Kinematically complete chemical reaction dynamics

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Abstract. Kinematically complete studies of molecular reactions offer an unprecedented level of insight into the dynamics and the different mechanisms by which chemical reactions occur. We have developed a scheme to study ion-molecule reactions by velocity map imaging at very low collision energies. Results for the elementary nucleophilic substitution (SN2) reaction Cl− + CH3I → ClCH3 + I− are presented and compared to high-level direct dynamics trajectory calculations. Furthermore, an improved design of the crossed-beam imaging spectrometer with full three-dimensional measurement capabilities is discussed and characterization measurements using photoionization of NH3 and photodissociation of CH3I are presented.

1. Introduction
Collisions of atoms and molecules with well-defined momentum vectors and angle- and energy-resolved detection have been used for many years to obtain a wealth of information on the reaction dynamics of neutral molecules [1, 2, 3, 4]. To study ion-molecule reactions at low energy with high resolution, we have developed a crossed-beam imaging spectrometer that allows us to measure these reactions in a kinematically complete way [5]. It is based on the technique of velocity map imaging [6], which projects ions with the same transverse velocity vector onto the same spot on the detector surface.

For comparison with neutral-neutral scattering it is instructive to calculate the scattering rate for ion-molecule reactions in crossed beams. The probability that an ion traversing a molecular beam undergoes scattering is given by

\[ p_{\text{scatt}} = \frac{knd}{v_{\text{rel}}}, \]

where \( d \) is the path length of the ion through the molecular beam and \( v_{\text{rel}} \) is the relative velocity between the ion and the neutral. The ion-molecule reaction rate coefficients \( k \) is about few times \( 10^{-10} \) cm\(^3\)/s and the target density \( n \) is typically \( 10^{12} \) cm\(^{-3}\). For \( d = 1 \) mm and \( v_{\text{rel}} = 3000 \) m/s one obtains a scattering probability of \( 3 \times 10^{-5} \). For a typical value of \( 10^4 \) ions per ion pulse one obtains a 30% probability for a reactive event per pulsed beam intersection.

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For a typical repetition rate of 10 Hz this leads to an event rate of a few events per second. For small relative velocities the rate may increase beyond 10 per second and for low reaction rate coefficients it may be as small as 0.1 per second. With this small event rate it is advantageous that a velocity map imaging spectrometer has an effective solid angle of almost $4\pi$ and that position sensitive detectors can measure ion impact positions with above 50% detection efficiency. Furthermore, the intrinsic noise of an imaging spectrometer can be smaller than 0.1 noise events per second, which provides a significantly large dynamic range in the reaction rate for a variety of experiments.

Using our ion-molecule crossed beam imaging spectrometer we have studied the cation-neutral reaction of $\text{Ar}^+ + \text{N}_2$ and found interesting dynamics [5, 7]. More recently we have studied the anion-molecule reaction $\text{Cl}^- + \text{CH}_3\text{I}$ [8]. Details of this experiment will be presented in the next section. Recently, we have improved the electric field design of our crossed-beam spectrometer and we have integrated a time-of-flight measurement and thereby set up a full three-dimensional velocity vector measurement. These improvements have been characterized with photoionization imaging of $\text{NH}_3$ and with photodissociation imaging of $\text{CH}_3\text{I}$. This is presented in section 3.

2. Crossed beam imaging of a nucleophilic substitution reaction

A model system for a polyatomic chemical reaction that shows already many of the emerging properties of complex reactions is the nucleophilic substitution ($\text{S}_2\text{N}_2$) reaction

$$X^- + \text{CH}_3\text{Y} \rightarrow X\text{CH}_3 + Y^-.$$  \hspace{1cm} (2)

Here $X^-$ is the approaching nucleophile that forms a bond with the central carbon atom. As a consequence a leaving group $Y^-$ is removed from the molecule. In the simplest realizations $X^-$ and $Y^-$ are halogen anions, but they could also represent polyatomic molecular anions. $\text{S}_2\text{N}_2$-reactions are important in chemical synthesis because they allow the replacement of one molecular group with another one. This can be used to synthesize large organic molecules. Also living cells make use of $\text{S}_2\text{N}_2$-reactions.

According to the sum formula of Eq. (2) the hydrogen atoms are not affected during this reaction. It turns out, however, that the reaction inverts the “umbrella” of the three hydrogen atoms in order to establish a near-tetraedric structure of the product molecule. Thus, the coupling of the hydrogen degrees of freedom to the halogen motion is important for the reaction dynamics.
Figure 2. Measured initial velocity distributions of the Cl\(^{-}\) and CH\(_3\)I reactant beams in the laboratory frame of reference. The solid arrows denote the average beam velocities in the laboratory frame. From them the center of mass velocity (white solid arrow) and the reactant velocities in the center of mass frame are calculated (dashed arrows). In this Newton diagram the velocity vector of the I\(^{-}\) reaction product lies by conservation of energy and momentum within the dotted circle.

We have selected the elementary S\(_N\)2-reaction with X\(^{-}\) being a chlorine anion that reacts with methyl iodide CH\(_3\)I for the experimental investigation with our crossed-beam spectrometer [8]. The potential energy curve for this reaction along the reaction coordinate is depicted in Fig. 1. Characteristic of this and other anion-molecule reactions are the two relatively deep potential minima separated by an intermediate barrier. In the reaction studied here this barrier lies submerged below the energy of the reactants. Nevertheless it strongly influences the reactivity in that the reaction occurs at only 10% of the Langevin or capture rate.

Details of the experimental setup have been described already previously [5]. In this experiment a pulsed beam of Cl\(^{-}\) is formed by co-expanding CCl\(_4\) gas and argon in a supersonic beam that is passed into vacuum by a piezo-electric valve [9]. Electron impact ionizes the gas and efficiently allows slow secondary electrons to dissociatively attach to CCl\(_4\) and produce Cl\(^{-}\) and CCl\(_3\) radicals. This delivers packets of about 10\(^4\) ions with a tunable kinetic energy in the range from 0.5 eV up to several electronvolts. The typical energy spread amounts to 0.2 eV (FWHM). The slow Cl\(^{-}\) ions are brought to collision with a supersonic beam of the CH\(_3\)I target, which is prepared in a pulsed supersonic beam of CH\(_3\)I in helium, using a second piezo-actuated pulsed valve.

The CH\(_3\)I velocity distribution is directly measured by ionizing the molecules in collisions with 1 keV electrons and then imaging the CH\(_3\)I\(^+\) ions onto the position sensitive detector. The impact position of an ion on the imaging detector is linearly transformed into the ion’s transverse velocity [5]. The momentum transfer during ionization is only a small correction to the initial beam velocity and is neglected. The resulting distribution is shown on the left side of Fig. 2. The velocity origin is calibrated by imaging an isotropic thermal cloud of argon or xenon and measuring its center of gravity.

The Cl\(^{-}\) velocities are measured in a similar way but operating the imaging spectrometer with opposite polarity. The imaging electrodes are pulsed on when the ions are in the interaction volume. The neutral target beam is deactivated. The resulting distribution is depicted on the right side of Fig. 2. The figure also shows the full Newton diagram of the reaction kinematics, the reactant velocities in the center of mass frame (dashed arrows) and the range of product I\(^{-}\).
velocities that are in accord with energy and momentum conservation (dashed arrow and circle).

To observe reactive scattering both the ion and the neutral reactant beam are synchronously activated with a repetition rate of 10 Hz. A few microseconds after both beams have started to cross each other the high voltages of the velocity map imaging electrodes are pulsed on within a few tens of nanoseconds. Then the I\(^-\) product ions and the non-reacting Cl\(^-\) ions are projected onto the imaging detector. To avoid saturating the detector with the chlorine reactants the detector gain is electronically gated to the arrival time of the iodine mass. In fact, the time-window of the detector gain is reduced even further to accept only events where the reactive scattering occurs in the plane parallel to the detector, which is referred to as slice imaging [10, 11]. In this way the recorded images directly reflect the differential scattering cross section.

Two types of transformations need to be applied to the data. First, the transformation to the center of mass frame is calculated for each scattering event, which involves a translation and a rotation of the image parallel to the relative velocity vector. Second, the loss of fast moving reaction products needs to be corrected. Product ions with high laboratory velocities have a chance to leave the spectrometer volume that can be imaged onto the position-sensitive detector. To correct for this, an empirical function is used to provide events with large laboratory velocities with a larger weight than events with small velocities. This correction function is independent of the scattering angle. Furthermore, the same correction function is used for all collision energies.

The differential cross section images for two relative energies, 0.39 eV and 1.9 eV, are shown in Fig. 3 [8]. At the low energy an isotropic distribution of product velocities is observed. This is indicating a long-lived intermediate complex that decays on the time scale of several rotational periods and thus looses the information of the direction of the incoming particles. The measured velocity magnitudes are much smaller than the maximum velocity possible at this energy. This maximum is indicated by the largest circle superimposed onto the distribution. At 0.39 eV therefore a large fraction, about 84\%, of the available energy is partitioned into internal degrees of freedom of the CICH\(_3\) product molecule. This amount of internal energy can be explained by a statistical branching of the available energy over all product states [8]. This is another indication that at this collision energy the specific properties of the initial state have no influence on the dynamics. A very different behavior is observed at 1.9 eV relative energy. Here the I\(^-\) ions scatter preferentially backward with respect to the direction of the incoming CH\(_3\)I. Also their velocity is found very near the maximum possible velocity. This can be explained by a fast and direct reaction mechanism where the I\(^-\) leaves the reaction approximately co-linearly with the incoming Cl\(^-\) anion.
Figure 4. Snapshots of two selected trajectories for the reaction Cl$^-$ + CH$_3$I, obtained with direct dynamics calculations. a) The direct nucleophilic substitution mechanism, which is found in about 90% of the trajectories. b) The indirect roundabout mechanism, where the CH$_3$I molecule undergoes a single rotation before the substitution occurs.

In order to understand the details of the measured differential cross sections comparison with theoretical calculation is essential. However, the theoretical description of polyatomic reactions that involve more than four atoms is very difficult. The present reaction involves six atoms and therefore twelve internal degrees of freedom. Such a large system can not be calculated quantum mechanically and one has to resort to significant approximations. These are either quantum scattering calculations in reduced dimensions (typically four) [12] or calculations that treat the electronic structure quantum mechanically but propagate the nuclei classically on the Born-Oppenheimer surface [13, 14].

The latter approach was used to calculate the reaction dynamics of the Cl$^-$ + CH$_3$I reaction at 1.9 eV relative collision energy. The calculations were carried out using the approach of “direct dynamics” [15], where at each point along the 12-dimensional trajectory the electronic eigenenergy and its gradient are calculated within the Born-Oppenheimer potential. This information is then used to propagate the trajectory further. This approach is numerically very demanding, but it circumvents the requirement of a global Born-Oppenheimer hypersurface. In the present study the electronic structure was calculated at the MP2(fc)/ECP/aug-cc-pVDZ [8] level of theory.

The calculated trajectories show that at 1.9 eV collision energy a direct reaction mechanism governs the nucleophilic substitution reaction. This mechanism is depicted in the upper sequence of Fig. 4. The Cl$^-$ ion moves into the umbrella of the hydrogen atoms and forms a bond with the central carbon atom. Roughly co-linearly to this motion the I$^-$ product ion is moving away after the three hydrogen atoms have inverted to form the ClCH$_3$ product molecule. This numerical result corresponds directly to the back-scattering observed in the experiment.

The trajectory calculations also revealed another reaction mechanism that occurs with about 10% probability. In this mechanism, which is depicted in the lower panel of Fig. 4 the CH$_3$I reactant undergoes a single 360° revolution about an axis perpendicular to the C-I bond. Only after this revolution the substitution occurs. This mechanism, which we named the “roundabout mechanism”, is found to go along with a large energy partitioning into internal degrees of freedom of the neutral product molecule. Therefore the translational energy of the reaction products is smaller than for the direct mechanism. This nicely agrees with the observed structures in the measured differential cross sections at small I$^-$ velocity (see Fig. 3b), which we attribute to the roundabout mechanism [8].
3. Improved crossed beam ion imaging

3.1. Second generation imaging electrodes

In crossed-beam ion imaging a much larger interaction volume needs to be imaged onto the position sensitive detector as compared to applications in photodissociation and photoionization. To improve the resolution of the spectrometer under these conditions and to minimize the influence of stray fields from outside the spectrometer, we have constructed a second generation configuration of the electric fields.

The setup consists of six plates and the microchannel plate detector with phosphor screen and CCD camera. The classical velocity map imaging detector consists of planar plates. In contrast, we have changed the geometry of our electrodes in order to shield the interaction region from electric potentials, which are applied to ion optics elements close to the stack. We also added rims on the upper surface of the electrodes [16], which we found in simulations to lead to an improved imaging resolution. The shielding of the second electrode has 12 cylindrical holes for the beams with a diameter of 10 mm. In order to increase the interaction volume we use six instead of three field plates.

Fig. 5 shows a simulation of our new velocity map imaging stack carried out with SIMION [17]. It shows ion trajectories of two pairs of ions starting in the same plane parallel to the detector. By choosing the correct combination of potentials on the electrodes the ions with the same velocity vector are focused onto the same spot.

To characterize the performance of the new spectrometer we have measured the velocity spread and the rotational spectrum of ammonia seeded in a supersonic expansion of argon out of the pulsed piezo valve. We used the frequency doubled output of a Nd:YAG pumped tuneable pulsed dye laser in the range of 63760 to 63940 cm$^{-1}$ for (2+1) REMPI of Ammonia via the vibration-less C-state [18]. The produced ions are imaged on the detector.

The measured velocity distribution is shown in Fig. 6a. We find that the determined spread corresponds to an effective translational temperature of the NH$_3$ molecules of below 1 K, in the reference frame of the supersonic argon beam. The rotational spectrum is recorded scanning the
Figure 6. a) Measured velocity distribution for NH$_3$ molecules seeded in a supersonic beam of argon, obtained by 2+1 REMPI and subsequent velocity map imaging. The translational temperature corresponds to below 1 K b) Rotationally-resolved spectrum of NH$_3$ in the seeded supersonic beam. The observation of only one rotational transition starting from the J=1, K=1 state indicates a rotational temperature of at most 7 K.

dye laser wavelength and measuring the integrated ion yield. As shown in Fig. 6b, only a single Q-branch transition persists that starts from the ground state J=1, K=1 of the ortho hyperfine manifold (for the para ground state J=0, K=0 no Q-branch transition exists). According to simulations of the rotationally resolved spectrum this measurement implies an upper bound on the rotational temperature in the supersonic beam of about 7 K. This shows that the expansion cools very efficiently the translational and the rotational degrees of freedom. Furthermore, blurring of the obtained image introduced by electric field inhomogeneities has to be smaller than 3%.

3.2. Three-dimensional ion imaging

Two dimensional velocity map imaging brings along several shortcomings, as usually the reaction products fly away in all 3 directions. In order to retrieve information such as the kinetic energy distribution from the measured images a certain class of velocity components in one direction is selected and the other two components are displayed. Usually the fixed component is the one perpendicular to the detector and the produced slice is around its zero value.

There are two methods to obtain slices through the three-dimensional product velocity distributions using two-dimensional velocity map imaging. The first method uses an inverse Abel transformation on the image integrated over the third velocity component (perpendicular to the detector surface). Several numerical algorithms have been developed for this purpose [19]. The second method is the slicing technique [10, 11] that we also applied in the SN$_2$ reactive scattering experiment (see section 2).

Both methods describe the 3D product velocity distribution in 2D and rely on cylindrical symmetry in the process under study. In crossed-beam scattering experiments this is in principle often the case, as the scattering cross section for spherical reactants is cylindrically symmetric around the relative velocity vector. However, the symmetry is quickly lost due to unsymmetric broadenings induced by the distribution of reactant velocities. The Abel inversion can then no longer be used and instead forward reconstruction algorithms [5] or direct slicing is needed. Furthermore, if spatially aligned molecules are brought to collision the symmetry is directly lost. Then the full 3D distribution has to be measured.

A solution to this problem is to measure the time-of-flight of each ion in addition to its impact position and deriving the full three-dimensional velocity distribution from these measurements. In order to do this we have integrated a high-resolution time-of-flight detector into our velocity map imaging spectrometer. A photo-multiplier (Hamamatsu R7402-20, transition time spread 230 ps, risetime 780 ps) is used to detect the light pulses on the phosphor screen that are induced by ion impacts on the microchannel plate detector. After conversion to an electronic logic pulse
with a constant fraction discriminator (Ortec 583) this signal is used as a stop signal for a time-to-digital converter (TDC, ATMD GPX). The start trigger is provided by the pulse generator (Quantum Composers 9520, < 200 ps jitter) that triggers the entire experiment. In a test measurement with logic pulses replacing the photomultiplier signals, the overall time resolution of the electronics was measured to be 140 ps RMS. Attention has to be paid to the correct assignment of the TDC data to the camera data as the data transmission from the camera to the computer as well as the online image analysis are CPU time-consuming.

This setup now allows 3D imaging if the event rate is smaller than the read-out rate of the camera and TDC system, which has been increased to 20 Hz. Considering the typical reaction event rates (see section 1) this is no significant limitation for the experiments. For a first characterization of the time-of-flight setup we have imaged the well-known photodissociation of CH$_3$I into CH$_3$ + I at 266 nm [20, 21] using the fourth harmonic of a Nd:YAG laser polarized parallel to the detector surface. The pulse energy is attenuated in order to detect about one ion per camera frame. The I atom product is ionized by three additional photons from the same laser pulse.

Fig. 7 shows measured I$^+$ velocity distributions and derived kinetic energy distributions. The upper panel is obtained by setting in the offline analysis a 20 ns cut on the measured time-of-flight around the mean of the time-of-flight distribution and the lower one by an Abel transformation of the entire projected data set. One can see from the high-velocity ring segments that the dissociation probability is proportional to $\cos^2 \theta$, as expected for a parallel transition, where $\theta$ is the angle between the polarization axis of the laser and the C-I bond. The events near the center of the images are likely due to non-resonant multiphoton ionization and fragmentation of CH$_3$I. The energy distributions show that position and width of the peaks quantitatively agree with each other, well within the experimental accuracy.

4. Conclusion and outlook

The presented crossed-beam imaging spectrometer for low-energy ion-molecule reactions has developed into a robust and versatile tool. Further experiments on anion-molecule nucleophilic substitution reactions are under way. It will be interesting to investigate the role of direct and indirect reaction mechanisms in these and other systems. Also further studies of quantum mechanical effects in ion-molecule reactions will be carried out. Particularly important will be to understand the role of quantum scattering resonances in chemical reactions, where only very few have been identified up to now.

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**Figure 7.** Measured kinetic energy distributions for the I fragment after CH$_3$I photodissociation.  
a) Obtained by slicing the measured events based on the time-of-flight measurement  
b) Obtained by Abel-inversion of the projection of all events. The insets show the corresponding two-dimensional velocity distributions, sliced and Abel-inverted respectively.

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