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## Interaction dynamics in collisions of ions with molecules and clusters

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# Chapter 6

## Summary and Outlook

### 6.1 Summary

This thesis features a pioneering experimental study of keV ion interactions with *polycyclic aromatic hydrocarbon molecules* (PAHs) [20]. To investigate the sub-keV range of ion kinetic energies a molecular dynamics code was developed and employed. In addition to these studies we constructed and commissioned a new setup that allows to perform detailed kinematic studies of ions interacting with molecules and clusters. This setup entailed the development of a supersonic jet molecular beam source serving as a cold and localized target, to be crossed with a projectile beam, and a *recoil ion momentum spectrometer* (RIMS). Such a crossed-beam detector combination allows to determine a wealth of kinematic parameters involved in the ion-PAH reaction. The workings of such a machine and proof-of-principle results are presented in chapter 5.

The experimental study of ion interactions with PAHs is presented in chapter 3. Time-of-flight mass spectra for keV proton and  $\text{He}^{2+}$  collisions with the polycyclic aromatic hydrocarbon anthracene ( $\text{C}_{14}\text{H}_{10}$ ) are reported. Substantial fragmentation as well as formation of multiply charged fragments is observed. For  $\text{He}^{2+}$  projectiles, more and smaller fragments are formed as compared to proton impact. Increasing projectile velocity leads to an increase in fragmentation and a shift to smaller fragment masses for both projectiles. For  $\text{He}^{2+}$  projectiles in contrast to protons, the degree of hydrogenation of the cationic anthracene fragments suggests that sufficient energy is deposited to suppress the influence of the molecular structure on the fragmentation pattern. An electronic stopping model based on realistic anthracene electron densities is employed to estimate the molecular excitation due to electronic stopping. It is concluded that 30 keV  $\text{He}^{2+}$  and 10 keV  $\text{H}^+$  induce equal electronic stopping. The major difference in fragmentation between both projectiles is attributed to double electron capture by the  $\text{He}^{2+}$  projectiles, which is a weak channel for protons.

Chapter 4 elaborates on the development of a molecular dynamics code and its application to interactions of H and He projectiles in the sub-keV kinetic energy range interacting with PAHs and in particular the anthracene molecule. The results are compared to the work of Micelotta et al. [11] where the authors approach the problem using an analytical binary collision approximation between the projectiles and a carbon atom.

In the molecular dynamics simulation intra molecular interactions are modeled using a Tersoff-Brenner *reactive bond order potential*. Projectile interactions with the molecular constituents are modeled through the 'universal' ZBL *screened-Coulomb* potential.

When targeting specific atomic sites within the molecule it becomes apparent that direct fragmentation as a result of projectile impact is greatly overestimated in the binary collision approximation theory of ref. [11]. Direct fragmentation requires projectiles of kinetic energies much higher than 10 eV He, or equivalently a kinetic energy transfer of 7.5 eV to the molecule. Rather, He projectiles with a kinetic energy of some 43 eV (H projectiles of 99 eV) are required for complete single knock-out of a carbon atom, or equivalently an energy transfer to the molecule of some 27 eV.

Next to determining the energetics for direct fragmentation, we determined the range of energy transfers of He projectiles of various kinetic energies to the anthracene molecule. This allows one to determine a probability for dissociation of the molecule in competition with relaxation through Infra-Red (IR) photon emission. The dissociation of the molecule is assumed to be described by an Arrhenius process with a characteristic energy  $E_0=4.6$  eV. The temperature of the system is taken as the geometric mean of an effective temperature upon excitation of the molecule and the effective temperature after a given number of IR photon emissions. The probability for dissociation of the molecule is a function of an 'average' energy transfer of the projectile to the molecule. The average energy transfers in our work are taken to be the average of the energy transfer spectrum using the minimum value of 4.6 eV. This procedure yields similar excitation energies as in the work of ref. [11], which only deviate for low kinetic energies.

The total interaction cross sections determined in our work are larger than those in ref. [11]. This is to be expected though, because we determine total cross sections including all events above a lower limit for energy transfer of the projectile to the molecule of 4.6 eV, whereas in the work of ref. [11] a lower limit of 7.5 eV for energy transfer is assumed. A second cause is that in anthracene there is an outer circumference of hydrogen atoms enlarging the geometric cross section compared to a carbon skeleton of just 14 carbon atoms. A third point is that in our simulations the molecular nature of the target is taken into account as well, whereas in ref. [11], by definition, this is not the case.

In conclusion, energy transfers of the projectile to the molecule are similar in the models, however, dissociation probabilities are sensitive to variations in the energy transfer parameter through an exponential dependence in the Arrhenius equation. The collision rates in interstellar environments are expected to be larger due to enhanced cross sections determined in the computer simulations.

The second focus of this thesis is the construction and commissioning of a new setup, which combines a supersonic jet molecular beam source and a recoil ion momentum spectrometer. Such a machine allows us to perform kinematically complete measurements of the interactions of highly charged ions with clusters and molecules. The basics of supersonic beam production and how such a device can be used as a tool for cluster production are briefly introduced. A short overview of the thermodynamics and fluid dynamics of jet sources is also included. The degree of clustering in the jet may be estimated from the stagnation conditions in the source such as temperature, pressure and nozzle diameter using scaling laws reported in the literature. The newly constructed molecular beam source is characterized for different

stagnation conditions by crossing it with beams of highly charged ions and by subsequently measuring the charged interaction products by means of a high resolution reflectron time-of-flight mass spectrometer. In these measurements we detected charged argon clusters (fragments) in the time of flight spectra when this was expected from the scaling laws for certain pressure and temperature stagnation conditions. Clusters were absent in the spectra when the stagnation conditions were such that only monomers were expected from the scaling laws. This confirms the desired proper behavior of the molecular beam source.

In these first characterization measurements we determined kinetic energy releases occurring in interactions of highly charged ions and argon clusters.

After a characterization of the supersonic molecular beam source we combined it with our newly constructed recoil ion momentum spectrometer. We discussed the basic principles of such a spectrometer and how multi-hit coincidence measurements of position of impact and time of flight of charged fragments can be used to calculate the vectorial momenta of those fragments. First test measurements with the new setup of interactions of argon clusters with highly charged ions were successful in recovering time of flight spectra of argon and its clusters. Also successful position detection of charged interaction products was reported. These measurements allowed us to determine the speed of the supersonic jets under various initial conditions. The results agree well with estimates from theory models. From CO fragmentation measurements also the multi-hit detection capability of the setup is demonstrated.

We conclude that the newly constructed setup for kinematically complete measurements of interactions of highly charged ions with clusters and molecules operates according to design specifications.

## 6.2 Outlook

In an outlook we envision a systematic kinematics study of argon clusters with highly charged ions. Among other things this might reveal the more intricate details of argon dimers and larger clusters and their possible survival after charge transfer. Also the addition of a small vapor oven to the setup allows for the possibility of investigating molecular targets, which can be evaporated. The supersonic jet of carrier gas is passed through a vapor of molecules of interest, or the vapor is co-expanded with the carrier gas, before reaching the interaction point where it is crossed with a beam of highly charged ions or a different projectile. The supersonic jet *picks up* the molecules in the vapor carrying them to the interaction point where they may interact with a beam of highly charged ions. A first candidate for such experiments will be polycyclic aromatic hydrocarbon molecules to further elucidate the details of their interactions with highly charged ions, which may provide a greater insight into their behavior in interstellar space. Larger molecules, which cannot be intactly evaporated, may be electro-sprayed and collected in a ring-electrode trap from which dense bunches may be released for crossed beam experiments. Such an interface allows for detailed research into the interaction of large ( $>50$  C atoms), astro-physically important PAH molecules with (highly charged) ions and other projectiles.

