

INDC International Nuclear Data Committee

Summary Report of
Final IAEA Research Co-ordination Meeting

Data for Molecular Processes in Edge Plasmas

Prepared by
R.E.H. Clark

IAEA Headquarters, Vienna, Austria
1-2 November 2004

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Abstract

Eleven international experts discussed in detail the outcomes of their research at the final Research Coordination Meeting (RCM) on “Data for molecular processes in edge plasmas” at IAEA Headquarters on 1-2 November 2004. Participants summarized their results obtained in the course of the Coordinated Research Project (CRP), and the impact of the data generated on the modelling and design of fusion devices. Data needs still exist, and the specialists hoped that further research on these processes will be supported in the future. The discussions, conclusions and recommendations of the RCM are briefly described in this report.

February 2006

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1. Introduction

The final Research Coordination Meeting (RCM) on “Data for molecular processes in edge plasmas” was held on 1-2 November 2004, at IAEA Headquarters, Vienna. The main aims of this RCM were to review the research activities of the participants, summarize the outcomes of the Coordinated Research Project (CRP), and identify additional data needs for plasma diagnostics which require and merit further research. A summary of the various outputs and outcomes was also formulated.

2. Meeting Proceedings

A. Nichols (Section Head, Nuclear Data Section) welcomed the participants on behalf of the IAEA. He stressed that fusion research continues to be an important topic within the IAEA Nuclear Data Section. There are many processes of importance in the modelling of the edge region in fusion devices, where temperatures and densities lead to the formation of a variety of molecules, and he acknowledged that this CRP has provided much new and significant data of this type. He also stated that the IAEA is grateful to the hard work and dedication of the CRP participants.

R. Clark (Scientific Secretary) reviewed the proposed agenda, which was accepted without change (Appendix 1).

2.1 Summary of current research activities

The eleven participants in the RCM are experts in the various fields that encompass the molecular processes important in quantifying the behavior of plasmas in the edge regions of fusion energy devices (Appendix 2). Each participant reviewed their research activities, and their Power point presentations were collected electronically and distributed on CD. Only brief summaries of the presentations are given below.

M. Capitelli presented recent work on the elementary processes, transport and kinetics of molecular plasmas. Work on elementary processes included calculation and compilation of cross-section data for a number of processes. State-to-state vibrational resolved electron molecule cross sections for the triplet-triplet transitions in molecular hydrogen have been calculated by means of the impact parameter method. Work has progressed on the construction of a database for dissociative attachment of ro-vibrational states of H₂ and isotopes. A classical approach has been used to calculate the ionization cross sections for N₂ and O₂ in different vibrational states. The small effect of the rotational energy has been estimated. Cross sections and rate coefficients for the system H-H₂(v,j) were calculated by the quasi-classical trajectory method, and have been improved by using a new and more accurate potential energy surface (to be extended to isotopes). Transport cross sections of electronically excited states of atomic hydrogen have been derived by using semi-classical approaches. The data have been used to calculate the transport coefficients (viscosity, thermal conductivity and electrical conductivity) of thermal plasmas over a wide range of temperatures and pressures. These results show the strong influence of excited states on the transport coefficients of atomic plasmas, and were completed in 2003 and published this year. Transport cross sections of electronically excited nitrogen and oxygen atoms have also been derived. Five codes were used to describe the kinetics of the molecular plasmas (mainly hydrogen) in different non-equilibrium conditions, and have been applied to reproduce different experimental situations.

Y. Hatano summarized results for the dissociative excitation of molecules. A survey was presented of the dissociative excitation of molecules in photonic and electronic collisions in the energy range from 10 to 50 eV. Emphasis was placed on the formation and dissociation dynamics of molecular superexcited states. A synchrotron source was combined with coincidence or two-dimensional spectroscopy techniques for a photonic study of the molecules excited into optically-allowed states. Coincidence electron energy loss spectroscopy has been used to study electronic collisions into optically forbidden states. Molecules under study included simple diatomic and tri-atomic molecules up to a variety of polyatomic molecules. Specific examples of high importance to fusion edge regions included H₂, D₂, O₂, CO and C₁-C₂ hydrocarbons. Most of the observed excited states are high Rydberg states that are vibrationally and/or rotationally double or inner core excited and converge to each of the ion states. Dissociation dynamics and the products were found to be significantly different from lower excited states at energies below the ionization limit.

M. Chibisov reported on Coulomb Rydberg quenching by neutral atoms and atomic ions. Studies of collision L-mixing of atomic coulomb Rydberg A^{**} by neutral atoms B have taken place over the previous year. As reported earlier, the adiabatic approach was used to investigate the $A^{**} + B$ system when the Rydberg electron of the excited atom A^{**} experienced many collisions with the perturbing atom B . Others have used the single collision approach because the Rydberg orbit size is much larger than the size of the perturbing atom B . Therefore, the question of the collision velocity ranges where these approaches are applicable needs to be addressed. This question has been solved by means of an investigation of the Rydberg electron classical trajectories in two fields: the coulomb field, and the field of atom B . The classical pure coulomb trajectories are known to be closed as a result of the special four-dimensional symmetry of the coulomb field. After a first collision with atom B in both the coulomb and atom B fields, the Rydberg electron will soon move again in a pure coulomb field because the electron interaction with the neutral atom B decreases strongly by $\sim -\alpha/2r_{e,B}^4$ (α is the atom B polarizability) as the distance $r_{e,B}$ increases. Consequently, after the first collision with B , the Rydberg electron will move along the closed trajectory, and after a full revolution will again collide with atom B independent of the scattering angle. Calculations were presented for a Rydberg electron with energy $E = -1/2n^2$ (principal quantum number $n = 30$) that collided with a Cs atom 10, 20, or 30 times, depending on the collision phase (collision velocity $v_{Cs} = 10^{-4} v_0$, where $v_0 = 2.1877 \cdot 10^8$ cm/sec; $E_{Cs} \sim 300K$). Therefore, the adiabatic approach is applicable for the description of the system $A^{**} + B$ for Rydberg states with principal quantum numbers $n < (v_0/v_B) = 10^4$, although the single collision approach is correct for $n > 10^4$. Detailed results are presented in a paper being prepared by Chibisov and Moskovkin for publication in JETP.

T. Maerk reported on electron impact ionization/dissociation for molecules of relevance to edge plasmas. The overall goal of the research was to provide data needed for fusion plasma edge modelling and diagnosis - data were acquired, assessed and compiled for use in established databases. Processes under study included volume reactions and plasma-wall reactions. Volume reactions covered the processes of electron ionization of atoms, molecules and ions, and electron attachment to ions, while plasma-wall interactions included secondary ion emission. Experiments on electron impact ionization involved high-resolution measurements, including a detailed study of the total kinetic energy release distribution and identification of any released fragments. Results have been compared with other experiments, and calculations have also been undertaken.

P. Defrance reviewed the results of electron impact ionization and dissociation of $C_m H_n^+$ ions. Absolute cross sections for electron impact single ionization (SI), and fragment

production resulting from dissociative excitation (DE) and dissociative ionization (DI) of H_2^+ , D_2^+ , D_3^+ , C_2H_2^+ and C_2H^+ , and CH_n^+ or CD_n^+ ($n = 1-4$) were measured for electron energies from the corresponding thresholds to 2.5 keV by means of an animated crossed electron-ion beam experiment. Product ions were separated by means of a large angular acceptance, double-focusing analyzing magnet. The product velocity distribution observed in the laboratory was analysed in order to (i) separate contributions from the different reaction channels (DE and DI) leading to the same fragments production and (ii) determine the kinetic energy release distributions (KERD). Absolute total cross sections have been measured for electron impact dissociative excitation and dissociative ionisation of H_2^+ and D_2^+ in the energy range from 5 to 3000 eV. While for C_2H_2^+ and C_2H^+ , absolute cross sections have been measured for SI and for the production of each of the possible fragment ions H^+ , H_2^+ , C^+ , CH^+ , CH_2^+ and C_2^+ . Results were compared with other values from the literature.

I. Schneider reported on reactive collisions between electrons and molecular ions of hydrogen and oxides relevant for fusion plasma kinetics. Results have been calculated using multichannel quantum defect theory (MQTD). Reactive collisions between electrons and $\text{H}_2^+(v = 0, 1, 2)$ ions were obtained at low energy (0.0001–1 eV), including the processes of dissociative recombination (DR), superelastic collisions (SEC), inelastic collisions (IC) and elastic collisions (EC). These calculated values were compared with TSR storage ring experimental data. Cross sections for DR and SEC between electrons and $\text{H}_2^+(v = 0, 1, \dots, 7)$ ions have been calculated at very low energy (0.01–100 meV) and compared with experimental data from the TSR storage ring. A rigorous theory at intermediate energy (< 10 eV) for dissociative excitation (DE) was developed. Calculations were carried out for the following:

- (a) DE of $\text{HD}^+(v = 0)$ ions at low energy (3–6 eV), and compared with experimental data from the TSR storage ring and older theoretical results;
- (b) DE of $\text{H}_2^+(v = 0, 1, \dots, 6)$ ions at low energy (3–6 eV), and compared with crossed beam experimental data - a critical update of molecular data (states and interactions) for H_2 and isotopes was also undertaken;
- (c) rotationally-resolved DR of HD^+ at low energy (0.01–350 meV), and compared with experimental data from the TSR storage ring;
- (d) rotationally-resolved DR of DT^+ at low energy (0.01–350 meV);
- (e) DR, IC and DE of $\text{DT}^+(v = 0)$ ions (illustrating the isotope effect) at energies of 0.0001–15 eV.

Lifetimes of the vibrational states of $X \ ^3\Pi_g$ ground state of CO^{++} were calculated and compared with other theoretical results. Rate coefficients for DR, IC, SEC and EC of $\text{NO}^+(v = 0, 1, \dots, 9)$ ions at energies of 0.0001–10 eV were calculated and compared with Flowing Afterglow Langmuir Probe plasma experiments.

V. Tarnovsky reported on studies of the electron impact ionization of radicals along the primary and dissociative channels. A review of experimental techniques was presented, and the importance of radicals in a number of areas was summarized:

- (a) ionization cross sections for NO , NO_2 and N_2O have been measured in which several persistent ambiguities that exist in the literature regarding the ionization

properties of NO, NO₂ and N₂O were addressed, and various questions were answered;

- (b) ionization cross sections for diborane were reported;
- (c) silane and SiH_x (x = 1–3) radicals were studied in an attempt to resolve large discrepancies between their previously reported cross sections- measurements of silane were carried out using a double-focusing mass spectrometer, while relative partial parent ionization cross sections for each of the three free radicals of SiD_x (x = 1–3) were determined in the fast-beam apparatus from threshold to 200 eV, followed by a measurement of the relative partial cross sections for the corresponding fragment ions;
- (d) absolute partial cross sections for the formation of positive ions followed by electron impact on WF₆ from threshold to 900 eV were measured by means of a time-of-flight mass spectrometer - dissociative ionization processes dominate and result in seven different singly-charged ions (F⁺, W⁺, WF_x⁺, x = 1–5) and five doubly-charged ions (W₂⁺, WF_x²⁺, x = 1-4);
- (e) absolute cross sections for SiCl₄ have now been obtained, and a comprehensive series of absolute partial ionization cross section measurements is being carried out for SiCl_x (x = 1–3) radicals using the fast-beam apparatus.

All experimental ionization studies were supported by continuing efforts to extend and refine a semi-classical approach to the calculation of total single ionisation cross sections for molecules and free radicals. An overall level of agreement between calculation and experiment of better than 20% (and in many cases better than 10%) has been achieved. Significant upgrades to the experimental facilities are also being carried out.

U. Fantz reviewed work performed on the effective rate coefficients for the molecular processes of hydrogen and hydrocarbons in edge plasmas. The TraDiMo computer code (developed at Augsburg University) is used to calculate Franck-Condon factors and transition probabilities on the basis of the potential curves and electronic transition dipole moments for hydrogen. An almost complete input database was compiled from the literature for electronic levels up to quantum number n = 4 (united atom approximation) for the singlet and triplet system of the hydrogen molecule. Vibrational energy levels, Franck-Condon factors and vibrationally resolved transition probabilities for H₂, D₂, T₂, HD, HT and DT were determined. Calculations were also carried out for transitions of C₂, CH, CD and CT that are accessible by emission spectroscopy. These calculations formed the basis for an improvement of an existing collisional radiative model for molecular hydrogen which is also linked with another model for atomic hydrogen. A major improvement was the resolution of the n = 3 levels in the singlet and triplet system into the six electronic states. Differences of the order of a factor of ten in population densities were obtained in comparison with the assumed pre-interaction population throughout these states and according to their statistical weights. The link between the models for H₂ and H offers the possibility of calculating the influence of molecular processes on the population of excited states in hydrogen.

Z. Herman reported on collisions of slow hydrocarbon ions C₂H_n⁺ and C₃H_n⁺ with carbon surfaces. Survival probability was determined for these ions at the incident angle of 30° with respect to the surface, and incident energies of 11 to 45 eV, both for room-temperature (covered with hydrocarbons) and 600° C (hydrocarbon-free) surfaces. Fragmentation product

ions from these collisions were determined, and chemical reactions between radical cation projectiles and CH₃-groups of the surface hydrocarbons were described for hydrocarbon-covered surfaces. Specific reactions were hydrogen-atom transfer to the projectile cations and carbon build-up reactions of C₂-hydrocarbons to form C₃-hydrocarbon product ions. The effect of the internal energy of the projectile hydrocarbon ions on the extent of fragmentation after surface collision was investigated: initial internal energy of the projectile ions appears to be fully available for the fragmentation process.

S. Matejcek reported on the electron impact ionization of small hydrocarbon molecules and the effect of the gas temperature. Electron impact ionization reactions were studied in crossed electron/molecular beam experiments. The appearance energies (AE) of the ions formed via electron impact ionization on these molecules were measured at two different gas temperatures of 293 and 693K. Generally, a decrease of the appearance energies of the ions with increasing gas temperature occurred, and isotopic effects in the appearance energies at room and elevated temperatures were observed in deuterated methane (CH₃D). These observations can be explained in terms of the zero point energies of the molecules. An investigation of the temperature effects on the AE of propane is in good agreement with previous studies with ethane and methane, where red shifts of 0.19 – 0.3 eV and 0.14 eV have been observed, respectively. The increase of the gas temperature from 293 to 693K resulted in a decrease of the AE for cations of propane in the range of 0.21 ± 0.09 eV up to 0.42 ± 0.1 eV that can be explained by the higher internal energy of the molecules (i.e., population of higher vibrational and rotational states). Comparisons of the present AE values at 293K with equivalent data from previous studies show decreases for most of the cations. These differences can be explained in terms of the high detection efficiency of the apparatus and long accumulation time of the ion signal which allows the detection of very weak ion efficiency yields (i.e., higher sensitivity of the present experiment).

M. Larsson presented results from the experimental measurements of product branching ratios in the recombination of hydrocarbon ions. This work focused on experimental studies of dissociative recombination of H₃⁺ and hydrocarbon molecules C_xH_y⁺. Considerable progress has been made to understanding and quantifying the recombination of the H₃⁺ ion - a controversial topic for many years. New experiments at CRYRING during 2002 with an ion source delivering rotationally cold ions was an important milestone, and these studies were carried out simultaneously with theoretical work by Greene's group at JILA, Boulder, Colorado. The data reduction and preparation of a complete description of the CRYRING experiments has been extremely time consuming, and a short note was published in *Nature*, April 2003. Agreement between experiment and theory is now very good for H₃⁺ in the lowest vibrational level, and permits theoretical calculations of the recombination of vibrationally excited H₃⁺ with confidence - something that is extremely difficult to do in a controlled way with experimental techniques. One experiment has been carried out on hydrocarbon ions during the reporting period, and much effort has been devoted to data reduction from earlier experiments. Thus, papers have appeared on C₃H₇⁺, C₂H⁺ and C₂H₄⁺, C₃H₄⁺, C₂D₅⁺, while another on C₃D₇⁺ and C₄D₉⁺ is almost ready for submission. Dissociative recombination of hydrocarbon ions produces more free radicals than previously believed, and the carbon-carbon bond is broken for all hydrocarbon ions studied so far (for some cases in more than 50% of the event).

3. Specific Outputs and Outcomes

During the course of the CRP, new data have been generated for a variety of processes impacting on a number of issues in the edge region of fusion plasmas. Essentially all the goals of the

original work plan have been fulfilled during the course of the CRP, with the generation of new theoretical and measured cross sections for a variety of processes in molecules relevant to fusion plasmas. A great deal of the data has now been made available in electronic form for several modelling codes, and has already had a positive impact in a number of fusion applications. Data have also been added to the database maintained by the Atomic and Molecular Data Unit for direct and cost-free use by all fusion researchers.

Discussions during the final session of the RCM indicated that even with the large amount of data generated, there are still significant areas involving molecular processes and edge plasmas that merit further research. A pressing need is the systematic development of scaling methods to fill gaps in the molecular data. The overall consensus of the CRP participants was that additional work is extremely important in this area of the fusion process.

4. Concluding Remarks

The CRP on “Molecular processes in edge plasmas” has been extremely successful in achieving all the specific objectives specified at the beginning of the project. All participants have published their resulting work in refereed journals over the course of the CRP, are making their data available in electronic form, and have prepared summary articles for a dedicated issue of *Atomic and Plasma-Material Interaction Data for Fusion* (IAEA publication).

**Final IAEA Research Co-ordination Meeting on
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1-2 November 2004, IAEA Headquarters, Vienna, Austria

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Agenda

Monday 1 November

Meeting Room: F-01-21

09:30-10:00 Opening, Adoption of Agenda, A. Nichols, R. Clark

Session 1: Progress Reports I

Chairman: V. Tarnovsky

10:00 – 10:45 M. Capitelli Progress on elementary processes, kinetics and transport properties of H₂ plasmas

10:45 – 11:15 *Coffee Break*

11:15 – 12:00 Y. Hatano Dissociative Excitation of Molecules

12:00 – 12:45 M. Chibisov Coulomb Rydberg quenching by neutral atoms and atomic ions

12:45 – 14:00 *Lunch*

Session 2: Progress Reports II

Chairman: Y. Hatano

14:00 – 14:45 T. Märk Electron impact ionization/dissociation of molecules relevant in fusion edge plasmas

14:45 – 15:30 P. Defrance Electron impact ionization and dissociation of C_mH_n⁺ ions

15:30 – 16:00 *Coffee Break*

16:00 – 16:45 I. Schneider Reactive collisions between electrons and molecular ions of hydrogen and oxides, relevant for fusion plasma kinetics

16:45 – 17:30 V. Tarnovsky Electron impact ionization of radicals along the primary and dissociative channels

Tuesday 2 November

Session 3: Progress Reports III

Chairman: T. Märk

09:00 – 09:45	U. Fantz	Effective rate coefficients for molecular processes of hydrogen and hydrocarbons in edge plasmas
09:45 – 10:30	Z. Herman	Collisions of slow hydrocarbon ions with carbon surfaces: C ₂ and C ₃ hydrocarbon ions
10:30 – 11:00	<i>Coffee Break</i>	
11:00 – 11:45	S. Matejcek	Electron impact ionization of small hydrocarbon molecules, the effect of the gas temperature
11:45 – 12:30	M. Larsson	Product branching ratios in recombination of hydrocarbon ions
12:30 – 14:00	<i>Lunch</i>	

Session 4: Review of work plan and outcomes, formulation of CRP conclusions

Chairman: M. Larsson

14:00 – 15:30	All	Discussion
15:30 – 16:00	<i>Coffee Break</i>	
16:00 – 17:00	All	Discussion

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Summaries from Participants

Summary of Work Performed as Part of the Coordinated Research Program (CRP) on Data for Molecular Processes in Edge Plasmas

K. Becker

Stevens Institute of Technology, Hoboken, USA

The work performed by our group falls into 4 categories:

1. Experimental Determination of Electron Impact Ionization Cross Sections of Molecules and Radicals;
2. Calculations of Total Ionization Cross Sections of Molecules and Radicals (in collaboration with Prof. T.D. Märk, Innsbruck and Prof. H. Deutsch, Greifswald);
3. Experimental Modifications;
4. Plasma-induced Decomposition of Hydrocarbons on Metal Surfaces.

Specifically, we completed the following tasks (either totally or partially):

1. Experimental Determination of Electron Impact Ionization Cross Sections of Molecules and Radicals

Ionization of NO, NO₂, and N₂O: We carried out absolute partial ionization cross section studies for the 3 nitrogen-oxygen compounds NO, NO₂, and N₂O. These measurements constitute the first effort to measure absolute partial ionization cross sections for all three nitrogen-oxygen compounds in the same apparatus using the same experimental technique. NO and NO₂ are considered oxides of nitrogen. Both molecules have an unpaired electron and are thus classified as radicals. N₂O is a symmetric non-linear molecule with a bond angle of about 134°. N₂O, “laughing gas”, is a linear molecule which cannot easily be represented by a single valence bond picture. The molecule has the O atom at one end and “oscillates” between three resonance structure involving double and triple bonds. Several persistent ambiguities that existed in the literature regarding the ionization properties of NO, NO₂, and N₂O were addressed in the course of our work and open/unresolved questions were answered.

Ionization of B₂H₆: Diborane has a very unusual molecular structure, which is very different from other molecules such as C₂H₆, C₂F₆ and Si₂H₆. There is no direct chemical bond between the two B atoms in B₂H₆. Two BH₂ groups lie in a plane with the B atoms facing each other. The molecule is held together by 2 B-H-B lobes which are perpendicular and on opposite sides of that plane. The intensities of the ions BH₃⁺, BH₂⁺, and BH⁺ are distinctly higher in our mass spectrum compared to the NIST standard data table, which may be attributable to a higher detection efficiency in our experiment for ions formed with significant excess kinetic energy. We also found ion signals for the three ions H⁺, H₂⁺, and H₃⁺. No appreciable ion signals were detected that corresponded to the formation of doubly charged ions. The formation process leading to H₃⁺ fragment ions could not be uniquely identified. The cross-section curves of all ions show a very similar shape as a function of impact energy. The cross sections increase rapidly from threshold to a maximum and then decrease slightly with higher impact energy. The maximum for the B₂-containing ions was found to be in the range between 40 and 70 eV and at higher energies around 80 eV for the B-containing ions and H⁺. The total ionization cross-section curve of diborane exhibits a maximum at 70 eV with a peak value of 10.74 x 10⁻¹⁶ cm².

Ionization of Silane and its Radicals: Even though electron-impact ionization cross sections of silane and of its radicals, SiH_x (x = 1–3) have been studied by several authors, there were

serious discrepancies between the results from various experiments. We carried out measurements using a double focusing mass spectrometer for silane. For each of the three free radicals SiD_x ($x = 1-3$), relative partial parent ionization cross section were measured in the fast-beam apparatus from threshold to 200 eV followed by a measurement of the relative partial cross sections for the corresponding fragment ions. The measurements were limited to singly charged ions, since cross sections for the formation of doubly charged ions were found to be at or below the detection sensitivity of the fast-beam apparatus (i.e. peak cross sections below $0.05 \times 10^{-16} \text{ cm}^2$).

There are notable similarities between the SiD_x cross sections and the cross section data obtained previously for CD_x and SiF_x . Similar to SiD_x , the ionization of the CD_x radicals was also dominated by parent ionization and the parent ionization cross section had essentially the same value for all CD_x targets. Furthermore, dissociative ionization of the CD_x radicals was dominated by a single channel which involved the removal of a D atom. However, the SiD_x cross sections are typically larger by more than a factor of 2. On the other hand, the previously measured SiF_x ionization cross sections showed maximum values comparable to the present SiD_x cross sections. Dissociative ionization channels were found to be much more important for SiF_x . The presence of strong dissociative ionization channels appear to be characteristic for all fluorine-bearing molecules and radicals.

Ionization of WF_6 : We measured absolute partial cross sections for the formation of positive ions followed by electron impact on WF_6 from threshold to 900 eV using a time-of-flight mass spectrometer. Dissociative ionization processes resulting in seven different singly charged ions (F^+ , W^+ , WF_x^+ , $x = 1-5$) and five doubly charged ions (W^{2+} , WF_x^{2+} , $x = 1-4$) are the dominant ionization channels. The ion spectrum at all impact energies is dominated by WF_5^+ ions. At 120 eV, the partial WF_5^+ ionization cross section has a maximum value of $3.92 \times 10^{-16} \text{ cm}^2$ (43% of the total ion yield). The cross section values of all the other singly charged fragment ions at 120 eV range from $0.39 - 0.73 \times 10^{-16} \text{ cm}^2$. The ionization cross sections of the doubly charged ions are more than one order of magnitude lower than the cross section of WF_5^+ . Double ionization processes account for 21% of the total ion yield at 120 eV.

SiCl_4 and SiCl_x radicals: SiCl_4 has a similar structure to fluorinated and hydrogenated targets that we studied in the past (SiF_4 , SiH_4). No ionization cross section data are available for the molecule. Perhaps most importantly, the SiCl_4 molecule is a candidate for electron-impact ionization studies on thin deposited SiCl_4 films. This affords a unique opportunity to explore how the ionization properties of a molecule change from the gas phase to the condensed phase. Absolute cross sections for SiCl_4 have now been obtained and we are in the process of carrying out a comprehensive series of absolute partial ionization cross section measurements for the SiCl_x ($x = 1-3$) radicals using our fast-beam apparatus.

2. Calculations of Total Ionization Cross Sections of Molecules and Radicals

All experimental ionization studies were also supported by our continuing effort to extend and refine our semi-classical approach to the calculation of total single ionisation cross sections for molecules and free radicals. In general, we now have achieved a level of agreement between calculation and experiment of better than 20% (and in many cases of better than 10%). This level of agreement gives us confidence as to the predictive capabilities of our approach for molecules for which no experimental data are available.

3. Experimental Modifications

We have installed a new dual-detector system from Roentdek GmbH in Germany. One fast position-sensitive MCP detector replaces the channeltron in the fast-beam apparatus and serves as the final product ion detector. The second detector will be installed as an alternative to the Faraday cup and will serve as a monitor of the fast neutral beam and the product ion beam prior to entering the electrostatic energy analyzer. This will allow us to obtain information about the excess kinetic energy of the fragment ions. We also replaced the electron gun with a different design that achieves a much higher current density and thus allows us to significantly reduce the interaction volume.

4. Plasma-induced Decomposition of Hydrocarbons on Metal Surfaces

We study the interaction of a novel capillary non-thermal ambient pressure plasma with contaminated Al and other metal surfaces and in an effort to develop a new technology that is suitable for the destruction and removal of organic contaminants from metal surfaces.

The project has four main objectives:

- Characterization of the discharge plasma used in the present application.
- Development of a laboratory-scale experimental system.
- Investigation of plasma jets firing against conductive and non-conductive surfaces.
- Investigation of an atmospheric-pressure plasma discharge system for controlled cleaning of Al and other metal surfaces contaminated with selected hydrocarbons.

Consistent with the objectives of the project the following tasks were executed:

- Construction of a discharge plasma reactor for atmospheric-pressure operation.
- Characterization of the plasma jets.
- Assessment of destruction of oils and VOCs on non-conducting and conducting surfaces.
- Assessment of HC destruction and by-product analysis.

We characterized the hydrocarbon removal process by standard surface characterization studies supported by a detailed mass balance. The macroscopic properties and the spatial distribution of the capillary plasma were examined in order to determine the effects of the treated material on the characteristics of the plasma (back-diffusion of volatile surface reaction products into the plasma!). In order to characterize the effect of the plasma on a treated surface, we used an SEM analysis of the surface. Several samples of Al alloy 6061 were prepared for testing. A control sample was prepared and was always compared to the treated samples. The samples were subjected to the following conditions:

- Sample 1: control – no plasma; one hour elapsed - ambient air oxidation
- Sample 2: Plasma treated for two minutes at high power.
- Sample 3: Plasma treated for five minutes at low power.
- Sample 4: Plasma treated for five minutes at high power.
- Sample 5: Plasma treated for twenty minutes at high power.

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Elementary Processes, Transport and Kinetics of Molecular Plasmas

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We report the results obtained since the last meeting in Vienna, 12-14 May 2003, in the three topics covered by our group

Elementary Processes

- State to state vibrational resolved electron molecule cross sections for the triplet-triplet transitions in molecular hydrogen have been calculated by using the impact parameter method. The calculations have been finished last year and published this year.
- The construction of a data base for dissociative attachment of ro-vibrational states of H₂ and its isotopes is in progress.
- A classical approach has been used for calculating the ionization cross sections for N₂ and O₂ in different vibrational states. The small effect of the rotational energy has been estimated.
- Cross sections and rate coefficients for the system H-H₂(v,j), calculated by the quasiclassical trajectory method, have been improved by using a new and more accurate potential energy surface. The extension to isotopes is in progress.

Transport Properties of H₂ Plasmas

- Transport cross sections of electronically excited states of atomic hydrogen have been derived by using semiclassical approaches. The data have been used to calculate the transport coefficients (viscosity, thermal conductivity, electrical conductivity) of thermal plasmas in a wide range of temperatures and pressures. The results, which show the strong influence of excited states on the transport coefficients of atomic plasmas, have been completed last year and published this year. Transport cross sections of electronically excited nitrogen and oxygen atoms have been also derived.

Plasma kinetics

We have implemented kinetic codes to describe the kinetics of molecular plasmas (mainly hydrogen) in different non-equilibrium conditions. These codes include

- a) quasi-homogeneous plasma model including a radiative-collisional model for atomic and molecular hydrogen;
- b) PIC-MCC (Particle In Cell with Monte-Carlo Collisions) for describing parallel plate hydrogen plasma reactors;
- c) 1D Euler code coupled with the kinetics of partially ionized gases to describe high enthalpy flows through nozzles of different geometries;
- d) DSMC (Direct Simulation with Monte Carlo collisions) model for describing shock wave propagation;
- e) zero dimensional code to reproduce the plasma kinetics in multipole magnetic plasmas.

The codes have been applied to reproduce different experimental situations. In particular the first model has been used to rationalize the experimental CARS

measurements of the vibrational and rotational temperatures in RF discharges obtained in our laboratory, while the PIC-MCC code has been used to reproduce different experimental quantities obtained in other laboratories.

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Summary Report 2005

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Optical Spectroscopy of Nuclear Fusion Plasma was the main subject of our investigations during the last three years. The new summation rules for Coulomb wave function products (M.Chibisov *et al.*, PRL, 84, 3, 451 2000; JETP, 90, 2, 276, 2000; J. Phys. B, 34, 49, 2001) were the basis for the renovation of this topic. It was found that properties of Coulomb Rydberg states, perturbed by neutral atom, differ essentially from properties of unperturbed states (M. Chibisov *et al.*, J. Phys. B, 35, L193, 2002; PRA 66, 042709, 2002). In particular, Radiation Life Times of perturbed Rydbergs are in 3-7 times larger than unperturbed one's with principal quantum numbers $n=25-35$. Coulomb Rydberg states are present also in collisions of negative and positive atomic ions as a result of the charge transfer process and the inverse process: $A^+ + B^- \leftrightarrow A^{**}(nlm) + B$. Energy splittings at avoided crossings are expressed through the new sum of Coulomb wave function products and this sum has been investigated also (M. Chibisov, JETP, 93, 2, 256, 2001; Physics-Uspekhi (45) (1) 1-26, 2002). The cross sections of these processes depend strongly on properties of these sums. The collisions $H^- + H^+$ and He^{++} have been studied in details. The cross sections of the excitation (de-excitation) and single-electron capture processes in the collision $H^+ + He^*(1s, nLm)$ have been calculated in close coupling approach (M. Chibisov *et al.*, J. Phys. B, 34, 2631, 2001; J. Phys. B, 35, 5081, 2002). At large internuclear distances R in final states $H^*(nLm) + He^+(1s)$ the excited hydrogen is perturbed by the electric field of the He^+ ion and the hydrogen states should be Stark states. Energies of these states are changed proportionally R^{-2} and crosses the excited helium states at large distances R . As a result, the cross sections of the excitation (de-excitation) are very large, $10^{-14} - 10^{-13} \text{ cm}^2$ for $n = 3, 4, 5$, at collision velocities $10^6 - 10^8 \text{ cm/s}$. These processes play an important role in the radiative-collisional kinetics of Tokamak divertor plasmas, when seeded with He, as well as in the attenuation kinetics of diagnostic and heating neutral helium beams (particularly with a metastable atom admixture) when penetrating a fusion plasma. We study now another processes when the new summation rules of Coulomb wave function products are important.

Electron Impact Ionization and Dissociation of Polyatomic Ions

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Absolute cross sections for electron impact single ionization (SI), and for fragment production resulting from dissociative excitation (DE) and from dissociative ionization (DI) of H_2^+ , D_2^+ , D_3^+ , $C_2H_2^+$ and C_2H^+ , CH_n^+ or CD_n^+ ($n = 1-4$) are measured for electron energies from corresponding thresholds to 2.5 keV. The animated crossed electron-ion beam experiment is used. Product ions are separated by means of a large angular acceptance, double focusing, analyzing magnet. The initial inelastic process (I or E) leads to the formation of electronically excited states, which may dissociate, the internal energy in excess being converted into kinetic energy released (KER) to the fragments. The fragments exhibit wide energy and angular distributions so that it is difficult to collect all of them, especially for the lightest fragments. Reaction threshold energies are in the range from 5 eV (DE) to 20 eV (SI and DI).

The product velocity distribution observed in the laboratory is analysed in order to (i) separate contributions from the different reaction channels (DE and DI) leading to the same fragments production and (ii) determine the kinetic energy release distributions (KERD). Obtained results are compared with the available data from the literature.

For H_2^+ and D_2^+ , absolute total cross sections have been measured for electron impact dissociative excitation and dissociative ionisation in the energy range 5–3000 eV. In addition, the vibrational population of the primary ion beam has been analysed. A model calculation has been performed to interpret the different KER spectra. Observations are consistent with the measured vibrational population extending up to $v = 13$, as confirmed by the appearance threshold of the dissociative ionisation (DI) channel. A distinctive hump is also present around 9 eV that coincides with the maximum of the DI contribution.

For $C_2H_2^+$ and for C_2H^+ , absolute cross sections have been measured for SI and for the production of each of the possible fragment ion H^+ , H_2^+ , C^+ , CH^+ , CH_2^+ and C_2^+ . The partial contributions of DI and DE are determined. The results (cross sections and KERDs) are compared with the prediction based on scaling laws developed with respect to data obtained for neutral molecules. It is clearly seen that in some cases, the predictions do not reproduce accurately enough the experimental results. Similar conclusions hold for the ions of the methane sequence (CH_n^+ and CD_n^+ , $n = 1-4$), which has been systematically studied.

The high-energy dependence of the electron impact ionization cross section can usually be presented by the Bethe plot, which for atoms or ions shows that the cross section may be expressed in the following form:

$$\sigma = \frac{a}{EI} \left[\ln \left(\frac{E}{I} \right) + b \right]$$

where I is the threshold energy. The Bethe plot of present data for simple ionization cross section shows that this dependence extends down to relatively low energies, about 70 eV. The

Deutsch-Märk model for the estimation of the ionization cross section was adapted according to experimental results and, the recently calculated data were brought in a very good agreement with experimental results for ionization. Single ionization cross sections are found to contribute for about 1/3 of the total ionization cross section. Finally, it is worth mentioning that no evident isotopic effect could be observed nor for H_2^+ and D_2^+ , nor for CH_n^+ and CD_n^+ .

Effective Rate Coefficients for Molecular Processes of Hydrogen and Hydrocarbons in Edge Plasmas

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Hydrogen and hydrocarbons are some of the most dominant molecular species in edge plasmas of fusion devices. The recombination of hydrogen particles on surfaces leads to the formation of hydrogen molecules, whereas hydrocarbons are released from carbon (graphite) surfaces due to the chemical erosion process. The molecules penetrate into the plasma and can undergo a variety of reactions: vibrational excitation, dissociation, ionization, recombination, charge exchange - to name some of them. An insight in the role of molecules in edge plasma can be obtained by a combination of diagnostics and modelling. The wide parameter range (n_e , T_e) in which edge plasmas can operate requires a description of plasma processes by effective rate coefficients. A summary of the activities at the University of Augsburg is given in the following with emphasis on the progress made since the last meeting in May 2003.

Transitions of diatomic molecules: TraDiMo

The TraDiMo computer code (developed at Augsburg University) is used to calculate Franck-Condon factors and transition probabilities on the basis of potential curves and electronic transition dipole moments for hydrogen. An almost complete input database was compiled from literature for electronic levels up to the quantum number $n = 4$ (in the united atom approximation) for the singlet and triplet system of the hydrogen molecule. Vibrational energy levels, Franck-Condon factors and vibrationally resolved transition probabilities for H_2 , D_2 , T_2 , HD, HT and DT are calculated. The complete data set is already published in an IAEA report (INDC(NDS)-457) and available online from the AMDIS webpage. Selected examples are presented during the meeting and applications for diagnostic purposes are shown. In addition, these calculations formed the basis for an improvement of the collisional radiative model for molecular hydrogen. Calculations are also carried out for transitions of C_2 and CH, CD and CT which are accessible by emission spectroscopy.

Collisional radiative model for H_2 and H

The existing collisional radiative model for molecular hydrogen which is also linked with one for atomic hydrogen was further developed and improved. The influence of selected processes on the population of vibrational levels in the ground state is shown for H_2 and D_2 . Concerning the isotope effect similar populations are obtained which is confirmed by measurements. The dependence on T_e is presented. Effective emission rate coefficients and effective rate coefficients for processes such as charge exchange, dissociative attachment, ionization and dissociation were calculated as a function of n_e and T_e with and without taking into account the vibrational population. The enhancement of rate coefficients at low T_e was emphasized. Applications of these data to molecular flux measurements were shown. The calculations were validated by experimental results from measurements carried out at the divertor of ASDEX Upgrade. The effective 'photon efficiency', i.e. (S+D)/XB ratios were calculated for direct use in edge plasmas. The role of molecules in plasma recombination, especially in cold detached divertor plasmas, was emphasised and effective rate coefficients for these processes (MAR in comparison to EIR) were calculated as a function of T_e and n_e .

A major step in the improvement of the collisional radiative model was the resolution of the $n=3$ levels in the singlet and triplet system into its six electronic states, respectively. This is in particular of importance for the application to diagnostic purposes, as these states are easily accessible by emission spectroscopy. Differences in the order of a factor of ten in population densities are obtained in comparison to the before assumed population among these states according their statistical weights. The populations of several states in $n=3$ are validated in laboratory experiments where the plasma parameters are well known from other diagnostic methods. In a next step the vibrational structure of electronically excited states was resolved. First results were presented as a function of the vibrational population in the ground state and T_e and n_e .

The link between the model for H_2 and the model for H offers a possibility to calculate the influence of molecular processes to the population of excited states in hydrogen. Depending on T_e , n_e , neutral density to ion density and molecular ion to proton density the relevance of dissociative excitation and dissociative recombination was demonstrated for selected examples. The model provides population coefficients as a function of n_e and T_e for the coupling to the different species. Applications to linear plasma devices operating in the parameter range of edge plasmas were shown.

Dissociation models for hydrocarbons

Hydrocarbons (C_xH_y) which are released from graphite surfaces by the chemical erosion process are accessible by the radiation of the CH and C_2 radical. A relation with the parent molecule, i.e. CH_4 and C_2H_y particles, respectively and therefore quantification is given by the corresponding photon efficiencies. This means, effective dissociation rate coefficients and effective excitation rate coefficients are needed. For this purpose flexible dissociation models are developed for methane dissociation, taking into account in the first case only electron impact collisions. A second model represents a full model including heavy particle collisions and formation and dissociation of the C_2H_y family. A third model calculates the dissociation of C_2H_y particles into C_2 particles. On the basis of these models dominant dissociation paths are identified and CH/ CH_4 , C_2/CH_4 and C_2/C_2H_y particle density ratios are calculated as a function of T_e and n_e . Together with a compilation of the direct and dissociative excitation rate coefficients of CH and C_2 effective emission rate coefficients were presented. It was shown that for the case of CH radiation (A-X transition) the dissociative excitation channel from CH_4 and C_2H_2 plays a role whereas for C_2 radiation (Swan band) the direct excitation channel is always dominant. First results from this modelling indicate a good agreement with measured photon efficiencies in the divertor plasma of ASDEX Upgrade (taken in a certain parameter range for n_e and T_e), in particular for the case of C_2 formation from the C_2H_y group. Thus, it was shown that in quantification of erosion yields the formation of higher hydrocarbons can now be taken into account.

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I. Electron and Photon Driven

Photoionization Cross Sections of Simple Hydrocarbons:

As an extension of our research programs [1-8] the absolute photoionization cross sections of C₁-C₄ hydrocarbons have been measured using synchrotron radiation as a continuous-wavelength light source in the photon-energy range of 10-25 eV [9] where a major part of the interaction of photons with molecules exists. The absolute photo-absorption cross sections, neutral-dissociation cross sections, and photoionization quantum yields of these molecules have been also measured [9]. Some fine-structure peaks and shoulders which are attributed to high Rydberg states of a hydrocarbon molecule converging to each of the ion states have been observed in the obtained cross section curves for each of these hydrocarbon molecules as a function of the photon energy. The obtained results are compared in detail with those obtained by the dipole-simulation method using electron beams as the virtual photons [10]. By comparing the obtained cross sections of these hydrocarbon molecules with the energies of the ion states obtained from photoelectron spectroscopy and also with the Kuhn-Thomas-Reiche sum-rule, an overview has been presented of the behavior of the absolute magnitudes of these observed quantities as a function of the number of carbon atoms in a hydrocarbon molecule [10].

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Dissociative Excitation of Molecules in Photonic and Electronic Collisions with Molecules:

Dissociative excitation of molecules has been considered one of the most difficult processes to be studied experimentally as well as one of the most important fundamental processes in phenomena in ionized gases and condensed matter. In the present work, a survey is given of recent progress in experimental studies of the dissociative excitation of molecules in photonic and electronic collisions with molecules in the excitation-energy range of 10-50 eV with particular emphasis placed on the formation and dissociation dynamics of molecular superexcited states which have been recently substantiated experimentally [1-12].

In photonic collision experiments synchrotron radiation as an excitation photon source combined with newly developed coincidence or two-dimensional spectroscopy-techniques have been used for studying molecules excited into optically allowed states [1-9], while in electronic collision experiments newly developed coincident electron energy-loss spectroscopy has been used for studying those excited into optically forbidden states [10-12].

Molecules studied ranging from simple diatomic and triatomic molecules to a variety of polyatomic molecules. In the present work, examples of molecules relevant to fusion edge plasmas are H₂, D₂, O₂, CO, and C₁-C₃ hydrocarbons [1-14].

Most of the observed molecular excited states are high Rydberg states which are vibrationally (or/and rotationally), doubly, or inner-core excited and converge to each of ion states. Non-Rydberg states are also observed. Dissociation into neutral fragments in comparison with ionization is of unexpectedly great importance in the observed decay of each of these states. Dissociation dynamics as well as its products are remarkably different from those for lower excited states below about ionization thresholds [1-12].

These experimental results have motivated much new development of theoretical investigations of molecular superexcited states and their dissociation dynamics as well as of optical oscillator strength distributions [4]. These results are of great importance also in understanding further the dynamics of electron-ion recombination, electron attachment, and Penning ionization processes [1, 4].

Most of the phenomena in ionized gases and condensed matter are well described by fundamental processes induced by electron-molecule collision processes [15-19]. Cross section values for the ionization and excitation in electron-molecule collisions in the energy range greater than 10² eV are well elucidated quantitatively by the Born-Bethe approximation, while those in the energy range lower than 10² eV are estimated at least roughly also by this theory that is called the optical approximation [15-18]. The information obtained from photonic collision experiments is, therefore, of great importance also in understanding the phenomena induced by electronic collision processes [15-19].

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II. Neutral Driven

Collisional De-excitation of Excited Rare Gas Atoms by Atoms and Molecules:

Collisional de-excitation of excited rare gas atoms by atoms and molecules (as one of the typical heavy neutral-particle collisions following electronic energy transfer) has been extensively studied both experimentally and theoretically [1-4]. This process is of great importance also in the fundamental processes in ionized gases [5, 6].

Since the energies of the lowest excited states of rare gas atoms are much higher than the ionization threshold-values of most of the atoms and molecules, one of the characteristic features of this de-excitation process is to result in the ionization or/and the excitation into highly excited states of the target atoms and molecules [1-4]. This process is classified into two parts, i.e., the de-excitation of excited rare gas atoms in the metastable states and those in the radiative states. The former states are optically forbidden in the transition to the lower excited states and the ground state, whereas the latter states are optically allowed to the lower states and the ground state. The former process is explained by the electron-exchange mechanism, while the latter process by the dipole-exchange mechanism [1-4]. The absolute magnitudes of the de-excitation cross sections as well as their dependence of the collision energy are largely dependent on these two mechanisms, i.e., the electronic states of the excited rare gas atoms whether they are optically forbidden or allowed. The cross sections in the former process are smaller than those in the latter process and their collisional energy dependence whether they increase or decrease with increasing the collision energy is dependent on target atoms and molecules. The cross sections in the latter process almost always decrease with increasing collision energy [1-4].

The collisional de-excitation of excited rare gas atoms in resonant states, i.e., the optically allowed states against the ground state, is well explained by the Watanabe-Katsuura theory of

the dipole-exchange mechanism which was developed for the de-excitation by atomic targets not by molecular targets. In this theory, the photoionization cross sections of the target atoms at the photon energies corresponding to the excitation energies of excited rare gas atoms are of great importance in determining the de-excitation cross section values. Since the photoionization cross sections of molecules are much different from the photo-absorption cross sections at the excitation energies of rare gas atoms in the resonant states [7-11], the important questions have been raised whether the cross sections for photoionization or photo-absorption of target molecules should be used to explain the observed de-excitation cross sections by the Watanabe-Katsuura theory. Recently [12], this problem has been solved by the comparison between the de-excitation cross sections of the resonant states of neon, argon and krypton by atoms and molecules including simple hydrocarbons and the photoionization quantum yields, i.e., the ratios between the photoionization cross sections and the photo-absorption cross sections of the target atoms and molecules. The experimentally obtained de-excitation cross sections are well explained by the theory with photo-absorption cross sections, and not with photoionization cross sections.

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Chemical and Physicochemical Processes in Reactive Plasmas

Reactive plasmas, e.g. those in chemical vapor deposition and etching processes, are generally characterized as weakly ionized plasmas in which component polyatomic molecules have an important role [1]. Fundamental processes in these plasmas are classified into the following three groups:

1. Atomic and molecular processes in a bulk plasma
2. Atomic and molecular processes in the region of plasma-surface interactions
3. Atomic and molecular processes in solids

It is generally accepted that all three groups are of great importance in the control of reactive plasmas. In this paper only the first (1) is described.

The fundamental processes are composed of the physical, physicochemical and chemical stages. The physical stage is the primary activation of parent molecules in reactive plasmas through the collision of molecules with electrons in a wide energy range. Molecules thus receive energies from electrons and form reactive species such as excited or ionized states of molecules, free radicals and electrons of low energies.

These species interact with each other or with stable molecules. The succession of events in atomic and molecular processes that follow the primary activation is summarized in a recent review article [1]. The physicochemical stage is the reactions of ions, electrons, excited atoms and molecules such as electron, ion and neutral driven processes in this work plan. The chemical stage is the reactions of free radicals such as recombination, disproportionation, addition, and abstraction.

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Energy transfer, fragmentation and chemical reactions in collisions of ions with surfaces

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Considerable lack of information on molecular collision processes in plasma edge and in plasma-wall interactions and need for data on behavior of small hydrocarbon ions ($C_1 - C_3$ hydrocarbon ions) of energies 10-100 eV in collisions with surfaces led us to a systematic investigation of interactions of small hydrocarbon ions with carbon surfaces. Using the newly developed scattering method [1], we undertook a program of obtaining new experimental data on ion survival in ion-surface collision, on surface-induced dissociation processes and on chemical reactions with the surface material. Also, the data should serve to elucidate energy transfer in collisions with surfaces and the extent of inelasticity of the collisions and degree of incident-to-internal energy transfer for ions of increasing complexity. The scattering method makes it possible to direct a mass selected ion of energies 1-50 eV under a pre-selected angle to the surface (at room temperature or heated to about 600°C) and to measure mass spectra of the ion products as well as their translational energy and angular distributions.

In the first part of this work [1], a set of experiments was carried out on ion-surface collisions of small hydrocarbon ions CD_5^+ , CD_4^+ , and CD_3^+ and their isotopic H and $^{13}C,H$ variants with carbon surfaces at room and elevated (600°C) temperatures. Fragmentation processes of the projectiles, energy transfer and chemical reactions with the surface material were determined. On heated surfaces, only fragmentation of the projectiles, increasing in extent with increasing incident energy, was observed. The room-temperature surfaces were covered by a layer of hydrocarbons and, besides fragmentation of the projectile ions, also their chemical reactions with the surface hydrocarbons could be observed. These were (i) H-atom transfer from surface hydrocarbons to projectile radical cations to form protonated projectile ions (ii) carbon chain build-up reactions in interactions of the incident ions with the CH_3 - terminal group of the surface hydrocarbons, to form mainly C_2 - hydrocarbon ion products. The importance of hydrocarbons on carbon surfaces for the outcome of interaction with gas phase ions has been specifically stressed [2].

In a subsequent study, a set of scattering experiments was carried out on ion-surface collisions of C_2 hydrocarbon ions $C_2H_2^+$, $C_2H_3^+$, $C_2H_4^+$, $C_2H_5^+$ and their D-isotopic variants $C_2D_2^+$ and $C_2D_4^+$ with carbon surfaces at room and elevated (600°C) temperatures [3]. Again, dissociation, energy transfer and chemical reactions with the surface material were determined. Also, ion survival probabilities for the surface collisions were determined. In the same way, collisions of $C_3H_n^+$ ($n = 3-8$) hydrocarbon ions with the carbon surfaces were investigated.

Interaction of doubly-charged ions, in comparison with analogous singly-charged ions was studied in collisions with carbon surfaces at room temperature. Hydrocarbon ions $C_7H_8^{2+}$ ($C_7H_8^+$), $C_7H_7^{2+}$ ($C_7H_8^+$), and $C_7H_6^{2+}$ from toluene were investigated [4, 5]. The ion survival at the incident energy of 25 eV (incident angle 30° with respect to the surface) was found to be of the order of several percent and about twice as large for the di-cations as for the respective cations. Only singly-charged product ions were observed in collisions with the di-cations. Despite the fact that ions of different structures may be present in the cation and di-cation beams, the prevailing process appears to be dissociation of the projectiles via the tropylium structure of the projectile or fragment ion $C_7H_7^+$. Translational energy and angular distributions of the product ions were determined, too.

In a close collaboration with the group of Prof. Märk (University of Innsbruck), the effect of initial internal energy of small hydrocarbon ions on the extent of surface-induced dissociation was investigated. The projectile ions, prepared both with internal energy by electron impact and relaxed by gas-phase collisions (without internal energy), were CH_3^+ , CH_4^+ , CH_5^+ , C_2H_4^+ , C_2H_5^+ and C_2H_6^+ . It was found that the internal energy was practically fully available to drive the projectile ion dissociation [6, 7].

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Product Branching Ratios in Recombination of Hydrocarbon Ions ($C_nH_m^+$ $n > 0$, $m > 0$)

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In a plasma cold enough to contain molecules, dissociative recombination is the most important neutralizing process. In a fusion reactor, molecular ions are present in the fusion edge plasma, and in particular divertors. Hydrocarbon ion impurities are present because of the interaction of the plasma with the carbon-containing first wall or the divertor plate segments. Hydrocarbon molecules released into the plasma are ionized and subsequently dissociated. In order to model the edge plasma, information on the dissociative recombination of hydrocarbon ions is needed [1, 2]. The complexity of the process makes it impossible to rely on theoretical calculation, which means that laboratory measurements are needed. Presently there is only one technique which allows measurements of product branching ratios of the dissociative recombination of hydrocarbon ions, namely the ion storage ring technique. The Molecular Physics group at the Department of Physics, Stockholm University has carried out a systematic research programme aiming at determining product branching ratios in dissociative recombination of hydrocarbon molecular ions.

Table I lists all results for hydrocarbon ion branching ratios measured in CRYRING. The complete results are given for $C_nH_m^+$ ($n < 3$), whereas only the results for the C–C bond breaking is given for $C_nH_m^+$ ($n = 3$). The level of detail concerning H-atom loss channels differ for the isotopomers $C_3D_7^+$ and $C_3H_7^+$, with the more reliable results being those for $C_3D_7^+$ because the larger mass separation provided by the D-atoms. For $C_4D_9^+$ only the C–C bond breaking branching ratio could be determined. In general one can say that fragmentation is more abundant than had previously been anticipated based on chemical arguments.

The results from CRYRING including attempts to rationalize the data in terms of enthalpy changes in the reactions have been reviewed very recently [12].

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TABLE (a). Hydrocarbon ions studied in CRYRING

Molecule		Branching ratio	Reference
CH_2^+	C + H + H	0.63 ± 0.06	3
	CH + H	0.25 ± 0.04	
	C + H ₂	0.12 ± 0.02	
CH_5^+	CH ₃ + H + H	0.70 ± 0.01	4
	CH ₂ + H ₂ + H	0.17 ± 0.02	
	CH + H ₂ + H ₂	0.03 ± 0.01	
	CH ₄ + H	0.05 ± 0.01	
	CH ₃ + H ₂	0.05 ± 0.01	
C_2H^+	C ₂ + H	0.43 ± 0.03	5
	CH + C	0.39 ± 0.04	
	C + C + H	0.18 ± 0.04	
C_2H_2^+	C ₂ H + H	0.50 ± 0.06	6
	CH + CH	0.13 ± 0.01	
	C ₂ + H + H	0.30 ± 0.05	
	CH ₂ + C	0.05 ± 0.01	
	C ₂ + H ₂	0.02 ± 0.03	
C_2H_3^+	C ₂ H ₂ + H	0.29 ± 0.04	7
	C ₂ H + H ₂	0.06 ± 0.03	
	C ₂ H + H + H	0.59 ± 0.06	
	C ₂ + H ₂ + H	0.03 ± 0.01	
	CH ₃ + C	0.006 ± 0.002	
	CH ₂ + CH	0.03 ± 0.01	
C_2H_4^+	C ₂ H ₃ + H	0.11 ± 0.07	5
	C ₂ H ₂ + H ₂	0.06 ± 0.03	
	C ₂ H ₂ + H + H	0.66 ± 0.06	
	C ₂ H + H ₂ + H	0.10 ± 0.04	
	CH ₄ + C	0.01 ± 0.01	
	CH ₃ + CH	0.02 ± 0.02	
	CH ₂ + CH ₂	0.04 ± 0.02	
		0.04 ± 0.02	
C_2D_5^+	C ₂ D ₄ + D	0.12 ± 0.03	8
	C ₂ D ₃ + D + D	0.27 ± 0.04	
	C ₂ D ₂ + D + D + D	0.13 ± 0.03	
	C ₂ D ₂ + D ₂ + D	0.29 ± 0.03	
	CD ₃ + CD ₂	0.17 ± 0.01	
C_3H_4^+	C ₃ H ₃ + H	0.87 ± 0.04	9
	C ₃ H ₂ + H ₂	≤ 0.02	
	C ₂ H ₃ + CH	0.01 ± 0.01	
	C ₂ H ₂ + CH ₂	0.06 ± 0.02	
	C ₂ H + CH ₃	0.01 ± 0.01	
	C ₃ H ₂ + H + H	≤ 0.05	
C_3H_7^+	C–C bond breaking	0.34 – 0.39	10
C_3D_7^+	C–C bond breaking	0.44	11
C_4D_9^+	C–C bond breaking	0.39	11

Report on work accomplished

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In the framework of this project we have studied appearance energies (AE) for electron impact ionisation to the molecules CH₄, CH₃D, CD₄, C₂H₆ and C₃H₈ [1-4]. The electron impact ionization to molecules occurs in the plasma edge where at relatively low temperature besides electrons and atomic ions- and particles also a significant number of neutral hydrogen atoms, low-charged atomic and molecular impurities (produced and introduced for instance via plasma/wall interactions, via diagnostics or via cooling).

The crossed electron – molecules beams technique with mass analysis of the ion has been applied to measure the ion yields at the ionization thresholds. As the thermal conditions in the fusion reactors are apart the normal laboratory conditions, we have focused in the project on the effects of the gas temperature on AE of particular positive ions. Significant temperature effects for the appearance energies of the positive ions have been observed. Generally, the appearance energies have been decreasing with the increasing gas temperature. This feature has been measured for the first time experimentally. Moreover, the magnitude of the temperature shift was increasing with the size of the molecule. The larger the molecule, the larger the temperature shift. This phenomenon we have attributed to the rotational and vibrational excitation.

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Report on the scientific activity for the CRP on Data for molecular processes in edge plasmas

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Researchs subject:

Reactive collisions between electrons and molecular ions of hydrogen and oxides, relevant for fusion plasma kinetics.

Main results (advances in modelling and computed rates):

1. Reactive collisions between electrons and H_2^+ ($v = 0, 1, 2$) ions at low energy (0.0001-1 eV): Dissociative Recombination (DR), Superelastic collisions (SEC), Inelastic Collisions (IC) and Elastic Collisions (EC). Computation and comparison with TSR storage ring experimental data.
2. DR and SEC between electrons and H_2^+ ($v = 0, 1, \dots, 7$) ions at very low energy (0.01-100 meV): computation and comparison with TSR storage ring experimental data.
3. Rigorous theory for intermediate energy (< 10 eV) Dissociative Excitation (DE).
4. DE of HD^+ ($v = 0$) ions at low energy (3-6 eV): computation and comparison with TSR storage ring experimental data and older theoretical results.
5. DE of H_2^+ ($v = 0, 1, \dots, 6$) ions at low energy (3-6 eV): computation and comparison with crossed beam experimental data.
6. Critical update of molecular data (states and interactions) for H_2 and isotopes.
7. Rotationally-resolved DR of HD^+ at low energy (0.01-350 meV): computation and comparison with TSR storage ring experimental data.
8. Rotationally-resolved DR of DT^+ at low energy (0.01-350 meV): computation.
9. DR, IC and DE of DT^+ ($v = 0$) (0.0001–15 eV): computation.
10. *Lifetimes of the vibrational states of $X^3\Pi_g$ ground state of CO^{2+} : computation and comparison with other theoretical results.*
11. DR, IC, SEC and EC of NO^+ ($v = 0, 1, \dots, 9$) (0.0001–10 eV) : computation and comparison with Flowing Afterglow Langmuir Probe plasma experiments.

Publications and Communications

A. Articles

1. A.I. Florescu, V. Ngassam, I.F. Schneider, A. Suzor-Weiner, H_2 triplet states contribution to low energy dissociative recombination of H_2^+ , *J. Phys. B* **36**, (2003) 1205-1215.
2. V. Ngassam, A.I. Florescu, L. Pichl, I.F. Schneider, O. Motapon, A. Suzor-Weiner, The short-range reaction matrix in MQDT treatment of dissociative recombination and related processes, *European. J. Phys.* **D 26** (2003) 165.
3. V. Ngassam, O. Motapon, A.I. Florescu, L. Pichl, I.F. Schneider, A. Suzor-Weiner, Vibrational relaxation and dissociative recombination of H_2^+ induced by slow electrons, *Phys. Rev.* **A 68** (2003) 032704.
4. "Towards a model for dissociative recombination of the CO^{2+} dication: states and couplings", N. Vinci, N. De Ruelle, F. O. Waffeu-Tamo, O. Motapon, M. Fifirig, O. Crumeyrolle, X. Urbain, J. Tennyson et I. F. Schneider, *J. Phys.: Conference Series* **4**, 162, 2005.

5. “Quantum interferences of super-excited states: application to electron – molecular cation reactive collisions”, M. C. Stroe, A. I. Florescu, M. Fifirig, F. O. Waffeu Tamo, V. Ngassam, O. Motapon and I. F. Schneider, *Romanian Reports in Physics*, **57**, 748-772, 2005.
6. “Reactive collisions between electrons and NO⁺ ions: rate coefficients computations and relevance for the air plasma kinetics” O. Motapon, M. Fifirig, A. Florescu, F. O. Waffeu Tamo, O. Crumeyrolle, G. Varin-Breant, A. Bultel, P. Vervisch, J. Tennyson, I. F. Schneider, *Plasma Sources Science and Technology*, **15**, 23-32, 2006.

B. Invited lectures

1. V.N. Ngassam, A. Florescu, M. Fifirig, K. Laarej, O. Crumeyrolle, G. Varin-Bréant, O. Motapon, J. Tennyson, L. Pichl, A. Suzor-Weiner and I.F. Schneider, Reactive collisions between electrons and molecular ions in hydrogen, atmospheric and noble gases, XIIIth Symposium on Electron (Positron) – Molecule Collisions and Swarms“, Prague, 31 August – 1 July 2003.
2. I.F. Schneider, Reactive collisions between electrons and molecular ions: hydrogen, atmospheric and noble gases, 6th International Conference on Dissociative Recombination: Theory, Experiments and Applications, Mosbach, 12-16 July 2004.

C. Posters

1. O. Waffeu-Tamo et al, Dissociative recombination of CO⁺⁺ di-cation, 6th International Conference on Dissociative Recombination: Theory, Experiments and Applications, Mosbach, 12-16 July 2004, and 8th International Conference on Atomic and Molecular Physics, Rennes, 6-10 July 2004.
2. O. Waffeu-Tamo *et al.*, Energy Levels and Lifetimes of CO⁺⁺ di-cation, 6th International Conference on Dissociative Recombination: Theory, Experiments and Applications, Mosbach, 12-16 July 2004.
3. O. Waffeu-Tamo *et al.*, Reactive Collisions between NO⁺ Ions and Slow Electrons, 6th International Conference on Dissociative Recombination: Theory, Experiments and Applications, Mosbach, 12-16 July 2004, and 8th International Conference on Atomic and Molecular Physics, Rennes, 6-10 July 2004.
4. O. Motapon *et al.*, Dissociative excitation of di-atomic cations, 6th International Conference on Dissociative Recombination: Theory, Experiments and Applications, Mosbach, 12-16 July 2004, and 8th International Conference on Atomic and Molecular Physics, Rennes, 6-10 July 2004.

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