Studying the formation of product isomers in ion-molecule reactions with Velocity Map Imaging

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Over the last decades, velocity map imaging (VMI) has become a very powerful tool to study structural and dynamical properties in molecular systems and chemical reactions [1]. In the field of reaction dynamics, VMI has opened a new window towards probing experimentally the predictions of chemical dynamics simulations. In our group we use a combination of a crossed beam setup with a 3D-VMI spectrometer [2] to study the energy- and angle differential cross section of several types of ion-molecule reactions [3,4]. Our current interest relies on reactions that can form different isomers.
We will present recent results on two astrophysically relevant proton transfer reactions, namely CO + H_3^+ and CO + $HOCO^+$, both producing the HCO^+/HOC^+ isomers. The formyl and isoformyl cations are among the most important species in the interstellar medium (ISM) and their branching ratio and formation mechanisms have been widely investigated [5,6,7]. Our results show a very high degree of internal excitation at all collision energies ranging from 0.3–4.5 eV. Applying a fitting procedure on the obtained energy distributions an upper limit of 20% for the HOC+/HCO+ branching ratio is obtained at E_{col}=1.85 eV. This does not agree with two recent predicted trends for the branching ratio[5,8].
Furthermore, we will discuss new advances in our work on bimolecular nucleophilic substitution () reactions. The reaction between CN^- and CH_3I produces either acetonitrile ($NCCH_3$) or methyl-isocyanide ($CNCH_3$), the first channel being thermodynamically favored with a difference in exothermicity of 0.92 eV. In this contribution we present experimental velocity distributions of the S_N2-product I^- for a sequence of collision energies. The contribution of different mechanisms will be discussed and compared with electronic structure calculations performed in our group.
Finally, we present the status of the experiment for the investigation on extended carbon chains, where the S_N2 reaction mechanism will compete with an elimination process (E2). We plan to study the ratio of both mechanisms as a function of collision energy.

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