Reaction Kinetics in Soft and Condensed Matter 2014

ORLÉANS, FRANCE, 1-4 JULY 2014

Book of Abstracts

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SCHEDULE

TUESDAY, July 1st

8:40 Registration

9:00 Opening RKSCM 2014

9:10 **Alexander Doktorov** (L-1)

Recent development of the binary theory of multistage physicochemical processes in solutions based on the kinetic theory notions

10:00 **Masanori Tachiya** (L-2)

Onsager problem of reversible bulk ion recombination revisited

10:50 Coffee Break

11:20 **Mariusz Wojcik** (O-1)

Reaction kinetics in an irradiated system: Electron-ion recombination in liquid argon

11:50 **Peter Purtov** (O-2)

Modern problems of spin chemistry

12:20 **Nikita Lukzen** (O-3)

Diffusion-controlled radical recombination in magnetic field

13:00 Lunch

14:20 **Andrea Cannizzo** (L-3)

Investigating electronic and vibrational dynamics in proteins and molecular devices by femtosecond coherent optical spectroscopies

15:10 **Alexei Kornyshev** (L-4)

The unusual laws of electron transport through chain molecules in electrochemical environment

16:00 Coffee Break

16:30 **Arnulf Rosspeintner** (O-4)

Bimolecular photoinduced charge separation and recombination – now featuring ultrafast spectroscopy

17:00 **Stanislav Fedorenko** (O-5)

Kinetics of exciplex formation/dissipation in reaction following Weller Schemes I and II

WEDNESDAY, July 2nd

9:10 **Matthias Weiss** (L-5)

Crowding, diffusion, and biochemical reactions

10:00 **Doris Heinrich** (L-6)

Cellular kinetics - from intracellular transport to cell migration

10:50 Coffee Break

11:20 **Konstantin Ivanov** (O-6)

Kinetics of target searching by means of two diffusion-like motions

11:50 **Marek Litniewski** (O-7)

Relative diffusion in two dimensions. Breakdown of the standard diffusive model for simple liquids

12:20 **Josef Hamacek** (O-8)

Reaction kinetics in lanthanide-mediated supramolecular assemblies

13:00 Lunch

14:20 **Cait MacPhee** (L-7)

Fibrillar protein self-assembly: the link between kinetics and fibril morphology

15:10 **Alessandro Barducci** (L-8)

Hsp70 chaperones as non-equilibrium machines: ultra-affinity from energy consumption

16:00 Coffee Break

16:30 **Bernhard Lang** (O-9)

Farewell to flash photolysis, broadband transient absorption spectroscopy from femtosecond to microsecond time domain

17:00 **Volodymyr Dubinko** (O-10)

Effect of moving discrete breathers on reaction kinetics in crystals under irradiation

20:00 Social Dinner

THURSDAY, July 3

9:10 **Suliana Manley** (L-9)

Organizing principles of the bacterial z-ring and the eukaryotic centriole: tiny, multi-protein machines

10:00 **Huan-Xiang Zhou** (L-10)

Protein association in dilute and crowded solutions

10:50 Coffee Break

11:20 **Guillaume Tresset** (O-11)

Self-assembly kinetics of a norovirus nanocage

11:50 **Sergey Traytak** (O-12)

Solution of the diffusion equation in slender impermeable tubes of varying cross-section

12:20 **Gonzalo Angulo** (O-13)

Experimental Evidence of the Relevance of Orientational Correlations in Photoinduced Bimolecular Reactions in Solution

13:00 Lunch

14:20 **Giancarlo Franzese** (L-11)

Kinetics of bionano interactions: a multiscale approach

15:10 **Joachim Dzubiella** (L-12)

Solvent fluctuations in hydrophobic cavity–ligand binding kinetics

16:00 Coffee Break

16:30 **Dmitri Stass** (O-14)

Formation of exciplexes in X-irradiated alkane solutions for luminophores with short fluorescence lifetimes

17:00 **Günter Grampp** (O-15)

High pressure effects on the rates of electron transfer reactions in organic redox systems: an ESR-spectroscopic study

FRIDAY, July 4

9:10 **Dominik Wöll** (L-13)

Single molecule fluorescence microscopy to study molecular dynamics in polymer solutions and their relation to polymerization kinetics

10:00 **Sangyoub Lee** (L-14)

A new solution method for Fredholm integral equations and its applications to diffusion-influenced reaction kinetics

10:50 Coffee Break

11:20 **Kazuhiko Seki** (O-16)

Segregation of colloids by interference between entropic effect and thermophoresis

11:50 **Matteo Gori** (O-17)

Experimental detection of long-distance interactions between biomolecules through their diffusion behavior: Numerical study

12:20 Concluding remarks and Closing RKSCM 2014
13:00 Lunch

ABSTRACTS OF INVITED LECTURERS

Recent development of the binary theory of multistage physicochemical processes in solutions based on the kinetic theory notions

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Physicochemical processes (including chemical reactions) depending on spatial migration of reactants (for example, diffusion-influenced reactions) in con
densed media play an important role in different fields of science and technology. Among these are, for instance, electron excitation energy transfer, electron (or proton) migrations in photosynthetic systems, various chemical reactions occurring in colloid or polymer solutions, in nano- and bio- systems, or trapping and detrapping problems in semiconductors and many others. From this standpoint, development of the theory of reactions depending on mobility of reactants is crucial to understanding of the systems and application to complex problems. Many fundamental issues on theories have been addressed over many years. Primarily most of the theories referred to elementary geminate and bulk reactions, however, some simple multistage reactions significant in studies of biochemical reactions have also been investigated, as well as transfer reactions in luminescence and chemiluminescence and photo- and electrochemistry. An increasing interest in the consideration of different multistage reactions has stimulated formulation and development of general (matrix) theories of bulk multistage reactions including all possible elementary stages (bimolecular chemical exchange and addition reactions, dissociation and monomolecular transformation reactions) which is based on kinetic theory notions treating solution as a "gas" of reactants (Encounter Theory concept) dissolved in chemically inert continual solvent. Recently similar (matrix) approach has been developed for geminate multistage reactions of isolated pairs of reactants arising from external radiation that are another important class of reactions in solutions (general matrix kinetic theory of multistage geminate reactions of isolated pairs). In the framework of the developed approach, "internal" degrees of freedom, namely, classic (for example, reactants rotations) and quantum (for instance, spin states) have been included in the consideration, thus the reactions between reactants with anisotropic reactivity and those between paramagnetic particles (free radicals and radical ions), in external magnetic field also, can be studied.

This makes it possible to establish general detailed balancing principles: total balance of reacting particles, kinetic (microscopic and macroscopic) and thermodynamic balancing. Time behavior of geminate and bulk reacting systems (with multistage reactions) on the macroscopic time scale is considered, and long-term universal asymptotes of equilibrium attainment are established.

This communication is devoted to the analysis of the above-mentioned basic approaches to the development of the kinetic theory of physicochemical processes (geminate and bulk) in dilute solutions.

The authors thank the Russian Foundation of Basic Research (project 12-03-00058) for financial support.

Onsager problem of reversible bulk ion recombination revisited

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Onsager's theory of reversible bulk ion recombination [1] is attracting attention in connection with attempts to measure magnetic monopoles [2]. His theory deals with the following reactions in the presence of an external electric field.

$$P \rightleftarrows A^+ + B^-$$

where P is a neutral molecule and A^+ and B^- are positive and negative ions. Concerning recombination (left-directed arrow) Onsager used the result of Langevin [3] which was obtained by assuming that A^+ and B^- recombine when their separation becomes zero. Concerning dissociation (right-directed arrow) Onsager described it by the steady-state flow of B^- from the neighbourhood of the origin to infinity. He considered that when recombination and dissociation are in equilibrium, the rate of this flow is equal to the rate of the steady-state flow of B^- from infinity to the origin. By using this condition together with the result of Langevin for the recombination rate constant, Onsager calculated the dissociation rate constant when recombination and dissociation are in equilibrium. He further calculated the dissociation constant and investigated the effect of an external electric field on the dissociation constant.

However, concerning recombination it is more appropriate to assume that A^+ and B^- can approach only up to a finite distance R and recombine there by back electron transfer at a finite rate constant k_{bet} [4]. Concerning dissociation it is more appropriate to assume that when P dissociates into A^+ and B^- by forward electron transfer at a finite rate constant k_{fet}, A^+ and B^- are initially generated with a separation R [5]. They subsequently perform Brownian motion under the influence of mutual Coulomb potential and the external electric field, and recombine at the rate constant k_{bet}, whenever their separation becomes R. In this talk I extend Langevin and Onsager theories of irreversible and reversible bulk ion recombination by properly taking into account these effects.

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Investigating electronic and vibrational dynamics in proteins and molecular devices by femtosecond coherent optical spectroscopies

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In the last twenty years, ultrafast spectroscopy has dramatically changed our way to investigate matter. Now we can indeed follow in real time all the photo-inducible transformations occurring out of equilibrium states with femtosecond resolution, and our comprehension of excited state physics and chemistry has undergone a breathless leap. A less evident quality is that now we can directly access times where thermal fluctuations occur, mainly time resolving spectral diffusion processes. This has given us on the one hand the unique capability to disentangle homogenous and inhomogeneous line shape broadening, on the other hand novel methodologies (the so-called multidimensional optical spectroscopies) to track down collective motions and long-range interactions within a molecule, which are quickly covered or even destroyed by incoherent fluctuations. These unique capabilities make such techniques the methodology of choice to investigate intramolecular interactions as well as charge and energy transfer phenomena in macromolecules.

In this talk I will illustrate the capabilities of femtosecond spectroscopies with few examples from my research activity and literature.

The unusual laws of electron transport through chain molecules in electrochemical environment

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Measurement of electronic current mediated by chain molecules linking an electrode and an STM tip has revealed several unusual properties of conductance in such systems, which are of potential interest to molecular electronics.

In my talk I will

- Overview the principles of the theory of electron transport through a chain molecule with rotational degrees of freedom, for the plain tunneling or superexchange mechanisms;
- Rationalize the mysterious dependence of apparent activation energy of conductance (as revealed from Arrhenius plots) on the length of the molecule;
- Describe the predicted effect of rectification of electronic current which should take place

if the molecule is longer than the Debye (Gouy) length in the electrolytic solution;

- Highlight the difference of the current voltage characteristics form the popular 'bell-shaped-curves' predicted and described theoretically, and observed in the case if a redox-center containing molecules.

The results will be compared with available experimental data. Suggestions of new experiments will be discussed, as well as avenues of exploitation of these effects.

Crowding, diffusion, and biochemical reactions

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Diffusion is the main mode of molecular transport in living cells. Diffusion not only leads to a dispersion of molecules, but it also is the driving force behind biochemical reactions and pattern formation. Macromolecular crowding in cellular fluids equips macromolecule diffusion with properties that deviate significantly from dilute conditions in the test tube and therefore can be expected to alter biochemical reactions as compared to dilute conditions. Indeed, hindered and anomalous diffusion due to crowding have been observed in cells and biochemical reactions are affected differentially by these (see [1] for a recent review).

In this contribution, we will discuss the emergence and detection of anomalous diffusion due to macromolecular crowding, the nature of the random walk that emerges in crowded media [2-4], and the impact of anomalous diffusion on simple biochemical reactions [5,6]. An outlook on additional phenomena, e.g. in the context of cell division, will be given at the end.

References

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Cellular kinetics - from intracellular transport to cell migration

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Living cells exhibit exceptional dynamic properties, caused by the presence of ATP-driven motion. In particular, intracellular transport of cargos proceeds by successive phases of diffusion and directed movement along microtubules via dynein and kinesin motors. While diffusion allows for intracellular transport of molecules on the nanoscale, it becomes inefficient for transport of large proteins, vesicles and organelles on the scale of a whole cell (Fig. 1). We developed a time-resolved identification method for motility state signatures of cytoplasmic tracers in living cells. Such an approach is both, experimentally challenging and of fundamental importance for our understanding of intracellular transport processes. A rolling-average algorithm [1] is based on the analysis of the local mean-square displacement (MSD) and directional persistence of an intracellular tracer path, to reliably separate diffusion and directed motion of particles in cells. This two-state motility model yields distributions for state durations, velocity during directed phases and the diffusion coefficient else. This analysis can be extended to sub-diffusive intracellular transport states [2-5] and further to motion states of the entire cell, migrating on structured surfaces [6]. By further applying spatially and temporally defined external boundary conditions to these cells, like precisely monitored chemotaxis gradients [7,8] or by cell motility assays on pre-ordered 3D topologies, we induce changes in cellular function and therefore control cell migration [9].

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Fibrillar protein self-assembly: the link between kinetics and fibril morphology

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Amyloid and amyloid-like fibrils are self-assembling protein structures [1], of interest for their robust material properties [2] and inherent biological compatibility as well as their putative role in a number of debilitating mammalian disorders. Understanding fibril formation is essential to the development of strategies to control, manipulate or prevent fibril growth. From the viewpoint of useful nanomaterials [3], control over self-assembly allows control over fibril mechanics and the viscoelastic properties of fibrillar gels. I will describe the emerging predictive link between the kinetics of fibril self-assembly and the morphology of the resulting aggregates. I will describe the macroscopic implications of models in which secondary processes such as secondary nucleation, fragmentation, end joining and branching may dominate the assembly pathway.

References

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Hsp70 chaperones as non-equilibrium machines: ultra-affinity from energy consumption

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70-kDa Heat shock proteins are ATP-driven molecular chaperones that perform a myriad of essential cellular tasks. Although structural and biochemical studies have shed some light on their functional mechanism, the fundamental issue of the role of energy consumption, due to ATP-hydrolysis, has remained unaddressed. Here we establish a clear connection between the non-equilibrium nature of Hsp70, due to ATP hydrolysis, and the determining feature of its function, namely its high affinity for its substrates. Energy consumption can indeed decrease the

dissociation constant of the chaperone-substrate complex by several orders of magnitude with respect to an equilibrium scenario. We find that the biochemical requirements for observing such *ultra-affinity* coincide with the physiological conditions in the cell. Our results rationalize several experimental observations and pave the way for further analysis of non-equilibrium effects underlying chaperone functions.

References

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Organizing principles of the bacterial z-ring and the eukaryotic centriole: tiny, multi-protein machines

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Our goal is to inform quantitative models for the architecture and biophysics of protein assemblies, using single molecule and superresolution fluorescence imaging. In two recent studies, we use our imaging technology developments to reveal the organizing principles of tiny structures involved in cell division. First, we created a high throughput modality of photoactivated localization microscopy, HTPALM, which enables automated 3D PALM imaging of hundreds of synchronized bacteria during all stages of the cell cycle [1]. We used HTPALM to investigate the nanoscale organization of the bacterial cell division protein FtsZ in live C. crescentus. We observed that FtsZ predominantly localizes as a patchy mid-cell band, and only rarely as a continuous ring, supporting a model of "Z-ring" organization where FtsZ protofilaments are randomly distributed within the band and interact only weakly. Second, we optimized chemical buffers to increase resolution by nearly a factor of two, and applied this to study the organization of the key centriolar protein HsSAS-6 [2,3]. This is the first time its nine-fold symmetry was observed in situ in mammalian cells.

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Protein association in dilute and crowded solutions

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Most biological processes are mediated by protein association, which is often under kinetic rather than thermodynamic control [1]. We have developed the transient-complex theory for protein association, which presents a framework for elucidating the mechanisms of protein association and for predicting the association rate constants [2]. The transient complex refers to an intermediate along the association process, in which the two associating molecules have near-native separation and relative orientation but have yet to form the short-range specific interactions of the native complex. Our theory rationalizes the variations in association rate constants over 10 orders of magnitude and its computational implementation gives accurate prediction of the rate constants based on the structures of the native complexes [2-4]. We find that disordered proteins bind to their targets often via a dock-and-coalesce mechanism, whereby a segment of the disordered protein first docks to its cognate subsite and the remaining segments subsequently explore conformational space and coalesce around their cognate subsites [5]. We propose that intrinsic disorder allows proteins to form complexes that are highly specific and yet short-lived, twin requirements for signaling and regulatory purposes [6]. In the cellular context, association processes occur in the presence of a high concentration of bystander macromolecules [7]. We have developed methods to model the effects of the crowded cellular environments on the affinities and rate constants of protein association [8,9]. These studies allow us to achieve a quantitative understanding of biological processes in the cellular context, based on physical principles.

References

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Kinetics of bio-nano interactions: a multiscale approach

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The recent exploitation of nanoparticles in commercial and medical applications has increased the possibility that people could enter in direct contact with these materials. Thousands of products in the market, such as fabrics, cleaning products and cosmetics, include nanocomponents. Nanomaterials are already used in medical treatments, electronics or as food additives, generating millions of dollars in sales. Human exposure to nanomaterials, smaller than a thousandth the diameter of a hair, raises important issues about if the interactions between nanomaterials and biological systems can have adverse health effects. Therefore, it is fundamental to study the BioNano Interactions and to understand how we can control them. This is relevant both for the technological applications and for the social impact. In fact, a distorted knowledge or a superficial control of the nanoparticle effect for the health could generate a social concern. For example, in the past years these issues have generated a strong reaction to the OGM food, limiting the research and its possible benefits. The starting hypothesis of our research is that water dominates the structure and the organization of the biosystems at the molecular level. Water properties are paramount in BioNano Interactions. The presence of water in living organisms is responsible for much of the structural and physicochemical properties of biomolecules because of the unique water ability to form hydrogen bonds. In this paper I will present the recent results of my group in describing the formation of the "protein corona" around the nanoparticles when these are in aqueous solutions with biomolecules. With great simplification, chemical molecules interact directly with the biological elements, while nanoparticles are coated with proteins and lipids. These macromolecules adhere so strongly to the nanoparticle surface that the exchange times with the solution are extremely long. As a consequence, the biological identity of the particles depends largely of the protein corona, instead of the nanoparticle material.

Solvent fluctuations in hydrophobic cavity–ligand binding kinetics

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In this contribution I present results on the role of water in the binding kinetics of a ligand to a prototypical hydrophobic pocket studied by explicit-water molecular dynamics (MD) simulations and implicit diffusional approaches [1]. We observe that the concave pocket in the unbound state exhibits wet/dry hydration oscillations whose magnitude and time scale are being amplified by the approaching ligand. In turn, the ligand's stochastic motion intimately couples to the slow hydration fluctuations, leading to a sixfold-enhanced friction in the vicinity of the pocket entrance. The increased friction considerably decelerates association in the otherwise barrierless system, indicating the importance of molecular-scale hydrodynamic effects in cavity–ligand binding arising due to capillary fluctuations. We derive and analyze the diffusivity profile and show that the mean first passage time distribution from the MD simulation can be accurately reproduced by a standard Brownian dynamics simulation if the appropriate position-dependent friction profile is included. However, long-time decays in the water–ligand (random) force autocorrelation demonstrate violation of the Markovian assumption, challenging standard diffusive approaches for rate prediction. Possible extensions of standard diffusion approaches to coupled reaction-diffusion systems are discussed. The spatiotemporal hydrodynamic coupling observed in our generic system may be of biological importance, providing the time needed for conformational receptor–ligand adjustments, typical of the induced-fit paradigm.

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Single molecule fluorescence microscopy to study molecular dynamics in polymer solutions and their relation to polymerization kinetics

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The reaction kinetics in soft and condensed matter is often diffusion-controlled. Therefore, only a detailed analysis of diffusional processes in these systems allows for their basic understanding and opens up ways towards materials with tailored properties. One of the main foci of our research is the observation of single molecule diffusion in polymer solutions, and how diffusion slows down with increasing conversion during radical polymerizations. In contrast to previous studies on polymerization kinetics and their relation to the mobility of monomers and polymer chain,[1] single molecule fluorescence microscopy allows us to follow the trajectories of individual (molecular, macromolecular and colloidal) tracers and determine heterogeneities in their motion.[2] The distributions of diffusion coefficients can vary significantly for different polymerization systems[3] and are essential for a complete description of polymerization kinetics. Such distributions can only be accessed by single molecule approaches, in contrast to ensemble measurements that basically measure mean values of diffusion coefficients.

The authors want to thank the Zukunftskolleg and the Department of Chemistry of the University of Konstanz for administrative and financial support. Furthermore, we appreciate financial support from the German Research Foundation (DFG).

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A new solution method for Fredholm integral equations and its applications to diffusion-influenced reaction kinetics

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Recently we proposed a new method of solution for the Fredholm integral equation of the second kind, which would be useful when the direct iterative approach leads to a divergent perturbation series solution [1]. A main advantage of the new method comes from the fact that the solution has the same structure as the exact solution. Hence the new method usually gives much more accurate results than Pade approximation method for the same computational cost.

By using the method, we had obtained an accurate expression of the propagator for diffusive dynamics of a pair of particles interacting via an arbitrary central potential and hydrodynamic interaction [1]. We tested the accuracy of the propagator expression by calculating the diffusion-controlled geminate and bimolecular reaction rates. It was shown that our propagator expression provides very accurate results for the whole time region [1,2]. We also derived a very accurate expression for the steady-state rate constant of diffusion-influenced bimolecular reactions involving long-range reactivity. We considered the general case in which the reactants interact via an arbitrary central potential and hydrodynamic interaction. The rate expression becomes exact in the two opposite limits of small and large reactivity, and also performs very well in the intermediate regime [3].

Very recently, we have investigated the effects of like-particle interactions on the diffusion-influenced bimolecular reactions by extensive computer simulations, and the results have been compared to a theoretical rate expression constructed by using the new solution method of integral equations [4].

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ABSTRACTS OF CONTRIBUTED COMMUNICATIONS

Reaction kinetics in an irradiated system: Electron-ion recombination in liquid argon

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An interesting feature of fast physicochemical processes taking place in irradiated systems is that they involve highly non-uniform spatial distributions of reacting species. The primary effect of irradiation is an ionization of the medium, which results in creating a distribution of electron-ion pairs along the radiation track. When the ionization density is very low, the produced electron-ion pairs are independent of one another, so their subsequent recombination can be described by the Onsager theory of geminate reactions. On the other hand, at a high ionization density, the electron-ion pairs are separated by short distances and form cylindrical structures. The recombination reactions in such structures are described by the theories of columnar recombination, such as the classical Jaffe theory.

In recent years, there has been a renewed interest in studying electron-ion recombination in irradiated liquefied rare gases. This is related to the construction of large elementary-particle detectors, such as ICARUS or ATLAS (part of the Large Hadron Collider), which use liquid argon as the detecting medium. Because the electron motion in liquefied rare gases cannot be treated as an ideal diffusion, the classical recombination theories are not fully applicable to these systems.

In this work, a computer simulation methodology is used to describe the electron-ion recombination in radiation tracks in liquid argon. The simulation is based on realistic models of electron transport and electron-ion reactions [1], and is capable of modeling large cylindrical structures of charged particles. The simulation results well reproduce the dependence of the recombination probability on the ionization density obtained from the ICARUS experiments. An agreement with experiment has also been achieved in interpreting the results of the ArgoNeuT project (FermiLab, USA) that show the dependence of the recombination probability on the angle between the track axis and the collecting electric field [2]. An application of our methodology in the search for Dark Matter will also be discussed.

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Modern problems of spin chemistry

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In this paper we consider some important aspects of Spin Chemistry. Spin Chemistry emerged about 40 years ago. It is currently a complete section of Physical Chemistry. It has its own problems, their own methods and approaches to their solution. Of course such methods as a CIDNP or a CIDEP have become universal methods of studying chemical reaction. New problems appear frequently in Spin Chemistry. However, often it is well forgotten old.

For example we consider Zeno chemical effect, i.e., chemical process influence on singlet - triplet evolution. The influence of recombination rate of radical pairs on the efficiency of singlet-triplet transitions is the well-known fact in spin chemistry. The cause is smearing of energy levels, and, as a consequence, transition resonance disturbance. Really, it has much in common with the influence of measurement process on quantum system evolution. However, the analogy is incomplete.

Measurement in spin chemistry is an important issue. For instance, under certain conditions switching of mw-pumping or external magnetic field retards spin evolution. Even more fine effects can be encountered in spin chemistry, for example, magnetic field of mw-range serves to detect CIDEP spectra and at the same time participates in the formation of this effect. It is necessary to distinguish the effect of CIDEP and the CIDEP spectrum. A similar feature exists in the CIDNP.

Particular attention will be paid to the influence of a magnetic field and the CIDNP effect in weak magnetic fields. Basic laws of magnetic and spin effects in weak magnetic fields have been established theoreticaly 30 years ago. Unfortunately, many do not know them.

For this time numerous investigations show that commonly the effect of a magnetic field on chemical reactions is insignificant with impact less than 10 percent. However, there are some papers that point to the observation of external magnetic field effect on chemical and biochemical systems actually having a significant impact on the reactions. We consider some models explaining how an applied weak magnetic field might influence the steady state of a non-equilibrium chemical system. External magnetic field may be responsible for the violation of the stationary state stability condition, and change radically the system properties.

Diffusion-controlled radical recombination in magnetic field

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Free radicals play an important role in many numbers of chemical and biological processes. Magnetic field effects in chemical reactions are due to spin selectivity of the radical recombination process, the presence of re-contacts during their diffusional encounter in solution and due to magnetic interaction of the unpaired electron spins with the external magnetic field and magnetic nuclei. The magnetic field effects are well known and studied in detail for geminate radical pairs. However, for the bulk radical recombination there are only a few [1-3] theoretical studies. In these works, radical recombination in the presence of a strong magnetic field was considered and the effects of paramagnetic relaxation were taken into account. These considerations did not take into account the hyperfine couplings of the unpaired electron spins with magnetic nuclei as well as the case of weak or arbitrary magnetic field. The latter is the subject of our study. We present analytical and numerical results of calculation of magnetic field effect for radical bulk recombination. Effects of electron spin relaxation, singlet-triplet mixing of spin levels of encounter radicals by an external (arbitrary magnitude) magnetic field and by hyperfine couplings were considered. The size of possible magnetic field effects on radical recombination rate constant has been estimated.

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Bimolecular photoinduced charge separation and recombination – now featuring ultrafast spectroscopy

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Electron transfer (ET) constitutes the simplest and at the same time most elementary "chemical" reaction rendering it a benchmark for the understanding of basically every other chemical reaction.

In this communication we will try to emphasize the peculiarities that arise as soon as this simple charge transfer step becomes interwoven with the reactants' mutual spatial diffusion. While the body of theoretical work on the influence of diffusion on electron transfer reactions is vast,[1] its only since the advent of ultrafast spectroscopies that its experimental counterpart is catching up and putting theories to a test.

Here, we compare and rationalize our recent results on bimolecular photoinduced charge separation and geminate recombination in liquid solution,[2,3] which have been obtained using state-of-the-art femtosecond time-resolved fluorescence and visible transient absorption spectroscopy. In particular, we are going to dwell on:

- Comparison of driving force dependence for bimolecular charge separation and recombination
- Charge separation in solvents of different dielectric permittivity
- Non-equilibrium effects on charge recombination
- Charge recombination in inert and reactive solvents

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Kinetics of exciplex formation/dissipation in reaction following Weller Schemes I and II

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The quenching of an excited electron donor, , by charge transfer to an electron acceptor, , resulting in the formation of either exciplex, , or ion pair and , has attracted a lot of attention for many years. Exciplex formation can proceed in two ways (so called Weller's Scheme I and Scheme II) [1], [2]. In a nonpolar medium exciplex formation occurs at the contact of the excited electron donor and acceptor, followed by contact dissociation of the ion pair (Scheme I). On the contrary, in polar solvents quenching of excited donors occurs in the main by distant electron transfer from donor to the acceptor, forms ions and , which can associate into exciplex at contact encounter (Scheme II). The Weller Schemes I and II are considered by means of Integral Encounter Theory. The general kinetic equations are obtained for excited and charged reactants involved into reaction. Detailed comparison of kinetics behaviour of reactions is made. The special attention is given to the important case of irreversible remote ionization of primary excited electron donor. The corresponding kinetic equations are solved for getting the stationary and kinetics characteristics of exciplexes formation and fluorescence as well as excitations and charges dissipation. Exciplex kinetics was shown (Fig. 1) to be qualitatively different at short times (during geminate stage) and at long times when reaction proceeding in bulk is controlled by bimolecular processes. The geminate processes are governed by bi-exponential relaxations within the cage while the bulk reaction proceeds as power law kinetics determine by bimolecular charge recombination. At low light pumping both stages are well separated in time while at stronger pumping the bulk stage starts much earlier. Such two-stage kinetics takes place only in the diffusion-assisted regime. In process of transition to a kinetic limit (dotted lines) bi-exponential geminate stage disappears.

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Kinetics of target searching by means of two diffusion-like motions

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A theoretical approach to stochastic searching of a small target is developed, which can be applied, for instance, to searching for a damaged site on the DNA molecule by a DNA repair enzyme. It is assumed that the searching molecule moves along a chain of sites by means of stochastic jumps to the adjacent positions (one-dimensional 'sliding'); the second motion models diffusion in three dimensions. A general expression is obtained for the flux to the damaged site. A special case is analyzed where the second motion is treated as effective 1D diffusion; the effective searching time is estimated. It is shown that the faster second motion shortens the searching time. A more realistic case where the second kind of motion leads to jumps not only to the adjacent site is also treated: it is shown that the diffusional search is facilitated even further.

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Relative diffusion in two dimensions: Breakdown of the standard diffusive model for simple liquids

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Using molecular dynamics simulations for a liquid of identical soft spheres we analyze the relative diffusion constant and the self diffusion constant D_n where r is the interparticle distance and n = 2, 3 denotes the dimensions number. We demonstrate that for the periodic boundary conditions, D_n is a function of the system size and the relation:, where L is the length of the cubic box edge, holds both for n = 2 and 3. The simulations show also that for n = 2 both and $D_2(L)$ increase logarithmically with its argument. According to both theoretical and simulation models $D_2(L\to\infty)$ should diverge[1]. Our simulations do not question this result. However, we found that the diffusive process for large two dimensional systems is very sensitive to perturbations. The sensitivity increases with L and even a very low perturbation limits the increase of $D_2(L\to\infty)$. Due to the functional form of the standard assumption for the Smoluchowski type models of reaction kinetics at three dimensions: leads to giant errors if applied for n = 2.

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Reaction kinetics in lanthanide-mediated supramolecular assemblies

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After a strong development of structural supramolecular chemistry in 1990s, people started to be more interested in thermodynamics and kinetics of self-assembly processes. These studies were particularly rare for lanthanide-containing systems due to low coordination preferences and high coordination numbers of these metal ions. The first self-assembly, a dinuclear triple-stranded helicate, was thus characterized only in 2003 by us.

In this contribution we will focus on kinetic aspects of self-assembly in polynuclear lanthanide helicates [1,2]. We will present the mechanistic study of dinuclear systems and the key reaction steps in details. When the system complexity increases, the kinetic evolution slows down due to increased number of self-repairing steps. This behaviour will be discussed for lanthanide assemblies derived from tripodal polytopic ligands [3,4].

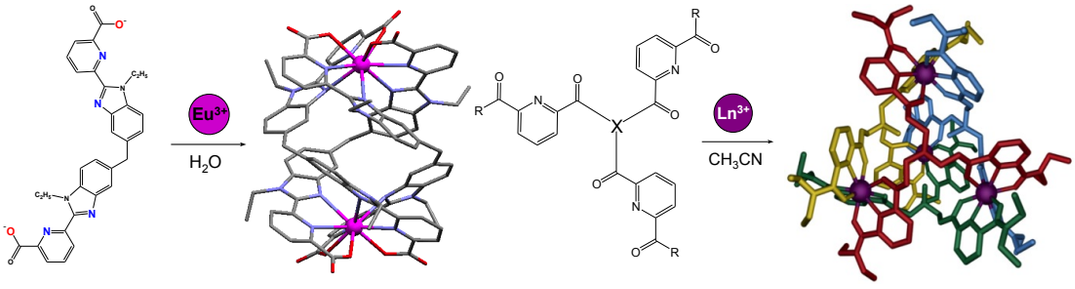

Figure. Self-assembly of a) dinuclear and b) tetranuclear helicates.

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Farewell to flash photolysis, broadband transient absorption spectroscopy from femtosecond to microsecond time domain

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Laser flash photolysis has been an important tool for the research on photoinduced processes over the past six decades. However, the achievable time resolution is limited by the duration of the excitation pulses and the spectral irradiance of the employed probe light. The limit of a couple of to tens of nanoseconds can be undercome by using picosecond laser diodes [1], however, at the cost of a narrow-band detection.

We have combined sub-nanosecond photo excitation with femtosecond super continuum probing to extend femtosecond transient absorption spectroscopy into the nanosecond to microsecond time domain [2]. The time delay between excitation and probe pulse is measured with a high precision time delay counter to overcome the intrinsic jitter of the employed passively Q-switched Nd:YAG pump laser. A time resolution of 350 ps is achieved with sub-picosecond excitation. Single-shot referencing of the super continuum probe with two identical spectrometer / CCD arrangements together with rapid sampling of kinetics yields an excellent signal-to-noise ratio in short to moderate accumulation times. The time overlap of almost an order of magnitude between fs and ns excitation mode permits to extend ultrafast transient absorption experiments seamlessly into time ranges traditionally covered by laser flash photolysis, with the added benefit of a broadband detection which covers the entire visible spectral domain and the near UV. Vice versa it is possible to study ultrafast parts of the dynamic beyond the time resolution of a typical flash photolysis set-up without changing the detection system.

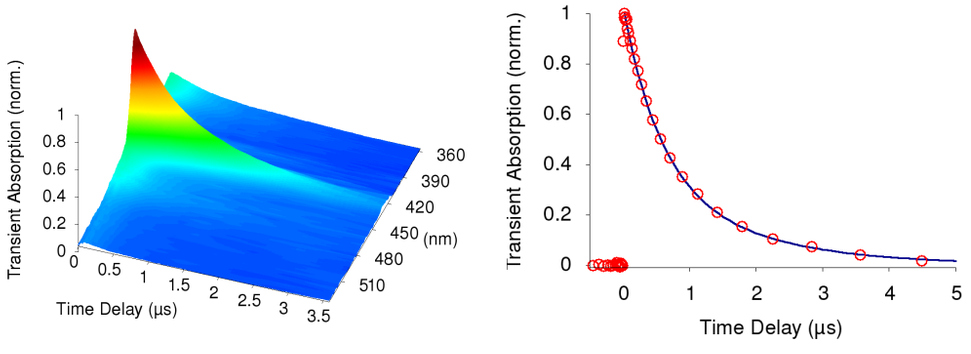

Fig. 1: Transient absorption of the triplet state of dibromoanthracene in acetonitrile (left panel) and kinetics at the maximum of the band at 425 nm (right panel).

Fig. 1 shows a transient absorption measurement of dibromoanthracene in acetonitrile. The signal centred at 420 nm is due to the absorption of the triplet state which is populated after inter-system crossing upon $S_0 \leftarrow S_1$ excitation at 355 nm. The right panel depicts the kinetics of this absorption at its maximum. The typical accumulation time for such a measurement amounts to a couple of minutes.

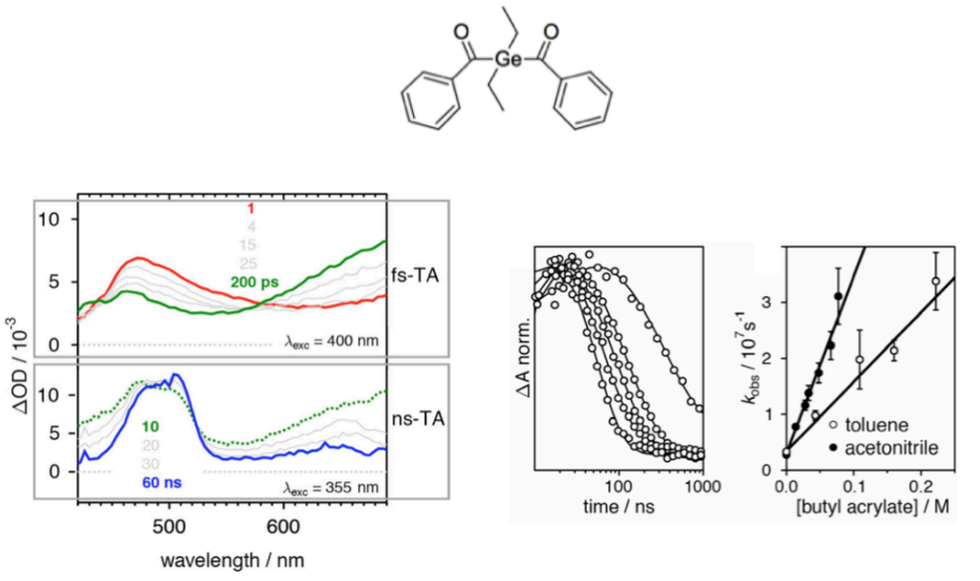

Fig. 2: Transient absorption on an acygermane photoinitiator reaction. Left transient spectra from femto to nansosecond time domain, Stern-Vollmer plot of the addition of butyl acrylate as a follow-up reaction.

Fig. 2 demonstrates the capability to follow a photochemical reaction from the initially photo excited state over inter-system crossing and bond breaking to a new bond formation [3]. After photo excitation of the S_1 state of acylgermane, a band due to the S1 excited state absorption appears around 480 nm (upper plot, red curve). Within 200 ps the system changes to the triplet manifold (upper plot, green curve). Bond breaking occurs from there on a 10 ns time scale. The green curve in the lower plot displays the spectral signature of the resulting acylgermane radical. Upon addition of butyl acrylate, the final product is formed within 60 ns (blue curve lower plot). The right panel of Fig. 2 depicts the kinetics and a Stern-Vollmer plot of the latter reaction. Further applications, including also magnetic field effects on kinetics, will be shown at the conference.

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Effect of moving discrete breathers on reaction kinetics in crystals under irradiation

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Interaction of moving discrete breathers (DBs) with a vacancy, edge dislocation and free surface in BCC Fe is analyzed using large scale MD simulations in 3D space. Scattering of DBs on lattice defects is shown to results in the localized atomic excitations, leading to the amplification of the reaction rates involving these defects due to effective reduction of the underlying reaction barriers. The amplification mechanism is based on modification of the classical Kramers escape rate from a potential well due to a periodic modulation of the well depth (i.e. the reaction barrier height), which is an archetype model for chemical reactions since 1940 [1]. Control parameters of the reaction facilitation, such as the amplitude and standard deviation of energy fluctuations, excitation time and the total transferred energy, are evaluated and compared with those obtained in two-dimensional lattices with pairwise Morse potentials [2].

The model results are applied for a quantitative analysis of experimental evidence of long-range effects in solids exposed to irradiation including radiation-enhanced diffusion in Fe [3], radiation-induced softening of Al, Cu, Fe [4] and enhancement of the annealing rate of defects in Ge by super low energy plasma irradiation [5].

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Self-assembly kinetics of a norovirus nanocage

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Noroviruses are the first cause of non-bacterial gastroenteritis in humans, as well as in animals, causing about 250 million cases of gastrointestinal distress and over 200,000 deaths each year. They are made up of a protein nanocage called the capsid (~20-40 nm in diameter), enclosing the genetic material, or genome, in the form of RNA. For noroviruses and many other viruses, the capsid consists of 180 copies of a single structural protein arrayed in an icosahedron, i.e. a solid with 20 triangular faces and 12 vertices [1]. Remarkably, the norovirus capsid proteins can self-assemble reversibly *in vitro*, without the assistance of the genome or any cellular components, solely by the interplay of solution pH and ionic strength [2].

The self-assembly kinetics of viral capsid is a multiscale process that requires heterogeneous molecular species with nanometer sizes to be probed over a time scale ranging from milliseconds to hours. We have thus investigated the formation of norovirus capsids by time-resolved small-angle X-ray scattering with a synchrotron source [3]. We devised a kinetic model with three main species – dimers, intermediates and capsids – exchanging matter at reaction rates that were determined by fitting the experimental data. The three-dimensional structure, at nanometer resolution, of the intermediate species was obtained by *ab initio* shape determination from its extracted form factor.

The analyses revealed that in the first step, some ten dimers combine to form a stave-shaped intermediate, possibly made of two pentamers of dimers connected by an interstitial dimer (see Figure). In the subsequent, slower step, which takes hours, these intermediates interlock into a capsid. In contrast, capsids form by sequential addition of dimers in many other viruses such as the hepatitis B virus.

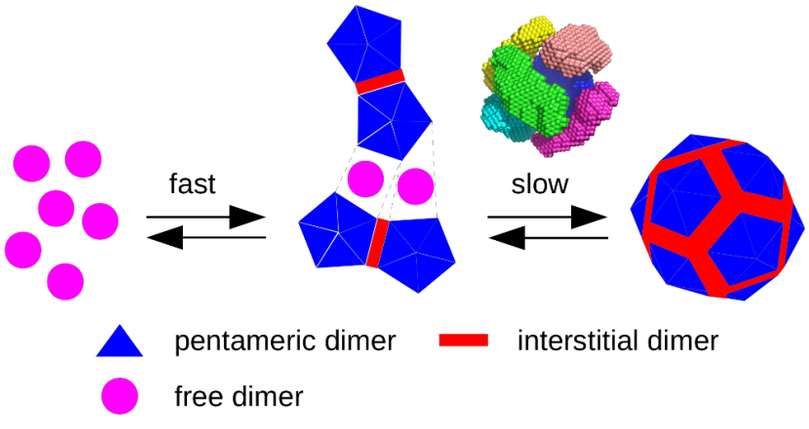

Figure 1. Kinetic scheme of norovirus capsid assembly. Above the last assembly step, a representation of interlocking intermediates is given as a possible mechanism. Six intermediates, each in a different color, have been positioned above the six contiguous fragments made of two pentamers of dimers connected by an interstitial dimer.

By clarifying the kinetics involved in norovirus assembly, this study provides a better

understanding of the physical processes at work in the self-assembly of a viral nanocage. It could also advance efforts to treat or prevent these infections, and it could be applied to engineer viral nanoparticles to make diagnostic agents and tailored therapeutics.

The authors gratefully acknowledge the ESRF and the SOLEIL facility for allocation of synchrotron beam time. The research was partly funded by ANR, Triangle de la Physique and CNRS.

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Solution of the diffusion equation in slender impermeable tubes of varying cross-section

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The anisotropic 3D equation describing the pointlike particles diffusion in slender impermeable tubes of revolution with cross section smoothly depending on the longitudinal coordinate is the object of our study. This problem is of great importance for numerous applications dealing with artificial and natural diffusion-influenced transport processes, however, it appeared to be fairly tricky. In this connection, researchers usually use an approximate reduction of the original diffusion equation describing the local particles concentration field to an effective time-dependent 1D equation [1].

In this study we apply singular perturbations approach to find the rigorous asymptotic expression for the local particles concentration as an expansion in the ratio of the characteristic transversal and longitudinal diffusion relaxation times. The corresponding leading-term approximation is a generalization of well-known Fick-Jacobs approximation. It is important to note that contrary to previous investigations we do not impose any This result allowed us to delineate the conditions on temporal and spatial scales under which the Fick-Jacobs approximation is valid. A striking analogy between solution of our problem and the method of inner-outer expansions for low Knudsen numbers gas kinetic theory is established. With the aid of this analogy we clarify the physical and mathematical meaning of the obtained results.

The full description of the method used and obtained results are presented in our recent paper [2].

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Experimental Evidence of the Relevance of Orientational Correlations in Photoinduced Bimolecular Reactions in Solution

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A major problem in the extraction of the reaction probability in bimolecular processes is the disentanglement from the influence of molecular diffusion. One of the strategies to overcome it makes use of reactive solvents in which the reactants do not need to diffuse to encounter each other. However, most of our quantitative understanding of chemical reactions in solution between free partners is based on the assumption that they can be approximated by spheres because rotation averages their mutual orientations. This condition may not be fulfilled when the reaction takes place on time scales faster than that of molecular reorientation. In this work, the fluorescence quenching of two very similar polyaromatic hydrocarbons with different electric dipole moments is measured. The concentration of a liquid electron-donating quencher is varied from very dilute solutions to pure quencher solutions. In both cases, the thermodynamics of the reactions are very similar and, according to the Marcus expression, the kinetics are expected to proceed at similar rates. However, one of them is 10 times faster in the pure quencher solution. This difference starts at relatively low quencher concentrations. An explanation based on the fluorophore−solvent dipole−dipole interaction and the consequent orientational solvent structure is provided. The orientational correlation between fluorophore and quencher is calculated by means of computer simulations. Important differences depending on the fluorophore dipole moment are found. The kinetics can be explained quantitatively with a reaction−diffusion model that incorporates the effects of the presence of the dipole moment and the rotational diffusion, only in the highest quencher concentration case, but not in dilute solutions, most likely due to fundamental limitations of the kinetic theory.

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Formation of exciplexes in X-irradiated alkane solutions for luminophores with short fluorescence lifetimes

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In case of X-ray generation of excited molecules via the step of radical ion pair recombination another molecule, corresponding to the second partner of the pair, is always found next to the excited molecule formed upon recombination. As a result, not only the expected emission of the excited molecule becomes possible, but also the formation of excited complexes, such as exciplexes. Thus X-ray generation opens the way to exciplexes for systems with a very short fluorescence lifetime of the luminophore molecule, as the excited molecule and its partner are close to each other.

This work reports the spectra of photo- and X-generated luminescence from several donor-acceptor systems in alkane. One component (DMA, positive charge acceptor) was held constant, and as the other component (electron acceptor, luminophore) were chosen molecules with lifetimes of the electronically excited state τ_f from about 100 ns to about 10 ps. We also studied the sensitivity of the emission spectra to external magnetic field, and obtained the close to maximally possible under these experimental conditions magnetic field effect (up to 20%) in exciplex emission band for the system diphenylacetylene/DMA having $\tau_f = 8$ ps in *n*-dodecane [1]. Theoretical description is currently under development.

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High-pressure effects on the rates of electron transfer reactions in organic redox systems: an ESR-spectroscopic study

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Electron transfer reactions are among the most important reactions in chemistry, physics and biology. From simple redox reactions to complex photosynthesis, electron transfer is always involved. To understand the basic principles of these reactions many investigations have been undertaken to measure the rate constants and the activation parameters.

The extensive theory of R.A. Marcus and others helps quite a lot in understanding the experimental data obtained. One of the most fundamental reactions are the so-called electron-self exchange reactions, where no bond is broken or newly formed. Such reactions are characterized by pure electron exchange.
Dynamic ESR (Electron Spin Resonance Spectroscopy) is one method to measure the rate constants of such reactions.

According to Marcus-Theory the activation energy of an electron transfer reaction is mainly given by the inner-sphere reorganization energy describing the changes of bond-lengths and angles upon electron transfer and the outer-sphere reorganization energy responsible for the reorientation of the solvent dipoles caused by the charge transfer. Up to now several investigations describe the solvent dependence of electron-transfer reactions in the sense of Marcus theory very well, provided the solvents show a polarization effect. Also the activation parameters, like activation enthalpy and activation entropy, obtained from temperature dependent measurements of the rate constants are well understood, now.

We report here on the pressure dependence of electron-self exchange reactions in classical organic solvents [1,2] as well as in ionic liquids. These are molten salts at room temperature consisting of an organic cation and an inorganic anion. Electron transfer in these solvents is found to be diffusion controlled.

From Arrhenius-type plots one can gets the activation volumes at constant temperature. From pressure dependent plots at constant temperature the activation volumes are obtained. Astonishing is the fact that some of the measured activation volumes show a positive sign, indicating a looser arrangement in the activated complex compared with the ground-state precursor complex. This is in agreement with theory, but not fully understood up to now. Beside the experimental and theoretical results, also experimental details will be given [3].

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Segregation of colloids by interference between entropic effect and thermophoresis

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Recently, various distribution of colloids under well controlled temperature gradients have been measured. [1-2] Movement of particles under temperature gradients is called thermophoresis. When polymer suspensions were heated locally by a focused laser, migration of polymers from the hot region to cold region by the polymers' thermophoresis was observed. If the other colloids also have tendency to move from the hot region to cold region and the concentration of colloids is much higher than that of polymers, the distribution of polymers is affected by the non-uniform distribution of colloids. The particle motion driven by concentration gradients is called diffusiophoresis. In experiments, segregation of polymers from the other colloids was observed. In some cases, polymer concentration at hot region was higher than that at cold region in the presence of other colloids. [1,2] Even ring formation around the hot spot was observed. [2]

We theoretically study the segregation of polymers from other colloids by taking into account the entropic effect by excluded volume interaction. We show that various non-uniform distribution of polymers including the ring can be formed by the interference between the entropic effect and thermophoresis. The ring can be formed when the temperature gradient is increased above the threshold value causing nonlinear response of the polymer profile. In experiments, three phases of polymer distribution, such as depletion, accumulation, and ring profile, were observed. These phases were expressed in the 2D diagram, where one of the axis was the concentration of colloids and the other axis was the polymer size. [2,3] Previously, the polymer size-dependence was not theoretically explained. Our theory reproduces the phase diagram including the polymer size-dependence. [4]

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Experimental detection of long-distance interactions between biomolecules through their diffusion behavior: Numerical study

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The dynamical properties and diffusive behavior of a collection of mutually interacting particles are numerically investigated for two types of long-range interparticle interactions: Coulomb-electrostatic and dipole-electrodynamic. It is shown that when the particles are uniformly distributed throughout the accessible space, the self-diffusion coefficient is always lowered by the considered interparticle interactions, irrespective of their attractive or repulsive character. This fact is also confirmed by a simple model to compute the correction to the Brownian diffusion coefficient due to the interactions among the particles. These interactions are also responsible for the onset of dynamical chaos and an associated chaotic diffusion which still follows an Einstein-Fick like law for the mean square displacement as a function of time. Transitional phenomena are observed for Coulomb-electrostatic (repulsive) and dipole-electrodynamic (attractive) interactions considered both separately and in competition. The outcomes reported in this paper clearly indicate a feasible experimental method to probe the activation of resonant electrodynamic interactions among biomolecules.

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