CECAM Workshop Scientific Report

Workshop: **Charge carrier dynamics in nanostructures: optoelectronic and photo-stimulated processes**

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Location: University of Bremen, Germany,
9th until 13th of October 2017

I. State-of-the-Art Summary

Advances of time-resolved experimental techniques, needed for a detailed understanding of charge carrier dynamics as they occur in real time, require matching progress in theoretical approaches. Applications to novel, emerging nanoscale materials, which ultimately lead to faster, more efficient and miniaturized devices, pose multiple theoretical challenges. Modeling time-resolved experimental data becomes a major goal of a theorist.

The proposed workshop became a forum to brainstorm ideas about solutions to important computational problems, and identify new directions for time-dependant electronic structure method development and challenging applications. In this way, we have been able to create an exchange mechanism to unite a core of developers in an interactive environment, in order to initiate design of a new generation software tools for quantum modelling of realistic complex systems and nanostructures in electronic ground and excited states. The delivery of this technology to a broad community will facilitate breakthroughs on high-impact materials science problems.

We have been successful to achieve the following key objectives:

- Bring together researchers from experiment and theory working on time-dependent charge carrier dynamics related to optoelectronic and photo-stimulated processes, in order to highlight recent progress, and to discuss challenges and opportunities in the materials aspect of tailor-made nanostructures and hybrid interfaces for highly efficient energy applications.
- Foster the exchange of methodological expertise and new developments between scientists working on different aspects of charge dynamics at surfaces, interfaces, and in 2D-materials and hetero-structures.
- Discuss possibilities for optimizing the materials properties and device design. The interdisciplinary character of the workshop did help finding solutions for overcoming current limitations.
- The Workshop has provided opportunity to form new worldwide interdisciplinary collaborations on time-dependent spectroscopy for the mutual benefit of theoretical, experimental and applied researchers, in particular including also young researchers on the Postdoc and PhD-level.

The program consisted of 34 invited talks of 40 minutes (35+5) each and one poster session presenting 41 posters. In addition, many social events (reception and

conference dinner) to allow for informal exchange were held. The invited talks were given by well-established scientists from the different theoretical and experimental communities, which acted as platform for interesting cross-/interdisciplinary discussions. The invited talks were followed by a poster session where the young researcher participants could show their scientific work/progress and exchange of ideas with a broad knowledge in computational chemistry, solid state physics and computational materials science. The organization was very compact with the scientists accommodated in the same hotel fostering exchange and discussion between the participants also outside the meeting room.

Financial support from the DFG, Psi-k Network, and the German CECAM node multi-scale modelling from first principles, cecam-mm1p.de at the University Bremen is gratefully acknowledged.

II. Scientific content, main outcome of key presentations, selected discussions

Currently, theoretical studies of light-induced processes at interfaces usually fall in one of two broad categories: i) modelling of the atomic structure and ground state electronic properties of complex interfaces and ii) simulation of light-matter interactions and electronic excited states in relatively simple systems. For example, several talks at the conference addressed the atomic surface structure of photocatalysts, such as titanium dioxide, and discussed the complex interaction of these surfaces with adsorbed atoms and molecules. Other talks addressed excited states of such photocatalysts with high-level methods, such as many-body perturbation theory. For a full understanding of photocatalysis and other light-induced processes at interfaces, it is necessary to combine these two aspects. We therefore expect and hope that in the near future more studies will attempt to bridge and connect these categories, i.e. simulate the interaction of light with matter at realistically complex systems.

For the light-matter interaction, there has been an increasing number of studies using the real-time formalism. These studies give important insights into the kinetics of light-induced processes at interfaces. However, the increased numerical effort of these simulations usually necessitates the use of approximate theories, such as time-dependent density-functional theory with its well-known limitations. Conversely, higher-level methods, such as quantum chemical wavefunction approaches or the Bethe-Salpeter equation, can only be applied with a linear-response framework. We expect that the next 2-3 years will see the transfer of high-level methods from the frequency-domain to the real-time domain. This would open up the description of exciton dynamics in heterogeneous systems, which are highly relevant to photocatalysis and photovoltaics.

Experiment

On the experimental side, the workshop has demonstrated enormous effort in the advancement of time-resolved experimental techniques probing the transient electronic structure after excitation of charge carriers with light or intense pulsed laser fields on nano- and attosecond scales.

- E.g., this includes the study of resonant energy transfer of triplet excitons from pentacene to lead selenide (PbSe) nanocrystals, where Akshay et al. [1] report on efficient resonant-energy transfer of molecular spin-triplet excitons from

organic semiconductors to inorganic semiconductors. They use ultrafast optical absorption spectroscopy to track the dynamics of triplets, generated in pentacene through singlet exciton fission, at the interface with PbSe nanocrystals.

- The direct imaging of microscopic structural changes on ultrafast time scales is another particular challenge in the natural sciences. Alongside ultrafast X-ray techniques, time-resolved electron microscopy, diffraction and spectroscopy yielded unprecedented insights into rapid physical, chemical and biological processes. Various incvited speakers in most recent years follow a variety of imaging approaches with ultrashort, highly coherent electron pulses to investigate the dynamics of ultrafast electronic and structural phenomena. Over the past few years, Feist and Schäfer et al. [2] have developed a novel implementation of Ultrafast Transmission Electron Microscopy ("UTEM"). The instrument employs a "pump-probe" scheme, in which two laser pulses are coupled into the column of a transmission electron microscope (TEM). A first laser pulse excites an electronic or structural change in the investigated sample. In a special photocathode, a second, delayed laser pulse generates an ultrafast electron pulse, which then probes the induced sample change in microscopy, diffraction or spectroscopy. By varying the relative pulse delay, the dynamics can be followed in time.

- Transition metal dichalcogenides (TMDs) are emerging as promising two-dimensional (2D) semiconductors for flexible optoelectronic, spintronic and photovoltaic devices. Their photophysical properties are of pivotal importance for the understanding and optimization of device operation. However, a microscopic explanation of the photophysics is still lacking. Cerullo and Pogna et al. [3] use femtosecond transient absorption spectroscopy, with pump pulse tunability and broadband probing, to monitor the relaxation dynamics of single-layer MoS_2 over the entire visible range, upon photoexcitation of different excitonic transitions. They find that, irrespective of excitation photon energy, the transient absorption spectrum shows simultaneous bleaching of all excitonic transitions and corresponding red-shifted photoinduced absorption bands. First-principle modeling of the ultrafast optical response reveals that a transient bandgap renormalization, caused by the presence of photoexcited carriers, is primarily responsible for the observed features.

- Multi-dimensional ultrafast pulsed coherent optical spectroscopy is more and more becoming the experimental method of choice to understand and control light-mater interactions in semiconductor nanostructures, see, Nardin and Cundiff et al. [4] and in photo-synthetic biological architectures [1]. In oxygenic photosynthesis, the initial charge separation occurs in the photosystem II reaction centre, the only known natural enzyme that uses solar energy to split water. Both energy transfer and charge separation in photosynthesis are rapid events with high quantum efficiencies. In recent nonlinear spectroscopic experiments, long-lived coherences have been observed in photosynthetic antenna complexes, and theoretical work suggests that they reflect underlying electronic–vibrational resonances, which may play a functional role in enhancing energy transfer. Using two-dimensional electronic spectroscopy, Fuller and Ogilvie et al. [5] report the observation of coherent dynamics persisting on a picosecond timescale at 77 K in the photosystem II reaction centre. In the opining lecture of the conference, Scholes gave an excellent overview of the current status of the field. He discussed different examples

how coherence may be use to enhance energy transfer in biological systems and presented new experimental data highlighting the importance of vibronic coupling for energy transfer[2].

- Coherent multidimensional electronic spectroscopy can be employed as well to unravel various channels in molecular chemical reactions. This approach is thus not limited to analysis of energy transfer or charge transfer (i.e. processes from photophysics), but it can also be employed in situations where the investigated system undergoes permanent structural changes (i.e. in photochemistry), see Nuernberger and Brixner et al. [6]. Kolano and Hamm et al. [7] recently introduced the method of transient 2D-IR spectroscopy, which extends conventional 2D-IR spectroscopy to the non-equilibrium regime, allowing one to make 'molecular movies' of fast conformational changes in proteins and “watch hydrogen-bond dynamics“.
- Coherent vibrational motion of molecular moieties can now be monitored experimentally, e.g. motion of fullerenes after ultra-short impulsive optical excitation of a polymer donor in a prototypical polymer/fullerene solar cell[3][8] as shown by Falke and Lienau et al. The comparison of the experimental data to first-principle theoretical simulations has been a major topic of the meeting. Molinari and Rozzi presented time-dependent density functional theory simulations that give evidence coherent electron transfer between donor and acceptor on a similar time scale as in experiment. They showed oscillations of the transferred charge with a 25-femtosecond period matching that of the observed vibrational modes. The results show that coherent vibronic coupling between electronic and nuclear degrees of freedom is of key importance in triggering charge delocalization and transfer in a noncovalently bound reference system.
- Two-dimensional electronic spectroscopy with 10-fs time resolution can reveal the coherent birth of polaron pairs in organic semiconductors. De Sio and Lienau et al.[4] find signatures of strongly coupled exciton and polaron pair state excitations in the two-dimensional spectra of P3HT polymer thin films. The study shows that the strong electron-phonon coupling in these materials results in a mixing of localized exciton and charge separated polaron pair excitations. Vibronic coupling thus induces exciton dissociation despite the large exciton binding energies in these materials. The experimental results were supported by multiconfiguration quantum dynamics simulations presented by Burghardt et al.[5] Similar experimental studies were presented by Scholes et al.[6] highlighting the effect of the sample morphology on coherent vibronic dynamics.
- Popmintchev gave an overview of laboratory-scale high harmonic sources. He discussed the substantial experimental progress made during the last years in creating isolated attosecond pulses in the VUV to X-ray regime. Specifically, the use of mid-infrared drivers has now allowed to create pulses with keV photon energies[7]. This offers exciting new prospects for atom-specific probing of charge dynamics in molecules and nanostructures.
- Trabatttoni and Calegari et al., have used such high harmonic sources to study charge migration in organic molecules in the gas phase on few-femtosecond time scales[8]. Visible pump / XUV probe experiments promise to give much new insight into charge migration processes. The current status of the theoretical discussion of those experiments has been presented by I.

Tavernelli. Mixed quantum-classical simulations suggest that vibronic couplings are of paramount important for these ultrafast charge motions.

- A promising route towards the development of ultrastable fiber laser sources has been presented by Leitenstorfer. Using the world-wide unique laser system developed in Konstanz, vacuum fluctuations of the laser field could be measured for the first time[9] and squeezed vacuum noise could be observed[10]. The system is tailor-design to study light-matter interactions and to coherently control light-driven currents[11] on an ultimate single cycle time scale.
- A unique approach towards studying ultrafast dynamics in molecules with atomic resolution has been discussed by Cocker et al. By combing a scanning tunneling microscope with Terahertz pulse excitation, signatures of the motion of van der Waals bound molecules at surfaces could be resolved[12].

Theory and computational studies

On the computational side, the theoretical groups as well have put a lot of effort to address the more and more advanced time-resolved spectroscopic data and provided atomistic insight into photo-induced processes.

- Real-time time-dependent density functional theory (TDDFT) constitutes one of the most promising way to model time-resolved experimental data. It provides both good accuracy and computational efficiency, allowing one to model hundred atom systems on femto- and pico-second time-scales. Ab initio DFT provides a more rigorous and transferrable tool that can be applied to nearly all classes of materials, with the system size limited to below 200 atoms. Tight-binding DFT, DFTB, can be used to model excited state dynamics in thousand atom systems; however, it requires careful parameterization, in particular when modeling new materials. Successful applications have been demonstrated in the talks by Oleg Prezhdo, Sergei Tretiak and Christian Sanchez.
- Nonadiabatic molecular dynamics (NAMD) allows one to describe combined electron-nuclear non-equilibrium evolutions that ensue following a photo-excitation or another perturbation. While TDDFT focuses on coupling of the electronic subsystem with electromagnetic radiation and subsequent evolution of electron density, NAMD enables one to combine electronic evolution with vibrational dynamics, and describe electronic energy dissipation into heat, charge and energy transfer driven by nuclear motions, nonradiative electron-hole recombination and related processes. A combination of TDDFT and NAMD is a particularly powerful tool capable of a comprehensive description of all non-equilibrium processes in modern materials.
- Extensive theoretical efforts are dedicated to modeling of far-from-equilibrium excited state dynamics in photovoltaic and photocatalytic systems, aimed at harvesting of solar light energy. In these systems, one is interested in competition between productive processes, such as charge and energy transfer, with counter-productive processes, such as energy dissipation to heat and charge recombination. The ultrafast timescales of photo-initiated dynamics makes it hard to employ traditional charge and energy transfer theories, which make (quasi-) equilibrium assumptions that are not satisfied on femto- and pico-second scales, motivating development and applications of TDDFT, NAMD and related theories.

- Hardy Gross in his talk *Potential energy surfaces and berry phases beyond the Born-Oppenheimer approximation: a novel approach to non-adiabatic dynamics* were facing the full Hamiltonian of the complete system of electrons and nuclei. He described an exact factorization of the full electron-nuclear wavefunction into a purely nuclear part and a many-electron wavefunction which parametrically depends on the nuclear configuration and which has the meaning of a conditional probability amplitude. The equations of motion for these wavefunctions lead to a unique definition of exact potential energy surfaces as well as exact geometric phases, both in the time-dependent and in the static case. They proposed novel mixed-quantum-classical algorithms whose unique feature is that the trajectories are coupled. Without recourse to Tully surface hopping and without any added decoherence correction, the new algorithm provides a rather accurate, (much improved over surface hopping) description of decoherence, which is demonstrated for the photo-induced ring opening of oxirane.
- Open quantum systems are ubiquitous in nature. While observation of quantum coherence in experiments has progressed, there is a need to understand and utilize the dynamics of quantum systems interacting with environment. Guanhua Chen reported the development of a time-dependent density-functional theory for open systems and its applications to study interference effect in molecular electronics. Successful application of the method is also demonstrated by Ignacio Franco in studying non-resonant laser pulse induced current in nanojunctions. The optical properties of nanojunctions have also been the topic of several theoretical studies. Heiko Appel, Thomas Niehaus and ChiYung Yam reported studies of absorption and emission processes in nanoscale systems by including light-matter interactions at quantum level.
- Hot carrier generation from plasmonic decay in metallic nanostructures are currently under intensely investigation because of their potential for technological applications in photocatalysis, photodetection and solar energy harvesting. Accurate theoretical description of these phenomena can guide experimental progress and device design. Different theoretical approaches to study plasmonic response in metallic nanostructures, including generation, transport and thermalization of hot carriers are reported, which account for both electronic structure and phonon effects. The undesired hot carrier thermalization in different materials due to electron-electron and electron-phonon interactions is studied, which provides clue to retain efficient light absorption while minimizing carrier thermalization.

III. Assessment of the results and impact on future direction of the field

A major obstacle to the accurate description of light-induced processes at interfaces is the intrinsic interdisciplinarity of the subject. The study of such processes requires knowledge of physics, chemistry, materials science and even biology. Therefore, advancing our understanding of photo-induced processes necessitates a joint effort from experts in different fields, including both experimental and computational studies. To enable such collaborations, it is of crucial importance to organize interdisciplinary workshops like ours to act as platforms for exchanging ideas and for bringing together researchers from different subject areas who work on different

aspects of the same topic. In the future, we will try to continue organizing workshop to achieve this goal on a biannual basis.

The workshop became a forum to discuss about possible solutions of improving the quality of hybrid interfaces for studying real time electron dynamics and charge transfer reactions and correlating experiment and theory on a highly predictive level.

IV. Infrastructure requirements to make advances in the field

As discussed above, the advancement of theories of light-induced processes at interfaces requires the development of novel theories and codes which can i) capture the inherent complexity of realistic interfaces and ii) contain sufficiently accurate description of physico-chemical processes, including photon-electron interactions, electron-hole coupling, electron-phonon coupling, etc. The development of such theories and the resulting computer software will benefit the broad community of theoretical researchers, but also have important impacts on experimental studies and industry. However, to achieve this, a continued investment is required, as method and code development usually occur on a longer time scale compared to the study of applications. This also requires the training of masters and PhD students not only in physics, materials science or biology, but also in computer programming (including parallelization of software) and use of high-performance computing resources.

V. *Impact to address the need of industry in driving economic growth*

Progress in the field of many body physics, time-dependent electron dynamics and wave function based correlated quantum chemistry is fundamental to many European industries connected to high-tech materials design and device applications. Examples are

• Advanced hybrid photovoltaics

• Nanomaterials with vibronically-enhanced transport properties for improved photovoltaics or quantum sensing

• Photo-catalytic processes in energy storage and pollutant degradation

• Hybrid nano/bio-systems for medical applications

• Molecular scale electronic devices and quantum computing

• Single-defect-based quantum optical and spintronic sensors and devices

• Ultrafast switchable photonic devices operating at THz speed

• Bio-inspired sensor concepts for ultrasensitive detection of electric and magnetic fields.

Such directions can be strengthened by focused research projects for the development of new materials and devices in key enabling technologies. The field of nanodevices is currently opening to new materials, especially 2D. The EU flagship on graphene and 2D materials is indeed expected with the aid of computational predictions to produce several new outcomes. However, technological innovation is not limited to these materials.

Community needs (minimum 1000, maximum 2000 characters)

Discuss the needs of the community in terms of computational infrastructure (e.g. existing codes, use of HPC resources), networking (e.g. outreach to other communities including experimentalists), event organization (e.g. should a series of CECAM workshops on this topic be considered and if so why?)

We should try to make a 2-year CECAM series out of this workshop Funding (minimum 500, maximum 1000 characters)

Summarize typical funding channels and identify possible new sources in upcoming calls e.g. Horizon 2020, funding schemes. Was the possibility of joint research proposals discussed during the meeting?

New sources: DFG Priority Programme on “Nonadiabatic dynamics and vibronic coupling in nanostructures”
ITN or other type of European Network on “Coherent charge carrier dynamics in nanostructures” - We have plenty of European Researchers - both theoretician and experimentalists at the workshop. Currently there is no funding scheme that allows for creating a joint consortium. I have tried to initiate a FET-Open with some of people at the workshop but this has not yet been successful.

Will these developments bring societal benefits? (minimum 1000, maximum 2000 characters)

Discuss potential societal benefits of the research topic of the workshop. For example, summarize economic through the use of our methods by industry; societal benefits such as sustainability; health benefits such as design. If possible reference funding opportunities related to these benefits.

The workshop has been extremely successful in bringing together experimentalists and theoreticians. There is a strong community need to establish a joint research effort towards CCDYN.

November 25th 2017

The Organizers

1. Engel GS, *et al.* Evidence for wavelike energy transfer through quantum coherence in photosynthetic systems. *Nature* **446**, 782-786 (2007).

2. Scholes GD, *et al.* Using coherence to enhance function in chemical and biophysical systems. *Nature* **543**, 647-656 (2017).

3. Falke SM, *et al.* Coherent ultrafast charge transfer in an organic photovoltaic blend. *Science* **344**, 1001-1005 (2014).

4. De Sio A, *et al.* Tracking the coherent generation of polaron pairs in conjugated polymers. *Nat Commun* **7**, 8 (2016).

5. Polkehn M, Tamura H, Burghardt I. Impact of charge transfer excitons in regioregular polythiophene on the charge separation at polythiophene-fullerene heterojunctions. *Journal of Physics B: Atomic, Molecular and Optical Physics*, (2017).

6. Song Y, Hellmann C, Stingelin N, Scholes GD. The separation of vibrational coherence from ground- and excited-electronic states in P3HT film. *J Chem Phys* **142**, 11 (2015).

7. Popmintchev T, *et al.* Bright Coherent Ultrahigh Harmonics in the keV X-ray Regime from Mid-Infrared Femtosecond Lasers. *Science* **336**, 1287-1291 (2012).

8. Calegari F, *et al.* Ultrafast electron dynamics in phenylalanine initiated by attosecond pulses. *Science* **346**, 336-339 (2014).

9. Riek C, *et al.* Direct sampling of electric-field vacuum fluctuations. *Science* **350**, 420-423 (2015).

10. Riek C, *et al.* Subcycle quantum electrodynamics. *Nature* **541**, 376-+ (2017).

11. Rybka T, Ludwig M, Schmalz MF, Knittel V, Brida D, Leitenstorfer A. Sub-cycle optical phase control of nanotunnelling in the single-electron regime. *Nat Photonics* **10**, 667-670 (2016).

12. Cocker TL, Peller D, Yu P, Repp J, Huber R. Tracking the ultrafast motion of a single molecule by femtosecond orbital imaging. *Nature* **539**, 263-+ (2016).