Kinematically complete reaction dynamics of slow ions

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Abstract. An experiment for crossed beam imaging has been developed for kinematically complete studies of the reaction dynamics of ion-molecule collisions. Here we report on this technique and on recent results regarding the charge transfer reaction of $\text{Ar}^+ + \text{N}_2$. We speculate that the experimental observation of $\text{N}_2^+$ product ions with unexpectedly high vibrational excitation may be caused by a Feshbach scattering resonance and propose further theoretical work on this reaction. Furthermore we discuss how future collision experiments of molecular ions and clusters will utilize a radiofrequency 22pole trap for internal cooling of the ions prior to the interaction.

1. Introduction
To study the quantum dynamics of molecular collisions and reactions, kinematically complete experiments with crossed molecular beams are an invaluable tool [1]. Such experiments yield energy and angle-differential scattering cross sections and allow one to unravel quantum-state specific dynamics of complex few-body scattering problems. In this way a Feshbach resonance in the scattering of $\text{F} + \text{H}_2$ forming $\text{HF} + \text{H}$ has been investigated in great detail [2]. We extend such crossed-beam studies to slow ion-neutral collisions in order to unravel quantum scattering properties such as resonances and product branching ratios under the influence of the long-range ion-dipole interaction. This is particularly interesting for the class of nucleophilic substitution $\text{S}_{\text{N}}2$ reactions of negative ions, $\text{X}^- + \text{R} \text{Y} \rightarrow \text{RX} + \text{Y}^-$ [3].

2. Crossed beam imaging of ion-neutral reactions
To carry out crossed-beam experiments with slow charged particles and to measure reactive scattering cross sections of ion-molecule collisions in a kinematically complete fashion, we have combined a crossed-beam imaging system with a source of low-energy ions as described in detail in Ref. [4].

The source for slow ions (see Fig. 1) is based on a pulsed piezo-electric valve that forms a supersonic beam of typically 100 $\mu$s duration. A 10 $\mu$s long pulse of electrons, which is emitted from a nearby hot filament and accelerated to about 100 eV, creates a package of between a few hundred and few thousand ions from the supersonic beam. Due to the small momentum transfer during ionization the ions drift further downstream with the supersonic beam velocity. The housing of the ionization region floats on a ‘platform voltage’ of between 0.2 and 5 V relative
Figure 1. (Colour online) View of the crossed beam spectrometer with the low-energy ion source (lower left), the pulsed neutral beam source (lower right) and the velocity map slice imaging spectrometer (center).

to the interaction region so that the ions are accelerated to this voltage when they enter the central scattering region of the spectrometer. A second pulsed supersonic beam brings the neutral collision partner into the interaction region, as also depicted in Fig. 1.

Product ions emerging from a reactive collision when the ionic and neutral reactant bunches cross are detected with a velocity map imaging detector either in projection mode [5] or using slice imaging [6]. Impact positions on the detector are linearly transformed into velocity components parallel to the detector surface. The scaling factor is obtained from SIMION 7.0 calculations [7] and the velocity origin by imaging ions created in the isotropic background gas by electron impact. The interaction region of the crossed ion and neutral beams is located between the two lowest plates of the electrode stack in Fig. 1. The average background gas pressure of typically below $10^{-7}$ mbar ensures that background gas collisions are negligible. To avoid any electric fields to perturb the ion-molecule scattering it is crucial to have the collisions take place with grounded electrodes. With fast high-voltage switches all imaging electrodes are then synchronously pulsed to high voltage. The exact pulse timing is determined from the counter-acting requirements that the pulsed reactant beams have had considerable time to cross each other and that at the same time the product ions have not yet left the source volume of the spectrometer. The end-caps of the supersonic beam chambers are pulsed together with the imaging electrodes to minimize distortions of the imaging fields.

An important advantage of the neutral beam source is that the supersonic expansion introduces significant translational and rovibrational cooling. This is demonstrated in a measurement of the velocity distribution of a pulsed supersonic beam of argon, produced with a stagnation pressure of 2 bar. Using electron impact ionization with 1 keV electrons $\text{Ar}^+$ ions are created in the centre of the interaction region of the velocity map imaging spectrometer. These ions are then projected onto the position sensitive detector and their impact position is transformed into the ion velocity magnitude. The result, shown in Fig. 2, is a narrow velocity distribution that peaks near 570 m/s with an r.m.s. width of about 45 m/s. The theoretical
Figure 2. Distribution of the magnitude of the projected velocity vector for a pulsed supersonic beam of argon, as measured with the velocity map imaging spectrometer. Its root mean square (r.m.s.) width of about 45 m/s corresponds to a translational temperature in the co-moving frame of not more than about 10 K.

The terminal velocity of a supersonic beam of constituents with $f$ degrees of freedom is given by

$$\sqrt{(f + 2) \frac{k_B T}{m}},$$

which yields 560 m/s for argon ($f = 3$), in good agreement with the measurement. The r.m.s. width $\sigma_v$ of the velocity distribution represents a measure of the translational temperature in the co-moving frame of the beam, $\sigma_v = \sqrt{k_B T/m}$. Here a value of about 10 K is obtained for the measured velocity distribution, which shows efficient cooling of the argon atoms due to the expansion. Note that this value represents an upper limit, because the measured velocity distribution could include an additional broadening due to a finite imaging resolution.

Measurements of the velocity distribution of the ions emerging from the source are also carried out with the imaging spectrometer. In this way the relative collision energy is determined with a minimum of systematic uncertainty, because the same spectrometer is used for measuring the reactant velocities and the reaction product velocities. The energy resolution of the ion beam is obtained to be typically 200 meV FWHM for kinetic energies between 0.2 and 5 eV, which is expected to be limited by stray fields in the ion source.

3. Angle-differential scattering of a charge transfer reaction

Using crossed-beam ion imaging we have studied charge transfer, one of the most fundamental ion-molecule collision processes. The collision system

$$\text{Ar}^+(2^3P_{3/2}) + \text{N}_2(v = 0) \rightarrow \text{Ar} + \text{N}_2^+(v')$$

was chosen, because it represents a very well studied ion-molecule reaction [8] and therefore allows for detailed comparison of our results with previous data. One of the most notable effects in this reaction is the predominant formation of N$_2^+$ products in the $v' = 1$ level at collision energies of few to few tens of electron volts. This is in violation of the Franck-Condon principle,
which would suggest no change in the vibrational level upon the transfer of the electron from the nitrogen molecule to the argon cation. This even changes reaction (2) from an exothermic to an endothermic reaction. The occurrence of product ions in \( v' = 1 \) is explained by a Landau-Zener curve crossing due to non-adiabatic couplings between the different potential energy surfaces \[9\], as shown schematically in Fig. 3.

In our recent work \[4\] we measured the differential cross section using crossed beam ion imaging for different relative collision energies between 0.6 and 2.5 eV. At the latter collision energy we observe only little momentum transfer upon charge transfer and the data are in agreement with \( \text{N}_2^+ \) product state \( v' = 1 \). For lower collision energies, however, different velocity distributions, which are proportional to the differential scattering cross sections, are measured (see Fig. 4). They show that reaction (2) exhibits distinctly more complex dynamics below 1 eV collision energy. This transition in the reaction dynamics manifests itself in large angle scattering as seen in Fig. 4 for 0.6 and 0.8 eV relative energy. In the same data sets we observe higher vibrational excitation of the \( \text{N}_2^+ \) product, specifically \( v' = 2 \), as indicated by the iso-energetic rings in Fig. 4 corresponding to the different product vibrational levels.

By integrating the velocity distributions over the scattering angle we obtain translational energy distributions. Energy conservation during the reaction links the \( \text{N}_2^+ \) translational energy to its internal excitation so that the branching ratio for the different product vibrational levels as a function of the collision energy can be extracted for reaction (2); rotational excitation is
assumed to be small compared to vibrational excitation [10]. The result is shown in Fig. 5, which combines the data of this study with data points from Liao et al. [11] obtained using guided ion beam techniques together with chemical probing. The recent calculation of Ref. [9] predicts an almost constant fraction of 70% in $v' = 1$ and 20% in $v' = 2$ over the collision energy range of Fig. 5. This is in disagreement with the experimental data, which show that $v' = 1$ is dominant only at large relative energies and that the $v' = 2$ channel shows a distinct peak near $0.8 \text{ eV}$.

With a full quantum scattering calculation for reaction (2) still at large, we allow ourselves a speculation of the reason for the higher product vibrational excitation near $0.8 \text{ eV}$. In the Landau-Zener calculation of Ref. [9] only the ground electronic states for Ar and N$_2$ are taken into account. However, N$_2^+$ possesses a low-lying electronically excited A-state of $^2\Pi_u$ symmetry. This state lies $1.1 \text{ eV}$ above the $X^2\Sigma_g$ ground state and thus represents an energetically closed channel for collision energies below $0.9 \text{ eV}$. The N$_2^+$ ground state interacts strongly with Ar leading to a total binding energy of the (ArN$_2$)$^+$ complex of more than $1 \text{ eV}$ [12]. If the A-state of N$_2^+$ features a similarly strong interaction with argon then this closed channel can in fact couple to the open Ar$^+$ + N$_2$ scattering channel for collision energies below $1 \text{ eV}$. This Feshbach-type coupling can lead to scattering resonances when a bound state in the closed channel is tuned into resonance with the continuum scattering state, as shown qualitatively in Fig. 3. Our suggestion is that the higher vibrational excitation of the N$_2^+$ product at 0.6 and $0.8 \text{ eV}$ collision energy may be a manifestation of such a resonance. The observed large angle scattering would be in support of this as well. Clearly, a theoretical treatment that includes the A-state would be highly desirable. Further experiments on this system are planned in particular to shed more light on the width of this resonance feature and to investigate if further resonances occur at different scattering energies.

4. Perspectives for scattering of molecular ions and ionic clusters

The pulsed low-energy ion source has been successfully employed to produce Ar$^+$ ions. Also Cl$^-$ anions have been formed by dissociative electron attachment to CCl$_4$. Experiments with
Figure 5. (Colour online) Branching ratio for vibrational levels $v'$ of the $\text{N}_2^+$ charge transfer product ion as a function of the relative collision energy, derived in this work (circles) and obtained from Ref. [11]) (triangles).

molecular and cluster ions, however, require a different ion source, in particular if the internal rovibrational excitation of the composite ions is to be well defined.

To prepare complex ions at a well defined temperature we have set up a radiofrequency 22pole ion trap [13]. This trap has already been used to study photodetachment of rotationally thermalized OH$^-$ anions, which has also allowed us to measure the spatial density distribution of the trapped ions [14]. Recently, evaporation of translationally thermalized Cl$^-$ ions has been used to study the effective trap depth and quantify the dynamical conditions that are necessary and sufficient for stable trapping [15]. As a next step we will develop the pulsed extraction scheme needed to bring the trapped ions into the interaction region of the imaging setup.

The path of ions extracted from the trap intersects the neutral supersonic reactant beam inside the imaging spectrometer at an angle of 60° (see Fig. 1). Compared to the 120° of the currently employed ion source this will further reduce the lowest attainable relative collision energy at a given laboratory kinetic energy down to about 100 meV.

5. Outlook

In the future we will make use of the unprecedented new view on low-energy ion-molecule reactions that has opened up with our crossed-beam velocity map imaging experiment. We are currently studying reactions of negative ions, specifically the nucleophilic substitution reaction of Cl$^-$ with CH$_3$I. Using the ion trap as source for cold clusters we will study S$_\text{N}$2 reactions of molecular OH$^-$ anions and of ions embedded into water clusters to study the effect of microsolvation [16]. Furthermore work is in progress to prepare laser-aligned CH$_3$I using a high-intensity infrared laser pulse [17]. Such laser-aligned molecules offer the possibility to directly visualize stereodynamic effects in molecular reactions.
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