

1. Анкетные данные

ФИО: Михайлова Татьяна Владимировна

Год рождения: 1995 г.

Образование:

Волгоградский государственный университет, 2017г., бакалавр по направлению «Физика».

Волгоградский государственный университет, 2019 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 0919798

ДОКУМЕНТ ОБ ОБРАЗОВАНИИ И О КВАЛИФИКАЦИИ

Регистрационный номер
ФКФм-006

Дата выдачи
05 июля 2019 года

Настоящий диплом свидетельствует о том, что

Михайлова

Татьяна Владимировна

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 № 6 от 25 июня 2019 г.

Председатель
Государственной
экзаменационной комиссии
Руководитель организации,
осуществляющей образовательную
деятельность



М.П.

Завьялов Д. В.

Тараканов В. В.

РОССИЙСКАЯ
ФЕДЕРАЦИЯ



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

ПРИЛОЖЕНИЕ
к ДИПЛОМУ
магистра с отличием
103418 1034293

Регистрационный
номер

ФКФм-006

Дата выдачи

05 июля 2019 года

1. СВЕДЕНИЯ О ЛИЧНОСТИ ОБЛАДАТЕЛЯ ДИПЛОМА

Фамилия **Михайлова**

Имя **Татьяна**

Отчество **Владимировна**

Дата рождения **18 октября 1995 года**

Предыдущий документ об образовании или
об образовании и о квалификации

Диплом бакалавра, 2017 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

Страница 1

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.	зачтено
Философия и методология науки	4 з.е.	отлично
Java-технологии	3 з.е.	отлично
Иностранный язык (английский)	2 з.е.	зачтено
Алгоритмы дискретной математики	2 з.е.	отлично
Современные проблемы физики	2 з.е.	отлично
Гидро и магнитогидродинамика	3 з.е.	отлично
Методы квантовой химии	3 з.е.	отлично
Элементарные химические процессы	3 з.е.	отлично
Web-программирование	3 з.е.	отлично
Кинетика фотохимических процессов	2 з.е.	зачтено
Компьютерная графика	4 з.е.	отлично
История и методология физики	2 з.е.	зачтено
Математические методы теоретической физики	3 з.е.	отлично
Специальный физический практикум: Компьютерные методы моделирования физических явлений	3 з.е.	отлично
Вариационный принцип в теоретической физике	2 з.е.	зачтено
Физика плазмы	2 з.е.	отлично
Дополнительные главы высшей алгебры	3 з.е.	отлично
Механика сплошных сред	3 з.е.	отлично
Компьютерное моделирование эволюционных уравнений	3 з.е.	отлично
Квантовые вычисления	3 з.е.	зачтено
Молекулярная спектроскопия	3 з.е.	отлично
Практики	51 з.е.	х
в том числе:		
Производственная практика, практика по получению профессиональных умений и опыта профессиональной деятельности	21 з.е.	отлично
Производственная практика, педагогическая	6 з.е.	отлично
Производственная практика, преддипломная	15 з.е.	отлично
Производственная практика, научно-исследовательская работа	9 з.е.	отлично
Государственная итоговая аттестация	9 з.е.	х
в том числе:		
Выпускная квалификационная работа (магистерская работа) "Моделирование сверхбыстрой кинетики фотоиндуцированного протонно-связанного переноса электрона"	х	отлично
Объем образовательной программы	120 з.е.	х
в том числе объем работы обучающихся во взаимодействии с преподавателем:	741 час.	х



4. КУРСОВЫЕ РАБОТЫ (ПРОЕКТЫ)	ОЦЕНКА

5. ДОПОЛНИТЕЛЬНЫЕ СВЕДЕНИЯ

Форма обучения: очная.
Направленность (профиль) образовательной программы: "Компьютерная физика"

БЕЗ ДИПЛОМА НЕДЕЙСТВИТЕЛЬНО

Руководитель организации,
осуществляющей образовательную
деятельность



Тараканов В. В.

Настоящее приложение содержит 4 страниц

3. Достижения в научно-исследовательской деятельности

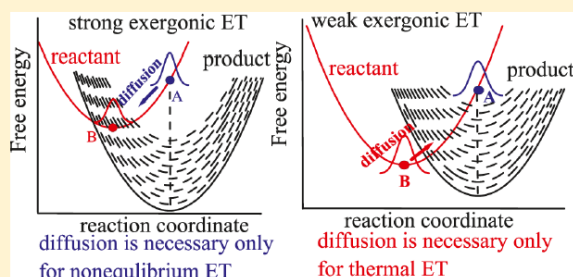
Dynamic Solvent Effect on Ultrafast Charge Recombination Kinetics in Excited Donor–Acceptor Complexes

Tatyana V. Mikhailova, Valentina A. Mikhailova, and Anatoly I. Ivanov*¹

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

ABSTRACT: Manifestation of the dynamic solvent effect (DSE) on the charge recombination (CR) kinetics of photoexcited donor–acceptor complexes in polar solvents has been investigated within the framework of the multichannel stochastic model. The model takes into account the reorganization of both the solvent and a number of intramolecular high-frequency vibration modes as well as their relaxation. The non-Markovian solvent dynamics is described in terms of two relaxation modes. The similarities and differences inherent to ultrafast charge transfer reactions occurring in the nonequilibrium and thermal regimes have been identified. The most important differences are as follows:

(1) the DSE is strong in the area of weak exergonicity and is weak in the area of strong exergonicity for thermal reactions, whereas for the nonequilibrium reactions, the regions of strong and weak DSEs are reversed; (2) an increase in the electronic coupling value results in a decrease in the magnitude of DSE for nonequilibrium electron transfer and in its increase for the thermal reactions; and (3) the two-staged regime most clearly manifests if the reorganization energy of the relaxation modes noticeably exceeds the CR free-energy gap. With an increase in electronic coupling, the kinetics approaches the exponential regime because in the limit of strong electronic coupling, the reaction includes only single, nonequilibrium, stage.



INTRODUCTION

The theoretical investigations of electron transfer (ET) reactions in polar solutions started with Marcus theory¹ that was generalized in the early 1980s to account for the dynamic solvent effect (DSE) on ET kinetics.^{2–4} This triggered extensive experimental and theoretical studies of charge transfer in solutions.^{5–19}

Theory of DSE^{2–4,18,20} allowed bridging between non-adiabatic and solvent-controlled regimes and answering the question of when the solvent relaxation, rather than microscopic electronic processes, constitutes the rate-determining step of ET.³ In the framework of the stochastic point-transition model, the ET rate constant is described by the equation³

$$k_{\text{ET}} = \frac{V_{\text{el}}^2}{\hbar(1+g)} \sqrt{\frac{\pi}{E_{\text{m}}k_{\text{B}}T}} \exp\left[-\frac{(\Delta G + E_{\text{m}})^2}{4E_{\text{m}}k_{\text{B}}T}\right] \quad (1)$$

where V_{el} is the electronic coupling, \hbar is the Planck constant, k_{B} is the Boltzmann constant, T is the temperature, E_{m} is the solvent reorganization energy

$$g = \frac{2\pi V_{\text{el}}^2 \tau_{\text{L}}}{\hbar} \left[\frac{1}{|\Delta G + E_{\text{m}}|} + \frac{1}{|\Delta G - E_{\text{m}}|} \right] \quad (2)$$

is the Zusman parameter determining crossover from the Golden rule to the solvent control, ΔG is the reaction free-energy change, and τ_{L} is the longitudinal dielectric relaxation time.

From eq 1, several important conclusions follow: (1) in the nonadiabatic limit, $g \ll 1$, the ET rate constant is proportional to

V_{el}^2 and is independent of the longitudinal relaxation time of the solvent, τ_{L} ; (2) in the opposite, solvent-controlled, limit, $g \gg 1$, the ET rate constant is inversely proportional to the longitudinal relaxation time of the solvent and is independent of the electronic coupling, that is, the dependence $k_{\text{ET}}(V_{\text{el}})$ is saturated; and (3) the upper limit for the ET rate is achieved in the activationless region, where it is close to $1/\tau_{\text{L}}$ for polar solvents with $E_{\text{m}} \approx 1$ eV. These predictions were partly confirmed in a series of experimental studies.^{21–29} Later, it was shown that the behavior of real systems can considerably deviate from these predictions. In particular, the observed rate constant may exceed the upper limit, $1/\tau_{\text{L}}$, by several orders of magnitude.^{27,30–37} Besides, it is appeared that the DSE is observed for relatively slow reactions occurring in the Marcus normal region and it is absent for fast ET occurring in the activationless or inverted regions.¹⁹


All of the regularities were shown to emerge from the multichannel stochastic point-transition model.^{38,39} It should be stressed that these conclusions were obtained for charge transfer occurring in the equilibrium regime when the initial state of the solvent and intramolecular degrees of freedom are close to the thermal equilibrium. At the same time, there is a wide class of important processes in which nonequilibrium charge transfer plays a central role. Such a nonequilibrium of the nuclear subsystem can be created by both the photoexcitation and chemical transformations.

Received: September 16, 2016

Revised: November 3, 2016

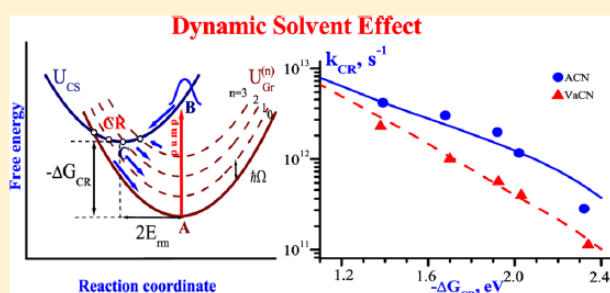
Published: November 3, 2016

Verification of Nonequilibrium Mechanism of Ultrafast Charge Recombination in Excited Donor–Acceptor Complexes

Tatyana V. Mikhailova, Valentina A. Mikhailova, and Anatoly I. Ivanov*

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

ABSTRACT: Control of charge transfer requires knowledge of its detailed mechanism. Due to the large number of known mechanisms, the identification of the mechanism in specific systems is a challenge so far. In this article we propose the idea of how to distinguish between thermal and nonequilibrium modes of charge recombination in excited donor–acceptor complexes. Simulations of the effect of solvent relaxation time scale on ultrafast charge recombination kinetics in photoexcited donor–acceptor complexes within the framework of the multichannel stochastic model have shown that a series of regularities inherent to the thermal and nonequilibrium charge transfer can strongly differ. Among them there are opposite regularities, for example, the dependence of the dynamic solvent effect on the free energy gap. In particular, theory predicts that in ultrafast charge recombination of excited donor–acceptor complexes the dynamic solvent effect is weak in the area of weak exergonicity and becomes stronger in the area of stronger exergonicity whereas for the thermal reactions an opposite trend is expected. Comparison of such trends with experimental data implemented in this article allowed establishing the regime in which the reaction proceeds. It is shown that observation of dynamic solvent effect in the region of strong exergonicity for ultrafast charge recombination is decisive evidence in favor of nonequilibrium mechanism.



INTRODUCTION

Photoinduced electron transfer being important for fundamental science and technological applications^{1–7} attracts much attention of the scientific community over the past decades.^{8–11} Despite the fact that there is a huge amount of information on charge transfer kinetic regularities and many details of charge transfer mechanism are known, the control of ultrafast charge transfer kinetics and the product yields remains a challenge. For example, low efficiency of modern photovoltaic devices (dye-sensitized solar cells) caused by ultrafast recombination of the charges immediately following primary photoinduced charge separation is one of such challenges.⁷

Studies of geminate charge recombination (CR) kinetics in donor–acceptor complexes (DAC) excited into a charge transfer band have shown for the first time that the role of the nonequilibrium of the nuclear subsystem in such reactions is important.^{12–14} The rate constant of CR in excited DACs, being monotonically decreasing function of the reaction exergonicity, does not show the Marcus normal region.^{15–17} The non-Marcus rate constant behavior can be accounted for if one accepts that excitation of a DAC by a short laser pulse initially creates a nonequilibrium population on the excited free energy surface far away from its minimum.^{12–14} It appeared that the CR rate constant dependence on free energy gap (FEG) calculated within the multichannel stochastic point-transition (MCSPT) model including the reorganization of the solvent and several intramolecular high-frequency vibrational modes can be well fitted¹³ to the experimental data.^{15–17}

At the same time, the very linear dependence of the CR rate constant on FEG does not prove a nonequilibrium mechanism, because such a dependence can be reproduced within the framework of both thermal and nonequilibrium theories.^{12,13,18–21} Therefore, the question of the ultrafast CR mechanism in the excited DACs is still open. To differentiate between the thermal and nonequilibrium modes, additional regularities should be exploited. The regularities showing opposite dependencies for different modes are the best suited. Indeed, MCSPT model simulations of the ultrafast CR kinetics in excited DACs have shown that the kinetic regularities of the charge transfer reactions occurring in nonequilibrium and equilibrium regimes can be strongly different.¹⁴ In the present article such a regularity has been found and used for the first time as a strong evidence of the nonequilibrium mechanism of ultrafast CR. This regularity is associated with the dependence of the CR rate constant on dynamic properties of solvent, namely, on the solvent relaxation time. This dependence is known as the dynamic solvent effect (DSE).²² In this article DSE is quantified as the relative change in the reaction rate constant with a variation in the solvent relaxation time, provided that the solvent polarity variation is minor. DSE is well pronounced in the solvent controlled regime when the solvent dynamics limits the electron transfer rate. In this regime the electronic coupling is sufficiently large and the electron

Received: March 17, 2017

Revised: April 14, 2017

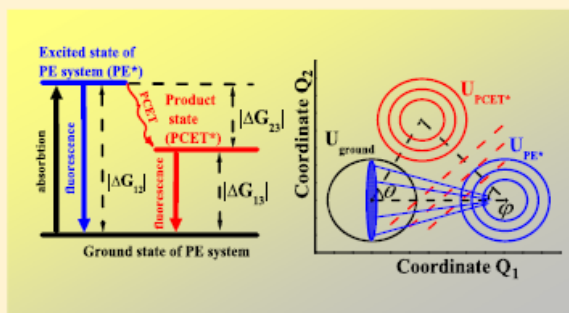
Published: April 14, 2017

Modeling Kinetics of Ultrafast Photoinduced Intramolecular Proton-Coupled Electron Transfer

Tatyana V. Mikhailova, Valentina A. Mikhailova, and Anatoly I. Ivanov*

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

ABSTRACT: A model of photoinduced intramolecular proton-coupled electron transfer is derived. The model includes three states as follows: the ground, excited, and product states. The charge transfer is associated with both stages, photoexcitation and product formation. A larger part of the model parameters can be extracted from the stationary absorption and fluorescence spectra of a particular fluorophore. Two different reaction coordinates are associated with the two stages, which are not independent. The angle between the reaction coordinates strongly influences on the kinetics of ultrafast product formation. The stochastic multichannel approach is exploited for simulations of the kinetics. The simulations well reproduce the kinetics of ultrafast intramolecular proton-coupled electron transfer in 2-((2-(2-hydroxyphenyl)benzo[*d*]oxazol-6-yl)methylene)malononitrile in a few solvents. The transfer is shown to occur totally or partly, depending on the solvent, in the nonequilibrium regime. Analysis of the kinetics of the excited-state decay has uncovered a significant decrease in the magnitude of the reorganization energies of slow nuclear modes with increasing the solvent polarity. Such an unusual behavior of the total reorganization energy can be rationalized under the assumptions: (i) a slow intramolecular reorganization of a significant magnitude associates with the transition between excited and product states and (ii) intramolecular slow reorganization is accompanied by a change in the dipole moment of the fluorophore.



INTRODUCTION

Proton and electron transfer are the simplest elementary and at the same time ubiquitous reactions in chemistry having diverse applications in emerging technologies.^{1–9} Such kind of reactions also plays a key role in biochemical transformations, including photosynthesis, respiration, energy transfer in cells, and enzyme reaction.^{1,8,9} Excited-state charge and proton transfer reactions may find their applications in a variety of modern technologies, for example, for designing suitable chemical and/or biological sensors and fluorescence sensing and imaging.^{7,9}

The number of compounds in which ultrafast photoinduced proton and electron transfers are observed is enormous. For the most part, the electron and proton transfer reactions are interrelated. In the literature, sequential and concerted mechanisms of proton-coupled electron transfer (PCET) are singled out.^{5,6,10–12} A sequential mechanism of PCET includes a stable intermediate product, when either the electron transfer (ET) proceeds before proton transfer (PT) or conversely the PT takes place prior the electron transition.¹³ The simultaneous transfer of the electron and proton in a single step without a stable intermediate product is interpreted as the concerted mechanism.^{5,6,11,12} However, in ultrafast processes, the discrimination of these mechanisms is impossible because the determination of a stable intermediate compound is difficult. Thus, a fast PCET is a more complex process which

attracts much attention of the scientific community.^{4,6,8,11,12,14–16}

Typical and well-studied examples of molecular structures in which such processes can proceed are salicylates, benzoxazoles, and hydroxyflavones.^{4,14,17–19} Among the last group of compounds, one of the most studied molecules where PCET takes place is 3-hydroxyflavone (3HF).^{14,18} In this molecular structure, an excited-state intramolecular PT (ESIPT) occurs between the oxygens of hydroxyl and carbonyl groups, which leads to the formation of a zwitter-ionic (bipolar) tautomer. Extensive studies of the 3HF molecule and some of its derivatives provided the quantitative data on the dynamics of the populations of excited states.^{4,14,18} The investigation of the detailed mechanism of the intramolecular PCET reactions proceeding after photoexcitation of a molecule is still one of the fundamental issues.^{4,14,18,20–23}

Chou and co-workers^{14,18,20–23} have synthesized and presented several examples of PCET molecular compounds.^{14,18} The first type of a PCET system is 4'-*N,N*-diethylamino-3-hydroxyflavone (further in text system I). The processes induced by optical excitation in I were interpreted within the three-level model assuming the excited state with considerable intramolecular ET to be directly populated by the

Received: September 17, 2018

Revised: October 17, 2018

Published: October 17, 2018





DOI: <http://dx.doi.org/10.15688/jvolsu1.2016.3.6>

УДК 541.14: 544.522

ББК 24.5

СТОХАСТИЧЕСКАЯ МОДЕЛЬ РАЗДЕЛЕНИЯ ЗАРЯДОВ В ФОТОВОЗБУЖДЕННЫХ МОЛЕКУЛЯРНЫХ ТРИАДАХ¹

Татьяна Владимировна Михайлова

Студент физико-технического института,
Волгоградский государственный университет
mikhailovavolsu@gmail.com
просп. Университетский, 100, 400062 г. Волгоград, Российская Федерация

Дарья Андреевна Рощина

Студент физико-технического института,
Волгоградский государственный университет
suhorukovadaria@mail.ru
просп. Университетский, 100, 400062 г. Волгоград, Российская Федерация

Елена Александровна Михайлова

Кандидат физико-математических наук, доцент кафедры теоретической физики
и волновых процессов физико-технического института,
Волгоградский государственный университет
mikhailova_ea@mail.ru, tf@volsu.ru
просп. Университетский, 100, 400062 г. Волгоград, Российская Федерация

Валентина Александровна Михайлова

Доктор физико-математических наук, заведующая кафедрой теоретической физики
и волновых процессов физико-технического института,
Волгоградский государственный университет
mikhailova.va@volsu.ru, tf@volsu.ru
просп. Университетский, 100, 400062 г. Волгоград, Российская Федерация

Аннотация. В рамках стохастического подхода проведено исследование сверхбыстрого разделения зарядов в фотовозбужденных донорно-акцепторных триадах, находящихся в полярном растворителе. Получено аналитическое выражение для вероятности переноса заряда на вторичный акцептор, протекающего параллельно с релаксацией полярного растворителя. Сделаны количественные оценки влияния распада продуктов на вероятность данного процесса.

Ключевые слова: фотоиндуцированные реакции переноса заряда, внутримолекулярная колебательная релаксация, молекулярная донорно-акцепторная триада, электрон, молекулярные системы.

Введение

В последние несколько десятилетий все больше внимания уделяется исследованию детальных механизмов фотоиндуцированных реакций переноса электрона в супрамолекуляр-