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RESEARCH CONFERENCES

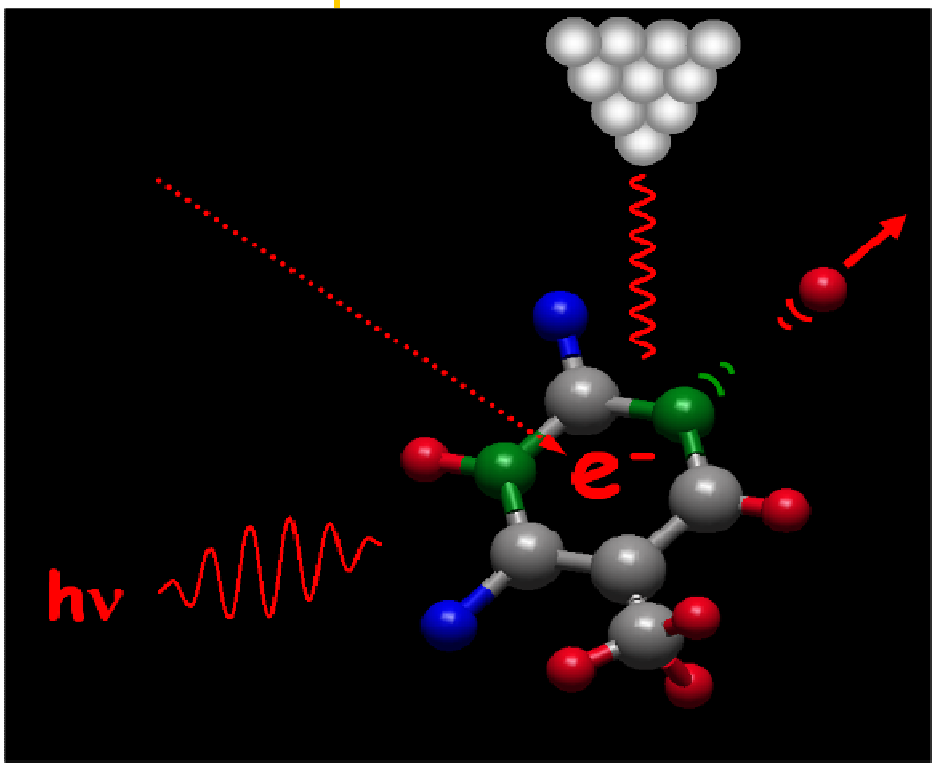
ESF-FWF Conference in Partnership with LFUI

Chemical Control with Electrons and Photons

Universitätszentrum Obergurgl
(Ötz Valley, near Innsbruck) • Austria
22-27 November 2008

Chair: **Petra Swiderek**, Universität Bremen, DE
Co-Chair: **Nigel Mason**, Open University, UK

www.esf.org/conferences/082561



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Conference Highlights

Please provide a brief summary of the conference and its highlights in non-specialist terms (especially for highly technical subjects) for communication and publicity purposes. (ca. 400-500 words)

The precise control over chemical transformations, both in terms of 'tuning' reaction products and allowing site specific chemical control is the subject of one of the most exciting and rapidly developing areas of modern science - introducing the potential for the creation of new materials and the development of new technologies with dramatic implications for advances in such fields as nanotechnology, quantum electronics and biophysics. Such research is driven by the emergence of new experimental tools and techniques. Ultrafast lasers provide light pulses with a duration of a few femtoseconds, the timescale on which the atoms in a molecule move, to manipulate molecular motion and control dissociation pathways. Electron beams, with very low energy, can break bonds in molecules at well defined sites while scanning tunnelling microscopes use atomically sharp tips to manipulate single molecules absorbed on surfaces. Together these three techniques offer the unique ability to select and 'tune' chemical pathways allowing us unprecedented control over chemical reactions.

This conference brought together leading experts from the fields of *electron*-, *laser*-, and *plasma-driven* chemical processing. Despite their common goals and synergies between the different approaches (e.g. in understanding molecular dissociation dynamics and fragmentation patterns) *this was the first time in any international research forum that the different communities exploring routes to chemical control were brought together at a single dedicated research conference.* The aim of this meeting was therefore to: (i) promote the awareness of a common research base and (ii) to discuss new opportunities and directions such as facile processes for surface functionalization and nanostructuring that may be developed through collaboration between the different communities.

The highly interdisciplinary nature of the conference with experts from many difference countries stimulated a very lively atmosphere in which the participants from each research area had the opportunity to learn about the concepts of the others. Four plenary lectures provided an insight into the state-of-the art of (i) chemical control using ultrashort and shaped light pulses, (ii) plasma technology for nanoscale fabrication (iii) the manipulation of single molecules using a scanning tunneling microscope and (iv) chemical control using low-energy electrons to produce novel nanoscale materials and to provide a fundamental understanding of radiation damage in biomolecules that may lead to development of new drugs for radiation therapy.

The conference clearly demonstrated that it is now possible to achieve chemical control using one of several different methodologies such that individual molecules can be positioned, isomerized, and fragmented along specific bonds at the behest of the experimenter. Such chemical control opens new routes for the fabrication of novel materials and devices and will play a major role on the development of nanotechnology as a commercially viable technology. Furthermore the insight gained by studying simple model systems on fundamental molecular reaction mechanisms can then be transferred to more complex macromolecular systems as was beautifully demonstrated in presentations where knowledge and control of the molecular dissociation pathways in biomolecules is leading to the development of new methodologies for improved radiation therapy.

x I hereby authorize ESF – and the conference partners to use the information contained in the above section on 'Conference Highlights' in their communication on the scheme.

Scientific Report

Executive Summary

(2 pages max)

The precise control over chemical transformations, both in terms of 'tuning' reaction products and allowing site specific chemical control is the subject of one of the most exciting and rapidly developing areas of modern science - introducing the potential for the creation of new materials and the development of new technologies with dramatic implications for advances in such disparate fields as nanotechnology, quantum electronics and biophysics. Such research has been made possible by the emergence of new experimental tools and techniques (e.g. ultrafast lasers, electron induced processing and scanning tunnelling microscopes) each of which may provide control of chemical reactions with high selectivity. The first method uses laser pulses with a duration of a few femtoseconds, the timescale on which the atoms in a molecule move, to manipulate molecular wavepackets and control dissociation pathways; the second uses very low energy electrons to dissociate the molecular target at well defined reaction sites while the third methodology uses scanning tunnelling microscopes to manipulate single molecules absorbed on surfaces. Together these three techniques offer the unique ability to select and 'tune' chemical pathways allowing us unprecented control over chemical reactions.

This conference brought together leading experts from the fields of *electron*-, *laser*-, and *plasma-driven* chemical processing. Despite their common goals and synergies between the different approaches (e.g. in understanding molecular dissociation dynamics and fragmentation patterns) *this was the first time in any international research forum that the different communities exploring routes to chemical control were brought together at a single dedicated research conference.* The aim of this meeting was therefore to (i) promote the awareness of a common research basis and (ii) to discuss new opportunities and directions such as facile processes for surface functionalization and nanostructuring that may be developed through collaboration between the different communities. The conference included not only reports of the fundamental aspects of molecular fragmentation and chemical control but also highlighted the applications of such knowledge in the areas of surface, material science and the ability to extend such knowledge to the study of biomolecular systems (e.g. in development of DNA as a functional engineering material).

The highly interdisciplinary nature of the conference, with experts from many difference countries, stimulated a very lively atmosphere in which the participants from each research area had the opportunity to learn about the methodologies and concepts of the other areas. Being aware of this aim, the senior speakers gave excellent presentations on their actual fields starting with clear descriptions of their fundamental concepts. In particular, four plenary lectures provided an insight into highly topical and state-of-the art examples of chemical control using (i) ultrashort and shaped light pulses, (ii) plasma technology for nanoscale fabrication (iii) the manipulation of single molecules with the scanning tunneling microscope, and (iv) chemical control using low-energy electrons to produce novel nanoscale materials and to provide a fundamental understanding of radiation damage in biomolecules that may lead to development of new drugs for radiation therapy. Many of the other Invited talks and Short talks built upon the material in the Plenary talks to highlight some of the most exciting recent advances and provided an unprecedented forward look at how such research may develop in the next few years.

The conference demonstrated that chemical control may be achieved using several different methodologies and that molecules can be positioned, isomerized, and fragmented along specific

bonds. However, several important steps remain before these may be directly applied in large scale commercial fabrication of novel materials and devices and thus allow nanotechnology (‘bottom up’) to replace current plasma processing (‘top down’). Furthermore the insight gained on the fundamental reaction mechanisms by studying simple model systems needs to be transferred to the study of larger macromolecules. That such a transfer of knowledge is feasible was beautifully demonstrated by the presentation of several examples where knowledge and control of the molecular dissociation pathways in biomolecules is leading to the development of new methodologies for improved radiation therapy.

Many participants were enthusiastic about the goal of the conference to bring together experts from the different research communities that try to achieve chemical control with different methodologies and believed that each community gains by interaction with the other communities. Various synergies were highlighted such as the prospect of using the current under the tip of a scanning tunneling microscope to locally perform electron-induced chemistry. Similarly, electron-induced reactions are important fundamental steps in plasma processes. New avenues may open up for example by realizing that specific molecular fragments produced by control of the reaction system by an appropriately shaped light pulse may also be used to trigger subsequent processes as already demonstrated by the surface modification or functionalization controlled by fragments stemming from selective electron-induced fragmentation. Many more opportunities exist and were discussed at the ‘forward look’ sessions of the conference that brought together the expertise from the different communities to identify common goals in the areas of *Control of molecular dissociation dynamics*, *Chemical control in biological systems*, and *Chemical control at the nanoscale and for building nanoarchitectures*. New contacts between the different communities and individuals were established at the conference and we are optimistic that this will lead to novel joint research directions on the long run. Consequently the question about repeating this conference were raised and will be pursued since it is vital to maintain the momentum established during the conference and ensure that these nascent links are encouraged to develop

Scientific Content of the Conference

(1 page min.)

- *Summary of the conference sessions focusing on the scientific highlights*
- *Assessment of the results and their potential impact on future research or applications*

The conference was organized in sessions focusing on

- Chemical control using ultrashort light pulses
- Chemical control using low-energy electrons
- Chemical control at the nanoscale using the scanning tunneling microscope (STM)

These three methodologies allow us to control the outcome of chemical processes in the sense that the reactions can be pushed towards the desired products. Additional sessions on

- Plasma processing and nanofabrication
- Chemical control of biomolecules

highlighted the application of chemical control (i) within plasmas aiming at producing surface structures of novel and superior quality and (ii) in controlling radiation damage to biomolecules, the latter being relevant to the radiation treatment of cancerous cells.

Designated poster sessions were arranged during two evenings allowing participants to discuss in more depth specific subjects from all of the different sessions but since the posters were on display throughout the meeting in the conference room there was an opportunity for informal discussions throughout the meeting.

The plenary talk on coherent control given by Tobias Brixner beautifully summarized the many successes in controlling chemical reactions using ultrashort light pulses. This includes, among other subjects, the use of polarized pulses that literally pull on a molecule in the desired direction as well as the use of infrared techniques to monitor the obtained products and thus give more specific feedback for the pulse shaping that controls the reactions. The ability to prepare molecules in specific orientations or conformations was demonstrated by talks of Olivier Faucher and Henrik Stapelfeldt while Petra Tegeder reported on reversible switching of the conformation of molecules adsorbed at surfaces. Another important issue concerned the use of ultrashort light pulses to control the vibrational state of complex systems such as carbon nanotubes (Sandro de Silvestri) and photosynthetic light-harvesting carotene molecules (Marcus Motzkus). An interesting result was also presented by Karl-Michael Weitzel who showed that the time delay between two femtosecond light pulses can control the relative abundance of different ionic fragments of the irradiated molecules.

Low-energy electron interactions with molecules provide another approach to site specific molecular fragmentation. Numerous examples were shown in a talk given by the pioneer of electron-induced chemistry Eugen Illenberger whose 65th birthday was also celebrated on the occasion of the conference. In these processes, specific fragmentation channels can be selected by tuning the electron energy. Anne Lafosse demonstrated that such reactions are also energy-specific when they occur in a condensed phase while Paul Scheier presented the use of He droplets as an ultracold model to study in more detail the effect of an environment on electron-induced reactions. The talk by Petra Swiderek discussed perspectives of such reactions for the modification of surfaces and molecular materials whereas the importance of theoretical approaches for an understanding of low-energy electron-controlled processes was stressed by Ilya Fabrikant and Jimena Gorfinkiel.

The control of molecular conformation but also of isomerization reactions within molecules adsorbed on surfaces using the STM was reviewed in the plenary talk by Karina Morgenstern. Similarly, Gérald Dujardin reported on switching of molecules between adsorption sites using the STM. The strength and the effect of an electrical current thus passing through single molecules was the subject of the talks given by Katharina Franke (experiment) and Martin Cizek (theory).

Finally, the application oriented sessions on nanofabrication and biomolecules offered even more highlights of the conference with Seiji Samukawa and Toshiaki Makabe reporting on novel plasma processes to obtain very precise surface architectures and Kurt Becker demonstrating the antibacterial activity of atmospheric-pressure plasmas. A most exciting and at the same time entertaining after-dinner talk was given by Armin Gölzhäuser who discussed the extraordinary physical properties of nanoscale molecular layers crosslinked under the effect of low-energy electron irradiation. Focused electron beams also enable the fabrication of metallic nanostructures as discussed by Cornelis W. Hagen and Ivo Utke. Finally, the impressive recent advances in understanding the action of drugs used in radiation therapy of cancer by experiments using low-energy electron irradiation were summarized by Léon Sanche.

The conference therefore clearly demonstrated that it is now possible to achieve chemical control using one of several different methodologies such that individual molecules can be positioned, isomerized, and fragmented along specific bonds at the behest of the experimenter. Such chemical control opens new routes for the fabrication of novel materials and devices and will play a major role on the development of nanotechnology as a commerically viable technology. Furthermore the insight gained by studying simple model systems on fundamental molecular reaction mechanisms can then be transferred to more complex macromolecular systems as was beautifully demonstrated in presentations where knowledge and control of the molecular dissociation pathways in biomolecules is leading to the development of new methodologies for improved radiation therapy.

Forward Look

(1 page min.)

- *Assessment of the results*
- *Contribution to the future direction of the field – identification of issues in the 5-10 years & timeframe*
- *Identification of emerging topics*

On the final afternoon of the conference three discussion sessions were held to provide a forward look on three topics which were determined by the conference as being areas in which chemical control would be advanced in the next few years. The three sessions were entitled;

1. Control of fragmentation dynamics
2. Chemical control at the nanoscale
3. Chemical control in biological systems

Each discussion group was then asked to provide a report on its deliberations to a general forum which then held a general discussion the following report is a summary of these discussions;

The development of new methodologies for chemical control are based on the ability on the control of fragmentation dynamics of molecular systems since these ‘prepare’ the reactants for subsequent chemical processes, to date such fragmentation control has been mostly in the gas phase but recently has been extended to surfaces and liquids. In principle such chemical control is possible in any molecule but at present most experiments have concentrated upon smaller polyatomic targets since it is easier to predict (and quantify) the fragmentation pathways of such

systems, however future applications of such chemical control will be most beneficial in larger macromolecules and biomolecules.

Control of fragmentation dynamics may be conveniently subdivided into those methods using light and those using electrons but they are not exclusive since light may liberate photoelectrons which can subsequently dominate the local chemistry. Indeed since light is easier to deliver in liquids and in some condensed phases photoelectron induced chemistry is a topic for further development.

Chemical control using light is now a mature field and we can expect to see a significant progress in methodologies for quantum control of fragmentation in the next few years, some methodologies using the 'time domain' others the 'frequency domain'. There remains some debate as to whether these two domains are "equivalent". More specifically in the frequency domain in the next few years the radio frequency regime will be exploited in the range from the kHz to the THz to achieve quantum control via state selection, while advances in the time domain will, in part, be influenced by the development of attosecond laser pulse technology. In both domains we can expect to see a more converging treatment and description of various aspects of phase to fragmentation dynamics.

One general question in fragmentation dynamics and the control thereof relates to transitions from adiabatic to non-adiabatic dynamics. The dynamics of fragmentation close to conical intersections has been the subject or considerable research in recent years and the applicability of Born-Oppenheimer approximation under such circumstances remains the subject of debate. However it appears that it may be possible to couple electron dynamics to nuclear dynamics by means of (ultra-)short laser pulses - this is, by definition, a non-Born-Oppenheimer regime.

The fundamental mechanism for *chemical control using electrons* is well quantified, with the process of Dissociative Electron Attachment (DEA) in which an incident electron is temporarily (resonantly) captured by the target molecule before the molecule fragments to provide commonly an anion and one of more neutral fragments. Such DEA processes have been shown to be highly site selective, cleaving particular chemical bonds at specific incident energies, a selectivity that occurs in both gas and condensed phases. However it is still often not possible to predict in advance the relative yields of the fragmentation products nor the energies at which such site selectivity will occur and major work is needed in developing the theory of low energy electron scattering from larger polyatomic targets whilst extension of such theory to condensed phase is still largely in its infancy. That such fragmentation dynamics is also strongly dependent upon the internal state of the target (e.g. degree of ro-vibrational excitation) is recognized but to date largely unquantified whilst electron-induced control of fragmentation dynamics from prepared electronically excited states through DEA is unexplored.

The STM may be considered as a bright electron source allowing **Chemical control at the nanoscale**. Indeed two step (or multistep) electron excitation may be induced in STM interactions with single molecules. Chemical control using STMs has been demonstrated for several systems but there are inherent differences between such STM control and single electron DEA that require further investigation by both electron and STM communities. Similarly the development of STM technology provides the opportunity for chemical control on unprecedented spatial scale and may provide a methodology for nanoscale processing but at present is inhibited by inherent slow molecule by molecule processing, the development of a multi-array of STM tips as a tool for nanolithography is therefore a topic for future instrumental research. The combination of STM and ultrafast photon technology has only recently been demonstrated with ultrafast laser pulses being used to generate short pulses of electrons from the STM tip, this is a topic that has great merit and

should be investigated further, most efficiently by an interdisciplinary collaboration drawn from participants of this meeting.

Having established the methodologies for chemical control it is necessary to explore how such chemical control at the nanoscale may be exploited for technological benefit. Here a fundamental question to be addressed pertains to the transfer of control from the molecular (microscopic) to the macroscopic scale, the latter leading to synthetic chemistry. Here the field merges with the development of nanotechnology and the desire to build chemical structures from the 'bottom up' rather than, as traditional surface processing, from the 'top down'. It is widely recognised that current surface processing and lithographic techniques (e.g. plasma etching) are nearing their technological limit and that the creation of 10nm structures may require bottom up technology to be made commercially viable. This in turn requires detailed assessment of the viability of chemical control methodologies as a tool for mass production.

The ability of electrons to functionalize surfaces and the combination of chemical control with self assembled monolayers may provide a methodology for such nanoscale lithography, with focussed (high energy) electron beam induced processing (FEBIP) being demonstrated as being capable of patterning on the nanoscale but inherent problems of providing low energy electron beams capable of DEA (and hence chemical selectivity) with nanoscale dimensions remaining. Whether FEBIP may be developed successfully commercially is still open to debate however it is clear that much greater information is needed on the role of secondary (low energy) electrons in such systems and the role of DEA. Indeed the kinetic energy spectrum of such secondary electrons must be quantified and to date the molecules used by the FEBIP community have not been studied by the electron/STM or photon community. Similarly there is a need to develop knowledge of the electron energy distributions and role of DEA in EUV induced lithography, another technique that has demonstrated its feasibility for producing sub 10nm structures. Collaboration between the fundamental research community and the FEBIP and lithographic communities is therefore vital and should include industrial partners at the earliest stage of such research.

One area where chemical control is being exploited and has shown great potential for challenging existing technology is in the study of radiation damage of biomolecules e.g. DNA (**Chemical control in biological systems**). The pattern of strand breaks induced in DNA by low energy electrons has been shown to be similar to that induced in DNA's constituent molecules through DEA, indeed such similarities have allowed the radiosensitivity of different molecules used in radiotherapy to be evaluated and the adoption of new techniques (e.g. incorporation of nanoparticles within the DNA as a therapeutic agent) to be explored. Nevertheless to date most research on biomolecules has been in the gas phase, a poor mimic of cellular systems. The study of biomolecules within clusters and as adsorbates provides a temporary means of exploring whether such gas phase studies are applicable to biological conditions but new methodologies for exploring such processes in liquid phase must be developed, for example generation of photoelectrons from a surface within a liquid using laser/synchrotron light.

In conclusion the meeting showed that whilst great advances have been made in chemical control (advances that were undreamt of even a decade ago) the development of methodologies and its exploitation in areas such as nanotechnology and bio/medical physics will require the collaboration of researchers from a wide range of disperate/interdisciplinary skills. The present meeting has provided, for the first time, a forum for such discussions and was seen by the majority of the participants as an essential step in the future of the field and in itself is a significant step forward in what promises to be one of the most exciting, innovative yet demanding fields of chemical/physical research.

- Is there a need for a foresight-type initiative?

The idea of a foresight initiative aimed at discussing how the fundamental research community represented at the meeting may develop its programme with the commercial (industrial) partners was a constant theme of the meeting. Bringing basic research methodology to large scale materials fabrication will require engagement with commercial partners and would be a very beneficial (and vital) function of the ESF.

Atmosphère and Infrastructure

- *The reaction of the participants to the location and the organization, including networking, and any other relevant comments*

Most of the conference participants were extremely enthusiastic about the primary goal of the conference - bringing together experts from the different research communities that seek to achieve chemical control to discuss synergies and opportunities for collaboration. The very impressive location stimulated continuing the discussions in a leisurely manner during the afternoon hours and until late at night, whilst the smooth organisation from the side of the ESF also contributed much to the success of the event. Consequently many participants expressed the wish to see such a meeting repeated in the future and opportunities for developing collaborations/networks through EU/ESF schemes were discussed (e.g. Cost Actions; ESF Research Network, Framework VII programme). Some examples of comments received by the chair after the meeting read as follows:

“I enjoyed the place and most of speakers, informal and inviting atmosphere.”

“Congratulation to you for the successful ESF research conference!… Heartily looking forward to joining the conference next year.”

“It was a very nice conference and I would like to express you my thanks to get me in.”

Confidential Issues

▪ *Any other issues, not to be included in the published report.*

None

Date & Author: