

Symposium Resonant Energy Transfer and Interatomic Coulombic Decay (SYET)

jointly organized by
the Molecular Physics Division (MO) and
the Quantum Optics and Photonics Division (Q)

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Energy transfer between microscopic quantum systems has been studied by the Quantum Optics and Molecular Physics communities from very different points of view. In Quantum Optics, Förster resonant energy transfer is a process whereby an electronically excited system decays by emitting a photon which is subsequently resonantly absorbed by a second system. In Molecular Physics, on the other hand, the decay of an electronically excited system can proceed via an energy transfer to (and ionization of) the immediate chemical environment in a mechanism known as Interatomic or Intermolecular Coulombic Decay.

Both phenomena, Resonant Energy Transfer and Interatomic Coulombic Decay, are currently of high interest due to their relevance in both biological and technological contexts. Resonant Energy Transfer is a key mechanism underlying photosynthesis in light-harvesting complexes, while also being a decisive factor in the engineering of efficient solar cells. Interatomic Coulombic Decay mechanisms, in turn, have been proposed as a source of genotoxic low-energy electrons, providing new insights into the radiation damage on a microscopic level, and ideas for possible future concepts for radiation therapy.

Overview of Invited Talks and Sessions

(Lecture room RW HS)

Invited Talks

SYET 1.1	Thu	11:00–11:30	RW HS	The quantum design of photosynthesis — ●RIENK VAN GRONDELLE
SYET 1.2	Thu	11:30–12:00	RW HS	On systems with and without excess energy in environment: ICD and other interatomic mechanisms — ●LORENZ CEDERBAUM
SYET 1.3	Thu	12:00–12:30	RW HS	Molecular QED of Resonance Energy Transfer: Pair and Many-Body Theory — ●AKBAR SALAM
SYET 1.4	Thu	12:30–13:00	RW HS	The Experimental Investigation of Interatomic/Intermolecular Coulombic Decay — ●UWE HERGENHAHN

Sessions

SYET 1.1–1.4	Thu	11:00–13:00	RW HS	Resonant Energy Transfer and Interatomic Coulombic Decay
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SYET 1: Resonant Energy Transfer and Interatomic Coulombic Decay

Time: Thursday 11:00–13:00

Location: RW HS

Invited Talk SYET 1.1 Thu 11:00 RW HS
The quantum design of photosynthesis — ●RIENK VAN GRONDELLE — Department of Biophysics, Faculty of Sciences, VU University Amsterdam, De Boelelaan 1081, 1081 HV Amsterdam, The Netherlands

In photosynthesis absorbed sun light produces collective excitations (excitons) that form a coherent superposition of electronic and vibrational states of the individual pigments. Two-dimensional (2D) electronic spectroscopy allows a visualization of how these coherences are involved in the primary processes of energy and charge transfer. Based on quantitative modeling we identify the exciton-vibrational coherences observed in 2D photon echo of the photosystem II reaction center (PSII-RC). We find that the vibrations resonant with the exciton splittings can modify the delocalization of the exciton states and produce additional states, thus promoting directed energy transfer and allowing a switch between the two charge separation pathways. We conclude that the coincidence of the frequencies of the most intense vibrations with the splittings within the manifold of exciton and charge-transfer states in the PSII-RC is not occurring by chance, but reflects a fundamental principle of how energy conversion in photosynthesis was optimized.

Invited Talk SYET 1.2 Thu 11:30 RW HS
On systems with and without excess energy in environment: ICD and other interatomic mechanisms — ●LORENZ CEDERBAUM — Heidelberg University, Heidelberg, Germany

How does a microscopic system like an atom or a small molecule get rid of the excess electronic energy it has acquired, for instance, by absorbing a photon? If this microscopic system is isolated, the issue has been much investigated and the answer to this question is more or less well known. But what happens if our system has neighbors as is usually the case in nature or in the laboratory? In a human society, if our stress is large, we would like to pass it over to our neighbors. Indeed, this is in brief what happens also to the sufficiently excited microscopic system. A new mechanism of energy transfer has been theoretically predicted and verified in several exciting experiments. This mechanism seems to prevail “everywhere” from the extreme quantum system of the He dimer to water and even to quantum dots. The transfer is ultrafast and typically dominates other relaxation pathways.

Can there be interatomic/intermolecular processes in environment when the system itself (again, an atom or small molecule) does not possess excess energy? The answer to this intriguing question is yes. The possible processes are introduced and discussed. Examples and arguments are presented which make clear that the processes in question play a substantial role in nature and laboratory.

Work on the interatomic processes discussed can be found in the Bibliography: <http://www.pci.uni-heidelberg.de/tc/usr/icd/ICD.refbase.html>

Invited Talk SYET 1.3 Thu 12:00 RW HS
Molecular QED of Resonance Energy Transfer: Pair and

Many-Body Theory — ●AKBAR SALAM — Department of Chemistry, Wake Forest University, Winston-Salem, NC 27109-7486, USA

One of the successes of the theory of molecular QED [1] in the area of inter-particle interactions is the unified description it furnishes of resonance energy transfer (RET) [1]. This process is viewed as arising from the exchange of a single virtual photon between an initially excited donor species and a ground state acceptor moiety. Asymptotic limits of the Fermi golden rule transition rate reveal a radiationless Förster type of exchange in the near-zone that has inverse sixth power separation distance dependence, and a radiative inverse square law behaviour in the far-zone.

In this talk, pair RET is briefly reviewed before recent results are presented concerning the influence that one and two additional passive polarisable molecules have in modifying the transfer rate [2-4]. Insight is gained into migration of energy in an environment of bath molecules by comparing these microscopic models of RET occurring between individual particles with polariton based approaches [5] in which direct excitation energy transfer is facilitated by medium-dressed photons.

[1] A. Salam, *Molecular Quantum Electrodynamics*, Wiley, Hoboken, 2010. [2] A. Salam, *J. Chem. Phys.* 136, 014509 (2012). [3] D. L. Andrews and J. S. Ford, *J. Chem. Phys.* 139, 014107 (2013). [4] D. Weeraddana, N. Premaratne and D. L. Andrews, *Phys. Rev. B* 92, 035128 (2015). [5] G. Juzeliunas and D. L. Andrews, *Phys. Rev. B* 49, 8751 (1994).

Invited Talk SYET 1.4 Thu 12:30 RW HS
The Experimental Investigation of Interatomic/Intermolecular Coulombic Decay — ●UWE HERGENHAHN — Leibniz-Institut für Oberflächenmodifizierung, Leipzig — Max-Planck-Institut für Plasmaphysik, Greifswald

In this talk I will review the experimental investigation of Intermolecular Coulombic Decay (ICD). The notion that ICD involves an energy transfer between two sites, often depicted as the exchange of a virtual photon, implies that a description of the system using separate sites is meaningful, *i.e.* it is supposed to be weakly bonded. Intermolecular Coulombic Decay originally was predicted on theoretical grounds for hydrogen-bonded clusters [1], but first experiments were done on van-der-Waals bonded rare gas clusters. Meanwhile, it has been established that ICD and related processes are present in a wide range of systems and settings, and they have been studied by various experimental methods. Recent highlights include a view on ICD in the time domain, and the study of cascade processes consisting of Auger decay and non-local decay steps.

Often it is tacitly assumed that ICD takes place between neighbouring atoms or molecules. Recently, we presented studies in which a surprisingly large fraction of decays to the second coordination shell is seen. Finally, I will discuss results on the quantitative determination of the branching ratio for ICD vs. other relaxation channels, which highlight the importance of ultra-fast proton transfer in water aggregates (clusters and liquid water).

[1] L. S. Cederbaum *et al.*, *Phys. Rev. Lett.* 79, 4778 (1997).