Eur. Phys. J. D **35**, 173–176 (2005)
DOI: 10.1140/epjd/e2005-00229-y

THE EUROPEAN
PHYSICAL JOURNAL D

Editorial

Electron-driven molecular processes: A general introduction

E. Illenberger[1] and P. Swiderek[2]

[1] Institut für Chemie - Physikalische und Theoretische Chemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin, Germany
[2] Institut für Angewandte und Physikalische Chemie, Universität Bremen, Leobener Strasse, 28334 Bremen, Germany

Electron-driven molecular processes are present in many areas of pure and applied science such as plasma processes, photochemistry on surfaces, tunnelling microscopy, lithography, and molecular processes in biosystems relevant for radiation damage or radiotherapy. This wide range of current research topics shows that the study of processes driven by low-energy electrons has nowadays evolved into a mature and truly interdisciplinary field, and the joint effort of many groups, both experimentalists and theoreticians, is providing an increasingly more complete picture of these processes. The aim is to control reactions in which low-energy free electrons, tunnelling electrons, or photoelectrons at surfaces or in the condensed phase play a key role in either starting such reactions or in guiding their evolution into specific products. Such processes can nowadays be studied on a molecular scale with high resolution in electron energy, spatial coordinate, and time.

This topical issue gives an account of the most recent progress in the field of electron-driven molecular processes that has recently gained momentum thanks to collaborative efforts within the European networks EPIC (*Electron and positron induced chemistry*), RADAM (*Radiation damage in biomolecular systems*) and EIPAM (*Electron-induced processing at the molecular level*). While the fundamental steps of electron-molecule interactions are now accessible in unprecedented detail due to progress in instrumentation, experimental methods, and computational approaches, as is addressed by the section "*Fundamental processes in the gas phase*", present research also focuses on a broad range of applications as demonstrated by the sections "*Plasmas and high pressure measurements*", "*Surface processes*", and "*Processes in biomolecules*" of this issue. Experimental work in all areas of research is complemented and guided by theoretical work: through this fruitful collaboration, much new insight has been gained in the recent years on a broad variety of electron-driven processes.

In the first part a series of papers illustrates some of the fundamental processes concerning the interaction of low energy electrons with gas phase molecules. Recent advances in measurements and theoretical predictions of electron scattering and attachment cross-sections [1] are crucial, e.g. for the modelling of any of the plasmas used in industrial plasma processing [2,3] The SF_6 molecule which is widely used as effective electron scavenger in high power high voltage devices, represents a particularly interesting example: owing to its widespread industrial application as gaseous insulator the system SF_6/SF_6^- is probably the most extensively studied system with respect to electron capture and anion formation [4]. In spite of that, very basic properties like the lifetime of the transient negative ion formed upon attachment of free electrons, the electronic structure of the SF_6^- anion or its vertical detachment energy are still under debate. The Kaiserslautern group (**Braun et al.**) presents an extended high-resolution study (energy resolution around 1 meV) using the Laser Photoelectron Attachment (LPA) method to study SF_6^- and SF_5^- formation in a supersonic beam at different nozzle temperatures. The latter is a product of dissociative electron attachment, which competes with the autodetachment of the extra electron from SF_6^-. The contribution by **Fabrikant** complements this work by modelling the SF_6 problem, but also CO_2 clusters, using a theoretical approach. This paper describes calculations of electron attachment cross-sections for ground state and vibrationally excited particles based on a generalization of the multi-channel effective range theory (ERT). A very good agreement is achieved with the high-resolution measurements of the Kaiserslautern group demonstrating the high quality of both experiment and theory.

Cluster studies are very much needed in order to make the link between processes taking place in the gas phase and the condensed phase [5] Consequently, several contributions to this issue, both experimental and theoretical, focus on electron interactions with different molecular clusters. The group from Villetaneuse (**Seydou et al.**) uses electron transmission and Rydberg electron transfer spectroscopy to study electron attachment to clusters of formamide. This system is a fundamental model that serves to study effects of hydrogen bonding that are ubiquitous in nature. Strongly polar systems as formamide also represent good examples for a study of the competition between simple attachment into a molecular valence orbital, into a diffuse multipole-bound state, or as a solvated electron. The coupling between these different states is expected to play an important role in intramolecular electron transfer processes. **Sommerfeld and Knecht** consequently show how to address this problem using a high-level quantum chemical ab initio approach for the example of the strongly polar cyanoacetylene molecule.

Electron capture by hydrogen halides is another example that still presents unresolved questions, among them the role of cluster anions in reaction channels induced by the attachment. The paper by **Rauk and Armstrong** therefore uses ab initio calculations to identify the nature and energetics of anion states formed by electron attachment to hydrogen chloride trimers. On the other hand, the Prague group in collaboration with Domcke (**Horacek et al.**), using calculations applying the non-local resonance model, shows that even seemingly simple systems can still produce surprises upon closer inspection as exemplified by a newly predicted inverse isotope effect.

Another important theoretical approach to electron-molecule interactions is the R-matrix theory that was initially developed nearly 60 years ago for the study of nuclear reactions. Implementations of R-matrix theory capable of treating collisions of electrons with polyatomic molecules were developed during approximately the last 25 years. The contribution by **Gorfinkiel et al.** discusses the range of problems that can at present be studied with this approach. Finally, the joint study of the Lille-Liège group (**Duflot et al.**) gives an example of the use of ab initio calculations for the assignment of inner-shell molecular excitations that can be observed with inner-shell electron energy loss spectroscopy (ISEELS).

Fundamental experimental studies on electron-driven processes are required for a reliable understanding of the elementary reactions that can occur under plasma processing conditions. Halogen-substituted hydrocarbons are important plasma processing gases and as such very much of primary interest. A systematic study on the effect of the molecular structure for C_3 hydrocarbons on electron-scattering cross-sections is therefore presented by the paper of **Makochekanwa et al.** With the same aim, the Bratislava group (**Ipolyi et al.**) presents a study of the temperature dependence of (dissociative) electron attachment to $CHCl_2Br$. Such data are important whenever $CHCl_2Br$ is used as a feed gas for plasma processing in which the molecules are often present at elevated temperatures [6].

Electron attachment to gas phase C_{60} shows unique features as it generates the non-decomposed anion which is observable (on the mass spectrometric time scale) at energies up to more than 10 eV. The attachment mechanism, in particular at very low energy (is *s-wave attachment* symmetry forbidden?) and the attachment behaviour at different temperatures has been the subject of many controversial papers over the last 10 years. **Prabhudesai, Nandi and Krishnakumar** revisite these problems by means of a crossed beams experiment and conclude from their temperature behavior that strong *s-wave* capture is present near zero eV.

G. Karwasz reviews the field of the interaction of positrons (the antiparticle of the electron) with molecules. While many phenomena are similar to electron scattering and electron attachment, the interaction of positrons with molecules can lead to the formation of a positronium (a hydrogen like particle consisting of a positron and an electron) or electron-positron annihilation creating two high energy photons with anti-parallel momentum. It is their detection which provides indicators for the above processes.

As mentioned above, gas-phase studies are directly relevant for the understanding and modelling of plasma processes and its numerous applications are discussed in the contribution by **Becker**. In this review the emission characteristics of atmospheric-pressure plasmas in three different electrode configurations, namely the microhollow cathode discharge (MHCD), the capillary plasma electrode discharge (CPED), and a cylindrical barrier discharge (C-DBD) are analysed and conclusions are drawn on how the spectroscopic studies can serve to elucidate the underlying collisional and radiative processes. Another study dealing with emission properties is contributed by **Borghesani et al.** and investigates the infrared fluorescence in a rare gas mixture under the effect of an ionising electron beam. Such results are also of importance in, for example, laser applications.

Fundamental quantities as electron attachment or ionisation energies and cross-sections as well as rates of these processes are required to model the behaviour of potential plasma processing gases. They can be measured accurately as described by the different contributions on high-pressure electron-driven processes by swarm techniques. The paper from the Birmingham group (**Mayhew et al.**) describes an improved version of their electron swarm apparatus and its application to the measurement of thermal attachment rate coefficients for two derivatives of SF_6 and two perfluorocarbons. The former are suspected to be potential greenhouse gases so that possible decomposition pathways need to be quantified. The latter are of importance in industrial semiconductor processing. Similarly, the contribution by **Barszczewska et al.** presents new data for different halopropanes and haloethanes. Finally, the paper from the Belgrade group (**Maric et al.**) discusses methods that are used to establish from experimental data coefficients for electron ionisation which are of importance not only in gas discharges but also for the development of particle and ionising radiation detectors [7].

Our understanding of low-energy-electron-driven chemical reactions at or near surfaces has been much enlarged recently by experiments performed at the macroscopic scale by use of well-defined incident electron energy beams or at the molecular scale by using the tip of the scanning tunnelling microscope (STM). This is the topic of the third part of this issue. Single-molecule electron-driven chemistry has been demonstrated previously in key experiments on the O_2/Pt(111) and C_6H_5I/Cu(111) systems [8,9]. Nowadays, and as demonstrated by contributions to this topical issue, insight is gained into the mechanism of such surface reactions by both vibrationally resolved scanning tunnelling microscopy and theoretical calculations. The paper by **Pascual** thus reviews a number of recent single-molecule experiments by inelastic electron tunnelling spectroscopy (IETS) with STM that yield information on both the mechanism of vibrational excitation under the tip of the STM and on reactive deactivation processes as for example the mode-selective manipulation of NH_3 on Cu(100). The Toulouse group (**Lorente and Ueba**) approaches a related problem from the theoretical point of view by studying the dynamics of CO induced by tunnelling electrons on different surfaces. Calculations of excited state lifetimes, of intermode couplings, and of the strength of the CO-metal interaction lead to an explanation of the different reactivity that was earlier observed experimentally. The contribution by **Gawronski et al.** presents results on electron-induced displacement processes of H_2O adsorbed onto Au(111) as studied on a single-molecule level by means of STM.

Exposure of surfaces to electrons with energies of only a few eV induces specific reactions on a macroscopic scale that allow us to couple to a surface not only single atoms as shown previously for fluorine attachment to and oxidation of amorphous hydrogenated silicon under electron exposure to thin films of CF_4 or H_2O condensed at the surface [10,11]. The same technique also opens a way to attachment of more complex molecular units as shown in the paper by **Lafosse et al.** This is the first example of such a complex surface functionalisation controlled by very low-energy electrons. The controlled modification of the surface of nitro-substituted self-assembled monolayers reported previously and applied for so-called chemical lithography that opens a new way to a nanoscale chemical patterning of surfaces has been another milestone in the use of low-energy electrons as a tool to tailor surfaces [12]. The contribution from the Bremen laboratory (**Swiderek**) presents a related study on the kinetics of electron-induced reactions in nitromethane. The experiments use the low-current electron beam from a high-resolution electron-energy-loss spectrometer to gain information on the role of the molecular environment in the electron-driven reaction of the nitro-group. In summary, a true understanding and control of electron-induced chemistry at surfaces appears to now be within reach of experiments and theory.

The interaction of low energy electrons with biologically relevant molecules has attracted much interest within the last few years: the last part of this issue therefore concentrates on biomolecules and their model systems. The interest is based on the accepted notion that the interaction of low energy electrons with biomolecules is a crucial step in the exploration of the molecular mechanisms associated with *radiation damage* and at the same time with the molecular mechanisms responsible for the action of *radiosensitizers* used in radiotherapy. After the discovery of X-rays, radioactivity and nuclear fission it became soon obvious that the exposure of living beings to high energy radiation (particles and photons) can result in fatal effects for the concerned individual. The variety of such effects is subsumed under the term *radiation damage.* It includes damage of biological material on a short time scale, i.e. the immediate collapse of living cells eventually resulting in the death of the individual within hours or days but also effects appearing on a much longer time scale. Instead of a complete damage of cells, radiation can result in genotoxic or mutagenic effects, associated with a change in the genetic expression of DNA or to DNA strand breaks.

Countless numbers of articles have been published in relation to radiation damage and we refer only to one earlier [13] and a recent monograph [14]. It appears that phenomenological aspects of radiation damage are well documented. There is, however, a very fundamental lack in the description of the initial steps following irradiation. This became obvious after it has been demonstrated that sub-ionisation electrons can effectively induce single and double strand breaks in plasmid DNA [15]. Very recently it has been shown that in plasmid DNA even sub-excitation electrons (0–4 eV) induce single strand break [16].

To understand the effect of high energy radiation to a living cell (DNA and its environment) one can follow this primary interaction through the secondary reactions in a chronological order. As an example, the *primary* interaction of a high-energy photon removes electrons from essentially any occupied state (via absorption and scattering), from valence orbitals to core levels. Depending on the energy of these ionized electrons they induce further ionisation events, etc. thereby being slowed down within the medium. The estimated quantity is 10^4 *secondary* electrons per 1 MeV primary quantum. These electrons are usually assigned as *secondary* although they are the result from primary, secondary, tertiary etc. interactions, including electrons from Auger processes generated during relaxation of the core holes. Taking a snapshot at some femtoseconds after the primary interaction we have then multiple charged sites within the complex molecular network (eventually undergoing Coulomb explosion), single ionized and electronically excited sites and, last but not least, an exceeding number of low energy secondary electrons with an energy distribution extending to a few tens of eV. Although the double and single ionized sites as well as electronic excitation can result in the rupture of chemical bonds, the major effects are induced by the large number of secondary electrons. In the course of successive inelastic collisions within the medium they are thermalized within picoseconds before they reach some stage of solvation, then becoming a chemically rather inactive species.

It is believed that damage of the genome in a living cell by ionizing radiation is about one third *direct* and two third *indirect.* Direct damage concerns reactions by energy deposition directly in the DNA and its closely bound water molecules. Indirect damage results from energy deposition in water and other biomolecules in the surrounding of the DNA. It is also believed that almost all the indirect damage is due to the attack of the highly reactive hydroxyl radical OH. In tracking direct damage to DNA by electrons the current efforts approach the problem from two limits concerning the complexity of the system. One side concerns the electron induced processes in plasmid DNA by the Sherbrooke group (Léon Sanche et al.) consisting of thousands of DNA base pairs and on the other side the gas phase experiments on single DNA building blocks performed by the groups in Innsbruck (Tilmann Märk, Paul Scheier et al.), Berlin (Eugen Illenberger et al.), Orsay (Robert Abouaf et al.) and Lincoln (Paul Burrow et al.). These experiments revealed very interesting results demonstrating that sub-excitation electrons effectively drive decomposition of the isolated DNA bases [17–20] but also of the sugar molecules. It became also obvious, that low energy electrons (in striking contrast to photons) can induce bond selective [21] and even site selective [22] decompositions in DNA bases — a very remarkable observation in light of strong efforts to induce the breaking of particular bonds by tailored, ultra-fast laser pulses [23]. In spite of the rather detailed information on the DNA building blocks, however, the molecular mechanism how low-energy electrons damage DNA is still unknown.

In the present issue, **Sanche** gives an excellent up-to-date review which deals with the overall problem by considering experiments on plasmid DNA but also the relevant gas phase experiments on the building blocks. The article from the Innsbruck group (**Denifl et al.**) describes cation and anion formation in 5-bromouridine which is used as a radiosensitizer in radiotherapy. The particular behavior of the purine nucleobases guanine and adenine (as opposed to thymine and cytosine) is investigated in a beam experiment by **Abdoul-Carime et al.** Very interesting insight into the action of low energy electrons to different gas phase DNA bases including some halogenated forms is possible by measuring elastic and inelastic electron scattering in addition to anion formation as shown by the work of **Abouaf et al.** Tetrahydrofuran (THF) represents an analogue to the furan structure of the sugar in the DNA backbone. **Milosavljevic et al.** therefore present an extended analysis of the elastic electron scattering cross-section from THF. In the article by **Gianturco et al.** the formic acid is used as a model system to theoretically explore the position and nature of resonance in a hydrogen bonded systems which is of particular importance in biology. These calculations are compared with experiments performed in molecular beams. Another theoretical study by **Dabkowska et al.** also approaches the problem from the starting point of a model system by dealing with possible contributions of concerted H radical and electron attachment to reactions occurring in an anhydrous nucleotide of cytosine. **Solomun et al.** finally presents a very interesting new approach to study electron damage to DNA by using oligonucleotides of defined size and sequence which are immobilized on a solid surface. Although the employed fluorescence technique in combination with a micro-array technology is not able to specify the damage, it represents an important step to bridge the gap between gas phase building blocks and plasmid DNA.

The ability to describe, manipulate and control processes at a molecular level is one of the great challenges of the 21st century. Apart from its intellectual demand, it the basis for the development of new technologies like nanolithography. As can be seen from the present collection of articles from rather different areas (connected by the action of low energy electrons), the research on electron-molecule interactions bears many new and interesting opportunities in basic and applied research. The present topical issue will thus hopefully contribute to attract further colleagues to the field. Last but not least, the guest editors would like to thank the editorial office of EPJ D and especially Solange Guéhot for doing a marvelous job in helping us to create this issue.

References

1. H. Hotop, M.-W. Ruf, M. Allan, I.I. Fabrikant, Adv. At. Mol. Opt. Phys. **49**, 85 (2003)
2. K.H. Becker, Elementary collision processes in plasmas, in *Low Temperature Plasma Physics*, edited by R. Hippler, S. Pfau, M. Schmidt, K.H. Schoenbach (Wiley-VCH Berlin, 2001)
3. L.G. Christophorou, J.K. Olthoff, *Fundamental Electron Interactions with Plasma Processing Gases* (Kluwer Academic/Plenum Publishers, New York, 2004)
4. *Gaseous Dielectrics X*, edited by L.G. Christophorou, J.K. Olthoff, P. Vasiliou (Springer, New York, 2004)
5. E. Illenberger, Electron Attachment Processes to Free and Bound Molecules, in *Photoinonization and Photodetachment*, Advanced Series in Physical-Chemistry, edited by Cheuk-Yiu Ng (World Scientific, Singapore, 2000), Part II, Vol. 10B
6. L.G. Christophorou, J.K. Olthoff, Adv. At. Mol. Opt. Phys. **44**, 155 (2001)
7. W.-F. Schmidt, *Liquid State Electronics of Insulating Liquids* (CRC Press, Boca Raton, 1997)
8. B.C. Stipe, M.A. Rezaei, W. Ho, S. Gao, M. Persson, B.I. Lundqvist, Phys. Rev. Lett. **78**, 4410 (1997)
9. S.-W. Hla, L. Bartels, L. Meyer, K.-H. Rieder, Phys. Rev. Lett. **85**, 2777 (2000)
10. W. Di, P. Rowntree, L. Sanche, Phys. Rev. Lett. **52**, 16618 (1995)
11. D. Klyachko, P. Rowntree, L. Sanche, Surf. Sci. **346**, L49 (1996)
12. W. Eck, V. Stadler, W. Geyer, M. Zharnikov, A. Gölzhäuser, M. Grunze, Adv. Mat. **12**, 805 (2000)
13. C. von Sonntag, *The Chemical Basis for Radiobiology* (Taylor and Francis, London, 1987)
14. *Charged Particle and Photon Interactions with Matter. Chemical, Physicochemical and Biological Consequences with Applications*, edited by A. Mozumder, Y. Hatano (Marcel Dekker, New York, 2004)
15. B. Boudaiffa, P. Cloutier, D. Hunting, M.A. Huels, L. Sanche, Science **287**, 1658 (2000)
16. F. Martin, P.D. Burrow, Z. Cai, P. Cloutier, D. Hunting, L. Sanche, Phys. Rev. Lett. **93**, 068101 (2004)
17. G. Hanel, S. Denifl, P. Scheier, M. Probst, B. Farizon, M. Farizon, E. Illenberger, T.D. Märk, Phys. Rev. Lett. **90**, 188104 (2004)
18. R. Abouaf, J. Pommier, H. Dunet, Int. J. Mass Spectrom. **226**, 397 (2003)
19. S. Gohlke, H. Abdoul-Carime, E. Illenberger, Phys. Rev. Lett. **92**, 168103 (2004)
20. A.M. Scheer, K. Aflatooni, G.A. Gallup, P.D. Burrow, Phys. Rev. Lett. **92**, 068120 (2004)
21. S. Ptasinska, S. Denifl, V. Grill, P. Scheier, T.D. Märk, S. Gohlke, M.A. Huels, E. Illenberger, Angew. Chem. Int. Ed. **44**, 1647 (2005)
22. S. Ptasinska, S. Denifl, P. Scheier, E. Illenberger, T.D. Märk, Angew. Chem. Int. Ed. (2005, in press)
23. C. Daniel, J. Full, L. Gonzales, C. Lupulescu, J. Manz, A. Merli, S. Vajda, L. Woeste, Science **299**, 536 (2003)