but also the rate of the backward electron transfer into the ground state.²⁶

Theoretical investigations of the effect of intramolecular high frequency vibrational modes excitation on photoinduced electron transfer also have been carried out.^{27–29} In particular, the excitation of high-frequency vibrational modes was shown to increase the photoinduced electron-transfer rate in both regions of strong and weak exergonicity and to decrease at moderate exergonicity in the vicinity of the barrierless region.^{28,29}

Received: January 18, 2016

Revised: March 7, 2016

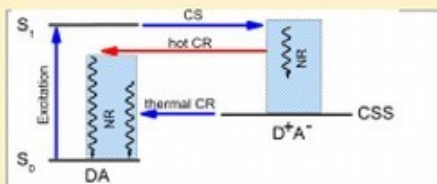
Published: March 8, 2016

Free-Energy-Gap Law for Ultrafast Charge Recombination of Ion Pairs Formed by Intramolecular Photoinduced Electron Transfer

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ABSTRACT: In this article, regularities of ultrafast charge recombination (CR) kinetics in photoinduced intramolecular electron transfer in polar solvents are studied. The kinetics of charge separation and ensuing ultrafast CR are simulated within the framework of the multichannel stochastic model. This model accounts for the reorganization of both the solvent and a number of intramolecular high-frequency vibrational modes. The solvent relaxation is described in terms of two relaxation modes. For ultrafast CR, the free-energy-gap law strongly depends on the parameters: the electronic coupling, reorganization energy of intramolecular high-frequency vibrational modes, and the vibrational and solvent relaxation times. The semilog dependence of the CR rate constant on the free-energy gap varies from a parabolic shape to a nearly linear one with increasing the electronic coupling and decreasing the vibrational relaxation time. The dynamic solvent effect in CR is predicted to be large in the area of strong exergonicity and small in the area of weak exergonicity. This regularity is opposite to that observed for the thermal reactions.



■ INTRODUCTION

Light-induced charge separation is one of the most common processes when photoexcitation is exploited as the driving force for photochemical transformations. Thus, photoinduced electron transfer (ET) is of paramount importance in both fundamental science and technological applications.^{1–7} Such processes often have low efficiency because of the short lifetime of the charge-separated states (CSSs), which considerably inhibits a quantum yield of the desired products. Typically, back electron transfer (BET) is responsible for the decay of ion pairs generated in the intermolecular photoinduced electron-transfer reactions. Hence, it is essential to establish strategies to achieve long-lived photoinduced CSSs. The main obstacle is that the dependencies of the ultrafast BET rate constants on many controlling parameters are still unknown because a detailed mechanism of BET reactions is mostly not understood in spite of their importance in the control of the photochemical process effectiveness.⁷ The essential feature of the ultrafast charge-transfer mechanism is a strong nonequilibrium of the nuclear subsystem. The regularities of such reactions may be significantly different from those observed for the thermal reactions.⁸

Free-energy gap (FEG) is the most common parameter controlling the charge-transfer rate. The dependence of this rate on the FEG, known as the Marcus FEG law, predicts the ET to be slow in the regions of both strong and weak exergonicity but fast in between, reaching the maximum at $-\Delta G = E_{\text{reorg}}$.⁹ Such a bell-shaped free-energy dependence was experimentally confirmed for several kinds of charge transfer. The intramolecular charge shift was the first among them.^{10,11} Later, it was observed for many other types of ET.^{12–20}

One of the reactions that demonstrates non-Marcus dependence of the rate constant on the reaction free energy is the geminate charge recombination (CR) in donor–acceptor complexes (DACs) excited into the charge-transfer band.^{21–23} For this reaction, the Marcus normal region (MNR) is absent and the logarithm of the rate constant decreases nearly linearly with increasing the reaction exergonicity. To account for such a behavior of the CR rate constant, Mataga and co-workers suggested that the CR in the excited DACs is associated with the reorganization of intramolecular vibrational high-frequency modes and the solvent plays a minor role.²²

A fundamentally different explanation was proposed by Tachiya and Murata.²⁴ They considered that a short laser pulse populates a nonequilibrium initial vibrational state of a DAC. However, this explanation encountered two problems:²⁵ (1) a good fit required too large electronic coupling values and (2) the model predicted a strong time dependence of the rate constant, in disagreement with most experimental data.²⁵ Later, it was shown that both the problems are related to oversimplification of the model due to full neglect of the reorganization of intramolecular high-frequency modes.²⁶ Indeed, a rather good fitting of the available experimental data on the FEG dependence of the CR rate constant in excited DACs was obtained within the multichannel stochastic point-transition model, including the reorganization of the solvent and several intramolecular high-frequency vibrational modes.²⁶ At the same time, the CR kinetics appear to be close to exponential.²⁷ The multichannel stochastic point-transition

Received: October 19, 2016

Revised: November 30, 2016

Published: January 1, 2017



Principals of simulation of ultrafast charge transfer in solution within the multichannel stochastic point-transition model[†]



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ARTICLE INFO

Article history:
Received 14 July 2016
Received in revised form
14 September 2016
Accepted 19 September 2016
Available online 3 October 2016

Keywords:
Brownian trajectory
Surface hopping
Vibrational manifold

ABSTRACT

We introduce `banKinetic`, an implementation of the stochastic multichannel point-transition approach to simulation of the charge transfer kinetics in molecular systems with reorganization of many intramolecular high-frequency vibrational mode in solvents with several relaxation timescales. The software provides simulation of the charge transfer kinetics in the molecular systems with many electronic states involved in photochemical transformations. It also allows simulating the charge transfer occurring in both equilibrium and nonequilibrium regimes. `banKinetic` is open-source software distributed under the terms of the GPL, without additional components. Software is implemented on multiple computing platforms. It exploits Matsumoto and Nishimura source code for pseudorandom number generator and a hierarchy of custom parallelization of the stochastic trajectories built on MPI.

Program summary

Program Title: `banKinetic`

Program Files doi: <http://dx.doi.org/10.17632/ywd9kwzzx9.1>

Licensing provisions: GPLv3

Programming language: C++

Supplementary material: MPI

Nature of problem: Simulation of dynamics and kinetics of charge transfer in solution.

Solution method: Brownian simulation method for diffusional dynamics, stochastic point-transition approach for electronic and vibronic transitions.

Additional comments including Restrictions and Unusual features: Binary search of transition-points for each diffusion step on crosses of vibrational manifolds, initial electron-vibrational distribution includes pump pulses characteristics, classical description of the solvent fluctuations, description of the vibronic states in terms of populations ignoring the quantum coherence, usage of the diabatic basis, parabolic terms.

Reference:

- [1] M. Matsumoto, T. Nishimura Dynamic Creation of Pseudorandom Number Generators, in book Monte Carlo and Quasi-Monte Carlo Methods, 1998, Springer, 2000, 56–69.

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[†] This paper and its associated computer program are available via the Computer Physics Communication homepage on ScienceDirect (<http://www.sciencedirect.com/science/journal/S00104655>).

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<http://dx.doi.org/10.1016/j.cpc.2016.09.015>
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1. Introduction

Electron transfer as one of the most widespread reaction in the nature plays a central role in many chemical, biological and physical processes [1–6]. It can occur on timescale covering huge area from seconds to few femtoseconds [7]. Such reactions are of primary importance in the emerging areas of molecular electronics, for example, dye/semiconductor systems applied in dye-sensitized solar cells [6,8,9]. Intensive investigations of

Excitation Frequency Dependence of Ultrafast Photoinduced Charge Transfer Dynamics

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Received 26 June 2017; revised 23 August 2017; accepted 28 August 2017

DOI 10.1002/kin.21129

Published online in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The dependence of the photoinduced charge transfer rate constant on the pump pulse carrier frequency is shown to be strong, and it is considerably affected by the value of the reorganization energy of low-frequency modes at the stage of excitation. In the area of small values of the reorganization energy, the dependence of the charge transfer rate constant on the pump pulse carrier frequency is strongly nonmonotonic that is caused by vibrational resonances and variation of the initial position of the wave packet on the term of the locally excited state. Increasing the reorganization energy smoothes the dependence. The smoothing is caused by the broadening of the vibrational resonances and their overlapping. The high-frequency vibrational mode excitation typically accelerates the charge transfer in both areas of high and low exergonicity and decelerates it in the vicinity of the Marcus barrierless region.
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INTRODUCTION

The study of the ultrafast electron transfer kinetics from nonequilibrium states attracts growing interest [1–19]. The term ultrafast electron transfer is typically used to refer to reactions proceeding on timescale and, hence in parallel with, relaxation of the nuclear subsystem of the reactants and the surrounding medium [20–24].

The nonequilibrium of nuclear subsystem can be created by both the pump pulse and the reaction itself at its separate stages [25]. Obviously, the kinetics of nonequilibrium reactions is rather complex and cannot be described in terms of a single rate constant [26–28]. The nonequilibrium manifests not only in nonexponential kinetics but also in a dependence of the kinetics on the pump pulse carrier frequency [17–19,26–28].

Population of a locally excited electronic state by a pump pulse can lead to the excitation of intramolecular high-frequency modes of a dye and brings the surrounding medium in a nonequilibrium state. There are a number of experimental investigations showing the effect of excitation of high-frequency vibrations on the charge transfer kinetics [1–8,10–15]. Such an effect

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Contract grant sponsor: Russian Science Foundation.

Contract grant number: 16-13-10122.

Supporting Information is available in the online issue at www.wileyonlinelibrary.com.

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Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

Journal homepage: www.elsevier.com/locate/jphotochem

Effect of charge separation free energy gap on the rate constant of ultrafast charge recombination in ion pairs formed by intramolecular photoinduced electron transfer



Alexey E. Nazarov, Georgy G. Eloev, Anatoly I. Ivanov*

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ARTICLE INFO

Article history:

Received 22 November 2017
 Received in revised form 10 March 2018
 Accepted 11 March 2018
 Available online 13 March 2018

Keywords:

Non-equilibrium electron transfer
 Solvent relaxation
 Free energy gap law

ABSTRACT

Regularities of ultrafast charge recombination kinetics in photoinduced intramolecular electron transfer in polar solvent are investigated. The multichannel stochastic model is used to simulate kinetics of charge separation and ensuing ultrafast charge recombination. The rate constant of ultrafast charge recombination occurring in non-equilibrium mode is shown to depend on the free energy gap of the preceding charge separation stage. This is a clear demonstration of violation of one of the fundamental principles of formal chemical kinetics, namely, the postulate of independence of elementary chemical reactions. The simulations revealed two main trends: (i) the charge recombination rate constant typically increases with decreasing the charge separation free energy gap, (ii) the maximum of the charge recombination rate constant, as a function of the charge recombination free energy gap, $[\Delta G_{CR}]$, shifts toward smaller values of $[\Delta G_{CS}]$ with decreasing the free energy gap at the previous, charge separation, stage of the reaction. The prediction of ultrafast charge recombination in donor–acceptor dyads with small charge recombination free energy gap is shown to be supported by the experimental data on the kinetics of charge recombination into the first excited state followed the charge separation from the second excited state.

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1. Introduction

Photoinduced charge separation (CS) attracts attention of researchers due to its important role in the nature and technological applications [1–8]. Typically, photoinduced CS is accompanied by ultrafast charge recombination (CR), which can heavily suppress the quantum yield of the desired products. For example, the effectiveness of a promising modern family of photovoltaic devices, dye-sensitized solar cells, is severely affected by ultrafast CR [7]. Since CR almost always accompanies photoinduced separation of charges, the example evidences that the problem of controlling the kinetics of ultrafast CR is of paramount importance for many technological applications. The solution of this problem includes the establishment of regularities determining the kinetics of CR. However, until now there is very limited information on the dependencies of the ultrafast CR rate constants on parameters of donor–acceptor pairs and the solvent characteristics, in spite of its importance [7].

One of the obstacles on the way to deducing regularities of ultrafast CR is its non-equilibrium nature. The ultrafast CR proceeds in non-equilibrium mode because the previous forward CS creates non-equilibrium distribution along the reaction coordinate that equilibrates in parallel with CR. The laws of non-equilibrium reactions, in contrast to thermal reactions, are less universal. Moreover, the regularities inherent in non-equilibrium and thermal reactions can vary greatly [9,10].

The second obstacle is caused by a dependence of the ultrafast CR kinetics on previous stages of the chemical transformations. Since the disequilibrium is created at individual stages of a complex reaction, the effect of the preceding stages on the succeeding stages is expected. The postulate of independence of elementary reactions is the fundamental principle of chemical kinetics, which is often silently implied. This postulate states that the rate constant of an elementary chemical reaction does not depend on other elementary reactions occurring in the system. It is well known that this postulate can be violated in non-equilibrium reactions. In this study the CR rate constant is shown to depend on the free energy gap of the preceding CS.

The results of experimental exploration of kinetics of CR ensuing photoinduced CS were reported in a number of articles

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