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Studies of cold chemistry in crossed and merged neutral beams

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L'infinito

Sempre caro mi fu quest'ermo colle, e questa siepe, che da tanta parte dell'ultimo orizzonte il guardo esclude. Ma sedendo e mirando, interminati spazi di là da quella, e sovrumani silenzi, e profondissima quïete io nel pensier mi fingo, ove per poco il cor non si spaura. E come il vento odo stormir tra queste piante, io quello infinito silenzio a questa voce vo comparando: e mi sovvien l'eterno, e le morte stagioni, e la presente e viva, e il suon di lei. Così tra questa immensità s'annega il pensier mio: e il naufragar m'è dolce in questo mare. - Giacomo Leopardi

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Abstract

In this thesis we present the design of two setups to study low-energy collisions between neutral species: an electron velocity map imaging for chemi-ionisation reactions and a merged electrostatic guide for polar molecules scattering.

In the past few years, chemi-ionisation of atoms and molecules by metastable He and Ne led to the measurement of the branching ratios between two possible reactive channels, namely Penning ionisation (PI) and Associative ionisation (AI). For molecular species, the reaction outcome is influenced by the redistribution of energy from vibrational excitation to translational energy. We designed an electron velocity map imaging spectrometer (e-VMI) to study chemi-ionisation of Kr, Ar, N₂, H₂ and D₂ by metastable He(${}^{3}S_{1}$) and Ne(${}^{3}P_{2}$) atoms in a crossed beam setup. A curved magnetic hexapole was used to guide the metastable atoms, specifically selecting the He(${}^{3}S_{1}$) and Ne(${}^{3}P_{2}$) states. Collision energies of 60 meV were reached by individually controlling the velocities of both reactants. In these experiments, electron kinetic energy distributions obtained using the e-VMI spectrometer were related to state specific reaction products. Detecting electrons, which are released in the first reaction step, we could characterise the reaction encounter complexes.

Merged beam experiments on neutral molecules allows molecular beam studies of reactive scattering below 1 K. We present the design and realization of a new merged beam setup that permits to study cold collisions between polar molecules, thus giving access to the investigation of dipole-dipole interactions in the sub-Kelvin range. The Stark effect was used to manipulate polar neutral molecules in an electrostatic guide. The electrodes structure required to merge two beams is highly complex and difficult to build by traditional methods. We used the 3D-printing metal coating approach, developed in our group, to realize a Y-shaped electrostatic guide in which two bent quadrupole guides are smoothly merging into a single hexapole guide. Simulations were performed to estimate the guide transmission as a function of the velocity in order to design the merged beams experiment. The correct functioning of the device was demonstrated by guiding ND₃ molecules.

Keywords

Cold chemistry, chemi-ionisation, electron velocity map imaging, merged neutral beam, 3D-printed metal coated electrostatic guide.

Sommario

In questa tesi presentiamo la progettazione di due configurazioni sperimentali per studiare le collisioni a bassa energia tra specie neutre : uno spettrometro per l'imaging della mappa di velocità degli elettroni nello studio di reazioni di chemi-ionizzazione e una guida elettrostatica congiunta per le collisioni di molecole polari.

Negli ultimi anni, la chemi-ionizzazione di atomi e molecole da parte di He e Ne metastabili ha portato alla misurazione dei rapporti tra due possibili canali reattivi, ovvero la ionizzazione Penning (PI) e la ionizzazione associativa (AI). Per le specie molecolari, l'esito della reazione è influenzato dalla ridistribuzione dell'energia da eccitazione vibrazionale in energia traslazionale. Abbiamo progettato uno spettrometro per l'imaging della mappa di velocità degli elettroni (electron-Velocity Map Imaging, e-VMI) per studiare la chemi-ionizzazione di Kr, Ar, N₂, H₂ e D₂ da atomi metastabili di He(${}^{3}S_{1}$) e Ne(${}^{3}P_{2}$) in una configurazione a fascio incrociato. Un esapolo magnetico curvo è stato utilizzato per guidare gli atomi metastabili, selezionando in particolare gli stati He(${}^{3}S_{1}$) e Ne(${}^{3}P_{2}$). Energie di collisione di 60 meV sono state raggiunte controllando individualmente le velocità di entrambi i reagenti. In questi esperimenti, le distribuzioni di energia cinetica degli elettroni ottenute utilizzando lo spettrometro e-VMI sono state correlate a specifici stati dei prodotti di reazione. Rilevando gli elettroni, rilasciati nella prima fase della reazione, abbiamo potuto caratterizzare i complessi di reazione.

Gli esperimenti con fasci congiunti su molecole neutre, consentono lo studio, con fasci molecolari, di collisioni reattive al di sotto di 1 K. Presentiamo la progettazione e la realizzazione di una nuovo esperimento a fasci congiunti che consente di studiare le collisioni a bassa temperatura tra molecole polari, dando così accesso allo studio delle interazioni dipolo-dipolo nell'intervallo dei sub-Kelvin. L'effetto Stark è stato utilizzato per manipolare molecole neutre polari in una guida elettrostatica. La struttura degli elettrodi necessaria per unire due fasci è molto complessa e difficile da costruire con i metodi tradizionali. Abbiamo utilizzato l'approccio di stampa 3D con rivestimento in metallo, sviluppato nel nostro gruppo, per realizzare una guida elettrostatica a forma di Y in cui due guide quadrupolari piegate si fondono gradualmente in una singola guida esagonale. Sono state eseguite simulazioni per stimare la trasmissione della guida in funzione della velocità al fine di progettare l'esperimento. Il corretto funzionamento del dispositivo è stato dimostrato guidando molecole di ND₃.

Parole chiave

Chimica a bassa temperatura, chemi-ionizzazione, imaging della mappa di velocità degli elettroni, fasci neutri congiunti, guida elettrostatica stampata in 3D rivestita in metallo.

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1 Motivation

A chemical reaction is the complex process of transformation of matter in which bonds are broken and new bonds are formed. This transformation of matter is the foundation of any phenomenon occurring around us and how this happens is the essential question of chemistry. A deep understanding of the reactions can only be possible studying elementary, two body, reactions. The advent of the field of reaction dynamics, in particular of gas phase dynamics, has enabled the investigation of chemical reactions at the microscopic molecular level, with effects on many areas of chemistry and natural sciences in general.

A reaction can also be viewed as a collision, in which the reactants approach each other with a certain kinetic energy. Their evolution, through transition states and intermediates, to final products will depend on their interaction potential, described by the potential energy surface (PES).

It is natural to consider the reaction partners as particles and treat them classically, however many aspects of the reactions rely on their wave-like behaviour which becomes evident at low temperatures, or from the point of view of a collision, low collision energies. In addition we should also remember that a large part of the chemistry that takes place in the universe, is at low temperatures. In interstellar clouds the temperature is between 2.7 and 100 K and even though the density is very low, the chemical environment is very active: indeed 200 molecules with up to 13 atoms, have been identified[1]. The study of reaction dynamics in the low collision energy regime, has become an important source of new insight in fundamental chemistry and a novel awareness on astrochemical relevant reactions[2].

We can differentiate two regimes: the cold regime usually refers to temperatures below 10 K and the ultracold to temperatures below 1 mK. In the former the collision partners are described by several partial waves and regulated by both classical and quantum mechanics. In the latter they can be described by single-partial waves and the system is governed essentially by quantum mechanics. As the collision energy is decreased it is possible to follow the transition from classical to quantum reaction dynamics. Quantum effects like tunnelling and scattering resonances, related to the wave-like behaviour, become significant and influence the reaction outcome[3–5].

Chapter 1. Motivation

Most of the reactions present a potential energy barrier, with respect to the reactants, that needs to be overcome to finally evolve to the products. When the collision energy is substantially lowered, the system doesn't have enough energy to overcome the energy barrier and the reaction rate will be extremely low. However, there are barrierless reactions allowed to happen at low collision energies. They can be atom-molecule, ion-neutral, radical, electronically and vibrationally excited states reactions or unimolecular decompositions[6]. Among all these possible reactions we here focus on the challenging study of barrierless reactions between neutral species.

The chemi-ionisation by a metastable atom or molecules is one of these: a long lived electronically excited atom, or molecule, ionises a ground state atom or molecule, through an electron transfer[7]. The ionisation goes through the formation of a reaction encounter complex in which the two reactants are bonded, in this step a free electron is emitted. The complex can either decompose and then ionise or directly ionise. The first step, in which the chemically bonded complex is formed, determines the redistribution of energy and angular momenta and establishes the final reaction outcome. The deep comprehension of the reaction is therefore related to the careful interpretation of the first reaction step.

In order to paint a picture of it, we propose the use of an electron Velocity Map Imaging (e-VMI) spectrometer. Electrons released in the first reaction are detected and their energy distribution is not influenced by possible post-ionisation dynamics, offering a characterization of the reaction encounter complex. The basic principle of operation of a VMI spectrometer is the extraction of electrons in such a manner that they reach the detector at a position determined by their velocities but not by the position where they are generated. We designed and built an e-VMI spectrometer to experimentally study chemi-ionisation of atom and molecules by metastable Ne and He, in a crossed molecular beams configuration.

Another key aspect of a low collision energy reaction is the sensitivity to the weak longrange, van der Waals, interactions, whereas in the high collision energy regime the short-range interactions are dominant. In a pictorial view, we can say that the reactants approach each other slowly and start to interact already when they are far away. In addition, due to their small relative motion, they spend a long time at large distances, therefore before that the short-range interactions become dominant. More precisely, the approach will mainly be influenced by the long-range tail of the potential if the relative velocity of the reactants, i.e. the collision energy, is negligible compared to the well depth of the interaction potential. In this case the radial wave functions associated with the relative motion of the particles are sensitive to any variation of the mutual interaction[2].

There are different kinds of long-range interactions, depending on the nature of the involved species: induced dipole-induced dipole, dipole-induced dipole and dipole-dipole[8]. We are interested in the study of dipole-dipole interactions between neutral polar molecules. In principle, the interaction of two polar molecules depends on their mutual orientation. However, at room temperature all orientations are possible and the resulting potential is attractive and scales with temperature as T^{-1} . When temperature tends to zero the thermal agitation is also reduced to zero and the rotational motion is quantized, leading to a mutual orientation

of the molecules, thus the interaction can be either attractive or repulsive. In the cold or ultracold regime, the long-range van der Waals interactions depending on the permanent charge distribution can therefore influence the reaction dynamics.

We propose the use of a merged electric guide to investigate, in molecular beam experiments, the role of dipole-dipole interactions in collisions between polar neutral molecules. We designed and built a 3D-printed metal coated merged electric guide with a peculiar Y-shape: two S-bent quadrupole guides, i.e. having a double curvature with opposite concavity, merge in a hexapole straight guide. This characteristic shape enables to have a single device to guide two different molecular beams from the beginning to the interaction region.

As a proof of principle, we demonstrate that polar molecules are transmitted through a guide with this atypical shape. The application of this new kind of merged beam experiment can highlight some hidden feature of neutral molecules collisions and expand our knowledge on the role of dipole-dipole long-range interactions.

The thesis is structured as follows:

Chapter 2 introduces the theoretical and experimental methods, common to the two projects. In particular are introduced the crossed beams technique, an overview of the methods used in cold chemistry, including the merged beam, and the guiding methods.

Chapter 3 presents the velocity map imaging of chemi-ionisation study. The theoretical aspects of chemi-ionisation are presented, followed by the simulation and design of the velocity map imaging spectrometer and the description of the experimental setup. The result of chemi-ionisation by metastable Ne and He of rare gases, Ar and Kr, and small molecules, N_2 , H_2 and D_2 are presented and discussed.

Chapter 4 presents the 3D-printed merged electric guide. As sample molecule to demonstrate the efficiency of the guide we choose ND_3 and a overview of the molecular characteristics is given at the beginning of the chapter. The theoretical simulations of the guide transmission are discussed. The guide manufacturing procedure and the experimental setup are described. Finally we show the results that prove the guiding efficiency of the 3D-printed guide and we propose a prospect of possible scattering experiments.

Chapter 5 exposes the conclusions of the thesis presenting the perspectives that the introduced techniques open for the investigation of low-collision energy reaction dynamics.

2 Introduction

This chapter presents the crossed beams technique, the collision kinematics, an overview of the methods used in cold chemistry and the Stark and Zeeman effects.

2.1 Reaction dynamics in crossed molecular beams

Research in reaction dynamics addresses the fundamental question of elementary reactions at the microscopic level, to determine interactions between molecules during the collision[9]. In order to get the microscopic description of the reactive system it is necessary to know the nature of the reactive products, the differential cross sections, the branching ratios of the different reactive channels and the evolution of the reaction on the Potential Energy Surface (PES). This information can be experimentally obtained by measuring products velocities and angular distributions for a certain collision energy and crossing angle.

Traditionally, reaction dynamics have been investigated by the use of the crossed molecular beams technique (CMB)[10]. Here two supersonic molecular beams cross at 90° and the reaction products are detected with a rotatable mass spectrometer, as shown in Fig. 2.1. The use of supersonic molecular beams provides internally cold reactants, i.e. the molecules are in the vibronic ground state and only few rotational states are populated[11].

The crossed molecular beams technique was first used in 1950's by Datz and Taylor to study alkali metals reactions[12]. In the 1960's Lee et al.[10; 13] improved the technique by the use of a more general detector, a rotatable mass spectrometer, allowing the study of a larger number of chemical reactions and the measurements of differential cross sections. When using a mass spectrometer, in principle, any reaction can be experimentally studied. Since then, the technique has been widely applied in the field, in general in combination with theoretical studies.

Many modified versions of the original setup have been developed over the years by different groups[14]. Noteworthy developments were, for example, the introduction of Velocity Map Imaging (VMI)[15; 16], in order to have velocities and angular distributions in a single measurement; the use of soft ionisation detection which enabled to study polyatomic reactions with multiple reaction channels[17; 18]; the state and velocity selection of reactants by magnetic or

electric guides[19]; the use of state-specific detection techniques like Resonance Enhanced Multiphoton Ionisation (REMPI)[20], Laser Induced Fluorescence (LIF)[21] or H-atom Rydberg tagging[22] to state select the reaction products.

The velocities of supersonic beams and the crossing angle, $\alpha = 90^{\circ}$, make the CMB technique suitable for studies in the collision energy range above 50 K (≈ 4 meV).



Figure 2.1: Schematic representation of a crossed molecular beams setup.

2.2 Collision kinematics

In a reactive collision between two structureless particles A and B, the quantities that are conserved are the total energy of the system and the total angular momentum. The total energy is the sum of kinetic energy T and potential energy V(R),

$$E_{tot} = T + V(R). \tag{2.1}$$

In the laboratory frame of reference (LAB) the kinetic energy is the sum of the kinetic energies of the two colliding particles

$$T = T_A + T_B = \frac{1}{2}m_A v_A^2 + \frac{1}{2}m_B v_B^2, \qquad (2.2)$$

where m_A and m_B are the masses and v_A and v_B the velocities of the two particles. A simpler frame of reference to describe the collision is the center-of-mass frame (CM). When using the CM frame, the center of mass of the system is considered at rest, so only the distance between the particles r and the relative velocity v_{rel} are the important quantities

$$\boldsymbol{r} = \boldsymbol{r}_A - \boldsymbol{r}_B, \tag{2.3}$$

$$\boldsymbol{v_{rel}} = \boldsymbol{v_A} - \boldsymbol{v_B}.\tag{2.4}$$

The relation between the two frames is illustrated in Fig. 2.2. In order to specify the collision in the CM frame we need to define the total mass *M* and the reduced mass μ :

$$M = m_A - m_B, \tag{2.5}$$

$$\mu = \frac{m_A m_B}{M}.\tag{2.6}$$

The position r_{CM} and the velocity v_{CM} of the center-of-mass in the LAB frame are

$$\boldsymbol{r_{CM}} = \frac{m_A \boldsymbol{r_A} + m_B \boldsymbol{r_A}}{M} \tag{2.7}$$

$$\boldsymbol{\nu_{CM}} = \frac{m_A \boldsymbol{\nu_A} + m_B \boldsymbol{\nu_B}}{M}.$$
(2.8)

Using Eq. 2.7, Eq. 2.8 and the following equation of the center of mass

$$m_A \boldsymbol{v}_A + m_B \boldsymbol{v}_B = 0, \qquad (2.9)$$

we can define the particle positions r_A , r_B and velocities v_A , v_B in the LAB frame:

$$\boldsymbol{r}_{\boldsymbol{A}} = \boldsymbol{r}_{\boldsymbol{C}\boldsymbol{M}} + \frac{\mu}{m_{\boldsymbol{A}}}\boldsymbol{r} \tag{2.10}$$

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Figure 2.2: Definition of the coordinates and velocities in the reference frame of the laboratory and in reference frame of the center-of-mass.

$$\boldsymbol{r}_{\boldsymbol{B}} = \boldsymbol{r}_{\boldsymbol{C}\boldsymbol{M}} - \frac{\mu}{m_{\boldsymbol{B}}}\boldsymbol{r} \tag{2.11}$$

$$\boldsymbol{v}_A = \boldsymbol{v}_{CM} + \frac{\mu}{m_A} \boldsymbol{v}_{rel} \tag{2.12}$$

$$\boldsymbol{v}_{\boldsymbol{B}} = \boldsymbol{v}_{\boldsymbol{C}\boldsymbol{M}} - \frac{\mu}{m_B} \boldsymbol{v}_{\boldsymbol{rel}}.$$
(2.13)

The kinetic energy *T* in the two frames of reference must be the same, so we can apply the transformations in Eq. 2.10-2.13 and obtain:

$$T = \frac{1}{2}m_A v_A^2 + \frac{1}{2}m_B v_B^2$$
(2.14)

$$=\frac{1}{2}M\boldsymbol{v_{CM}}^2 + \frac{1}{2}\mu\boldsymbol{v_{rel}}^2.$$
 (2.15)

As shown by Eq. 2.15, in the CM frame we can divide the kinetic energy into two components: the kinetic energy of the center-of-mass $T_{CM} = \frac{1}{2}M\boldsymbol{v_{CM}}^2$ and the relative kinetic energy, or collision energy E_{coll}

$$E_{coll} = \frac{1}{2} \mu \boldsymbol{v_{rel}}^2. \tag{2.16}$$

In the LAB frame the collision energy is given by

$$E_{coll} = \frac{1}{2}\mu(v_A^2 + v_B^2 - 2v_A v_B \cos \alpha), \qquad (2.17)$$

where v_A and v_B are the magnitudes of the velocity vectors of the particles in the LAB frame and α is the angle between the particles, as illustrated in Fig. 2.2.

The collision energy E_{coll} , as shown by Eq. 2.16, depends only on the relative velocity. To experimentally reduce the collision it is necessary either to slow down the colliding particles or, as shown in Fig. 2.3, to reduce the crossing angle.



Figure 2.3: Schematic representation of scattering experiments for different interaction angles, α . For $\alpha = 90^{\circ}$ the collision energy, E_{coll} , is independent on the scattering angle. For $\alpha < 90^{\circ}$ E_{coll} depends also on the scattering angle, thus resulting in a lower E_{coll} .

2.3 Cold chemistry: methods and application

In the low collision energy range (below 10 K) several features emerge and influence the evolution of the reaction: the wave-like nature of matter, tunnelling phenomena through reaction centrifugal barriers, resonance shapes and long-range interactions. In addition, most of the experimental methods used in the field can achieve the full control of the reaction parameters like the reactant quantum states, reactants polarization and orientation. Also state selective detection techniques can be employed leading to a deeper knowledge of the influence of each variable on the reaction outcome.

The average energy *E* of the collision system is often defined through the temperature *T* of the system. The two quantities are related by the equation $E = k_B T$ where k_B is the Boltzmann constant. Low collision energy corresponds therefore to low temperature and the terms are used indistinctly in the field. However, in molecular beams experiments the system is not thermalized and K is used merely as an energy unit.

From the experimental point of view, there are two ways to achieve low collision energies: reduce the reactants velocities in the laboratory frame of reference or reduce the collision angle. On overview of the experimental methods used in cold chemistry and of the results obtained is given in the following. We initially describe the methods based on the reactants cooling.

The first experimental studies at low collision energies were reported for atoms which can be stopped by laser cooling and trapped in magnetic traps[23]. Molecules have a more complicated internal structure and the application of laser cooling becomes more difficult[24] for this reason different techniques have been developed. As an example, ultracold sample of several polar alkali-metal diatomic molecules in their vibrational and rotational ground electronic state, such as ⁴⁰K⁸⁷Rb[25], RbCs[26], LiCs[27], ⁸⁷Rb₂[28] and Cs₂[29], were produced by magneto-association of ultracold atoms to a weakly bound Feshbach resonance which is then converted to a ground state molecule by a stimulate Raman adiabatic passage (STIRAP). The study of low collision energy scattering between polar neutral molecules has allowed to explore the influence of long-range dipole-dipole interactions on the reaction dynamics. Dipolar collisions in the ultracold molecular fermionic gas of ⁴⁰K⁸⁷Rb were reported by Ni et al.[25]. In this experiment the lifetime, monitored as inelastic loss, of the fermionic polar molecules trapped in an optical dipole was found to depend on the atom exchange reaction. The application of an external electric field induced a dipole moment and the dipolar longrange interaction modified the height of the reaction barrier. Dipolar interactions were found to be strongly anisotropic: the barrier was lowered for head to tail reactions and increased for side-by-side reactions.

The cold heteronuclear dipole collision $OH+ND_3$ with state selected reactants was experimentally studied by Sawyer et al.[30], by using a combination of Stark deceleration, magnetic trapping and buffer gas cooling. The main result was the measurement of an increase of total cross section upon application of an electric field which was suggested to be the effect of dipolar interactions.

Molecular ion-atoms collisions were studied combining sympathetic cooling and magneto-

optical trapping[31; 32]. Willitsch and co-workers studied the prototypical charge exchange reaction $N_2^++Rb \rightarrow N_2+Rb^+$ at 20 mK[33]. Molecular nitrogen cold ions are generated in a linear Radio-frequency ion trap and sympathetically cooled down by interaction with laser cooled Ca⁺ to form Coulomb crystals. The crystals were then translated, using an electric field, and overlapped with Rb atoms laser cooled in a magneto-optical trap. The dependence of the reaction on the electronic state of Rb was understood as the result of long-range capture due to the interaction between the charge of the ion and the electric quadrupole moment of Rb and the existence of a near resonance between reactants and products channels. Hudson and co-workers developed a similar experimental device, an hybrid ultracold atom ion trap co-located with a magneto-optical trap. They observed the synthesis of the mixed hypermetallic oxide BaOCa⁺ via the barrierless reaction of electronically excited Ca atoms and BaOCH⁺₃, in the temperature range 0.005-30 K[34].

Several experimental techniques based on the reduction of the crossing angle have been developed.

Van de Meerakker and co-workers used a Stark decelerated NO radical beam crossing at 5° with He produced by a cryogenic valve to study the atom-molecule reaction He+NO[35]. They observed resonance shapes in the low collision energy range and measured state-to-state integral and differential cross sections. The bimolecular collision OH+NO was also studied in a similar manner by Kirste and al.[36]. Stark decelerated OH molecules were crossed with hexapole focused NO molecules and the state purity of the collision partners made possible to measure state-to-state inelastic scattering cross sections.

Intrabeam experiments have been performed by Zare and coworkers. The principle of this technique is to make the collision happening in a single beam, the speeds of the co-expanding beams are similar, and the collision angle is small, reducing the temperature in the range 0-5 K. Using this method Zare and coworkers studied, for example, the rotationally inelastic collision of HD with H_2 and $D_2[37]$. The reactant HD was aligned parallel or perpendicular to the relative velocity by a Stark Induced Raman Passage (SARP) and they remarked that the rotational relaxation depends on the bond axis alignment, meaning that the reaction evolution is influenced by its stereodynamic. The technique of intrabeam collision has also been coupled with the VMI detection by Suits and co-workers. The scattering between Rydberg and ground states Xe atoms in the millikelvin range was found to be characterized by l-changing collisions[38]. The rotationally inelastic collision of vibrationally excited NO with Ar has been studied by the same group in near copropagating beam, with a collision angle of 4°[39]. They measured fully quantum state to state differential cross sections and showed that the reaction outcome was influenced by the attractive part of the interaction potential. Intrabeam experiments were performed also by Gawlas et al.[40]. In the reaction between He atom triplet Rydberg state and NH₃ about 1 K the energy transfer was demonstrated to be the result of a resonant electric dipole-dipole interaction affected by the energy level shift of the collision partners. The CRESU apparatus first introduced by Rowe and Marquette is based on the isoentropic expansion of a mixed beam from a high pressure reservoir into vacuum[41]. The technique was first applied to ion-molecules reactions and then expanded to neutral-neutral reactions and allowed to study reaction kinetics in the temperature range 7-160 K[42; 43]. Low, but

non zero, scattering angle experiments were performed by Bergeat et al.[44]. As an example, they performed the study of inelastic collision CO(J = 0)+He using two straight beams and a variable crossing angles between 90° and 12.5° reaching collision energies around 4 cm⁻¹[45]. They demonstrated a quantum dynamical resonance in the rotational excitation to CO(J = 1). In the merged beam approach the collision angle is reduced to zero $\alpha = 0$. In this way Eq. 2.17 becomes

$$E_{coll} = \frac{1}{2}\mu(v_A - v_B)^2,$$
(2.18)

and by choosing $v_A = v_B$ it is possible to achieve zero collision energy, independently on the beams velocities in the laboratory frame.

In order to merge one beam into the other, at least one of the two has to be bent so it is necessary to have a tool to control the motion of the collision partners. The technique was first used to study ion-molecule reactions[46–49] because ionic species can be easily guided. Magnetic or electric guides for neutrals based on Zeeman and Stark effect, developed in the context of beam deceleration, and already used for reactant selection[19; 50–52], were used to extend the merged beam technique to the study of neutral species reactions.

Merkt and co-workers used a merged beam approach to study ion-molecules reactions, in the range 5-60 K. The ionic collision partner is a Rydberg state of a molecule which can be deflected using a surface-electrode Rydberg Stark deflector and merged with the secondary molecular beam. The method was used to study the reaction $H_2^++H_2$ and the observed reactivity enhancement at low collision energy was explained as an effect of the interaction between the charge of H_2^+ and the rotational quadrupole moment of H_2 [53].

Merged neutral beam experiments were reported by Narevicius and coworkers and by our laboratory. Narevicius and coworkers by using two supersonic molecular beams merging in a magnetic quadrupole were able to observe the first shape resonance in the cold regime for the Penning ionisation of H_2 and Ar by metastable He atoms[3]. The latest introduction of a electron-ion coincidence VMI spectrometer has allowed the same group to report the existence of a Feshbach resonance for the reaction He^{*}+Ar[54].

In the merged beam setup developed in our laboratory the low collision angle between the two beams is achieved by the combination of two curved guides, a magnetic hexapole and an electric hexapole. Using this setup several Penning ionisation reactions including of Ne+NH₃[55], He+NH₃[56] and Ne+CH₃F[57] were studied. More recently low collision energy stereodynamic experiments of chemi-ionisation were performed by introducing a rotatable magnetic field in the interaction zone to orient the metastable Ne. A steric effect has been observed in the branching ratio of the reaction channels[58–60].

2.4 Manipulation of neutral species

In the experiments here presented we use the Stark and the Zeeman effect to manipulate the motion and guide, respectively, polar and paramagnetic species.

2.4.1 Stark effect

The Stark effect is the energy shift W_S of a molecule in the presence of an electric field. The first order shift originates form the existence of a dipole moment μ , related to the asymmetric charge distribution of the particle. When a polar molecule, characterized by the dipole moment μ , is in an electric field it will experience a potential energy W_S . This potential is influenced by the electric dipole moment μ orientation to the external field E[61]

$$W_S = -\boldsymbol{\mu} \boldsymbol{E},\tag{2.19}$$

In an inhomogeneous electric field, as the one represented in Fig. 2.4a), the Stark force F_S on the molecule is created by the gradient of the potential energy

$$F_{\mathbf{S}} = -\nabla W_{\mathbf{S}}.\tag{2.20}$$

A particle can gain or loose energy in increasing electric field, depending on the orientation of the dipole moment relative to the electric field. Thus, the Stark effect provides a force to manipulate the motion of a polar neutral molecule in the space.

The permanent dipole moment is an intrinsic property of the molecule and it is possible to define it by knowing the nuclei positions and the structure of the electron shell. A permanent dipole moment leads to a first order Stark effect. An external electric field can also induce a dipole moment, μ_{ind} that depends on the polarizability α of the molecule in the external field

$$\boldsymbol{\mu_{ind}} = -\alpha \boldsymbol{E}. \tag{2.21}$$

The energy shift due to an induced dipole moment is a second order Stark effect and since it is at least 1000 weaker than the linear Stark effect it can be neglected in our case.

We define here the first order Stark effect for a polar symmetric top molecule because in our experiments we will use the symmetric top molecule ND₃. For a rotating polar molecule, the components of the dipole moment orthogonal to the total angular momentum J are cancelled. The only remaining component is $\langle \mu_J \rangle$ which is parallel to J. The parallel component $\langle \mu_J \rangle$ is then reduced to the projection of J into the external field axis because the angular momentum precedes around the external electric field. For a symmetric-top molecule the dipole moment is aligned along the symmetry axis of the molecule. The quantum numbers K and M are therefore used. The former gives the projection of J on the symmetry axis of the molecule and the latter, defined as $-J \leq M \leq J$, the projection into the external field axis. A rotational state splits into 2J + 1 components that differ by their projection of J on the electric field axis.



Figure 2.4: a) Cross section of electric field norm in an electric hexapole. b) Definition of the rotational quantum numbers *J*, *K* and *M*.

The definition of the rotational quantum numbers is shown in Fig. 2.4b). The first order Stark effect on a polar symmetric top molecule is given by

$$W_S = -\frac{|MK|}{J(J+1)}\mu E.$$
 (2.22)

The guiding force is due to the presence of a dipole moment and so only molecules with a suitable dipole moment can be guided in an electric guide. In addition, the guiding probability depends on the rotational state defined by the quantum numbers M and K[52]. Rotational states defined by MK = 0 don't experience any Stark energy shift and are not guided. States defined by $MK \neq 0$ can either gain or loose energy in an external electric field, depending on their orientation to the field, as shown in Fig. 2.5 for the symmetric top molecule ND₃. The former are called low field seeker (lfs) and are attracted by low field regions and the latter are called high field seeker (hfs) and are attracted by high field regions. The zero field splitting arises from the inversion splitting of ammonia and will be discussed in Chap. 4.

By creating a 3D field minimum it is possible to confine polar molecules in the lfs states with static electric fields[62]. Time-dependent fields are necessary to confine hfs states.[63].

2.4.2 Zeeman effect

The Zeeman effect is similar to the Stark effect but induced by a magnetic field. In this case the permanent magnetic moment is the origin of the energy shift. There are two kinds of magnetic moment involved: the spin moment, μ_S , which is an intrinsic property of the particle and the one created by orbiting motion of the electrons, μ_I . The spin magnetic moment is

$$\boldsymbol{\mu}_{\boldsymbol{S}} = -2\frac{\mu_B}{\hbar}\boldsymbol{s},\tag{2.23}$$

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Figure 2.5: Schematic representation of Stark shift for ND₃.

where μ_B is the Bohr magneton. The orbital magnetic moment of a particle having a charge -qe and an angular momentum l is

$$\boldsymbol{\mu}_{\boldsymbol{l}} = -q \boldsymbol{e} \frac{\boldsymbol{\mu}_{B}}{\hbar} \boldsymbol{l}. \tag{2.24}$$

When taking into account the spin and the orbiting moments, the magnetic moment is

$$\boldsymbol{\mu}_{\boldsymbol{e}} = 2\frac{\boldsymbol{\mu}_{B}}{\hbar}(2\boldsymbol{s}+\boldsymbol{l}). \tag{2.25}$$

In the Russell-Saunders coupling approach, the total angular momentum **J** of the atom is given by

$$\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}. \tag{2.26}$$

where

$$\boldsymbol{L} = \sum \boldsymbol{l}_{\boldsymbol{i}} \tag{2.27}$$

$$\mathbf{S} = \sum \mathbf{s}_{i} \tag{2.28}$$

the magnetic moment of the atom becomes

$$\boldsymbol{\mu} = -\frac{\mu_B}{\hbar} (2\boldsymbol{S} + \boldsymbol{L}) = -\frac{\mu_B}{\hbar} (\boldsymbol{J} + \boldsymbol{S}).$$
(2.29)

The Zeeman effect is the energy shift W_z that particles will experience in a external magnetic field **B**, as the one shown in Fig. 2.6a), and it is related to the orientation of the magnetic dipole moment to the field axis

$$W_Z = -\boldsymbol{\mu}\boldsymbol{B},\tag{2.30}$$

that becomes

$$W_Z = -\mu_z B,\tag{2.31}$$

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if the external magnetic field **B** is oriented along the *z*-axis and μ_z is the component of the dipole moment along the same axis. The quantum numbers used describe the atom are the angular momentum *J* and the quantum number *M*, defined as the projection of *J* along the external magnetic field. Thus, the state of the atom is given by $\langle \alpha JM | B\mu_z | \alpha JM \rangle$, where α include all the other quantum numbers. The Zeeman energy is be given by

$$W_{Z} = -\langle \alpha J M | B \mu_{z} | \alpha J M \rangle = -\mu_{B} B M \left(1 + \frac{\langle \alpha J M | \mathbf{J} \cdot \mathbf{S} | \alpha J M \rangle}{\hbar^{2} J (J+1)} \right).$$
(2.32)

Using the common abbreviation

$$g_{\alpha J} = 1 + \frac{\langle \alpha J M | \boldsymbol{J} \cdot \boldsymbol{S} | \alpha J M \rangle}{\hbar^2 J (J+1)}, \qquad (2.33)$$

Eq. 2.32 becomes

$$W_Z = g_{\alpha J} \mu_B B M. \tag{2.34}$$

If we consider the product $\mathbf{J} \cdot \mathbf{S} = \frac{1}{2}(J^2 + S^2 - L^2)$

$$g_{LSJ} = 1 + \frac{\langle \alpha JM | \mathbf{J} \cdot \mathbf{S} | \alpha JM \rangle}{\hbar^2 J(J+1)} = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$
(2.35)

where g_{LSJ} is called the Lande' g-factor. As shown in Eq. 2.34, the Zeeman effect depends on the quantum number M, meaning that the magnetic guide operates a selection of states differing only for the quantum number M.

Zeeman effect of Metastable Neon and Helium

The ground state of the Ne atom, like all closed shell atoms, has no permanent magnetic moment. However, when the Ne is excited into higher states, there will be a single electron orbiting and the atom can become paramagnetic. In particular, an electron from the 2p orbital can be lifted to the 3s orbital. The presence of an electron into the 3s orbital gives 4 rotational states ${}^{1}P_{1}$, ${}^{3}P_{0,1,2}$. In the J-J coupling, used to describe the Ne atom, the selection rules for an electric dipole transition are $\Delta J = 0$ (for $J \neq 0$), ± 1 and $\Delta M_J = 0, \pm 1$. The transition from one of the excited states ${}^{3}P_{0}$ to the ground state ${}^{1}S_{0}$, would require $\Delta J = 0$ for J = 0 and the transition from the excited state ${}^{3}P_{2}$ would require $\Delta J = 2$. Both transitions are not allowed and for this reason, the lifetimes of excited states ${}^{3}P_{0}$ and ${}^{3}P_{2}$ are long and they are called metastable states. The ${}^{3}P_{2}$ has a lifetime of 24.4 s[64] and the ${}^{3}P_{0}$ has a lifetime of 430 s[65]. In Tab. 2.1 are listed the Zeeman energy shifts for different excited states of Ne. The states defined with the quantum number M = 0 don't experience any energy shift and are not transmitted. The states defined by $M \neq 0$ have a Zeeman shift which depends on the magnetic moment and are transmitted. Fig. 2.6b) shows the Zeeman energy shift for the different components of Ne ${}^{3}P_{2}$. The first electronically excited state of He, labelled as ${}^{3}S_{1}$, can be formed by promoting one of the 1s electrons into the 2s orbital. As in the case of excited Ne, the presence of a single electron makes the excited He paramagnetic. De-excitation to the ground state ${}^{1}S_{0}$ is doubly forbidden.



Figure 2.6: a) Cross section of magnetic field in a magnetic hexapole (Adapted from Ref. [66]). b) Zeeman energy shift diagram for $Ne({}^{3}P_{2})$.

Table 2.1: Zeeman effect W_z/B for Ne ${}^{3}P_{2,1,0}$ and He ${}^{3}S_1$ states as defined by Eq. 2.34.

Atom	State	g lsj	M_J	W_z/B
	${}^{3}P_{2}$	$\frac{3}{2}$	2	$3\mu_B$
			1	$\frac{3}{2}\mu_B$
Ne		_	0	0
110	3 D	3	1	$\frac{3}{2}\mu_B$
	$^{\circ}P_{1}$	$\overline{2}$	0	0
	${}^{3}P_{0}$	0	0	0
	30	0	1	$2\mu_B$
не	3_1	Ζ	0	0

In this case we can use the Russell-Saunders coupling and the selection rules are $\Delta L = 0$ (for $L \neq 0$), ± 1 and $\Delta S = 0$. The excited and the ground state have the same quantum number L = 0, which forbids a single photon transition and in addition the transition would require $\Delta S \neq 0$. For this reason this excited, or metastable, state has a very long lifetime, around 7870 s[67]. As discussed above for Ne, all the states having $M \neq 0$ have a Zeeman shift and can be transmitted in a magnetic guide. The Zeeman effect for metastable He is also listed in Tab. 2.1.

2.4.3 Guiding neutral species in electric and magnetic fields

Straight guide

In a hexapole guide, electric or magnetic, the field is zero at the center and increases quadratically. The maximum is reached at the edge of the inner opening, defined by the electrodes or the magnets. The potential has a perfect harmonic behaviour when the electrodes or the



Figure 2.7: a) Cross section of the electric field along *x*-axis for a real hexapole with a ratio between rods radius and inner opening of 0.5 (red line) and harmonic potential for an ideal haxapole (black line). b) Cross section of the electric field along *x*-axis for a real hexapole with a ratio between rods radius and inner opening of 0.565 (blue line) and a harmonic potential for an ideal haxapole (black line).

magnets have hyperbolic shape. Hyperbolic electrodes are difficult to produce and cylindrical electrodes are commonly used instead. It has been demonstrated that the use of cylindrical rods for which the ratio between the radius of the electrodes rods and radius of the inner opening is 0.565 produces the best approximation of an ideal hexapole[68], see Fig. 2.7b). But even the geometry in which the ratio between the electrodes radius and the inner opening radius is 0.5 produces a potential which differs less than 6% from a perfect harmonic potential[68], as shown in Fig. 2.7a).

A hexapole field produces a harmonic potential when the Stark or Zeeman effect is linear. The Zeeman effect for metastable rare gas atoms is linear. The Stark energy for ND₃ molecules in a hexapole is described well with a harmonic potential. The two-dimensional potentials described act like a 2D trap for the lfs states. Particles are confined in the *xy*-plane if the Stark or Zeeman energy at the inner opening is lower than the kinetic energy of the particles in the *xy*-plane. In contrast, hfs states will experience a maximum of the potential energy and will be pushed towards the magnets or the electrodes. Particles that are guided oscillate transversally around the minimum of the potential with a specific frequency, ω , these oscillations are called betatron oscillations and their length depends on the rotational state[69].

Curved guide

In a curved guide the transversal oscillations that the particles experience, while moving in the forward direction, can prevent them to follow the radius of curvature and push them outside the guide. In order take into account the effect of the curvature on the guide transmission we used an approximated model based on the contribution of a centrifugal force F_c to the motion


Figure 2.8: Definition of the particle position inside a hexaphole curved guide and of the radius of curvature of the guide.

of the particles

$$F_c = \frac{mv_l^2}{R+x},\tag{2.36}$$

where *m* is the mass of the particle, v_l is the longitudinal velocity, *R* is the radius of curvature and *x* is the distance of the particle from the centre of the guide, see Fig. 2.8. The centrifugal effect is defined by a pseudo-potential W_c [66]

$$W_c = -mv_l^2 lnR + x. ag{2.37}$$

The effective potential that a molecule feels in a curved guide is the sum of the pseudopotential and the potential of the guiding force. The radius of curvature of the guide is, generally, much bigger than the inner opening radius and the pseudo-potential can be considered linear. We can assume the guiding potential to be harmonic:

$$W_g = W_{gmax} \frac{x^2}{r^2},\tag{2.38}$$

where W_{gmax} is the Stark effect at the inner opening.

The effective potential is minimized when the centrifugal force and the guiding force are balanced, and this allows us to define an equilibrium radius r_{eq}

$$r_{eq} = \sqrt{\frac{R^2}{2} + \frac{mr_{max}}{2W_{gmax}}v_l} - \frac{R}{2},$$
(2.39)

where r_{max} is the inner opening radius, W_{gmax} is the Stark effect at the inner opening, m is the mass of the particle, v_l is the longitudinal velocity and R is the radius of curvature of the guide. At a specific longitudinal velocity v_{max} , the equilibrium radius corresponds to the inner opening and particles which have a velocity larger than v_{max} are not guided. The maximum guidable velocity is defined as

$$v_{max} = \sqrt{\frac{2W_{gamx}}{m} \left(1 + \frac{R}{r_{max}}\right)}.$$
(2.40)

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The trajectory of the particles travelling through the curved guide oscillate around r_{eq} and the maximum amplitude of the oscillation is given by $r_{max} - r_{eq}$. This means that for faster molecules less transversal velocities are accepted.

3 Velocity Map Imaging of Chemi-Ionisation

This chapter presents the e-VMI crossed molecular beams study of chemi-ionisation of rare gas atoms and small molecules by metastable Ne and He atoms. First a brief theoretical overview of chemi-ionisation is given, followed by the simulation and design of an e-VMI spectrometer, the description of the experimental setup, the experimental results and the discussion.

3.1 Chemi-ionisation

The term chemi-ionisation is used here to indicate the ensemble of different reactions in the collision between an atom, or a molecule, in an electronically excited state A^* and a ground state atom or molecule *B*.

In the simplest case of atomic collision partners the reaction is described by:

$$A^* + B \to A + B^+ + e^-.$$
 (3.1)

The collision between an electronically excited state of the atom A^* which has higher energy than the ionisation potential of the collision partner *B* can lead to the ionisation of *B* and the ejection of an electron[70]. The reaction, called Penning ionisation and first observed in 1927[71], is an electron rearrangement: one of the outer-shell electrons of *B* is transferred into the inner-shell vacancy of A^* . The reaction is believed to happen via the formation of two collisions intermediates $[AB]^*$ and $[AB]^+$ [72]

$$A^* + B \rightleftharpoons [AB]^* \to [AB]^+ + e^- \tag{3.2}$$

the second intermediate can evolve through different reaction channels:

$$[AB]^+ \to A + B^+ \tag{3.3}$$

$$[AB]^+ \to AB^+ \tag{3.4}$$

$$[AB]^+ \to A + X^+ + Y \tag{3.5}$$

$$[AB]^+ \to AX^+ + Y \tag{3.6}$$

The first channel, Eq. 3.3, is called Penning Ionisation (PI); the ionic complex can also ionise to AB^+ through the associative ionisation (AI) channel, Eq. 3.4; in the case of molecular collision partner dissociative ionisation (DI), Eq. 3.5, and rearrangement ionisation (RI), Eq. 3.6, can also take place.

The redistribution of translational energy, angular momenta and internal state energy happens in the primary ionisation process, that leads to the formation of the ionic complex $[AB]^+$, and defines the evolution of the system into its final state.

Two reaction mechanisms have been used to describe the chemi-ionisation: the radiative mechanism, and the exchange mechanism. In the former, which is dominant at long-range, the excited electron of the metastable specie relaxes to the ground state after transferring energy to the collision partner, which ionise; in this case only Penning ionisation can take place. The latter, is dominant at shorter distance, an electron of the collision partner is transferred to the vacant orbital of the metastable, this process requires orbital overlap and it is believed to lead to both Penning and associative ionisation.

3.1.1 Optical potential for Penning ionisation

The reaction is described by an optical potential W(R) defined as a combination of a real, $V^*(R)$, and an imaginary part, $\Gamma(R)$,

$$W(R) = V^*(R) - \frac{1}{2}\Gamma(R).$$
(3.7)

The real part describes the dynamics of the reactants approach on the entrance potential energy surface V^* . The imaginary part, $\Gamma(R)$ also called coupling function, defines the electronic rearrangement within the intermediate $[AB]^*$ to give the ionic complex $[AB]^+$. This step is described with an imaginary function because it is considered to be irreversible. It involves the release of a free-electron that is accompanied by a drastic change in electronic arrangement and signals Born-Oppenheimer breakdown[73]. It describes the disappearance probability of reactants with the transformation into products and it can also be defined as a transition rate K(R) since $\Gamma(R) = (h/2\pi)K(R)$. The Penning ionisation can be fully described through these functions. The relative importance of the two components, real and imaginary, is expected to vary with internuclear distance *R*. A schematic representation of the potential energy curves is shown in Fig. 3.1.

An important experimental observable is the ejected electron energy $E_k(e)$ which is directly



Figure 3.1: Schematic representation of chemi-ionisation potential curves.

related with the potential energy functions and the collision energy

$$E_k(e)(R) = E_{coll} + V^*(R) - V^+(R).$$
(3.8)

The resonance width is assumed to be independent on collision energy and angular momentum of the collision, in other words the nuclear motion. Therefore, the evolution of the complex $[AB]^*$ can be considered independent of the exit channel potential $V^+(R)$.

3.1.2 Cross section of Penning ionisation

The cross section of Penning ionisation in function of the collision energy can be estimated, in a classical treatment, describing the process in a one-dimensional PES. The derivation follows the one proposed by A. Niehaus[74]. Assuming the optical potential

$$W(R) = V^*(R) - \frac{1}{2}\Gamma(R),$$
(3.9)

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the PI probability P(R), for a particular intermolecular distance R and for a system having an initial angular momentum l, can be expressed as

$$P_l(R) = 1 - exp\left(-\int_{R_l}^{\infty} \frac{\Gamma(R)}{\hbar v_l(R)} dR\right),\tag{3.10}$$

where the local velocity, $v_l(R)$, is given by

$$\nu_l(R) = \sqrt{\frac{2}{\mu} \left(E_{coll} + V^*(\infty) - V^*(R) - \frac{l(l+1)\hbar^2}{2\mu R^2} \right)},$$
(3.11)

where μ is the reduced mass and R_l is the *l*-dependent turning point on $V^*(R)$ and defined through $\nu_l(R_l) = 0$. The total cross section is

$$\sigma(E_{coll}) = \frac{\pi\hbar^2}{2\mu E_{coll}} \sum_{l=0}^{\infty} (2l+1)P_l.$$
 (3.12)

If we assume large values of *l* and we substitute $b\sqrt{2\mu E_{coll}}/\hbar = (l + \frac{1}{2})$ the equation is converted into the integral over the impact parameter *b*

$$\sigma(E_{coll}) = 2\pi \int_0^\infty P(b)bdb.$$
(3.13)

Provided that there are enough partial waves, *l*-values, taking part to the collision, the cross section quantum effects are averaged, this means that the result given by the classical treatment, Eq. 3.13 can be considered accurate.

The collision energy dependence of the PI cross section can be classified into two types: if $\frac{E_{coll}}{D^*} \ll 1$, which means that the collision energy is smaller than the well depth D^* of the interaction potential V^* , the attractive part of the potential will be dominant in the interaction; if $\frac{E_{coll}}{D^*} \gg 1$, meaning that the collision energy is much higher than D^* , the repulsive part of the potential will dominate the interaction.

We can define b_c as the impact parameter at the turning point $R_c(b)$ where, $v_l(r_c) = 0$. In the low collision energy region, for large values of R, $b > b_c$ the ionisation probability P is low and the values of the impact parameter above b_c can be disregarded in Eq. 3.13. For $b < b_c$ the trajectories are mainly defined by the attractive forces and can be considered independent on the impact parameter b. The cross section simplifies to

$$\sigma(E_{coll}) \approx 2\pi \int_0^{b_c} P(b)bdb \approx \pi \overline{P} b_c^2, \qquad (3.14)$$

 \overline{P} is the average ionisation probability considered independent on the energy. The dependence of b_c on the energy is determined by the long-range attractive forces contributing to V^* . There are different kind of long-range forces such as dispersion forces, induced dipole interactions, dipolar interactions, or ionic forces and they have a different behaviour with respect to R. If we define a potential parameter s and we assume that for large R the potential is $V^* \propto R^{-s}$ then we can estimate $b_c \propto E_{coll}^{-\frac{1}{s}}$. Therefore the energy dependence of the cross section will be

$$\sigma(E_{coll}) \propto E_{coll}^{-\frac{2}{s}},\tag{3.15}$$

For example in the case of van der Waals attraction $\sigma(E_{coll}) \propto E_{coll}^{-\frac{1}{3}}$.

In the high collision energy region the potential V^* can be approximated by a purely repulsive potential and assuming a small ionisation probability for each collision the probability can be approximated by

$$P(b) \approx 2\pi \int_{R(b)}^{\infty} \frac{\Gamma(R)}{\hbar \nu(b,R)} dR,$$
(3.16)

and the cross section becomes an integral over distance

$$\sigma(E_{coll}) \approx \int_{R(0)}^{\infty} \frac{4\pi R^2 \Gamma(R)}{\hbar \sqrt{\frac{2}{\mu}} [E_{coll} - V^*(R)]} dR.$$
(3.17)

The potential can be approximated by $V^* = Cexp(-\frac{R}{F})$ and the coupling function by $\Gamma(R) = \hbar Aexp(-\frac{R}{B})$, with $\frac{R}{B} \gg 1$ so we obtain the energy dependence of the cross section

$$\sigma(E_{coll}) \approx 2A \left(\frac{\mu}{2B}\right)^{\frac{1}{2}} (BF\pi)^{\frac{3}{2}} \left(ln\frac{C}{E_{coll}}\right)^{2} \left(\frac{E_{coll}}{C}\right)^{\frac{F}{B}-\frac{1}{2}}.$$
(3.18)

3.2 Simulation and design of the e-VMI setup

In order to find the best VMI setup for the purposes of our experiment a series of SIMION[75] simulations has been performed on different electrode configurations.

Initially we concentrated on the classical 3-plates setup used by Eppink and Parker[15] and on the slicing scheme with larger number of electrodes proposed by Suits and co-workers[76]. Because of the high kinetic energy of the electrons released in chemi-ionisation, we finally decided to use the 11-plates Thick-Lens (TL) Velocity-Map Imaging developed by Kling et al.[77]. This spectrometer is characterized by high resolution for high kinetic energies (above 10 eV). A technical advantage of this setup is that the distance between the repeller plate and the detector, i.e. the flight tube, is small, 133.6 mm in the original setup. The smooth decrease of voltages, from repeller to ground, allow to take the charged particles to the detector and separate them, with no need of a long flight tube. Starting from the original TL-VMI design we carried out a further optimization to be able to apply it to our peculiar experimental conditions. To approach the problem in a systematic manner we performed trajectory simulations of electrons using SIMION for different geometries and voltages. The simulations are performed in 3D using the geometry shown in Fig. 3.2, which shows a slice of the cylindrical symmetry of the VMI spectrometer.

3.2.1 Particle distribution

The initial positions and the velocity distributions of the particles were selected to reproduce the experimental conditions.

Regarding the positions we used a distribution of particles on a circle, d = 1 mm, parallel to the detector and equidistant from the repeller and the extractor, which is the position of the interaction region centre. The velocity is uniformly distributed in the two velocity components in the interaction plane. Two sets of particles were used: with and without velocity component in the direction of the extraction.

3.2.2 Simulation parameters

From the point of view of the geometry the important features to optimize are: electrodes size, holes size, distance between adjacent electrodes and the total length of the time of flight tube. Although the focusing ratio between repeller and extractor is known, the mapping is very sensitive to voltages and so they have also been optimized.



Figure 3.2: a) The geometry of the TL-VMI used in the SIMION[75] simulations presented with the equipotential lines. The repeller plate is placed 172 mm away from the detector. b) Voltage distribution along the electrodes stack for $V_{rep} = 150$ V.

3.2.3 Velocity map imaging characteristic

The performances of VMI setup can be verified taking into account the following characteristics:

- The image size
- The linear relationship between the image size and the expansion speed, which quantifies the mapping efficiency
- The energy resolution

3.2.4 Results

Compared with the original VMI setup by Eppink and Parker, the TL-VMI spectrometer has a larger distance between repeller and extractor plate, and thus gives a larger voltage drop between them. The exit ring of the spectrometer together with the flight tube and the front of the MCP stack are set to ground potential.

In table 3.1 are presented, as an example, the results for 3 of the different arrangements tested here.

	r(mm)	$\sigma(mm)$
3-plate	11.0	0.2
4-plate	8.03	0.2
TL-VMI	15.06	0.02

Table 3.1: Variation of image radius and impact radius standard deviation for three different VMI arrangements.

The 3-plate setup is the standard Eppink-Parker setup[15] and the 4-plate setup is the arrangement proposed by Suits[76], the TL-VMI is based on the one of Kling et al.[77] but optimized for our experimental conditions. To quantify the mapping capability we analyse the image size radius r, and standard deviation σ , in the radial distance of the electron impact with the detector.

We observe that the TL-VMI setup produces the image with the largest radius and the smallest impact radius standard deviation. This means that the blurring of the image related to the ionisation volume can be kept as small as possible. It is important to notice that for very high electron kinetic energies (more than 3 eV) the image expands too much and doesn't fit any more on the imaging detector. A way to solve this problem is to increase the repeller voltage. To maintain the mapping ratio, all the other voltages need to be increased too. Higher voltages means that electrons are accelerated more in the extraction direction and have less time to expand in the detector plane directions, thus, the resulting image is smaller. As a consequence the resolving power of electron with similar kinetic energies decreases. We calculated that in the chemi-ionisation processes we want to study, the energy of the released electrons can vary between ≈ 0.6 eV and ≈ 6.0 eV. For this reason, we decided to optimize two sets of voltages (we refer at the two sets of voltages using the repeller voltage $V_{rep} = -150$ V and $V_{rep} = -700$ V) for two kinetic energies ranges (0.6-1 eV and 1-6 eV). The energy resolution will be as high as possible for each energy range.

The mapping efficiency is estimated by the linear relationship between the initial energy of the particles versus the square of the image radius R^2 . Fig. 3.3 shows the results for two sets of voltages optimized. The linear fit of the simulated data is in agreement with the trend $E \propto R^2$ and it is confirmed by the small residual plotted in Fig. 3.3b), c). This simple relationship facilitates the calibration of the energy axis.

The energy resolution $\frac{\Delta E}{E}$ can be calculated as:

$$\frac{\Delta E}{E} = 2\frac{\Delta R}{R},\tag{3.19}$$

where for each particle distribution *R* is the mean value of the impact radius, ΔR is the difference between the maximum impact radius and the minimum impact radius within the the same particle distribution.

The energy resolution for two sets of voltages is shown in Fig. 3.4 and it is possible to observe that a good resolution can be obtained with this detector especially for higher kinetic energies.



Figure 3.3: a) Simulation of R^2 vs. initial electron kinetic energy for -150 V (red) and -700 V (blue). Linear fits to the data are shown as a solid lines (black). b) Residual of the linear fit for -150 V. c) Residual of the linear fit for -700 V.

The width, ΔR , of the simulated rings goes from 1.6 mm, for the lower kinetic energy E = 0.2 eV, to 0.74 mm, for the higher kinetic energy E = 6.0 eV.

If the particles have also a component of the velocity in the direction of the extraction it is not expected that a uniform radius of impact is formed, because the image will be a 2D-projection of a 3D-sphere. This situation reproduces more accurately the experimental conditions. The main property of the imaging is still valid and a linear relationship between the particle expansion speed and its radius of impact on the detector has to be observed under focusing conditions.

A way to analyse this relationship is to plot the speed of the simulated particles in the detector plane as a function of the radius of impact, an example for two set of electrons with different kinetic energies is shown in Fig. 3.5. Different repeller voltages are used to simulate the two different kinetic energies. The linear relationship between the two quantities can be evaluated by the coefficient of determination, R^2 , that approaches 1 in both cases.

Based on these results we found the best geometrical parameters and the best voltages to be used in our experiment.



Figure 3.4: Energy resolution for two different repeller voltages -150 V (red) and -700 V (blue).



Figure 3.5: Speed at impact as a function of the radius at impact, for two electron kinetic energies a) $E_K = 1.0 \text{ eV}$ at repeller voltage -150 V b) $E_K = 2.0 \text{ eV}$ at repeller voltage -700 V. The black lines are the linear fits and the coefficients of determination, R^2 , are extracted from the graphs.



3.2 Simulation and design of the e-VMI setup

Figure 3.6: Schematic representation of the home-built TL-VMI spectrometer.

3.2.5 TL-VMI Design

A rendering of the home-built TL-VMI spectrometer is shown in Fig. 3.6.

It is composed of 11 electrodes made out of 1 mm thick non-magnetic stainless steel. The outer diameter of each plate is 51 mm. The repeller plate doesn't have any hole, the following 10 electrodes have holes with diameter increasing in 2 mm steps, starting from 40 mm for the extractor. The spacing between the repeller and the extractor plate is 12 mm, the spacing between the others electrodes is 6 mm. The electrodes are spaced by polyether-ether-ketone (PEEK) spacers. The first four plates are directly connected to power supplies, and the remaining are connected in a resistor chain with 1 M Ω resistors between adjacent electrodes. The voltages smoothly drop until the last plate which is grounded. The reaction takes place at the middle point between repeller and extractor plate.

The flight tube, from the interaction point to the detector, is 166 mm long and the entire electrodes stack is surrounded by two concentric μ -metal tubes (1 mm thick) to shield all magnetic fields which otherwise will influence the electrons' trajectories.

Electrons are detected on a stack of two 70 mm diameter MCPs in chevron configuration with a phosphor screen (Photonis). A charged-coupled device (CCD) camera (Basler) is used to record light flashes on the phosphor screen.

3.3 Experimental setup



Figure 3.7: Schematic representation of the experimental setup.

All the experiments described in this chapter were done in a crossed molecular beams configuration.

The experimental setup is shown in Fig. 3.7. The supersonic beam of metastable Ne or He is expanded into a differentially pumped source chamber and it is then skimmed before entering the curved magnetic guide. The guide, based on the Zeeman effect (Chap. 2), acts as a filter for the ${}^{3}P_{2}$ state of Ne* and ${}^{3}S_{1}$ state of He*. At the end of the guide, the beam is collimated before crossing at 90 ° with a secondary molecular beam. Collisions take place between the repeller and the extractor plate of the e-VMI setup. The electrons produced during the reaction are accelerated by the static electric field produced in the VMI region and velocity-mapped on a position sensitive detector. The electron hits on the screen are recorded with a CCD camera and stored by a computer. The setup is housed in a three stage differentially pumped high vacuum setup. The metastable beam source is pumped by Pfeiffer TMU 1600 MP (pumping speed 1400 l/s), the guide chamber by a Pfeiffer HiPace 700 (685 l/s) and a Pfeiffer HiPace 1200 (1300 l/s), the secondary beam source by a Pfeiffer TMU 521 YP (510 l/s) and the detector chamber by a Pfeiffer HiPace 700 (685 l/s). Three backing pumps are used: a Pfeiffer Duo 10 M and two Pfeiffer 20 M.

The collision energy is defined by:

$$E_{coll} = \frac{\mu}{2} (|\boldsymbol{v_1}|^2 + |\boldsymbol{v_2}|^2)$$
(3.20)

where v_1 is the velocity of the primary beam v_2 is the velocity of the secondary beam and μ is the reduced mass. The velocity of the primary beam can be varied by changing the expansion temperature, while the velocity of the secondary beam is fixed.

The repeller plate is switched on for $\approx 60 \ \mu$ s, and kept at ground for the rest of the time. The long extraction time, which is comparable with the duration of the beam pulses, allow us to detect all the electrons that are formed.

The spatial overlap of the two beams is assured by geometric constraint and the time overlap is found through variation and optimization of the valve timings relative to each other and to

the switching of the repeller plate.

The repetition rate is 5 Hz, limited by the pumping speed in the detector chamber. The detector is used in continuous mode since no mass selection is required and the CCD

camera has an opening time of 5 ms.

3.3.1 The supersonic beam sources

The requirement for the sources is to produce dense and cold atomic or molecular beams and this can be achieved by a supersonic expansion.

The speed of the supersonic beam can be calculated thermodynamically[11]

$$\nu = \sqrt{\frac{2k_B}{m}} \left(\frac{\gamma}{\gamma - 1}\right) (T_0 - T_{beam}),\tag{3.21}$$

where $\gamma = C_p/C_v$ is the ratio of the heat capacities at constant pressure and volume, *m* is the mass of the gas, T_0 is the stagnation temperature and T_{beam} is the beam temperature.

The source of Ne, or He, is a pulsed Even-Lavie source[78] equipped with a dielectric barrier discharge (DBD)[79] for the electronic excitation to the metastable state. The valve is used with a backing pressure of 8 bar. In order to control the velocity of the beam, and therefore the collision energy, we control the temperature of the expansion, T_{beam} in Eq. 3.21. The valve body is cooled with cold N₂ gas and then heated with an electric coil to the desired temperature, measured with a thermocouple. In the experiments here described the temperature is tuned over the range 150–300 K. The source of the secondary beam is a general valve (series 9, Parker-Hannifin corporation) and it is operated at a lower backing pressure, 2 bar, at room temperature.

3.3.2 Magnetic guide

Strong permanent NdFeB magnets (grade N35, nickel coated) are composing the magnetic guide. The remnant magnetization is $B_r = 1.17$ T.

The simulation of the magnetic field inside the guide can be seen in Fig. 3.8. The first part of the guide has a symmetric haxapole configuration and it is made by 3 straight segments each 300 cm long. Each one of the segments is tilted by 1° in the horizontal plane with respect to the previous one.

The second part has a very different geometry, the two magnets at the outside bend are removed and to keep the magnetic field strong enough to confine particles the top and the bottom magnet are replaced with wider ones. This peculiar geometry is needed when the magnetic guide is used in combination with a an electric guide, in a merged beam configuration[66].



Figure 3.8: a) Magnetic field in the first hexagonal part b) Magnetic field in the merging part. (Figure adapted from Ref.[66]).

3.3.3 Detector

The detector used for all the experiments is the home-built TL-VMI setup coupled with a position sensitive detector described in Sec. 3.2.5.

The image size depends on the energy of the electrons and on the repeller plate voltage. To make sure that high electron kinetic energies distributions will fit on the detector the repeller voltage has to be increased accordingly. In the experiments we used two sets of voltages, labelled as *A* and *B* in Tab. 3.2. Only the voltages of the first 4 plates are reported since all the others are connected to ground in a 1 M Ω resistor chain. The *A* set was optimized for Ne*+Ar and then used for the Ne* reactions, a part from the Ne*+Kr; the *B* set was optimized for Ne*+Kr and then used also for the He* reactions.

The front MCP, the first one that the electrons hit, is kept at ground, the back MCP at +2.0 kV, and the phosphor screen at +3.75 kV.

Voltage set	Repeller (V)	Extractor (V)	3rd plate (V)	4th plate (V)
A	-150	-140	-107	-98
В	-700	-680	-500	-450

Table 3.2: VMI voltages sets used in the experiment.

3.4 Abel inversion



Figure 3.9: Schematic representation of an electron imaging experiment. The relation between Newton sphere, velocity map and electron image is shown.

The reaction products formed during the collision expand from the interaction region and all the fragments having the same velocity are found, at any time, on the surface of a sphere, called Newton sphere. The result of a VMI experiment is an ion or electron image D(z, x). The image is the projection of the Newton sphere onto the detector plane. When performing an imaging experiment the goal is to determine the velocity map F(z, r). If we assume the images to be cylindrical symmetric around z, the axis perpendicular to the field created by the ion optics, the experimental map and the electron image depend only on two coordinates. All the information to obtain the map are contained in the image. The calculation of the Abel transform of a known map gives the image A(z, x), see Fig. 3.9.

$$A(z,x) = 2\int_{x}^{\infty} F(z,r) \frac{rdr}{\sqrt{r^{2} - x^{2}}}.$$
(3.22)

In the same way the map F can be calculated from the image A by the inverse Abel transform

$$F(z,r) = \frac{-1}{\pi} \int_{r}^{\infty} \frac{\partial A}{\partial x} \frac{dx}{\sqrt{x^2 - r^2}}.$$
(3.23)

The calculation described by Eq. 3.23 corresponds to the inversion of an almost singular matrix. Since the discovery of the VMI technique much effort has been put in solving the image reconstruction problem. In general the algorithms proposed either smooth or fit the data to some functional form to be able to apply Eq. 3.23.

The Abel inversion, from a mathematical point of view, corresponds to perform in sequence a Fourier transform and a Hankel transform[80] and in fact the first application of Abel to VMI

used a Fourier-Hankel method[81; 82].

Another method, first proposed by Pretzler[83], is called the matrix method. The data *D* is written as $(N \times M)$ matrix and in a similar way the map *F* and the simulated image *A* can also be written as matrices. Eq. 3.22 can be expressed as a matrix multiplication

$$\boldsymbol{A} = \boldsymbol{F}\boldsymbol{R},\tag{3.24}$$

by solving the equation system for *F* the image can be calculated.

Both the Fourier-Hankel and the matrix method produce a strong noise at the center line of the map F(z, r), that means for image points along the r = 0 line, because of the quasi-singularity of the matrix **R**. At the center line off the map very large positive and negative values can be found. The negative values do not have a meaning and for this reason other reconstruction methods have been proposed to avoid the center line artefact.

Among these methods one of the most used is "onion-peeling" [84; 85] which builds the reconstruction starting from large pixels. The outermost pixel can be reached only by particles with the largest available kinetic energy. For each pixel the maximum energy is calculated and its contribution subtracted to all the pixels in the same row. This procedure is repeated until the centre of the image is reached and in general gives a centreline about 4 pixels width. The class of algorithms called Basis Set Expansion (BASEX)[86] uses a different approach. The Abel inverse is exactly calculated from the analytical basis set expansion of the image. The data is reproduced with a linear combination of the basis set functions and when the inversion is performed the image is given as a linear combination of basis set functions, with the same expansion coefficients used for the data. The time demanding step is the calculation of the basis set functions.

The methods described require some smoothing or fitting before the inversion can be done and they don't employ a quantitative method to judge the quality of the reconstruction. A different approach is used in the class of methods called Maximum Entropy Velocity Image Reconstruction (MEVIR) proposed in 2014 by Dick[87]. The reconstructed map F is the one that gives the best simulation of the experimental data D for a Gaussian or a Poissonian particle statistics. In this way only the numerically stable forward Abel transform is used and any numerical modification of the data is avoided. Among the MEVIR class of algorithms we use the Maximum Entropy Legendre Expanded Image Reconstruction (MELEXIR) for our experimental data because it can avoid the center line artefact and give sharp peaks in the map even in the case of low signal level. These methods are described in the following paragraph.

3.4.1 MEVIR and MELEXIR algorithms

The basic idea of the MEVIR class of methods is to find the map F, defined as a slice cut along the *z*-axis of the velocity distribution[87], which, after Abel inversion, gives the best simulated image A for a given data set D. In other words, in order to maximize the probability of a calculated map, given the data, the elements of F are used as variational parameters[87]. The agreement is estimated by the likelihood estimator L. Since the number of variable parameters



Figure 3.10: Schematic of the MEVIR procedure (Figure adapted from Ref. [87]).

is similar to the number of data values to be fitted, many maps F have a likelihood estimator factor below the threshold. The process of maximization of the map probability allows us to choose the most likely map from this collection. This procedure can be considered as a maximization of the entropy function S for a strictly positive map

$$S = -\sum_{J=1}^{N_F} F_J \ln \frac{F_J}{eB_J}.$$
 (3.25)

The procedure followed by the MEVIR method is schematically showed in Fig. 3.10.

To make the simulated image agree with the data in the limit of a certain tolerance L the map is iteratively changed. The angular velocity distribution $Q_l(v)$ is given by the projection of the map F into Legendre polynomials. The hidden matrix H is introduced to take into account the correlation between adjacent rows in F[88]. The linear relation between F and H is defined as a linear transformation T which is a convolution process generally repeated several times. In each iteration the value of a pixel is replaced with a weighted average of this pixel and its 8 immediate neighbours. The optimization is done on the hidden maps H. The only constraint the velocity distribution has is to be rotationally symmetric around the z-axis.

The MELEXIR[89] approach is based on the assumption that few Legendre polynomials can be used to obtain the angular dependence of the velocity distribution[90]. The image data is also expanded in a series of Legendre polynomials and a projection of the image into Legendre polynomials in polar coordinates is used as raw data. The reconstruction of the velocity distribution can contain higher-order and odd-order Legendre contributions, important in multiphoton dissociation processes. Moreover, the sensitivity is higher and it is much faster than MEVELER. The schematic of the algorithm is shown in Fig. 3.11. The numerical velocity information is then given by a ($N \times M$) matrix Q which is in relation through an iterative



Figure 3.11: Schematic of the MELEXIR procedure (Figure adapted from Ref. [90]).

convolution with the hidden map H. The algorithm is programmed to directly transform Q into A. The velocity map F is not involved but it is possible to calculate it from the final result.

3.5 Experimental results

The images are divided into two groups according to the metastable atom used for the chemiionisation reaction. The collision energy is the same, $E_{coll} \approx 60$ meV, for all reactive systems presented here. In Fig. 3.12 it is shown the orientation of the two molecular beams in the interaction plane and consequently their projection onto the detector plane.



Figure 3.12: Schematic representation of the projection of the molecular beams orientation on the detector plane.

3.5.1 Ne* + X experimental velocity map images

Fig. 3.13 shows the experimental velocity map images for chemi-ionisation of different collision partners with $Ne({}^{3}P_{2})$.

In order to keep the collision energy constant for the different reactive systems the speed of the Ne(${}^{3}P_{2}$) is varied between $v_{Ne} = 780-790$ m/s.

The collision evolves through the reaction channels described in Sec. 3.1 and the two competing reaction channels are expected to be PI, in which X^+ is formed, and AI, in which NeX⁺ is formed. In the experimental images two or more rings are visible, meaning that electrons with different kinetic energies are formed. The kinetic energy of the released electrons can be associated with different internal states of the product ions.

In the case of atomic reactions the two spin-orbit coupling states, ${}^{2}P_{\frac{1}{2}}$ and ${}^{2}P_{\frac{3}{2}}$, of the product ions can be formed. In a similar way, for chemi-ionisation of molecular species, the ionic products can be formed in different vibrational states of the electronic ground state. Only states lying below the excitation energy of Ne*, 16.6191 eV, can be formed.

3.5.2 He* + X experimental velocity map images

Fig. 3.14 shows the experimental velocity map images for chemi-ionisation of different collision partners with He(${}^{3}S_{1}$). The speed of the metastable Helium beam is varied between $v_{He} = 1400-1600$ m/s. The energy of He^{*}, 19.8196 eV, is higher than the one of Ne^{*}.

Several rings are visible meaning that product ions can be formed in different internal states. For $\text{He}({}^{3}S_{1})$ +Kr, two rings are clearly visible and they reveal the two spin orbit coupling states of product ions. In the case of $\text{He}({}^{3}S_{1})$ +Ar the two spin orbit coupling states are not visible in



Figure 3.13: Experimental velocity map images for reactive scattering of Ne $({}^{3}P_{2})$ with different collision partners, as labelled. The collision energy is the same for all of them $E_{coll} \approx 60$ meV.

the image but will become more clear in the angular integration.

The reactive system $He({}^{3}S_{1})+N_{2}$ shows three broad rings that can be related to electronic states of the ionic products.



Figure 3.14: Experimental velocity map images for reactive scattering of He(${}^{3}S_{1}$) with different collision partners, as labelled. The collision energy is the same for all of them $E_{coll} \approx 60$ meV.

3.5.3 General features of the experimental velocity map images

There are two primary features in the images that should be highlighted and discussed. The images all show a strong asymmetry, with the intensity being higher for certain quadrants compared to others. Also, a small dip of the intensity can be observed for the larger images. For example looking at the Ne*+Ar image in Fig. 3.13 we can notice a higher intensity in the bottom-right region and a dip in the top-right region. Angular distributions of the products are in general considered an important experimental observable in VMI experiments carrying information about the dynamics. In the present case, the asymmetry has been understood to be an artefact. By rotating the imaging detector we could observe that the asymmetry rotates accordingly. As a consequence we have to assume that the detector has regions with different detection efficiency. The angular information will thus be discarded in the following discussion.

The other feature common to all the images is the presence of an intense spot in the centre. This 'central spot' has captured our attention for a long time and many tentative explanations were discussed, some of them are illustrated below.

- The presence of a reaction channel leading to zero kinetic energy electrons. This, for example, could be the case for the reaction $Ne({}^{3}P_{2})+N_{2}$, where the vibrational level v = 4 has an energy almost identical to the energy of Ne^{*}. A collision energy about 70 meV could be enough to lead to the additional formation of products in this vibrational level. Even at collisions energies substantially below 70 meV the spot persisted so we had to deduce that its presence was not related to ions in v = 4. Moreover the presence of the spot in all the images indicates that it cannot be related to reaction specific energy considerations.
- A reactants background. To investigate this possibility we recorded single beam images, with only metastable beam or only secondary beam, and we observed a homogeneous

background spread over the whole detector surface (accordingly with the different detection efficiency regions discusses above). This explanation, even if it is more general, has to be excluded too.

• The presence of Rydberg states of the Penning or associative ion just below the energy of the metastable reactant could lead to zero kinetic energy electrons. This phenomenon could explain the central spot but this means that at least one Rydberg state, with energy just below the energy of the metastable should exist. We calculated Rydberg states of the atomic ions Ar⁺ and Kr⁺ but they have energies above the energy of the Ne^{*} and He^{*} and cannot be accessed.

At this stage, we have not been able to clearly identify the source of this signal but this doesn't interfere with the data comprehension and interpretation. In fact, it corresponds to a concentration of signal in a small pixel area instead the other rings are spread over many pixels. When converting the images to velocity, i.e. energy, distributions the intensity at E = 0 meV, is, as it should be, low.

3.5.4 Application of MELEXIR and velocity distribution

The Abel inversion is performed with the MELEXIR algorithm using the program package MaxEntAbel. To be able to perform the inversion procedure the experimental raw images need to be prepared, since the MELEXIR algorithm required the images to be rotationally symmetric. In this case the images are circularized, symmetrized and, after the correct centre is found, moved to the centred position. All the manipulations required were performed using Python 3.0. Fig. 3.15 shows an example of the circularization and symmetrization procedure for the Ne*+Kr image.

The MELEXIR algorithm uses as input file the projection of the raw data onto Legendre polynomials in the polar coordinates of the 2D-image. The highest Legendre polynomial order requested to obtain the velocity maps from the raw images can be chosen between 0 and 6. In our case it is set to 4, giving the best angular integration results.

The angular integration of the images, i.e. the electrons velocity distribution, is given as an output at the end of the optimization.



Figure 3.15: Ne*+Kr: Circularization and symmetrization procedure.

3.5.5 Background subtraction

Independently of the inversion scheme used, if a finite background is present in the projected image, any reconstructed velocity distribution will show a nonzero baseline. The presence of this baseline can affect the accuracy of the information extraction. In order to remove it reliably we used an approach presented by Braun et al.[91].

A homogeneous background function is used to fit the velocity distribution, i.e. the chemiionisation electron spectrum, at high pixels values and then the fitted function is subtracted to the whole spectrum. The homogeneous background function used is the same derived in Ref. [91]:

$$P_S^B(r) = \frac{4}{\pi (r_0^2)} \frac{r^2}{\sqrt{r_0^2 - r^2}}.$$
(3.26)

Fig. 3.16 shows an example of the background subtraction procedure for the velocity distribution of the reactive system $Ne({}^{3}P_{2})$ +Ar. A similar process is applied to all the velocity distributions presented here.

3.5.6 Chemi-ionisation electron spectra

The information that can be extracted from the images is entirely contained in the velocity distributions. Before proceeding with the analysis the velocity distributions need to be converted to chemi-ionisation electron spectra. The *x*-axis of the velocity distributions are converted to energy. The conversion is done by using, as calibration data, literature values of Penning electron kinetic energies of Ne(${}^{3}P_{2}$)+Kr, Ne(${}^{3}P_{2}$)+Ar and He(${}^{3}S_{1}$)+Kr obtained by Penning Ionisation Electron Spectroscopy (PIES)[92]. In Fig. 3.17 are summarized all the chemi-ionisation electron spectra for the various reactive systems studied.

Within one spectrum each peak can be assigned to a group of electrons corresponding to the formation of different internal states of the atomic or molecular ion. The dashed vertical lines represent the theoretical kinetic energy of the Penning electrons E_0 , associated to the PI reaction channel, calculated assuming that the electron carries all the kinetic energy (a similar equation can be applied to He(${}^{3}S_{1}$)+X)

$$E_0 = E(Ne^3P_2) - IP(e, \nu)$$
(3.27)

where $E(Ne^{3}P_{2})$ is the energy of the metastable Ne (He) atom and IP(e, v) is the Ionisation Potential (IP) of the collision partner which depends on the spin-orbit state or on the electronic and vibrational state in which the product ion is formed. The total available energy of the system, a part from the energy of the metastable, includes also the collision energy and the internal energy of the collision partner. Their contribution to the electron kinetic energy will be further discussed.

The difference between the ground state of the Penning ion and associative ion is generally small, for example it has been measured around 74 meV for NeAr, 49 meV for NeKr[93] and estimated around 37 meV in the case of NeN₂[94]. This observation is reflected in very



Figure 3.16: Background subtraction procedure. a) Raw velocity distribution. b) The high pixels region of the raw velocity distribution is fitted to a homogeneous background. c) The fitted function obtained from panel b) is subtracted from the whole distribution (black line), to compare the raw velocity distribution is drawn (red line).

similar values of IP for the two expected reaction channels, PI and AI. Therefore, in the chemiionisation electron spectra we were not able to resolve electrons formed in the PI and AI. Nonetheless, a careful analysis of the electron energy distributions furnish, among the other information, knowledge about the ratio between the two reaction channels and it will be further presented and discussed.

Sharp and well resolved peaks can be observed in Ne(${}^{3}P_{2}$)+Kr, Ne(${}^{3}P_{2}$)+Ar and they are assigned to the two spin orbit coupling states, ${}^{2}P_{\frac{1}{2}}$ and ${}^{2}P_{\frac{3}{2}}$. In the Ne(${}^{3}P_{2}$)+N₂ spectra peaks are also well resolved and assigned to several vibrational levels. When colliding He(${}^{3}S_{1}$) with Kr, Ar and N₂ the peak cannot be completely resolved. For He(${}^{3}S_{1}$)+Kr the two spin orbit coupling states can be easily identified but for the system He(${}^{3}S_{1}$)+Ar the lower intense ${}^{2}P_{\frac{1}{2}}$ peak appears as a shoulder of the more intense ${}^{2}P_{\frac{3}{2}}$ peak. The He(${}^{3}S_{1}$)+N₂ spectrum shows 3 bands associated with three electronic states. The Ne(${}^{3}P_{2}$)+H₂ and Ne(${}^{3}P_{2}$)+D₂ spectra contains several peaks that, even though lower signal due to population spread over several vibrational levels, can be assigned.

The experimental linewidth is influenced by the presence of two possible reaction channels. The narrowest experimental linewidth is obtained for Ne*+Ar, using a repeller voltage $V_{rep} = -150$ V, and it is ≈ 110 meV at 0.89 eV. This result agrees well with the theoretical simulations of the VMI setup, presented in Sec. 3.2, that give an energy resolution $\Delta E = 120$ meV at 1 eV. Using the repeller voltage $V_{rep} = -700$ V the narrowest experimental linewidth is obtained for Ne*+Kr and it is ≈ 350 meV at 2.65 eV. Also in this case the results is in agreement with the theoretical simulations that give an energy resolution $\Delta E = 240$ meV at 3 eV.

3.5.7 Error handling and fit

The experimental data points are affected by an error on both the *x*-scale and on the *y*-scale. The error associated to the *x*-scale comes from the uncertainty in the determination of the position of electron hits on the CCD camera. It is first expressed as $\Delta(pixel)$, then converted in $\Delta(radius)$ and finally in $\Delta(E)$ (eV). Since the energy, *E* (eV), scales as the power of the radius a similar behaviour is expected for the error, $\Delta(E)$ (eV). The error associated to the *y*-scale is given by:

$$\Delta(n^{\circ}counts) = \sqrt{n^{\circ}counts} \tag{3.28}$$

where number of counts, $n^{\circ} counts$, is the intensity of the recorded signal on the CCD camera. The percentage errors, $\Delta(E)$ (eV) and $\Delta(n^{\circ} counts)$, are < 2% so the error bars have not been showed in the graphs.

In order to determine peak positions and peak areas, the spectra where fitted to Gaussian functions, here only the raw data are presented.

In the following sections will be presented the energy shift, this is the energy difference between the theoretical electronic kinetic energies E_0 , calculated as shown in Eq. 3.27, and the experimental peak values, ε_p . The error associated to these shifts is given by the error associated to the peak position $\Delta(E)$ (eV) since the theoretical values are assumed to be exact. The state populations, calculated in the following sections, are derived from the peak areas. Both the peak area and the associated error are given by the Gaussian fit.



Figure 3.17: Chemi-ionisation electron spectra for reactive scattering of $Ne({}^{3}P_{2})$ and $He({}^{3}S_{1})$ with different collision partners, as labelled.

3.6 Discussion

3.6.1 Ne*, He* + Ar and Ne*, He* + Kr

The feasibility and the simplicity of the title reactions facilitated many studies over the years, both theoretical and experimental and atomic PI reactions became a benchmark for more complicated systems. The reactive systems have been studied in molecular beam experiments in order to measure the energy dependence of the ionisation cross section[95–100]. Elastic angular distributions of the products[101] and differential elastic cross section[102] measurements contributed to the computation of the excited states optical potentials. The degree of AI has also been carefully studied[103; 104]. Ion imaging was applied to Ne*+Ar[105] showing, for the first time, the potential of this technique in chemi-ionisation experiments. The experimental results are supported by a large amount of theoretical calculation [106; 107]. In the last few years, with the idea to understand the reaction dynamics at low collision energy, stereodynamics experiments were carried out for Ne*+Ar, Kr and N₂[58; 94; 108]. Recently, a merged beam coincidence double VMI experiment for He*+Ar demonstrated the presence of a Feshbach resonance[54].

Thermal energy PIES of the reaction He*+Ar were among the first one to have been reported[72]. Since this first study, PIES experiments were also performed for the systems Ne*+Ar and He*, Ne*+Kr[92].

In order to prove the possibility to use an electron chemi-ionisation VMI spectrometer in crossed molecular beams experiments we decided to first concentrate on the investigation of these atomic systems. Due to the simplicity of electron images we first focus on the discussion of the results for these systems.

In Fig. 3.18a), c) are shown the chemi-ionisation electron spectra, obtained from the angular integration of the Abel inverted images, and the relative energy scheme, Fig. 3.18b), d), for chemi-ionisation of Ar and Kr by metastable Ne. In the energy schemes only the PI products are drawn, because of the small energy difference between the ground states of PI and AI products. Both spectra show a positive energy shift: the experimental peak, ε_p , is at higher electron kinetic energy compared to the theoretical value for the formation of the PI products, E_0 (dashed line in the figure), calculated with Eq. 3.27. The shift arises form the nature of the interaction, Ne*+Ar and Ne*+Kr, as well as He*+Ar and He*+Kr, are repulsive systems and when the autoionisation takes place, along the repulsive wall of the potential energy curve of the entrance channel $V(R)^*$, part of the asymptotic kinetic energy of the colliding partners, is converted into kinetic energy of the released electrons. The magnitude of the shifts is in good agreement with previous state selected thermal energies measurements reported in literature, see Tab. 3.3.

The high kinetic energy of the Kr⁺(${}^{2}P_{\frac{1}{2}}$) and Kr⁺(${}^{2}P_{\frac{3}{2}}$) peaks leads to a higher uncertainty on the energy shift values. The measured spin-orbit splittings are 179± 8 meV (theoretical value 178 meV) for Ar⁺ and 666±32 meV (theoretical value 665 meV) for Kr⁺. The peaks linewidths, (Full Width Half Maximum, FWHM) are ≈110 meV for Ar⁺ and ≈350 meV for Kr⁺.



Figure 3.18: $Ne({}^{3}P_{2})$ +Ar: a) Chemi-ionisation electron spectrum. b) Reaction energy scheme. $Ne({}^{3}P_{2})$ +Kr: c) Chemi-ionisation electron spectrum. d) Reaction energy scheme.

$Ne(^{3}P_{2}) + Ar$				
	$\varepsilon_p - E_0(meV)$			
Ref.	$Ar^{+}(^{2}P_{\frac{3}{2}})$	$Ar^+(^2P_{\frac{1}{2}})$		
This work	+31(6)	+30(6)		
Hotop et al. (PIES at 400 K)[92]	+29(4)	+28(4)		
$Ne(^{3}P_{2}) + Kr$				
	$\varepsilon_p - E_0(meV)$			
Ref.	$Kr^{+}(^{2}P_{\frac{3}{2}})$	$Kr^+(^2P_{\frac{1}{2}})$		
This work	+31(24)	+30(21)		
Hotop et al. (PIES at 400 K)[92]	+29(4)	+29(4)		

Table 3.3: Energy shift for chemi-ionisation of the listed systems.

As proposed by Hotop and Niehaus[70] the electron energy distributions can be interpreted in terms of potential energy curves involved in the chemi-ionisation process: $V(R)^*$, the entrance channel curve and $V(R)^+$, the exit channel curve. The schematic representations of potential curves and electron energy distribution are shown in Fig. 3.19. PI happens when the collision leads to the transition $V(R)^* \rightarrow V(R)^+$ and it is in general considered a vertical transition, meaning that the motion of the nuclei is assumed to be slow compared to the ejection of the electron.

The transition can happen for every value of the internuclear distance, *R*, leading to electrons with different kinetic energies:

$$E_k(e)(R) = V^*(R) - V^+(R) = V^*(\infty) - V^+(\infty) + \Delta E$$
(3.29)

where $\Delta E = \varepsilon_p - E_0$ is the peak shift to the theoretically expected value. The shape of the electron energy distribution is related to relative position and shape of the potential curves involved in the transition. The low energy part, near E_0 , results from the fact that the potential $\Delta V = V^*(R) - V^+(R)$ has a minimum near the value $\Delta V = V^*(\infty) - V^+(\infty)$.

The high energy tail of the electron kinetic energy distribution can give information about the amount of AI. In fact, for a certain collision energy, E_{coll} , depending on the interaction distance, R, we can identify two kind of collisions. For short collision distances the kinetic energy of the released electron is higher than $V(\infty)^* - V(\infty)^+ + E_{coll}$ and the AI product AB⁺ can be formed; if the interaction distance is larger the transition will produce electrons with kinetic energy lower than $V(\infty)^* - V(\infty)^+ + E_{coll}$ and the Penning ion B⁺ will be formed. Since all the possible interaction distances are probed, the result will be a distribution of electron kinetic energies. The region of the distribution where $E_k(e) > V^*(\infty) - V^+(\infty) + E_{coll}$ can be associated with electrons released in the formation of the AI product AB^+ , while the region where $E_k(e) < V^*(\infty) - V^+(\infty) + E_{coll}$ can be associated with electrons released in the formation of the AI product AB^+ , while the region where $E_k(e) < V^*(\infty) - V^+(\infty) + E_{coll}$ can be associated with electrons released in the formation of the AI product AB^+ , while the region where $E_k(e) < V^*(\infty) - V^+(\infty) + E_{coll}$ can be associated with electrons released in the formation of the AI product AB^+ .



Figure 3.19: a) Schematic diagram of the two potential curves relevant for chemi-ionisation. b) Kinetic energy distribution of the ejected electrons, the dashed area represents the AI region (Figure adapted from Ref. [70]).

the formation of PI product, B^+ . The two different regions are highlighted in the schematic electron energy distribution in Fig. 3.19. We can define a threshold electron kinetic energy for AI: $E_{AI} = V(\infty)^* - V(\infty)^+ + E_{coll}$.

Our experimental data can be interpreted following this representation.

With regard to the low energy side, in Fig. 3.18a), c) we can see that the peak intensity decreases fast for energies lower than the theoretical value and this can related to the small van der Waals well depths in the entrance channel. Hotop et al.[92], for example, calculated a well depth $D_e = 5.31 \pm 3$ meV in the case of Ne(${}^{3}P_2$)+Ar and $D_e = 8.68 \pm 4$ meV in the case of Ne(${}^{3}P_2$)+Kr. They showed that the well depth in the case of rare gases appears much smaller than for $Ne({}^{3}P_{2})+Hg[92]$. The latter system has a calculated $D_{e} = 54.9\pm3$ meV and the electron kinetic energies distribution is shifted to lower values compared to the theoretical ones. At the particular collision energy used in the present experiment ($E_{coll} \approx 60$ meV), which is one order of magnitude larger than the potential well depth, the collision takes place on the repulsive wall region of the entrance channel and it is not affected by the van der Walls attractive region. The high energy side, above the threshold energy E_{AI} , can be used to estimate the contribution of AI. Fig. 3.20a) shows the spectra of $Ne({}^{3}P_{2})$ +Ar, the dashed lines represent the theoretical energies, E_0 , and the threshold energy, E_{AI} , while Fig. 3.20b) shows the areas of each peak corresponding to the two channels. The electrons giving rise to the the low kinetic energy region of the distribution (orange area in the graph) should mainly come from PI, while the electrons in the high kinetic energy region (blue area in the graph) are released when the associative ion is formed.



Figure 3.20: Chemi-ionisation electron spectra of Ne(${}^{3}P_{2}$)+Ar. a) The dashed lines represent the theoretical energy E_{0} and the threshold energy for AI $E_{AI} = \Delta V + E_{coll}$. b) Area of each peak corresponding to the two reaction channels the orange area is associate to electrons released in PI formation and the blue area to electrons released in AI.

As expected the PI area is larger than the AI area. The calculation of the ratio $\frac{AI}{PI}$ as ratio between the two areas, considering both peaks, gives $\frac{AI}{PI} = 0.37 \pm 0.05$ which agrees rather well with the published results $\frac{AI}{PI} \approx 0.3[109]$. This value has to be considered as a rough estimation, based only on energetic considerations, and a precise determination of the ratio would be possible only for fully resolved reaction channels. PI is the most abundant channel in this collision but the cross section for AI is expected to be increasing for lower collision energies[109]. Stereodynamics experiments performed in our laboratory have shown that, at collision energies about 40 meV, by orientating the Ne^{*} relative to Ar, the ratio $\frac{AI}{PI}$ increases up to 0.7[94; 108]. The ratio $\frac{AI}{PI}$ strongly depends on the Ne^{*} quantum state. A further decrease of the collision energy causes the loss of the steric effect, which happens around 26 meV[58]. The increase of AI at low collision energy is expected to be reflected in the electron energy distributions. In a molecular beam collision energy dependence PIES study of Ne(${}^{3}P_{0,2}$)+Ar in the energy range 70-320 meV, Jacobs et al. [110], observed an increase in peaks shifts with increasing collision energy while the peaks asymmetry decreases. The mechanism can be described based on the optical potential proposed by Gregor and Siska in 1981[111]. The repulsive region at small distance forms a small tail in the electron energy distribution that extends to higher kinetic energies and leads to the associative ion if the collision energy is not too high. Our data, collected at a rather low collision energy, reproduce a small shift and a large peaks asymmetry due to the larger AI cross section. By considering the binding energy of the NeAr complex, $0.079 \pm 4 \text{ eV}[93]$, we can calculate the theoretical electron kinetic energies for the AI product in both the spin-orbit states. These theoretical values are plotted as dashed lines in the spectrum in Fig. 3.21 together with E_{AI} . In correspondence of these two theoretical values both peaks show a minor shoulder. The peaks slightly extend above the theoretical maximum kinetic energy.



Figure 3.21: Chemi-ionisation spectrum of Ne(${}^{3}P_{2}$)+Ar. The dashed lines represent the threshold energy for AI, $E_{AI} = \Delta V + E_{coll}$, and the theoretical electron energy, $E_{0}(AI)$, when the AI product NeAr⁺ is formed.



Figure 3.22: Chemi-ionisation spectrum of Ne(${}^{3}P_{2}$)+Kr. The dashed lines represent the threshold energy for associative ionisation, E_{AI} .

A similar interpretation can be applied also to the chemi-ionisation spectrum of Ne(${}^{3}P_{2}$)+Kr. In fact, the optical potential and resonance width[111] are similar, qualitatively and quantitatively, to the one for Ne*+Ar suggesting a similar reaction mechanism. Experimentally, we can observe that the chemi-ionisation peaks decrease fast in the low energy side and extend towards higher electron kinetic energies. Based on the energetic consideration used before the electron energies distribution can be divided into the PI an AI region. Fig. 3.22 shows the calculated threshold energy, E_{AI} , and the PI and AI regions highlighted in orange and blue. By using this method we can calculate the ratio $\frac{AI}{PI} = 0.62 \pm 0.05$ that it is almost double compared to previously reported value $\frac{AI}{PI} \approx 0.33[94]$ and has to be considered, also in this case, as an upper limit estimation.



Figure 3.23: $He({}^{3}S_{1})$ +Ar: a) Chemi-ionisation electron spectrum. b) Reaction energy scheme. $He({}^{3}S_{1})$ +Kr: c) Chemi-ionisation electron spectrum. d) Reaction energy scheme.

Similarly to what discussed for Ne*+Ar, stereodynamics measurements carried out in our laboratory, have shown that the $\frac{AI}{PI}$ can increase up to 0.7 at $E_{coll} = 40$ meV[94]. We have to notice that the collision energy of the present experiment, $E_{coll} = 60$ meV, is almost identical to the binding energy of the complex NeKr, 55 ± 3 meV[93], and this can in principle justify the large amount of AI. On the other side, as a consequence of this similarity, the theoretical electron kinetic energies for the formation of the AI products are almost identical to E_{AI} (for this reason are not plotted). This means that a large amount of the electron energy distribution expands beyond the maximum electron kinetic energy expected.

In Fig. 3.23a), c) are shown the chemi-ionisation spectra of $He({}^{3}S_{1})$ +Ar and $He({}^{3}S_{1})$ +Kr and the relative energy schemes, Fig. 3.23b), d).

$He(^{3}S_{1}) + Ar$				
	$\varepsilon_p - E_0(meV)$			
Ref.	$Ar^{+}(^{2}P_{\frac{3}{2}})$	$Ar^+(^2P_{\frac{1}{2}})$		
This work	+42(37)	+10(36)		
Brion et al. (PIES at 500 K)[112]	+44(5)	+44(5)		
$He(^{3}S_{1})+Kr$				
	$\varepsilon_p - E_0(meV)$			
Ref.	$Kr^{+}(^{2}P_{\frac{3}{2}})$	$Kr^+(^2P_{\frac{1}{2}})$		
This work	+37(45)	+30(42)		
Brion al. (PIES at 500 K)[112]	+35(5)	+35(5)		

Table 3.4: Energy shift for chemi-ionisation of the listed systems.

The ionisation cross section $\sigma_I = 8 \text{ Å}^2[72]$ at collision energy of 76 meV is smaller than the state selected ionisation cross section for Ne(${}^{3}P_{2}$)+Ar at similar collision energy $\sigma_{I} = 18 \text{ }^{2}$ [72]. The experimental shifts and the values available in literature are listed in Tab. 3.4. The $\operatorname{Ar}^+({}^2P_{\frac{1}{2}})$ shift is affected by high imprecision in the determination of the peak position, and the agreement with the literature is poor. Good agreement is found for the shift of more intense peak $Ar^+({}^2P_3)$ and let us conclude that the assignment is correct and that the resolving power is the limiting factor. The difference between the two peaks 240 ± 52 meV, is overestimated compared to the theoretical value 178 meV. The linewidth of the most intense peak is 280 meV. The peak shifts and shapes can be interpreted similarly to the Ne*+Ar case, and arise from the repulsive nature of the interaction. Compared to Ne*, the chemi-ionisation by He*, induces slightly higher shifts and the intensities of the peaks in the region near E_0 show a steeper decrease. This could be understood in terms of a steeper repulsive wall, the calculated well depth is about the same ≈ 5 meV[96; 113]. A smoothly repulsive potential is expected for this system[114]. Performing an energy dependent PIES study Longley et al.[115], have shown an increase of the energy shift and line widths with the collision energy. In the same study they measured the AI branching ratio from PIES for the singlet states of He* and they found it to be 10% at E_{coll} = 65 meV and to increase to 50% at E_{coll} = 20 meV. The AI threshold energy for the two states are E_{AI} = 3.9 eV and E_{AI} = 4.1 eV and they are plotted as dashed lines in the spectrum in Fig. 3.24a). We can see, by looking at $Ar^+({}^2P_{\frac{3}{2}})$, that it almost coincides with the peak and so a significant amount of AI could be formed at this collision energy. Because of the strong peaks overlap any attempt to estimate the AI/PI ratio from the spectrum would lead to erroneous results.

In the He(${}^{3}S_{1}$)+Kr spectra, Fig. 3.23c), the two spin-orbit coupling states are well resolved, the energy shifts are in good agreement with the literature and the high uncertainties is due to the high kinetic energy range probed. The energy difference between the two peaks is 672 ± 62 meV compared to a theoretical value of 665 meV. The shape of the distribution let us conclude the predominance of the repulsive interaction at this particular collision energy. In particular,


Figure 3.24: a) Chemi-ionisation spectra of $He({}^{3}S_{1})$ +Ar and b) $He({}^{3}S_{1})$ +Kr. The dashed lines represent the threshold energy for AI E_{AI} and the theoretical electron energy E_{0} when the PI products Ar⁺ and Kr⁺ are formed.

by looking at $\text{Kr}^2(P_{\frac{1}{2}})$ peak we can notice that the low energy part of the distribution, near E_0 , decreases faster compared to the Ne^{*} case. The linewidth is \approx 420 meV, so the peaks are clearly broader than in the Ne^{*} case and this could be interpreted as a larger propensity for the AI. The well depth is about the same, \approx 8 meV[96]. The threshold energies for the two peaks are $E_{AI} = 5.2$ eV and $E_{AI} = 5.9$ eV, are drawn as dashed lines in the spectrum in Fig. 3.24b). The ratio calculated from the spectrum is $\frac{AI}{PI} = 0.77 \pm 0.05$, is larger than the one measured for the Ne^{*} reaction.

The chemi-ionisation spectra also give access to branching ratio for formation of the two spin orbit coupling states, $I({}^{2}P_{\frac{3}{2}})/I({}^{2}P_{\frac{1}{2}})$. In Tab. 3.5 are summarized all the branching ratios calculated for the systems described in this section. They are calculated as the ratio between the area under each peak, as given by the Gaussian fit. The measured ratios for Ne(${}^{3}P_{2}$)+Ar and He(${}^{3}S_{1}$)+Kr are in good agreement with the literature values while for Ne*+Kr the branching ratio is overestimated of about 0.26 and for He*+Ar is underestimated of about 0.6. For Ne(${}^{3}P_{2}$)+Kr the larger branching ratio could be related with the larger amount of AI. The AI product could be formed more favourably in the ${}^{2}P_{\frac{3}{2}}$ state leading to the larger branching ratio. The difference between the ratios measured in this work and the literature for He(${}^{3}S_{1}$)+Ar it is related, once again, to the partial overlap of the peaks.

Collision system	Branching ratio
$Ne(^{3}P_{2}) + Ar$	
This work	1.50 ± 0.13
Hotop et al. (PIES at 400 K)[92]	$1.51 {\pm} 0.07$
$\frac{1}{Ne(^{3}P_{2})+Kr}$	
This work	$1.60 {\pm} 0.08$
Hotop et al. (PIES at 400 K)[92]	$1.34 {\pm} 0.06$
$He(^{3}S_{1}) + Ar$	
This work	1.34 ± 0.12
Brion et al. (PIES at 500 K)[112]	$1.94 {\pm} 0.05$
$He(^{3}S_{1}) + Kr$	
This work	1.82 ± 0.14
Brion et al. (PIES at 500 K)[112]	$1.8 {\pm} 0.05$

Table 3.5: Branching ratios ${}^{2}P_{\frac{3}{2}}/{}^{2}P_{\frac{1}{2}}$ for chemi-ionisation of the listed systems.

3.6.2 Ne* + N₂

The Penning ionisation of molecular nitrogen by either Ne^{*} and He^{*}, has received much attention over the years[95; 98; 102; 116–118] and N₂, because of its nonpolar character, has become the archetype of multiorbital reaction partners. There are two peculiar features that make molecular nitrogen so interesting: the presence of two or more ionisable orbitals in the molecule; the strong bond in N₂ and N₂⁺ that makes rearrangement (RI) and dissociative ionisation (DI) very unlikely to happen. The reactive collision with a metastable species will then lead only to the Penning and associative ions. Another characteristic is that the equilibrium distance of the electronic ground states of the molecular ion N₂⁺ increases only by 2% compared to the one of N₂.

In Ne(${}^{3}P_{2}$)+N₂ only the electronic ground states of N₂⁺ and NeN₂⁺ are energetically accessible. The theoretical optical potential of Ne(${}^{3}P_{2}$)+N₂ has been shown to be very similar to the one of Ne(${}^{3}P_{2}$)+Ar[102] suggesting a similar reaction mechanism. However, crossed and merged beams experiments have shown a sensible decrease, more than 60%, of the AI channel in N₂ compared to Ne(${}^{3}P_{2}$)+Ar[59; 60; 94].

Early PIES experiments[119] reported a significant vibrational excitation of the Penning ion, even though a quantitative calculation was not done. In a LIF experiment in neon afterglow Tsuji et al.[120] observed a similar behaviour and proposed the pre-dissociation (PD) of the associative ion or the pertubation of the N_2^+ curve by Ne* as possible mechanisms for the enhancement of the vibrational population. In a subsequent LIF experiment Sonnenfroh and Leone[121; 122] observed a bimodal rotational distribution in the spectra of N_2^+ giving an evidence of two possible reaction paths and supporting, indirectly, the PD mechanism. Fig. 3.25a) shows the chemi-ionisation spectrum and Fig. 3.25b) the reaction energy scheme, both



Figure 3.25: $Ne({}^{3}P_{2})+N_{2}$: a) Chemi-ionisation electron spectrum. b) Reaction energy scheme.

AI and PI pathways are reported. Only the electronic ground states, $X^2 \Sigma_g^+$, is accessible and 4 vibrational levels are populated. The collision energy of this experiment is not high enough to open the formation of v = 4.

The positive energy shift observed between the theoretical electron kinetic energies and the experimental values are reported in Tab. 3.6. The experimental line widths are about 150 meV. In previous PIES experiments[119] the shift wasn't, surprisingly, observed but the energy resolution of the measurements, about 20 meV, is in the same energy range of the shift we could measure.

As discussed in the atomic case the shift arises from the repulsive nature of the interaction[119]. The E_{coll} is also in this case larger than the well depth reported in literature, 3.5 meV at equilibrium distance $r_e = 5.4$ Å[72], and the reaction should not be affected by the attractive region. The shift is smaller than the one observed for rare gases and from the dynamical point of view a small shift in a repulsive system means that a large amount of the collision energy is tied up in the centrifugal motion. The vibrational spacings, calculated for the experimental peaks, are reported in Tab. 3.7 and they are in good agreement with the theoretical values calculated as the difference between adjacent vibrational energy levels of N₂⁺.

The vibrational population extracted from the electron distribution are listed in Tab. 3.8, within literature values from LIF experiments on PI products and Franck-Condon factors (FCF) obtained by photoelectron spectroscopy (PhES)[123]. The populations have a Franck-Condon nature. The vibrational level v = 0 is the most populated, but there is a clear enhancement of vibrational excitation. Our results are, within mutual errors, in agreement with vibrational population obtained by Sonnenfroh et al. and Tsuji et al. in N₂⁺ LIF experiments. Sonnenfroh et al. measured a similar population for v = 2 and v = 3 in contrast to what predicted by FCF and this is interpreted as a decay of Rydberg levels of N₂. In our data, instead, we can notice a similarity in the population of v = 1 and v = 2.

	$\varepsilon_p - E_0(meV)$					
	v = 0	<i>v</i> = 1	<i>v</i> = 2	v = 3		
This work	+19(7)	+20(6)	+29(5)	+27(3)		

Table 3.6: Energy shift in $Ne({}^{3}P_{2})+N_{2}$.

Table 3.7: Energy separation between adjacent N₂⁺ vibrational peaks.

	v' - v''(meV)				
	0 – 1	1-2	2 - 3		
This work	269 ± 9	256±8	264 ± 6		
Theoretical values	270	266	262		

Table 3.8: Relative vibrational population in $Ne({}^{3}P_{2})+N_{2}$.

Ref.	v = 0	<i>v</i> = 1	<i>v</i> = 2	v = 3
This work	100 ± 2	27±2	21±2	13±1
Sonnenfroh et al. (LIF N_2^+)[122]	100	$25.4{\pm}2.0$	16.3 ± 2.0	15.8 ± 3.0
Tsuji et al. (LIF N_2^+)[120]	100	24 ± 1	9 ± 1	20 ± 1
FCF Lofthus et al. (PhES)[123]	100	9	0.66	0.038

It is clear that a relation must exist between the vibrational level populations, the ratio between the PI and AI, and the probability of PD of the associative ion.

The PD of the AI product has been used to justify the lack of associative ion products[94] and could explain the vibrational excitation observed in the chemi-ionisation spectrum. When the collision complex [Ne-N2]⁺ is formed in a vibrationally excited level, vibrational energy can be transferred into translational energy along the Ne-N₂⁺ coordinate and enhance the bond breaking. If we assume that every AI product $NeN_2^+(v)$ pre-dissociate to $N_2^+(v-1)$, as shown in the graph in Fig. 3.25b), the amount of AI is hidden into the PI products. The populations of the excited vibrational levels of NeN_2^+ is transferred into vibrational levels of N_2^+ . Detection of the N_2^+ does not allow to distinguish between direct PI and PD of AI product. In the present experiment only electrons released during the primary ionisation process are detected, and the signal shouldn't be influenced by the PD pathway. However, for any vibrational level of the product ions, PI and AI electrons are not resolved and give rise to the same peak. This means that either in LIF detection of Penning ions, performed by Tsuji et al. and Sonnenfroh et al., or VMI detection of electrons, performed in the present experiment, PI and AI channel are not distinguished. As a consequence, the vibrational population are in both cases, LIF and e-VMI, a convolution of PI and AI and thus are reasonably similar one to the other even though the experiments are conceptually different.



Figure 3.26: Chemi-ionisation electron spectrum of $Ne({}^{3}P_{2})+N_{2}$. The black dashed lines represent the theoretical electron energy $E_{0}(AI)$ corresponding to the formation of the AI products.

The vibrational excitation, compared to FCF from PhES of N_2^+ , measured in this experiment, has to be related to a perturbation of the N_2^+ potential energy surface by the presence of Ne^{*}, meaning that the Ne-N2⁺₂ surface is substantially different from the N_2^+ surface.

A precise determination of the AI ratio, from the chemi-ionisation spectrum, cannot be performed but energetic considerations can reveal some interesting aspects. If we assume the binding energy of the complex NeN₂ to be $\approx 300 \text{ cm}^{-1}[94]$ we can calculate the energy of the electrons released in the AI channel. These are plotted as dashed lines in the spectrum in Fig. 3.26. The peaks don't have any asymmetry that could be an evidence for AI. One interesting feature we can notice is that the product NeN₂⁺ in v = 4 could be formed at this collision energy, the theoretical energy of the correlated electrons is also plotted in the spectrum. There is also no evidence for this barley open AI product. The absence of peaks asymmetry can be interpreted as an effect of the small probability of AI. The subsequent PD, enhanced by conversion of vibrational excitation of [Ne-N₂]⁺ into translational energy, causes a further reduction of AI product. A measurement of the velocity distribution of the ions would help in quantifying the efficiency of the conversion and its contribution to the break of the Ne-N₂ bond.

The favoured mechanism for the $Ne({}^{3}P_{2})+N_{2}$ reaction is believed to be the exchange mechanism, that takes place at short distances. Short-range interactions are the ones that lead to higher vibrational excitation. When the reaction takes place, one of the *p* electron of N₂ is moved to the vacant *p* orbital of Ne^{*}. The complex Ne^{*}-N₂ is formed and then it autoionise giving both AI and PI products.

3.6.3 He* + N₂

Penning ionisation of molecular nitrogen by metastable He^{*} can lead to the formation of the electronic ground state, $X^2 \Sigma_g^+$, and two electronically excited states $A^2 \Pi_u$ and $B^2 \Sigma_u^+$, which



Figure 3.27: $He({}^{3}S_{1})+N_{2}$: a) Chemi-ionisation electron spectrum. b) Reaction energy scheme.

Table 3.9: Energy shift in $He({}^{3}S_{1})+N_{2}$.

	$\varepsilon_p - E_0(meV)$				
Ref.	$X^2\Sigma_g^+$	$A^2\Pi_u$	$B^2 \Sigma_u^+$		
This work	+54(31)	[-12(27)]	+29(16)		
Hotop et al. (PIES at 400 K)[124]	+54(10)	+57(4)	+54(4)		

were first assigned in PIES experiments[124; 125].

An interesting aspect of the reaction, experimentally observed by Ohno et al.[126], is the magnitude of energy dependence of the partial ionisation cross section which is larger for the Π state than for the Σ states.

Fig. 3.27a) shows the chemi-ionisation spectrum and Fig. 3.27b) the relative energy scheme. The three accesible electronic states for the PI product, $X^2 \Sigma_g^+$, $A^2 \Pi_u$ and $B^2 \Sigma_u^+$ can be formed by removal of electrons, respectively, from a σ_g bonding, π_u bonding, and a σ_u^* antibonding orbital. The electrons in the π_u orbital are most strongly bonded and their removal leads to an increase in bond length which results in a long vibrational progression.

The first observation is the positive energy shift of the vibronic bands, due to the repulsive nature of the reactive interaction. The calculated van der Waals well depth is about 3 meV at an equilibrium distance of 6.1 Å[72]. Therefore at the collision energy of the present study the attractive part of the potential does not influence the reaction. The magnitudes of the energy shifts are reported in Tab. 3.9 with the experimental values obtained by Hotop et al.[124] in thermal energy measurements for a mixed beam containing both He(¹*S*) and He(³*S*). In the present work, the large errors associated to the shift are due to the high kinetic energy range we are probing. Good agreement can be observed for ground state, $X^2\Sigma_g^+$, while the Π state band appears to be unexpectedly shifted to lower kinetic energies. PIES experiments resolved 6 vibrational levels in the $A^2\Pi_u$ vibronic band with the most intense transition producing the

Ref.	$X^2\Sigma_g^+$	$A^2 \Pi_u$	$B^2 \Sigma_u^+$
This work	100 ± 7	69 ± 5	88±7
Hotop et al. (PIES at 400 K)[124]	100 ± 5	83 ± 9	113 ± 12
Ohno et al. (PIES at 70 meV)[126]	100 ± 5	75 ± 7	87 ± 15
Frost et al. (PhES)[127]	39 ± 3	52 ± 3	9 ± 2

Table 3.10: Relative population of ionic states in $He({}^{3}S_{1})+N_{2}$.

vibrational level v = 1. In the present study we cannot resolve the vibrational structure but we believe the vibrational population have a similar trend. The most intense transition should then be observed for v = 1 and this means that the vibrational band is peaking in the high energy side. Because of this, the peak position obtained by our Gaussian fit is erroneously found at higher energies. We suppose that the error associated with the shift is underestimated in our calculation and therefore we consider this shift inaccurate. The measured shift for $B^2 \Sigma_u^+$ is lower than the previously reported value but also in this case the associated error is large. The transitions to $X^2 \Sigma_g^+$ and $B^2 \Sigma_u^+$ states are vertical and only the first two vibrational levels are populated.

The measured electronic state population compared with literature[119; 126] and photoelectron spectroscopy data[127] are reported in Tab. 3.10. The results are in agreement, within mutual errors, with the most recent results published by Ohno et al.[126]. The most striking feature of chemi-ionisation is the substantial difference in electronic state population compared to photoelectron spectra. The contribution of the Π state to the ionisation is small compared to the other two states in contrast to what is obtained from a pure FC transition. In molecular chemi-ionisation, the difference with photoelectron spectroscopy, is recognized as a general feature and can be interpreted as a measure of the accessibility of molecular orbitals to attack by He^{*}. As briefly discussed above Ohno et al.[126] found that the relative population of the Π state increases more rapidly with the increase of collision energy than these for the Σ states. The energy shift of the PIES bands are correlated with the population, increasing in unequal way with the increase in collision energy. In He(${}^{3}S_{1}$)+N₂ the slope of the repulsive wall can be steeper for collinear reactions, favoured for the Σ states, than for perpendicular collisions, favoured for the Π state.

The ratio of PI and AI cross sections was found to be $\frac{\sigma_{AI}}{\sigma_{PI}} = 0.0013 \pm 3$ at $E_{coll} = 70$ meV[72] and falling rapidly with increasing collision energy. The rather small cross section for AI measured in energy dependent experiments let us believe that the electron energy distribution measured here corresponds essentially to the formation of the Pennning ion N₂⁺.

A comparison of the experimental results obtained for the He^{*} and Ne^{*} reaction with N₂ can be made. The experimental shifts observed for Ne(${}^{3}P_{2}$)+N₂ are in magnitude about 50% smaller than the one observed for He(${}^{3}S_{1}$)+N₂, meaning that the repulsive wall for the latter reaction has to be steeper and a greater amount of energy is converted in kinetic energy. The ionisation cross section for He(${}^{3}S_{1}$)+N₂ is smaller than the one for Ne(${}^{3}P_{2}$)+N₂, ≈8 Å² compared to ≈13.5 Å² meaning that a smaller impact parameter is driving the He^{*} reaction, leading to higher energy shifts. The high electronic excitation, in one case, and vibrational excitation, in the other, are related to the short-range nature of the interactions.

3.6.4 Ne* + H_2 and Ne* + D_2

The large majority of H_2 chemi-ionisation experiments were done with He^{*}[128–130]. The reaction evolves through PI, AI channels and also rearrangement (RI) and dissociation channels (DI). The cross section turned out to be an order of magnitude smaller than the atomic case He*+H[95] reflecting a change in the optical potential from strongly bonding to weakly repulsive. The repulsive behaviour was then confirmed by PIES experiments[131]. The ion-electron coincidence spectroscopy experiment by Munzer and Niehaus[132] showed that the AI channel coincided with electrons that leave H_2^+ in v = 0 and the RI channel with electrons that leave H_2^+ in $v \ge 4$. In fact all the electrons released when H_2^+ in v > 0 can pre-dissociate while the energy requirement for the RI reaction make it accessible only for highly excited vibrational levels. This result is accepted as one of the proofs of the two-complex mechanism with the formation of [HeH₂]* followed by ionisation. Energy dependent cross section measurements demonstrated that PI remains the dominant channel even at low collision energy[133; 134]. RI and AI becomes less important when E_{coll} is increased and DI is less important than in the photoionisation of molecular hydrogen. Many theoretical studies were also published with the idea to model the reaction mechanism[135; 136]. These studies have also been done for the isotopologues D₂ and HD.

In the case of Ne*+H₂ a lower number of experimental studies is available[137–140]. The energy dependence of the ionisation cross section is similar to the one of He*+H₂ showing an increase in the low energy side and levelling out in the higher energy side[98]. Elastic and inelastic differential cross sections were measured in a crossed molecular beams experiment by successfully distinguishing elastically and inelastically scattered products[139]. PIES measurements were conduct first by Hotop et al.[119] while Bussert et al.[138] presented a mass spectrometry experiment in a gas-cell. In a crossed molecular beams experiment Brunetti et al.[141] measured, by ion detection, the total ionisation cross section and branching ratio of Ne(${}^{3}P_{0,2}$)+H₂, D₂ and HD in energy range 0.04-0.3 eV. They concluded that PI is the dominant channel and that the RI is more efficient for the formation of NeD⁺ than for NeH⁺. For the reaction Ne*+HD the product NeD⁺ was found to be 1.5 times more abundant than NeH⁺. The optical potential they derived was then used to describe the reaction with a two steps model.

Fig. 3.28a) shows the chemi-ionisation spectrum and Fig. 3.28b) the reaction energy scheme for the PI channel of Ne(${}^{3}P_{2}$) + H₂. Only the electronic ground state, $X^{2}\Sigma_{g}^{+}$, of H₂⁺ is energetically accessible. From the energy diagram we can notice that 6 vibrational levels of H₂⁺ can be populated. The partial overlap of the peak is due to intrinsic peak broadness but also to the unfavourable S/N ratio. The small ionisation cross section, about 9 Å², and the spread of population over many vibrational levels made the signal intensity low.



Figure 3.28: $Ne({}^{3}P_{2})+H_{2}$: a) Chemi-ionisation electron spectrum. b) Reaction energy scheme.

	$\varepsilon_p - E_0(meV)$						
	v = 0	<i>v</i> = 1	<i>v</i> = 2	<i>v</i> = 3	<i>v</i> = 4	<i>v</i> = 5	
This work	+70±7	+30±7	+50±5	+50±5	+60±3	+70±2	

Table 3.11: Energy shift in $Ne({}^{3}P_{2})+H_{2}$.

Even an extremely long, about 80 hours, acquisition time of the two images presented in this section could only improve the S/N ratio moderately.

We can observe that the vibrational peaks are blue shifted, see Tab. 3.11. The shift, even though already observed in PIES experiments was never quantified. A shift about 70 meV was observed by Hotop et al. [119] for He^*+H_2 . Ne^*+H_2 is also a repulsive system with a strong similarity with the He^{*} reaction. The measured line width is \approx 130 meV. The low energy edge of the vibrational peaks near the theoretical values suggests a shallow well depth. The interaction between the metastable and the molecule and also between the ground state of Ne and the molecular ion is small and so the distance during the collision has to be large compared to the molecular equilibrium distance. The extended high kinetic energy tail of the vibrational peaks, suggests the formation of ions with kinetic energy lower than the asymptotic potential energy difference between the metastable and the Penning ion and could be interpreted as formation of a binding state. However, Brunetti et al., found the AI product and RI product (NeH⁺) to be respectively, ≈ 100 and ≈ 10 times less abundant than the PI product[141]. When the $[Ne-H_2]^+$ complex is formed with the molecular ion in a vibrationally excited state, vibrational energy can be converted into translational energy of the ions. A proof of the vibrational \rightarrow translational energy conversion comes from the measurements of the kinetic energy of the molecular products, performed by Tuffin et al.[140]. They found that H₂⁺ is formed with kinetic energy about 50 meV larger then the relative kinetic energy of the collision partners.

	v' - v'' (meV)					
Ref.	0-1	1-2	2 - 3	3 - 4	4-5	
This work	303 ± 10	236 ± 9	237±7	218±6	198±18	
Bussert et al. (PIES at 300 K)[138]	272±2	254 ± 2	241±2	229 ± 4	-	
Hotop et al. (PIES at 400 K)[119]	275 ± 10	255 ± 10	$240{\pm}10$	-	-	
Theoretical values	271.3	255.5	240.4	225.6	211.1	

Table 3.12: Energy separation between adjacent H_2^+ vibrational peaks.

Ref. v = 0v = 1v = 2v = 3v = 4v = 5This work 41 ± 12 76±10 100 ± 11 78 ± 10 58 ± 8 27 ± 6 Bussert et al. (PIES at 300 K)[138] 56 ± 3 96 ± 3 100 77±6 52 ± 12 Hotop et al. (PIES at 400 K)[119] 100 68 ± 8 93 ± 6 84 ± 6 -FCF Flannery et al. (PhES)[142] 52.1 92.0 100 87.9 68.4 50.4

Table 3.13: Relative vibrational population in Ne(${}^{3}P_{2}$)+H₂.

Tab. 3.12 lists the vibrational spacing compared with previous thermal energies measurements and theoretical values calculated as the difference between adjacent vibrational energy levels of H_2^+ . We have to consider that old experiments could not observe the vibrational level v = 5because of the high background near zero kinetic energy. A discrepancy can be noted, in fact our data are not in close agreement with the precisely known H_2^+ vibrational spacings, especially for the first two values. This would imply that the energy shift of the peaks depends on the vibrational level, in contrast to what has been previously observed. This experimental observation arises most probably from the difficulties in correctly defining the peak positions for v = 0, which appears very broad and just above the background levels, and v = 1, which has a very sharp intense feature that contrasts with the broad base.

The vibrational population of the nascent ion H_2^+ are presented in Tab. 3.13, compared with previous results[119; 138] and Franck-Condon factors[142]. The formation of the ion leads to an increase in bond length, from $r_e = 0.74$ Å to $r_e = 1.06$ Å and the vibrational progression is peaking at v = 2. The population measured in the present study are similar to FCF with a slightly higher vibrational excitation into v = 3. In fact v = 1 and v = 3 have almost the same relative population, in contrast to what has been previously observed. An inhomogeneous background level rising in the high kinetic energy range could have compromised the estimation of the population. The main differences are the values of v = 0 and v = 1 which appear to be underestimated.

Brunetti et al. observed that only v = 0 of H_2^+ is above the dissociation limit of NeH₂⁺[141]. This implies that when the complex is formed with the molecular ion in a higher vibrational level it won't be able to survive as an associative ion.



Figure 3.29: $Ne({}^{3}P_{2})+D_{2}$: a) Chemi-ionisation electron spectrum. b) Reaction energy scheme.

Always based on energetic considerations the authors suggest that the RI product NeH⁺ can be formed only for the complexes having the molecular ions in $v \ge 3$. The energy necessary to access this endoergic channel can only come from vibrational excitation.

In conclusion, the main experimental results of this study can be analysed in terms of the reaction mechanism generally accepted for the reaction. The large energy shifts observed are related with a small impact parameter, justified by the small ionisation cross section. The collision must happen on the repulsive wall near the classical turning point where the collision energy is efficiently converted into electron kinetic energy. The second step, the dissociation of the complex [Ne-H₂]⁺, is the one that determines the reaction branching ratio and it is mostly governed by vibrational excitation, that can be converted into ionic kinetic energy or used to open the RI channel. Vibrational population matches with FCF implying a small perturbation of the potential curve of the neutral by the presence of the metastable. The associative ion can be formed only in v = 0 so the vibrational population are not perturbed by PD.

The data of Ne(${}^{3}P_{2}$)+D₂ reaction can be discussed in a similar way. Fig. 3.29a) shows the chemi-ionisation spectrum and Fig. 3.29b) the energy scheme for the formation of the Penning product D₂⁺. The electronic ground states, $X^{2}\Sigma_{g}^{+}$, is the only energetically accessible and 8 vibrational levels of the nascent ion can be populated. The system is considered to be repulsive, moreover the similarity with H₂, would let us expect to see peaks shifted to higher kinetic energies. This behaviour is in fact observed for the vibrational level v = 0, 1, 2, 3, while the other peaks are shifted to lower kinetic energies, see Tab. 3.14. Measured experimental shifts were not reported in literature. The experimental line width is ≈ 110 meV. The broadness of the peaks should be considered as an evidence of conversion of vibrational energy into translational energy and not related to the formation of the associative ion. The branching ratio of the AI channel was found to be, also in this case, ≈ 100 times lower than the one of the PI channel. The RI channel, corresponding to the formation of NeD₂⁺, has a branching ratio about 10 times lower than PI[141].

	$\varepsilon_p - E_0(meV)$							
	v = 0	<i>v</i> = 1	<i>v</i> = 2	<i>v</i> = 3	<i>v</i> = 4	<i>v</i> = 5	<i>v</i> = 6	<i>v</i> = 7
This work	$+15\pm8$	$+50\pm7$	$+26\pm6$	+10±9	+10±5	-40 ± 4	-60±3	-70±1

Table 3.14: Energy shift in $Ne({}^{3}P_{2})+D_{2}$.

Table 3.15: Energy separation between adjacent D_2^+ vibrational peaks.

	$v^{'}-v^{''}(meV)$						
	0 - 1	1-2	2 - 3	3 - 4	4 - 5	5 - 6	6-7
This work	$154 {\pm} 10$	206 ± 9	178 ± 10	158 ± 10	169 ± 6	155 ± 5	122±3
Theoretical values	184	173	161	150	139	128	118

Table 3.16: Relative vibrational population in Ne(${}^{3}P_{2}$)+D₂.

Ref.	$\boldsymbol{v} = \boldsymbol{0}$	<i>v</i> = 1	<i>v</i> = 2	<i>v</i> = 3	<i>v</i> = 4	<i>v</i> = 5	<i>v</i> = 6	<i>v</i> = 7
This work	36 ± 5	84±13	100 ± 19	91 ± 17	80 ± 14	87±15	69 ± 10	9 ± 2
FCF Brunetti et al.[141]	52	92	100	87	68	50	36	25

The vibrational spacing between adjacent levels are listed in Tab.3.15 and they agree well with the theoretical values calculated as the difference between adjacent vibrational energy levels of D_2^+ . The relative vibrational population are reported in Tab. 3.16. As in the case of H_2 the vibrational progression is peaking at v = 2 and has a FC behaviour but with a small enhancement of vibrational excitation. Brunetti et al. reported the dissociation limit of the complex [Ne-D₂]⁺ at about 15.7 eV. This means the associative ion can be formed only if the molecular ion in the complex is in v = 0 or v = 1. The RI product can be formed only for molecular ions in $v \ge 4$. Comparing the results with the H_2 case we can say that the reaction proceeds through a similar mechanism, at the repulsive wall, and that the vibrational energy is efficiently converted into translational energy.

3.7 Conclusions and outlook

We presented the design of an e-VMI spectrometer and its application in the study of chemiionisation. We studied the chemi-ionisation of Kr, Ar, N₂, H₂ and D₂ by Ne^{*} and Kr, Ar, N₂ by He^{*} at $E_{coll} \approx 60$ meV in a crossed molecular beams setup.

The application of the e-VMI technique to these reactive systems has great importance in the understanding of the formation of the reaction encounter complex, [NeX]⁺ or [HeX]⁺. The electron kinetic energy distribution is not influenced by post-ionisation dynamics and reflects the energy redistribution that takes place in this reaction step.

The chemi-ionisation spectra were compared with PIES results present in literature. The most striking feature observed in the chemi-ionisation spectra is the peak shift to kinetic energies higher than the theoretical expected value ($E_0 = E(Ne/He) - IP$). This shift arises from the repulsive nature of the interaction between metastable and collision partner. The reaction happens at the repulsive wall and the excess of collision energy is converted into kinetic energy of the emitted electrons. For all the systems studied the magnitude of the measured shifts agrees well with the one measured in PIES experiments reported in literature.

The reactive systems studied are expected to evolve through PI and AI but due to the small energy difference between the ground states of the formed ions the two reaction channels were not resolved in the electron chemi-ionisation spectra. In the atomic case the analysis of the shape of the peaks observed in the spectrum, in terms of the involved potential energy curves, can lead to a rough estimation of the ratio between the PI and AI and the results obtained are coherent with published results.

In the molecular cases the analysis of the vibrational or electronic states population can give more insight on the reaction dynamics.

In the case of $Ne({}^{3}P_{2}) + N_{2}$ the observed vibrational excitation, which is in agreement with literature values, can be explained with a perturbation of the N_{2}^{+} curve by the presence of Ne^{*}. The lack of asymmetry of the peaks can be interpreted as a larger propensity for PI compared to AI. For the reaction $He({}^{3}S_{1}) + N_{2}$ the AI channel was already observed to be very small and the observed electronic state population is a reflection of the accessibility of the molecular orbitals to the attack of He^{*}.

For the reactive systems $Ne({}^{3}P_{2}) + H_{2}$ and D_{2} , the measured vibrational populations agree well with literature values. The deviation from FCF in these cases is small, meaning a small perturbation of the potential energy curves by the presence of Ne^{*}.

The results obtained can be rationalized in the terms of the, generally accepted short-range reaction mechanism.

As a prospective the collision energy dependence of the chemi-ionisation spectra can be studied. Low-collision energy can be reached performing the experiment in a merged beam configuration. However, in a merged beam experiment the collision between the beams takes place on a line, considerably complicating the achievement of focus condition of the e-VMI. A further modification of the e-VMI spectrometer will thus be required.

4 3D-Printed Merged Electric Guide

In this chapter we discuss the design of a 3D-printed merged electric guide. In the introduction we give a description of our merged beam setup. Then we review the molecular properties of ND_3 , and we present the merged electric guide simulations and design, and the preliminary experimental results to assess the guiding efficiency.

4.1 Introduction

The merged beam technique, as we discussed in Chap. 2, ensures low collision energy by reducing the crossing angle between two molecular beams. Our aim is to apply the merged beam technique to the investigation of collisions between two polar molecules. The essential requirement is the ability to guide and bend molecular beams. As discussed in Chap. 2, polar neutral molecules in lfs states can be guided in an electrostatic guide thanks to the Stark effect. In order to perform a merged beam experiment between two polar molecules, two electrostatic guides need to be combined, or a beam of polar molecules has to be inserted into an electrostatic guide. At first sight, this could be considered simple but there are some technical complications. At the edge of an electrostatic guide, in correspondence of the electrodes, the electric field has its maximum magnitude. When trying to insert a beam of polar molecules into an electrostatic guide, molecules are strongly repelled by this high field and cannot react with the guided beam.

Another possibility is to use a single Y-shaped device in which both beams are guided from the sources to the merging point. In this way, both molecular beams experience, from the beginning to end, the confining field of the guide. The merged electric guide we designed and built is a Y-shaped guide composed of two curved quadrupole guides merging to a straight hexapole. The bending required for the beam overlap is assured by the curvature of the quadrupoles. Each quadrupole has a particular S-shape, which means a double curvature with opposite concavity such that the guides initially are parallel to each other, a picture of the guide is presented in Fig. 4.1. The most challenging aspect in the design of the guide is the merging point, where the 8 cylindrical electrodes of the quadrupoles become the 6 rods of the hexapole.



Figure 4.1: 3D-printed metal coated Y-shaped guide: two quadrupoles merging in a hexapole.



Figure 4.2: Schematic representation of an inelastic scattering that promotes rotational excitation.

This means that two pairs of rods belonging to the quadrupoles must combine to form two rods of the hexapole. These geometric features, in particular the double curvature and the merging of cylindrical electrodes, imply that the guide is difficult to manufacture with traditional techniques. The 3D printing-metal coating approach developed in our group[143] allowed us to realize this innovative instrument. The guide is first 3D printed in plastic and the electrical conductivity, necessary to apply the required high voltages, is achieved by metal coating. We demonstrate the possibility to guide polar molecules in a merged 3D printed metal coated guide with the unconventional geometry described above. This represents the first step to perform the study of inelastic scattering between two state selected ND_3 molecules. The collision should lead to conversion of kinetic energy into rotational energy, similarly to what has been observed by Tkáč et al.[144] in the He+ND₃ scattering. The electrostatic guide yields a selection for the rotational states of the antisymmetric component of the ammonia inversion splitting. Collision between these selected states leads to rotational excitation. Rotational levels of both, the symmetric and the antisymmetric, components of the inversion splitting can be populated, a schematic representation of a possible transition is shown in Fig. 4.2. State selective REMPI detection can be used to reveal excitation to a rotational state, for example the 2_2 , in the symmetric inversion component.

4.2 Properties of deuterated ammonia

4.2.1 Inversion doubling of deuterated ammonia

The ammonia molecule, NH₃, and its deuterated isotopologue ND₃, are trigonal pyramids, symmetry group C_{3v}, with the three hydrogen, or deuterium, atoms forming the base and the nitrogen atom at the top[145]. The three N-D bonds are equivalent. The well known "umbrella" inversion of the ammonia arises from the double-well potential V(R) seen by the nitrogen atom along the coordinate *R* associated with the umbrella bending mode v_2 , as shown in Fig. 4.3. The coordinate *R* defines the distance of the nitrogen atom from the plane of the deuterium atoms. Each well represents the nitrogen on either side of the plane defined by the deuterium atoms. The two angles minima associated with these two positions are: $\rho = 68^{\circ}$ and $\rho = 112^{\circ}$, where ρ is the umbrella angle. The potential barrier is 2023 cm⁻¹ and it is possible for the nitrogen atom to tunnel through it, resulting in an inversion of the molecule. As a consequence of the tunnelling phenomenon, all the rovibrational levels below the energy barrier split into two levels with different energies and symmetries. We focus on the ground state vibrational level because it is the most populated at room temperature.

If we assume the potential barrier at R = 0 to be infinite the wavefunction at the barrier must go to zero. The wavefunction Ψ is located either in R > 0, described by Ψ_{up} , or in R < 0, described by Ψ_{down} . Because of the symmetry of the potential, the two wavefunctions are the same and the relative eigenstates have the same energy.

If the barrier is finite, the wavefunction in one well expands through the barrier and has a certain amplitude in the other well too. The two wavefunctions, Ψ_{up} and Ψ_{down} , represent the nitrogen atom when it is most probably localized in R > 0 or R < 0 but crossing into the other region. These wavefunctions are solution of the Schrodinger equation but they don't satisfy the requirement $\Psi(R) = \pm \Psi(-R)$. To satisfy this requirement we can form linear combinations of Ψ_{up} and Ψ_{down} [146]:

$$\Psi_a = \left(\frac{1}{\sqrt{2}}\right)(\Psi_{up} - \Psi_{down}),\tag{4.1}$$

and

$$\Psi_s = \left(\frac{1}{\sqrt{2}}\right)(\Psi_{up} + \Psi_{down}). \tag{4.2}$$

The two wavefunctions, Ψ_a , antisymmetric and Ψ_s , symmetric, are now mutually orthogonal. The energy of Ψ_s is lower than the energy of Ψ_a and the energy difference can be understood observing the evolution of the wavefunctions when lowering the potential barrier, as exemplified in Fig. 4.4. As the potential barrier decreases, Ψ_s expands in the barrier region and, in the boundary case in which the barrier goes to zero, the wavefunction is bell-shaped and represents the ground vibrational state of the system. When the barrier is lowered, Ψ_a shows a node at R = 0, which remains there also when the barrier goes to zero. Ψ_a represents, in this limit case, the first excited vibrational level. The energy levels associated with these wavefunctions go from being closely spaced to be fully separate. For ND₃ in the rotational level $J_K = 1_1$ (where J is the total angular momentum and K its projection on the symmetry axis) the energy difference, called inversion splitting, is $W_{inv} = 0.053 \text{ cm}^{-1}[147]$. The larger mass of



Figure 4.3: Double well potential experienced by the nitrogen atom in ND₃.

D compared to H, decreases the tunnelling probability and thus in the ND₃ the wavenfuctions are more similar one to the other and the inversion splitting of ND₃ is smaller compared to the one of NH₃, $W_{inv} = 0.79 \text{ cm}^{-1}$ [148]. Moreover, the vibration frequency is inversely proportional to the square root of the effective mass of vibration meaning that the zero point energy of ND₃ is lower than the one of NH₃. Therefore, the inversion barrier results higher for ND₃ than for NH₃. In the case of ND₃ the expansion of the wavefunction in the barrier region is more difficult explaining why the inversion splitting is smaller.

4.2.2 Rotational energy and rotational levels splitting

ND₃ is an oblate symmetric top molecule and the momenta of inertia *I* around the axes *a*, *b* and *c* are $I_A = I_B < I_C$. Rotations are described by the angular momentum, *J*, and its projections on the symmetry axis, *K*. In the rigid rotor assumption the rotational energy is given by

$$E_{rot} = BJ(J+1) + (C-B)(K)^2$$
(4.3)

where $B = \frac{h}{8\pi^2 c I_B}$ and $C = \frac{h}{8\pi^2 c I_C}$ are the rotational constants. The molecule exists in three nuclear spin configurations:

- A_1 for *J* odd, K = 0 and *K* multiple of 3;
- A_2 for *J* even, K = 0 and *K* multiple of 3;
- *E* for all *K* that are not multiple of 3.



Figure 4.4: Energy levels and wavefunctions as a function of the height of the barrier. a) With a finite barrier the wavefunctions have similar shape and the energy levels have similar energy. b) When the barrier is zero the wavefunctions becomes different and the energy levels separate.

The splitting of the vibrational levels due to the double well potential make the rotational levels to split into doublets (symmetric and antisymmetric component). The magnitude of the splitting, W_{inv} , depends on the rotational levels. The dependence of W_{inv} on the rotational quantum number *J* and *K* is an effect of the centrifugal distortion. Qualitatively, we can say that when the molecule is rotating mainly about the symmetry axis, the D atom are pushed outwards and the pyramid is flattened, resulting in a decrease of the potential energy barrier and thus an increase of W_{inv} . Rotations about the symmetry axis have K = J, and W_{inv} increases as K^2 . When the molecule is rotating about an axis perpendicular to the symmetry axis the pyramid is elongated and the distance between the D atoms decreases, inducing an increase of the potential energy barrier and a consequent decrease of W_{inv} . The decrease of W_{inv} will go as $[J(J+1) - K^2]$, which is the square of the angular momentum component perpendicular to the symmetry axis. The combination of these two opposite effects gives the dependence of the inversion frequency v_{inv} on the quantum numbers J, K

$$v_{inv} = v_{inv,0} - c_1 [J(J+1) - K^2] + c_2 (K)^2$$
(4.4)

where c_1 and c_1 are two positive constants with values that are empirically determinated by fitting the inversion spectrum of ND₃, and $v_{inv,0}$ is the inversion frequency of the $J_K = 1_1$ state[149]. The inversion of the state $J_K = 0_0$ is not allowed because, since the D atom is a fermion, the total wavefunction must change sign when two D atoms are interconnected. The dependence of v_{inv} and W_{inv} on the rotational state is small, and its magnitude can be neglected for the scope of our experiment. The rotational energy levels for the symmetric component are shown in Fig. 4.5 (the energy difference between the two inversion components



Figure 4.5: ND₃ rotational energy levels, J_K , up to $J_K = 3_3$.

is small, making difficult to distinguish them in the diagram).

Table 4.1: Inversion splitting and electric dipole moment of NH₃ and ND₃

	$W_{inv}(cm^{-1})$	$\mu(D)$
NH ₃	0.79	1.47
ND_3	0.053	1.50

4.2.3 Stark effect and state selection in an electrostatic guide

The first order Stark shift of ammonia in an external electric field *E* for a certain rotational state J_K , is given by

$$W(J, K, M) = \pm \sqrt{\left(\frac{W_{inv}}{2}\right)^2 + \left(\frac{MK}{J(J+1)}\mu E\right)^2}.$$
(4.5)

where W_{inv} is the inversion splitting, μ is the permanent electric dipole moment *J* and *K* are, as defined in Sec. 2.4.1, the total angular momentum and its projection on the symmetry axis, and M (-J < M < J) is the projection of the total angular momentum on the external field axis. The positive (negative) sign, in Eq. 4.5, identifies the antisymmetric (symmetric) component of the inversion splitting. The two components have different orientations with respect of the external electric field. This means that the rovibrational levels of the two components have different sign of the *M* quantum number and interact in a different manner with the electric field.

Fig. 4.6 shows the Stark energy shift for NH₃ and ND₃ in $J_K = 1_1$. The rovibrational levels from the antisymmetric component having MK < 0 are shifted to higher energies in increasing electric fields and are called low field seeker (lfs). The rovibrational levels from the symmetric component having MK > 0 are shifted to lower energies and are called high field seeker (hfs). The states with MK = 0 undergo only a very weak shift in an external field. The different



Figure 4.6: First order Stark shift energy diagram for the $J_K = 1_1$ state of ND₃ and NH₃.



Figure 4.7: Double well potential and components of the umbrella inversion of ND₃. Molecules in the lower symmetric component have only high field seeking states and molecules in the upper antisymmetric component have only low field seeking states.

magnitude of W_{inv} is responsible for the different Stark shift of NH₃ and ND₃ that can be seen in Fig. 4.6. The larger inversion splitting in NH₃ leads to a quadratic Stark shift for all levels up to large electric fields (about 10 kV/cm), in ND₃ instead the shift is nearly linear already at very low fields. The inversion splittings and the electric dipole moments of NH₃ and ND₃ are listed in Tab. 4.1. The electrostatic guide yields a state selection on ND₃. Molecules in the symmetric component, the hfs, diverge from the path along the guide and are expelled whereas molecules in the antisymmetric component, the lfs, experience a restoring force are confined inside the guide[150]. This situation is schematically shown in Fig. 4.7.

4.3 Detection method

For state selective detection of ammonia we used Resonance Enhanced Multiphoton Ionisation (REMPI)[151]. Multiple photons from a laser are used to ionise atoms or molecules through an excited state. This process increases the ionisation efficiency by orders of magnitude compared to direct ionisation. The photon energy, of a single or multiple photons, has to match the energy difference between the ground state and the excited state. We used a [2+1] REMPI scheme, as illustrated in Fig. 4.8, two photons promote the molecule to an excited electronic state and a third photon ionises the excited molecule. The photons have the same energy since they are from the same laser.



Figure 4.8: [2+1] REMPI scheme.

4.3.1 REMPI of ND₃

In the case of ND₃ the molecules are excited from the electronic ground state, \tilde{X} , to the electronically excited state, \tilde{B} and then ionised[151–153]. The symmetry of the excited state is planar, point group D_{3h}[154]. Considering the effect of the electronic degeneracy governing the transition to \tilde{B} , the rovibronic Hamiltonian H_{rve} is[151]

$$H_{rve} = T_v + BJ(J+1) + (C-B)K^2 - D_J J^2 (J+1)^2 - D_{JK}J(J+1)K^2 - D_K K^4 - 2C\zeta lK + \frac{1}{2}q((L_+^2 J_-^2 + L_-^2 J_+^2))$$
(4.6)

where T_{ν} is the energy of the vibronic state, *B* and *C* are the rotational constants, D_J , D_{JK} and D_K are the distortion parameters, and ζ is the Coriolis coupling constant. The values of the rotational constants of the states involved in the transition are summarized in Tab. 4.2. The wavefunction can be described as the product of a rotational $|JKM\rangle$ and a vibronic part $|l\rangle$. In the ground state l = 0 describes the vibronic part and in the excited state $l = \pm 1$ defines the vibronic part. The term $qL_+^2J_-^2$ couples the *l* levels and results in the *l*-type doubling. To find

a solution for the degenerate vibronic state a 2x2 matrix has to be diagonalized because the basis function $|JKM_J\rangle |-1\rangle$ and $|J(K+2)M_J\rangle |+1\rangle$ are coupled through the *q* term in Eq. 4.6.

Constant	$\widetilde{X}[155]$	$\widetilde{B}(v_2=5)[152]$	$\widetilde{B}(v_2=6)[152]$
$T_v (cm^{-1})$	$\pm W_{inv}(J,K)/2$	62993	63751
$B(cm^{-1})$	5.1426	4.4829	4.2780
<i>C</i> (<i>cm</i> ⁻¹)	3.1246	2.6949	2.6970
q (cm^{-1})	-	0.1589	0.1288
$D_J(10^{-6} \ cm^{-1})$	196.6	318	-428
$D_K(10^{-6} \ cm^{-1})$	-0.6364	789	346
$D_{JK}(10^{-6} \ cm^{-1})$	-347.94	-1209	102
ζ	-	0.8311	0.8412

Table 4.2: Rotational constants of the ground state \tilde{X} and the excited states $\tilde{B}(v_2 = 5, 6)$ of ND₃.

In view of this the energy E(J, K) is given by

$$E(J,K) = \frac{1}{2} \left[E_0'(J,K+2) + E_0(J,K) \pm \sqrt{\Delta E^2 + q^2 f(J,K)^2} \right]$$
(4.7)

where

$$\Delta E = E'_0(J, K+2) + E_0(J, K) \tag{4.8}$$

$$E_0(J,K) = T_v + BJ(J+1) + (C-B)K^2 + 2C\zeta K + \dots$$
(4.9)

$$E'_{0}(J, K+2) = T_{v} + BJ(J+1) + (C-B)(K+2)^{2} + 2C\zeta(K+2) + \dots$$
(4.10)

$$f(J,K) = \sqrt{[J(J+1) - K(K+1)][J(J+1) - (K+1)(K+2)]}.$$
(4.11)

Eq. 4.10 and Eq. 4.11 need to be extended accordingly with Eq. 4.6. The formula for the rovibrational selection rules for the two photon transition are:

$$\Delta J = 0, \pm 1, \pm 2$$
 (4.12)

$$\Delta K = \pm 1 \tag{4.13}$$

$$\Delta l = \pm 1. \tag{4.14}$$



Figure 4.9: Stark effect for ND₃, [2+1]REMPI schemes and wavelengths for detection of low and high field seeking states.

The application of the selection rules to the the vibronic transition implies that transitions must happen between vibrational levels of the ground, \tilde{X} , and the excited, \tilde{B} , electronic states with the same parity of the vibrational quantum number v_2 , because of the symmetry of this v_2 mode. Molecules in the symmetric component of the inversion doublet $\tilde{X}(s)$ can only be excited to vibrational levels $v_2 = even$ of the electronically excited state \tilde{B} . Molecules in the antisymmetric component of the inversion doublet $\tilde{X}(a)$ can only be excited to vibrational levels $v_2 = even$ of the electronically excited state \tilde{B} . Molecules in the antisymmetric component of the inversion doublet $\tilde{X}(a)$ can only be excited to vibrational levels $v_2 = odd$ of the \tilde{B} state:

$$\widetilde{B}(v_2 = even) \leftarrow \widetilde{X}(s), \tag{4.15}$$

$$\widetilde{B}(v_2 = odd) \leftarrow \widetilde{X}(a). \tag{4.16}$$

We can take advantage of the vibronic selection rules to differentiate lfs and hfs states, which in turn helps to distinguish between guided and non-guided molecules, as shown in Fig. 4.9. In fact, two vibrational transitions can be excited to selectively probe them. The non-guided, hfs, states are ionised through the transition

$$\widetilde{B}(\nu_2 = 6) \leftarrow \widetilde{X}(s) \tag{4.17}$$

and the guided, lfs, states are ionised through the transition

$$\widetilde{B}(\nu_2 = 5) \leftarrow \widetilde{X}(a). \tag{4.18}$$

4.4 Simulations

In order to get a quantitative knowledge of the trajectories of the molecules travelling through the guide and to find the best geometry, radius of curvature and length, we performed trajectory simulations.

The radius of curvature is important because, while in a straight guide all lfs states are guided independently on their forward velocity, in a curved guide molecules feel a guiding force and a centrifugal force. The centrifugal force depends on the radius of curvature and on the forward velocity (Sec. 2.4.3). They can be guided as long as the guiding force is larger than the centrifugal force and this defines the maximum guidable forward velocity (Eq. 2.40). In particular a crucial geometric aspect to analyse is the change of curvature concavity, due to the S-shape of the quadrupoles. This abrupt change may induce some transmission attenuation. A similar behaviour was already observed in storage rings for polar molecules, where the gap between the two semicircular guides creates field discontinuity and causes stop bands[156]. Another aspect is the merging point in which the shape of the electric field changes, as shown in Fig. 4.10. In a quadrupole the potential energy is linear and, if we approximate the Stark effect as linear, molecules feel a constant force towards the centre.

We developed a Fortran code that solves the equation of motion. The electric field and its gradients in *x*- and *y*- directions, inside the guide, which are necessary to calculate the confining force, are simulated with COMSOL[157]. They are saved and subsequently read and interpolated by our code. The equations of motion are written for an inertial frame of reference that moves along the centreline of the guide with a certain velocity. The Stark confining force and the centrifugal forces are considered as external forces and follow the inertial frame with the same forward velocity of the molecules. All the molecules, that during their motion through the guide, have a radial positions larger than the guide inner opening are considered ejected. The simulations are done for a quadrupole with rod of 2 mm radius and an inner opening of 2.3 mm radius. Using only a quadrupole and not simulating the merging into the hexapole is advantageous because we can consider the field constant in the forward direction. The simulation of the transition from quadrupoles to hexapole would instead require to adjust field and field gradients, accordingly with the molecules positions, in three dimensions instead of two. We can assume the merging region to a have a minor effect on the guide transmission because the zero field region is conserved.

4.4.1 Particle distributions and time step

The simulations are done using a conical distribution of velocities. The idea is to have a velocity distribution of the particles that accurately reproduces a distribution created by a supersonic expansion and a skimmer. The nozzle of the molecular beam can be approximated as a point source. At the beginning particles have a certain velocity magnitude defined by the supersonic expansion. This can be redistributed uniformly in the three velocity vector components. Only particles having a global velocity vector that geometrically fits into the



Figure 4.10: COMSOL simulated electric field norm in the merged guide at +10/-10 kV. The evolution of the electric field through the guide is shown. Electric field created by a) two separated quadrupoles, b) two approaching quadrupoles, c) a forming hexapole d) a hexapole.



Figure 4.11: Particle distributions used for the simulations: a) Initial velocity distribution. b) Initial position distribution.

conical shape of the skimmer are selected. The particle velocity distribution is shown in Fig. 4.11a).

Regarding their initial positions, particles are distributed on a circle with the radius that reproduces the radius of a real skimmer, 1.5 mm. They have zero initial forward position and a uniform distribution on the other two components. The initial position distribution of the particles is shown in Fig. 4.11b).

The sample molecule is the antisymmetric lfs inversion component of ND_3 , in different rotational states. Different applied voltages are also tested to analyse their effect on the transmission.

The optimized time step is 100 ns and it is the one used in all the simulations presented here.



Figure 4.12: a) Schematic representation of a U-shaped quadrupole guide. b) Schematic representation an S-shaped quadrupole guide.

4.4.2 Results

The effect of the concavity change on the guide transmission is investigated by comparing the simulated transmission of an S-shaped and a U-shaped guide. The two simulated guides are composed by 4 segments: a field free section, a straight segment, two curved segments. In the S-shaped guide the last two curved segments have different concavity, while in the U-shaped guide they have the same concavity, as shown in Fig. 4.12. Therefore, any difference in transmission between the two guides has to be related to the change of concavity of the S-shaped guide. The results for the lfs $J_{MK} = 1_{-1}$ of ND₃ at ±10 kV are presented in Fig. 4.13. For the the U-shaped guide the transmission decreases with increase of the forward velocity of the molecules. When molecules have forward velocity $V_x > 1600 m/s$ the guide transmission drops to zero. All the molecules for which the centrifugal force becomes larger than the guiding force have trajectories that exceed the guide inner opening radius and thus are ejected. Regarding the S-shaped guide we can say that, as in the previous case, molecules with low velocities are fully transmitted but we can observe a transmission dip around 750 m/s. At the local minimum at 684 m/s the transmission drops to 90%. This can be considered a nondestructive stop band. The electric field is continuous along the quadrupole and molecules are ejected because of the sudden change of concavity. The further attenuation of transmission for high forward velocities, compared to the U-shaped guide, also originates from the concavity change. These two effects don't cause a complete transmission loss and more than 80% transmission can be achieved for forward velocities above 800 m/s.

We then carried on simulation for an S-shaped guide to define the best radius of curvature and length. The simulated guide is composed of 5 segments: a field free section, a straight segment, two curved segments (of opposite concavity) and a final straight segment. Here we present the results for the chosen geometry: the total length of the simulated guide is 1.4 m, the radius of curvature is 9.6 m, as shown in Fig. 4.14. In Fig. 4.15a) we show the guide transmission results for different applied voltages, for the $J_{MK} = 1_{-1}$ of ND₃. In Fig. 4.15b) are shown the transmission curves for different ammonia rotational states at ±10 kV.



Figure 4.13: Transmission of the guide as a function of the forward velocity for a U-shaped and an S-shaped guide.



Figure 4.14: Schematic representation the simulated S-shaped quadrupole guide.

Higher fields lead to a larger guiding Stark force while the centrifugal force (Eq. 2.36) remains the same. Consequently, as the applied voltages increase, the maximum guidable velocity v_{max} (Eq. 2.40) increases. For applied voltages ±5 kV the transmission is zero for forward velocities around 1000 m/s. For voltages ±20 kV the transmission drops to zero only when the forward velocity is above 2000 m/s. The maximum guidable velocity depends also on the square-root of $\frac{MK}{J(J+1)}$. This results in a more efficient transmission of higher forward velocities for the state $J_{MK} = 2_{-4}$ compared to $J_{MK} = 1_{-1}$ and $J_{MK} = 2_{-2}$ [50; 51; 150]. In conclusion, the simulations allow us to say that in an S-shaped guide at ±10 kV, about 90% transmission can be observed for a pure ND₃ molecular beam, which has a velocity around

800 m/s. ND₃ can be seeded in a heavier gas to slow down the beam and observe even higher transmission.



Figure 4.15: a) Transmission of an S-shaped guide as a function of the forward velocity for $J_{MK} = 1_{-1}$ of ND₃ for different applied voltages. b) Transmission of an S-shaped guide as a function of the forward velocity for different rotational states J_{MK} of ND₃ at ±10 kV.

4.5 3D-printed metal coated Y-shaped guide

The 3D-printed Y-shaped guide is composed of 2 quadrupoles merging to a hexapole. It is made of 11 elements: a straight single quadrupole guide element (because one of the two quadrupoles is longer), 7 quadrupole curved segments, 2 merging segments and 1 fully merged hexapole segment. The rods have 2 mm radius. The inner opening of the quadrupoles has a radius of 2.3 mm and the one of the hexapole a radius of 4 mm. Overall, the guide is 1.4 m long and the radius of curvature is 9.6 m. A rendering of the merged guide is shown in Fig. 4.16. The elements are mounted on a stainless steel plate without gaps between adjacent segments. In order to ensure electric contact, the elements are also connected to each other with transformer wire insulted with ceramic beds.

The 11 pieces were 3D-printed out of polymethylmethacrylate(PMMA) (Resin Clear), in our laboratory, using a FormLabs Form 2 3D-printer. The size of the 3D printer defines the maximum length of a printed piece: about 12 cm. For this reason the guide has been partitioned in 11 pieces which were then assembled together. The printing technique is sterolithography (SLA)[158]. The vertical resolution is 25 μ m and the horizontal resolution, given by the laser spot, is specified by the producer as 140 μ m.

To create two separate and electrically isolated electrodes that have to be kept at opposite polarity the pieces were selectively electroplated, see Fig. 4.17. The coating was done by an external company (Galvotec GmbH, Switzerland) and it consists on the application of a layer of nickel, few tens of micron thick. The high quality of the surface is not ruined by some minor defects that should not alter the field distribution[143]. The smoothness of the edges should also avoid electrical breakdown[159]. Fig. 4.18 shows the fully assembled guide and an enlarged view of the merging region.

The advantage of this production technique is that essentially any shape can be 3D-printed and the metal coating offers robust, conductive elements. Moreover, the production time is greatly decreased. The printing of the guide here described took about 7 days and 10 more days were required for the metal coating.



Figure 4.16: Rendering of the merged electric guide.



Figure 4.17: One of the 3D-printed guide elements a) before and b) after the metal coating. c) Side view of a coated element. The coated and not-coated parts are separated by a dashed line. The positive and negative electrodes are electrically isolated.



Figure 4.18: 3D-printed metal coated guide: a) top view, the merging part is enlarged, b) front view.

4.6 Experimental setup



Figure 4.19: Schematic representation of the experimental setup.

A schematic representation of the experimental setup is shown in Fig. 4.19.

The 3D-printed merged guide is housed in a three-fold differentially pumped high vacuum chamber. Two supersonic molecular beam sources, placed in the first chamber staggered one to the other, produce two traslationally and rotationally cold beams that are skimmed and travel through a field free region of 1 cm before entering each of the two arms of the guide. A positive and a negative electrode of the merged guide are connected to High Voltage (HV) feedthroughs and the voltages are directly applied by two HV power supplies (FUG). The laser is aligned through the centre of the last chamber and focused, using a cylindrical lens, about 5 cm after the end of the guide. The ions are detected with a channeltron aligned with the end of the guide and positioned about 10 cm away from it. The signal is acquired by an Oscilloscope (Tektronik, series 3034) and stored by a computer.

The source chamber is pumped by a Pfeiffer TPU 1201 P (pumping speed 1200 l/s); the guide chamber by a Pfeiffer HiPace 300 (260 l/s) and a Pfeiffer HiPace 800 M (790 l/) and the detector chamber by a Pfeiffer TMU 521 YP (510 l/s). Two backing pumps are used, a Pfeiffer DUO 5M and an Edwards Dry Scroll nxDS10i. The pressure in source and guide chambers is in the low 10^{-7} mbar range and in the detector chamber in the low 10^{-8} mbar range.

The spatial overlap between the molecular and the laser beam is found by scanning the laser position and the time overlap is defined by the time delay of the molecular beam valve to time zero, defined by the laser. The timing are set using a delay generator (BNC, 577).

The laser has a frequency of 20 Hz and a pulse length of 10 ns. The molecular beams valves are operated at 10 Hz.

4.6.1 Supersonic beam sources

The ND₃ molecular beams are produced by two general valves (series 9, Parker-Hannifin corporation) and operated at a backing pressure of 2 bar.

The velocity of the beam is fixed and defined by the supersonic expansion. We use a seeded beam: 1 bar of ND₃ (99.9% in D, Sigma Aldrich) in 10 bar of Ar. The velocity of the molecular beam, defined by the supersonic expansion is $v_{ND_3/Ar} \approx 572$ m/s.

4.6.2 Laser

The second harmonic of a Nd:YAG laser (Innolas Spitlight 1000) is used to pump a tunable dye laser (Fine Adjustment Pulsare). The UV light, $\lambda \approx 317$ nm and $\lambda \approx 313$ nm, needed for the REMPI is obtained by doubling the frequency of the dye laser with a BBO crystal. The dye used in the experiment is DCIM. The power at 317 nm is about 12 mJ/pulse.

4.6.3 Detector

The detector is a channeltron (MAGNUM Electron Multiplier series 5900, Photonis). Positive ions are detected keeping the front of the channeltron at -1.7 kV and the back at ground.

4.7 Experimental Results and Discussion

4.7.1 Guide conditioning

To prepare the guide for operation, it is necessary to condition it to HV. Local field enhancement at the edges or in correspondence of small perturbations of the surface, like defects or dust pollution, can lead to extractions of electrons from the material and thus to arcing[159]. During the conditioning procedure the voltages are slowly increased in such a way to induce small and controlled arcs on the elements.

The guide is housed in vacuum and the pressure reaches the low 10^{-7} mbar range within few days signifying a good vacuum compatibility of the elements. Each of the 11 guide elements is individually conditioned. A positive and a negative electrode are connected to HV feedthroughs which are in turn directly connected to HV power supplies (Fig. 4.19), equipped with voltage and current readouts. The conditioning is done in three phases: the positive electrodes are conditioned up to +20.0/0 kV (by keeping the negative HV at 0 V); the negative electrodes are conditioned up to -16.0/0 kV (by keeping the positive HV at 0 V); finally both positive and negative voltages are applied, to the respective electrodes, up to +15.0/-10.0 kV. In each of these phases the voltages are increased by 100 V every 5 minutes, enlarging the time interval while increasing the voltages. During the single element conditioning we observe a small amount of intermittent arcs.

The same conditioning procedure is then repeated for the fully assembled guide reaching the maximum voltages +12.0/-5.0 kV. In the case of the fully assembled guide, more arcing is observed and the single arcs are also longer in time. Arcs are accompanied by pressure increase in the vacuum chamber, up to the low 10^{-5} mbar range. We observe the constant presence of a leak current. The magnitude of the leak current increases while increasing the voltages and reaches the maximum value of ≈ 0.06 mA. We also observe sudden spikes of current, above the base leak current. The current limit of the power supplies is 6 mA and frequently the current overcome this limit inducing the voltages to drop below the applied values. These phenomena are generally very short in time ($\approx 1-2$ seconds). The current then decreases and the voltages recover their initial values.

The base leak current is symmetric on the positive and negative electrodes. In addition, during the very intense spikes the current increases symmetrically on the positive and the negative electrodes. For this reasons we believe that current is flowing between the two electrodes, and not between one electrode and ground. Even though it is well known that plastic is an insulator, at very high voltages, we can observe a breakdown of the insulating property[159]. A surface current on the plastic that separates two adjacent electrodes could be the cause of the high leak current and current spikes. The larger amount of plastic surface in the full guide, compared to single pieces, explains why this phenomenon is more evident for it.

The occurrence of these effects highly reduces the stability of the guide and limits the voltages we could apply to the maximum values +11.0/-4.0 kV.

It is worth nothing that, during the conditioning and the operation of the guide, three guide elements were irreversibly damaged. Most probably an arc induced very high current on very



Figure 4.20: Guide on (+11.0/-4.0 kV) and guide off REMPI spectra for low field seeking states for the two quadrupole arms of the guide, and guide on (+11.0/-4.0 kV) and guide off REMPI spectra for high field seeking states for one of the two quadrupole arms of the guide.

small spot on the metallic surface, burning the plastic below the metal layer. The damaged pieces were substituted with new reprinted ones.

4.7.2 Guiding efficiency results and discussion

In order to show that ND_3 molecules are guided, through each quadrupole arm, we can take advantage of the vibrational level specificity of the REMPI transition, discussed in Sec. 4.3.1. Collecting spectra for two different vibronic transitions we can detect guided and not guided states[143]. Two sets of experiment are conduct:

- Guided, lfs, states are probed with the guide voltages off and on by measuring spectra for transition through the electronically excited state $\tilde{B}(v_2 = 5)$
- Not guided, hfs, states are probed with the guide voltages off and on by measuring spectra for transition through the electronically excited state $\tilde{B}(v_2 = 6)$

When the guide voltages are off, background ND₃ from the supersonic expansion is detected, in fact a portion of the molecular beam can always reach the detector chamber. When operating the molecular beam source the pressure in the detector chamber rises from the low 10^{-8} mbar to the low 10^{-6} mbar range. The left panel of Fig. 4.20 shows the guide off and on spectra of lfs states for each one of the two quadrupole arms.



Figure 4.21: a) Guide on (+11.0/-4.0 kV) experimental REMPI spectrum for low field seeker compared with PGOPHER simulation. b) Guide off experimental REMPI spectrum for low field seeker compared with PGOPHER simulation. Rotational levels of the vibrational ground state are assigned to each peaks.

The most striking feature is a clear enhancement of the signal intensity at +11.0/-4.0 kV compared to the guide off spectra. The right panel of Fig. 4.20 shows the spectra of hfs states, the experiment is done only for one of the molecular beams. The guide on REMPI spectrum doesn't contain any more signal from the hfs states[150], while background ND₃ can be detected when the guide is off. The combination of these spectroscopic observations is a convincing proof of the guiding efficiency of the 3D-printed guide. Lfs states are confined and efficiently transmitted until the end of the guide, while hfs states are attracted by the high electric field, at the edge of the guide, and therefore expelled.

The guide lfs spectra of the two molecular beams, Qudrupole 1 and Quadrupole 2 in Fig. 4.20, are not identical. The same rotational transitions are observed but with different relative intensities. This can be explained by a different rotational temperature of the supersonic beams, since they are produced by two different supersonic sources, or by a different transmission of the two quadrupoles.

Another proof of the guiding efficiency comes from the evident simplification of the lfs guide on spectrum. Rotational transitions can be assigned by comparing the experimental spectra with simulated ones, using the PGOPHER program[160]. Fig. 4.21 shows the guide on and off spectra, of Quadrupole 1, and the relative simulated spectra. Peaks are labelled according with the vibrational ground state rotational levels. The guide off spectra contains several rotational transitions. The guide on spectra reduces only to $J_K = 1_1$ and $J_K = 2_2$ transitions. In particular, comparing with the simulated spectra, we can observe that K = 0 transitions are not present in the guide on spectrum. These states experience only a weak Stark shift and, therefore are


Figure 4.22: a) REMPI signal intensity as a function of the applied voltage for the $J_K = 1_1$ transition at $\omega = 63020 \text{ cm}^{-1}$. The red coloured data point represents the signal intensity at +11.0/-4.0 kV, the voltages used to record the spectra shown above. b) Simulated guide transmission as a function of the voltage difference for ND₃ $J_{MK} = 1_{-1}$ with forward velocity $v_x = 570 \text{ m/s}$.

not guided[161].

The signal intensity as a function of the voltage difference across the guide electrodes gives the transmission curve of the guide, shown in Fig. 4.22a). The individual data points in the curve were measured by fixing the laser at $\omega = 63020$ cm⁻¹ corresponding to a $J_K = 1_1$ transition and collecting REMPI signal. We can observe that the signal intensity is almost zero when $\Delta V = 0$ kV and rapidly increases with the increase of the voltage difference. The signal intensity dependence on the electric field is in agreement to what observed when simulating the guide performance. The simulated transmission as a function of the voltage difference for ND₃ $J_{MK} = 1_{-1}$ with forward velocity $v_x = 570$ m/s is shown in Fig. 4.22b). A voltage difference at least equal to $\Delta V = 20$ kV is required to obtain 100% transmission. In the experimental transmission curve when increasing the voltage difference from $\Delta V = 15$ kV to $\Delta V = 20$ kV the signal intensity increases by a factor of two. In the simulations we can see that increasing the voltage difference from $\Delta V = 10$ kV to $\Delta V = 20$ kV the transmission increases by only 10%. This difference between simulation and experiments arises from the fact that in the simulations we approximated the Stark effect to be purely linear. The data point coloured in red in Fig. 4.22a) represents the signal intensity at the voltage difference used to acquire the spectra shown above. A further increase of voltages above this value would increase the signal intensity of the transitions observed in the spectra.

Unfortunately, as discussed in Sec. 4.7.1 we were not able to stably operate the machine above the threshold values +11.0/-4 kV because of the frequent voltage drops associated to the high intensity current spikes. A part from the risk of damaging the elements, frequent voltages drops mean that molecules don't experience, even if just for a short time, a confining electric field and any guiding experiment, in this condition, would be misleading.

We have to make clear that the guide became less stable over time. At the very beginning of

our experiments we could more easily apply very high voltages but after few months of use we were not even able to reach, in a stable way, the voltages used in the present experiment. The high current spikes and voltage drops became more frequent and eventually, neither voltage or current, would recover the original value. Even though we prove here that ND₃ molecules are guided the stability of the guide deteriorated in an irreversible way and we were not able to reproduce the results here presented and even less to conduct the ND₃+ND₃ inelastic collision experiment originally planned.

The fact that over time we observed high current intensity at lower voltages supports the theory of surfaces currents on the plastic. The longer voltages are applied the more surface current paths open and once a new path is open current will keep flowing through it, independently on the applied voltage.

4.8 Conclusions and outlook

We presented the design and building procedure of Y-shaped merged electric guide to study polar-polar low collision energy scattering processes. The most remarkable novelty is the building procedure itself. The guide has been designed and 3D-printed in plastic, in our laboratory, and then metal coated. Despite the successful demonstration of this technique for the 3D-printed beam splitter[143], the realization of the guide has implied, unexpected, complications in the achievement of the operation conditions, that hindered the project development. The production procedure followed for the two devices, guide and beam splitter, was the same. The main difference, that could have be the cause of the different behaviour, is the more complicated structure of the guide. The latter is longer and composed of more elements than the beam splitter. The only other dissimilarity is the use of two different versions of printing resin. In fact, between the realization of the beam splitter and the guide, the 3D-printer company released a new version of the resin which we decided to use for the guide. We don't know the exact chemical composition of the resin, because it is patent protected, but we believe that a modification of the composition could have contributed to the misbehaviour of the guide upon application of HV. We have to exclude that the cause is the coating because it has been performed in the same way for the beam splitter and the guide.

The experimental results presented, confirmed the possibility to guide neutral polar molecules in a 3D-printed metal coated electric guide. These preliminary results are just the first accomplishment, since our final goal remains the investigation of low energy scattering between two polar neutral molecules.

One of the experiments originally planned was the inelastic scattering $ND_3 + ND_3$ which we were not able to perform because of the unreliable functioning of the merged guide. There are two advantages that make this experiment suitable to demonstrate dipolar collision in merged beam: the use of two ND_3 molecular beams which simplifies the guiding and the well-known state selective detection of ND_3 .

More fascinating, even though more difficult to implement, is the idea to study reactive scattering. A good candidate is the highly exothermic HNO+OH reaction, that has been mainly studied in combustion flames experiments[162; 163]. The H atom abstraction that leads to H_2O+NO has no-energy barrier to the entrance channel[164], being suitable for merged beam experiments. HNO has a dipole moment of 1.67 D and its Stark shift has been reported[165]; OH has also a dipole moment of 1.67 D[166; 167]. The reaction product NO can be detected through a 1+1 REMPI scheme.

The realization of a scattering experiment, such as the ones here described, requires high stability of the experimental setup, especially of the electrostatic guide. The scattering probability is expected to be extremely low and a long acquisition time would be required to be able to detect scattering events. The current setup will probably require few modifications in order to be able to hold up HV for a long time. The conditioning procedure can be repeated in order to reach higher voltages and in a more stable way; the plastic surface between adjacent electrodes with opposite polarity can be modified increasing the path length of possible surface currents. In the worst case these changes won't give satisfactory results, it is also possible to decrease the length of the guide since it is has been observed a more reliable behaviour for single, short elements.

5 Conclusions

In this thesis, we presented the realization of two new experimental tools for low collision energy scattering studies.

The first is an e-VMI spectrometer we developed aiming to take a close look into the chemiionisation process. The use of electron imaging offers the advantage to directly observe the first reaction step, where electrons are released. The electron energies distributions can be used to recover information about the encounter collision complex and about the energy redistribution that accompanies the products formation.

The simulations and design of the e-VMI spectrometer has been presented within the results of the study of chemi-ionisation of atoms and small molecules. We studied reactions of metastable Ne with Kr, Ar, N₂, H₂ and D₂ and of metastable He with Kr, Ar, and N₂. The results obtained were compared with the literature and rationalized in term of the accepted reaction mechanisms. A general characteristic of the electron energy distributions was the peaks shift to high kinetic energies. The electrons gained some of the asymptotic collision energy because of the repulsive nature of the interaction between the metastable and the neutral. In the case of atomic collision partner the analysis of the shape of the electron energy distributions enabled us to estimate the ratio between PI and AI. The results, which have to be considered a rough estimation, because the two reaction channels are not resolved in the spectra, are in agreement with the literature. In the case of molecular collision partners the internal state population was related to the redistribution of energy taking place when the complex is formed and gave a confirmation of the expected reaction mechanisms. Chemiionisation of molecular nitrogen by either Ne* and He* provoked, respectively, vibrational and electronic excitation of the forming ions. The internal states excitation compared to FCF was interpreted as an indication of the perturbation of the potential energy surface of ionic nitrogen by the presence of the metastable. Internal state excitation is also a characteristic of a short-range interactions, which preferentially lead to PI. In agreement with this remark we noticed that, the measured spectra didn't contain any evidence of AI, meaning that this reaction channel has low probability to happen. Chemi-ionisation of H_2 and D_2 by Ne^{*} led to vibrational populations in agreement with FCF suggesting that the potential energy curves

were not perturbed by the presence of Ne^{*}. The recorded spectra did not show clear evidences of AI, which is expected to be very low for these reactive systems. The observed red-shift of the electron energies was understood as an effect of the conversion of vibrational energy into translational energy.

The results discussed showed that the use of an e-VMI spectrometer can undercover a large amount of information about the chemi-ionisation reaction mechanism.

The second tool is a 3D-printed merged electric guide. In the cold and ultracold field the exploration of the long-range dipolar collisions remains a challenge because of the difficulties in creating cold polar molecules, even though many studies have been conduct in the last few years. We simulated, designed and built a merged electric guide which can be used to study scattering process between polar molecules in a molecular beam experiment. Low collision energy is achieved by the reduction of the collision angle and doesn't require the reactants cooling. The characteristic Y-shape of the merged guide in which two quadrupoles were combined in a hexapole implied a difficult realization with traditional technique therefore the guide was 3D-printed in plastic and then metal coated. We demonstrated that ND₃ molecules are guided in a Y-shaped 3D-printed metal coated guide and that the transmission agrees well with the simulations. The production of the guide in plastic caused some difficulties in the application of HV, required to efficiently confine and transmit polar molecules. We found that the application of very HV, above +11.0/-4.0 kV, provokes a breakdown of the insulator properties of plastic and surface currents develop on the plastic between adjacent electrodes. The occurrence of surface currents led to high instability of the applied voltages and we were not able to pursue the study of inelastic scattering ND₃+ND₃.

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Curriculum Vitae

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