Hydrocarbon Characteristics in Fusion Edge Plasmas from Electron- Molecule and Ion- Surface Collision Experiments

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Abstract. The compatibility of reactor grade plasmas with plasma facing materials at the first wall is one of the present challenges in fusion research. In order to understand and elucidate the role of radiative and collisional processes in the edge plasma region, it is essential to have available detailed and quantitative knowledge on the corresponding elementary reactions proceeding in the volume before and at the wall. Surface processes involving hydrocarbons and their ions, which are probable vacuum contaminants in plasma devices, and the role of hydrocarbon chemistry and transport in divertor plasmas are some of the key components in modelling predictions for ITER based on atomic and molecular data. Improved data sets for hydrocarbons and detailed and accurate knowledge of the cross sections of the relevant plasma chemical volume and wall processes are needed. In this context we have carried out: electron (proton and helium) impact excitation/ionization reactions with possible plasma edge atoms, molecules and ions; determination of relevant differential, partial and total cross-sections and reaction rate coefficients for electron-molecule and ion-surface collisions; investigation of the temperature dependence of ionization energies and ionization cross sections and electron attachment cross sections; and calculations of inelastic interactions between electrons and atoms, molecules and molecular ions. The reported work supports the provision of essential data commonly needed for diagnostics and modelling across the fusion programme.

1. Introduction

Our investigations are primarily devoted to the understanding of reactive interactions between molecular ions / electrons with plasma facing surfaces, for parameters consistent with ITER plasma and first wall characteristics. The experimentally obtained atomic and molecular data contribute to the availability of detailed and quantitative knowledge on elementary plasma-wall reactions in particular for ITER edge modelling predictions. In this contribution we focus mainly on surface reactions involving different isotopes of small hydrocarbons (CHx) and their ions [1-3].

It is known about molecule and ion to surface collision processes that electron charge transfer in general dominates the reactions. The survival probability of ions ranges from 10-12%

percent down to less than 0.05% (see results in ref.[13], Fig. 5). In analogy to collision-induced dissociation in the gas phase, the internal energy deposition scales with the collision energy, but the distribution of internal energies is relatively narrow (~ 4eV FWHM). The efficiency of translational to vibrational energy transfer depends on the nature of the projectile and the surface, and amounts for example to around 30% for clean crystal surfaces and around 6% for hydrocarbon covered surfaces. The degree of inelasticity can vary with the projectile energy, normally in the range of 30-50%. The resulting velocity distributions can indicate if dissociation takes place at the surface or after scattering. In the context of fusion plasma-wall interactions we are thus interested to examine how this phenomenology changes for ITER-relevant surfaces made of beryllium (Be, on first wall), carbon fibre composites (CFC, on strike points) and tungsten (W, on rest of divertor surface). Also material transfer processes like sputtering can be observed qualitatively and how yields of ionized sputter products change with surface coverage by impurities.

2. Experimental facilities

The major experimental facility for ion-surface reactions in use at University of Innsbruck is the BESTOF apparatus (**B**-sector, **E**-field, **S**urface and **T**ime **O**f **F**light) described in detail in Refs. [4,5]. Projectile ions are produced in a Nier-type electron impact ion source operated at pressures of about 10^{-5} Torr. The ions produced are extracted from the ion source region and accelerated to 3 keV for mass and energy analysis by a double-focusing two-sector-field mass spectrometer. After passing the mass spectrometer exit slit, the ions are refocused by an Einzel lens and decelerated to the required incident energy before interacting with the target surface. Shielding the target area with conical shield plates minimized field penetration effects. The incident impact angle of the projectile ions was kept at 45° and the scattering angle (defined as a deflection from the incident beam direction) was fixed at 91°. The incident energy of ions impacting on the surface is defined by the potential difference between the ion source and the surface. The energy spread of the primary ion beam can be determined by measuring the (reflected) total ion signal as a function of surface potential. The energy resolutions (FWHM) of the of primary beam usually is determined around 1 eV, while the ion currents are around 100 - 500 nA, respectively, focused on a spot of roughly 2mm². A fraction of the product ions formed at the surface exit the shielded chamber through a 1mm diameter orifice. The ions are then subjected to a pulsed deflection-and-acceleration field that initiated the time-of-flight analysis of the ions. The second mass analyzer is a linear time-of-flight mass spectrometer with a flight tube of about 80cm length. The mass selected ions are detected by a double-stage multi-channel plate, connected to a multi-channel scaler (time resolution of 8 ns per channel) and a computer. The product ion intensities are obtained by integration of the recorded signals. The relative abundance of the product ions as a function of the incident projectile ion energy (collision-energy resolved mass spectra, CERMS curves) give insight into the characteristical interaction properties of an ion-surface combination, i.e., surface-induced dissociation (SID), charge exchange reactions (CER) and surface-induced reactions (SIR).

Material analysis is further carried out ex-situ at collaborating laboratories, for example by means of Rutherford back scattering (RBS) for the nondestructive, quantitative analysis of elementary surface composition and nuclear reactions analysis (NRA) for the determination of deuterium content in the SAK apparatus at IPP Garching. The content of deuterium in surface materials measured in SAK allows the calculation of the sticking coefficients when compared to the projectile beam intensity of BESTOF.
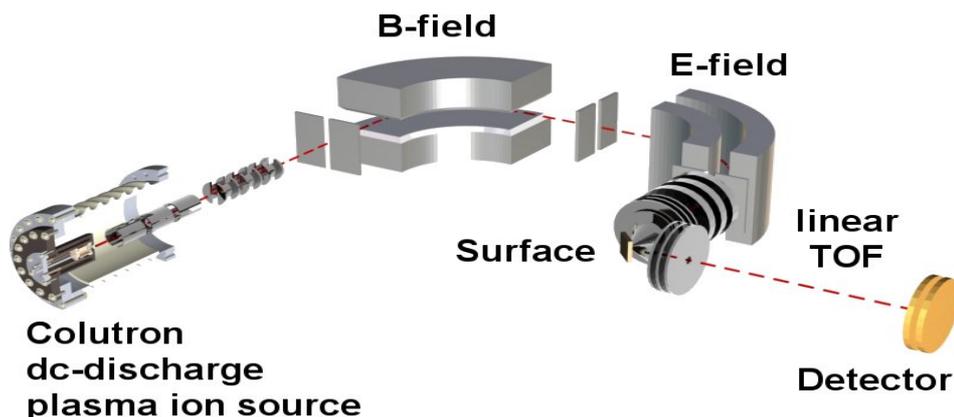
Fig. 1: BESTOF mass spectrometer for ion/molecule-surface interaction experiments.

The apparatus used in the total ionization cross-section is a double focusing two-sector-field mass spectrometer of reversed geometry with a Nier-type electron-impact ion source and has been described in detail in earlier publications [6-8]. A stagnant target gas is crossed by a well-characterized magnetically collimated electron beam with a FWHM energy spread of ~0.5 eV. Product ions are extracted from the ion source by a strong homogeneous electric field (3 kV/m) generated with a repeller (located in the back of the ion source) and lenses that are part of the front side of the interaction region of the electron beam and the neutral molecules. They are then accelerated to 3 kV before entering the analyzing part of the mass spectrometer through a narrow entrance slit. The ions then pass two pairs of perpendicular de-flection plates that allow the ion beam to be steered in the y- and z-direction. These deflection plates are used in cross section measurements to sweep the extracted ion beam across the en-trance slit [8] and to integrate the detected ion signal. After passing through a magnetic sector field followed by an electric sector field, the ions are detected by a secondary electron multi-plier operated in the pulse counting mode. The double focusing mass spectrometer corrects for the angular and spatial spreads of the starting points of the ions and for small variations in the kinetic energy within the deflection plane of the magnetic sector. The only way to compensate a velocity component perpendicular to the plane of the instrument (z-direction) is to apply a z-deflection voltage on a pair of plates right after the ion source. The ion yield, measured as a function of the z-deflection voltage, allows the determination of the kinetic energy distribution for a given fragment ion [6, 9-11].

3. Ion-surface collisions of small hydrocarbon molecules

Surface-induced dissociation (SID) properties of deuterated hydrocarbons impacting at incident energies in the range of about 0 to 100 eV on fusion relevant surfaces at room-temperature are investigated. Sample surfaces of graphite, plasma-sprayed tungsten, tungsten films (43nm on stainless steel) and beryllium films (2.5μm on stainless steel) are exposed to a beam of mass-selected singly charged hydrocarbon ions, e.g. CD_x^+ (x=2, 3, 4, 5), generated in a Nier-type electron impact ionization source.

Secondary ion mass spectra are recorded and secondary positively charged reaction products, formed upon the ion surface collisions with collision energies of up to 100eV, are monitored using the BESTOF linear time of flight mass spectrometer. Distinct changes in the survival probability of given projectile ions for different surfaces are observed by comparison of the spectra. At collision energies below about 5eV only inelastically scattered and reflected

projectile ions are observed. For higher collision energies, energy dependent fragmentation of primary ions, surface-induced reactions and sputtering of surface adsorbates are observed. One characteristic of measurements on Be is the much lower yield of positive ions, resulting in spectra with much higher background. We ascribe this to a much lower ion survival probability in the Be case.

In experiments carried out at the J.Heyrovsky Institute of Physical Chemistry on the scattering ion-surface beam apparatus EVA II, CD_3^+, CD_4^+ and CD_5^+ colliding with room-temperature highly oriented pyrolytic graphite (HOPG) at incident energies 3-10eV were investigated by analysing secondary ion mass spectra, angular and translational energy distributions of product ions [12]. In collisions of CD_4^+, product ions CD_4^+, CD_3^+, CD_2H^+, and CD_4H^+ were observed, indicating that the carbon surface was covered with hydrocarbons. At 10eV the survival probabilities of CD_5^+, CD_4^+, and CD_3^+ were found to be about 12%, 0.3% and 0.1%, respectively, decreasing to zero with decreasing incident energy.

Translational energy distributions in measurements with CD_5^+, measured at the same scattering angle, show that velocity distributions of inelastically scattered projectile ions and the fragment ions are the same: the assumption of unimolecular fragmentation after interaction with the surface is a good approximation even at low collision energies.

Further, collisions of slow ions C3Hn+ and C3Dn+ (n=2-8) with room temperature carbon surfaces were investigated with respect to mass spectra of product ions and the ion survival probability [13]. Collisions of slow hydrocarbon ions (3-10 eV) CD4*+, CD5+, C2D4*+, and C2H5+ with room temperature and heated tungsten surfaces have also been investigated [14].

4. Measurements and calculations of electron impact cross-sections of carbon compounds

We have performed systematic studies on electron-impact ionization of several compounds and hydrocarbons, including the determination of total, partial and differential cross sections, from threshold up to an energy of 1000 eV [9-11,15]. Our experiments contribute to the understanding of the dissociative ionization process by measuring the amount of kinetic energy release (KER) with which the ionized fragments are formed. In the case of several fragments it is found that substantial energy is released by the ionization process. Apart from the total ionization cross section measurements, we have initiated and successfully carried out first studies on the temperature dependence of the ionization energy cross sections, using monochromatized electrons from a trochoidal electron monochromator (TEM). The Deutsch-Märk (DM) formalism for molecules has been extended to the calculation of electron-induced ionization cross-sections [16,17], including simple hydrocarbon ions and carbon compounds, and to the ionization of negatively charged molecules [18]. In addition, calculations on SiCl(n) and other relevant molecules and on the temperature dependence of cross sections have been started.

5. Reflection properties of hydrocarbon radicals on W and CFC

The sticking coefficients of deuterium due to the collision of CD_2^+ and CD_3^+ ions on plasma-sprayed tungsten (PSW) and carbon fibre composite (CFC) surfaces, that were cut from ASDEX Upgrade tiles, have been determined for ITER-relevant divertor particle energy ranges [19].

The incident energies employed ranged from about 0 up to 100eV with a narrow energy distribution of ~100meV FWHM. The BESTOF apparatus produces a very stable beam with a

D flux of $\sim 10^{11}$ cm^{-2}s^{-1} and long time exposure. The targets had before undergone a pre-irradiation background analysis by NRA at SAK.

Results show an energy-dependent sticking coefficient S exhibiting its maximum at around 10 eV in case of CD$_3^+$ on PSW ($S \sim 0.05$-0.1) and around 30 eV for CD$_2^+$ on CFC ($S \sim 0.1$-0.4). Beyond this energy, the decrease in the sticking coefficient appears to be correlated to an increase in sputtering yields. It is found that the CFC surface retains deuterated compounds much more efficiently than plasma-sprayed tungsten [19].

6. Modeling of the formation of BeW compounds

We performed studies on the suitability of quantum chemical codes for the extension of our energy and property database towards the inclusion of Be-W clusters of various sizes and geometries. For the calculations of Be-W clusters we found that the LANL2DZ basis set for W, together with the D95V basis set for Be provide a possible and balanced description of the system. This also means that we can use the same basis set that was used previously for W-O, W-C and W-H systems. For Be-only and Be-H compounds we performed test calculations with a much larger basis set. With such basis sets and other theoretical methods like coupled clusters we can get an idea of the importance of the multitude of the electronic states. This is important even if in the final potentials and simulations we will have to restrict ourselves to a single Born-Oppenheimer surface.

Appendix I: Acknowledgements

Appendix II: References

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