Chapter 2

Coincidence Imaging and Pulsed Molecular Beams

The detection and in particular imaging of charged particles is the underlying principle of the photoelectron-photoion coincidence imaging machine that is used in all the experiments described in this thesis. Before the photoelectron-photoion coincidence apparatus is described in section 2.2.1, a short review of the developments in charged particle imaging is given. Subsequently, the calibration of the electron and the ion detector is discussed. Finally, the molecular beam and in particular the implementation of a cantilever piezo valve is described in detail in section 2.4.
Chapter 2

2.1 Introduction

For a good to complete understanding of many problems in molecular dynamics, e.g. molecular reactions, photoionization and photodissociation processes, the measurement of the momentum of the participating particles is required. In other words it requires the simultaneous measurement of the speed as well as the angular direction of the particles. In 1979 Chandler and Houston developed a technique to measure the initial momentum distribution of recoiling ions from a photodissociation experiment, the so-called ion imaging technique\(^1\). First the initial three-dimensional momentum distribution of the recoiling ions is projected onto a two-dimensional detector. Afterwards a mathematical recovery procedure (for example Abel inversion\(^2,3\)) is used to reconstruct the initial 3D-momentum distribution from the measured 2D ion image. The first disadvantage of the described experimental setup is the combination of the two-dimensional detector and the accompanying recovery procedure, because it requires that the initial momentum distribution had cylindrical symmetry and that projection was done in a direction perpendicular to that symmetry axis. Several techniques have been developed over time to circumvent this problem, starting with time-slice imaging\(^2,4–7\) and 3D-detectors (e.g. delay-line detector\(^8\) and Timepix\(^9\)). Since the central slice of the 3D-momentum distributions (containing the center of the sphere and symmetry axis, e.g. laser polarisation or k-vector) essentially contains the entire angular distribution information. This slice when rotated through 2pi about the symmetry axis reproduces the entire 3D-Newton sphere of the photoelectrons. This method of slicing through the center of the 3D-momentum distribution also works when there are two or more velocity distributions nested one inside the other, due to various ionization channels and appearance energies. While Abel inversion has to incorporate the projection of these nested spheres onto the same 2D-plane and then resolve the nested distributions, a central time slice through the concentric Newton spheres easily shows all the channels and their velocity distributions. In time-slice imaging, the detector is gated, while the 3D-detectors are able to directly measure the full 3D-coordinates of each event. The second limitation of the ion imaging technique is blurring of the imaging which limits the achievable resolution. The blurring of the image is a consequence of having dissociation processes taking place at different locations in the interaction region. This problem was solved by Eppink and Parker in 1997, who
invented the velocity map imaging technique (VMI)\textsuperscript{10}.

In VMI, a three plate assembly of open electrodes (called repellor, extractor and ground plate) is used to image the momentum of the particle onto the detector. The interaction region of the laser and molecular beam is in the centre in between the repellor and extractor plate. The voltage on the extractor plate is set to approximately 70-80\% of the repellor plate and the ground plate is set to zero. Hence, the charged particles are extracted and accelerated towards the ground plate and subsequently enter a field-free time-of-flight (TOF) tube towards the detector. The open electrodes create curved electric field lines in the acceleration region and these curved lines act as a lens which focuses the charged particles with similar momentum to a common point on the detector regardless of the position where the charged particles are formed. The mass of the charged particle can be retrieved from the TOF. An example of a VMI-image is shown in Fig. 2.1. The 3D-momentum distribution contained 4 different velocity components, which are mapped onto different positions of the detector. Because the 3D-distribution is projected onto a two-dimensional surface, each velocity component appear as a partially filled-in circle. The size of the rings is proportional to the speed and not the kinetic energy. Although the distance between the two outer rings is smaller than the distance between the two inner rings, the difference in kinetic energy is almost the same.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{vmi_image.png}
\caption{A) An illustration of a VMI-image containing 4 different velocity components. Note that the size of the rings is proportional to the speed and not the energy of the imaged particle. Panel B) shows the speed profile along the molecular beam direction and the corresponding kinetic energy distribution is shown in panel C).}
\end{figure}
The first electron imaging machine was developed in the group of Helm\textsuperscript{11,12}. This apparatus was the first electron detector that did not only measure the electron kinetic energy, but also measured the angle of the each electron.

Studying molecular dynamics using lasers to excite and ionize molecules yields an electron and an ion. Both particles contain information about the dynamics and therefore detection of only the electrons or the ions will irrefutably result in loss of information about the process. Photoelectron-photoion coincidence (PEPICO) techniques have been successfully employed for slightly more than forty years\textsuperscript{13,14}. However, the first photoelectron-photoion coincidence imaging apparatus to detect the momentum of both the electron and the ion simultaneously was demonstrated by Hayden \textit{et al.}\textsuperscript{15,16}. They investigated the dissociation dynamics in NO\textsubscript{2} with femtosecond time resolution using photoelectron-photoion coincidence imaging. In the same period another coincidence imaging technique called cold-target ion-recoil momentum spectroscopy (COLTRIMS) was demonstrated successfully\textsuperscript{17}. The really new thing about COLTRIMS was that delay-line detectors were used to directly obtain the full-3D momentum information of each electron and ion.

### 2.2 Photoelectron-Photoion Coincidence Imaging Apparatus

#### 2.2.1 Vacuum Apparatus

The coincidence imaging apparatus has been presented in detail previously\textsuperscript{18,19}. The machine consists of three differentially pumped UHV chambers, a source chamber, a buffer chamber, and the imaging chamber, see Fig. 2.2. The three chambers are pumped by magnetically levitated turbo molecular pumps, which are backed by an oil-free roots pump (Alcatel ATH 1300 MT). The source chamber is pumped by a 1250 l/s (Alcatel ACP28G). The source chamber is pumped by a 1250 l/s (Alcatel ACP28G). The source chamber is pumped by a 1250 l/s (Alcatel ACP28G). The source chamber is pumped by a 1250 l/s (Alcatel ACP28G). The source chamber is pumped by a 1250 l/s (Alcatel ACP28G). The source chamber is pumped by a 1250 l/s (Alcatel ACP28G). The source chamber is pumped by a 1250 l/s (Alcatel ACP28G). The source chamber is pumped by a 1250 l/s (Alcatel ACP28G). The source chamber is pumped by a 1250 l/s (Alcatel ACP28G). The source chamber is pumped by a 1250 l/s (Alcatel ACP28G). The source chamber is pumped by a 1250 l/s (Alcatel ACP28G). The source chamber is pumped by a 1250 l/s (Alcatel ACP28G).
Figure 2.2: left) Schematic overview (not on scale) of the photoelectron-photoion coincidence imaging machine for femtosecond experiments in a molecular beam. The apparatus consists of three differentially pumped chambers: source chamber (a), buffer chamber (b) and detection chamber (c). The chambers are pumped by 3 magnetically levitated turbo pumps with speeds of 1250 l/s (I), 400 l/s (II) and 2100 l/s (III), respectively. The pulsed molecular beam (red arrow), produced by a cantilever piezo valve\textsuperscript{20,21} is intersected by the laser pulse (green arrow) in the interaction region between charged particle lenses. Photoelectrons and photoions are extracted towards the detectors by switching the voltages on the charged particle lenses. right) On scale overview of the detector unit consisting of the VMI optics, electron and ion time-of-flight tube and the 2 detectors.

To use higher backing pressures. The piezo valve can operate both in pulsed mode and continuous mode and the gas was expanded through a nozzle with a diameter of 200 \( \mu \)m into the source chamber. Further downstream, the molecular beam is doubly skimmed. The first skimmer (d=1 mm) separates the source from the buffer chamber and is located about 2 cm after the nozzle. The second skimmer (d=200 \( \mu \)m) separates the buffer from the imaging chamber and is positioned approximately 12 cm after the first skimmer.

The molecular beam is intersected by the femtosecond laser pulses about 45 cm downstream of the nozzle. A lens (f=30-50 cm) focuses the femtosecond laser pulses down to a beam waist (Gaussian, FWHM) of approximately 100 \( \mu \)m in diameter. Light baffles are used at the entrance and exit ports of the laser beam to reduce the amount of scattered light reaching the detector.
Chapter 2

2.2.2 Ion and Electron Detection

Following the laser pulse excitation of the molecules, the electron and ion detection occurs on two separate TOF detectors in a velocity map geometry\textsuperscript{10}. In order to have optimal voltages and extraction field strength for both electrons and ions we operate the charged particle lenses numbers 1-4 in Fig. 2.3A) in a pulsed mode at the repetition rate of the laser system. The schematic of the operation is shown in Fig. 2.3.

Figure 2.3: A) Schematic overview of the charged particle lenses and the TOF tubes for photoelectron-photoion velocity map coincidence imaging apparatus. The molecular beam is intersected by the laser pulses in the interaction region between charged particle lenses. Photoelectrons and photoions are extracted by switching the voltages on the charged particle lenses. B) Schematic of the voltage conditions of a charged particle lens for electron and ion extraction. Before the laser interaction, the voltages are set to electron extraction mode \( V_1 = 0 \text{ V}, V_2 = -525 \text{ V}, V_3 = -385 \text{ V}, V_4 = -270 \text{ V} \) and electrons are detected in the first 200 ns after the laser interaction. Thereafter, the voltages are switched in about 50-70 ns (Behlke HV switches) to detect ionic fragments. After 25 \( \mu \text{s} \), sufficiently long after all masses of interest have reached the detector, the voltages are switched back in about 10 \( \mu \text{s} \) to the values for electron detection. All switching is at the repetition rate of the laser system (1 kHz in the present example). C) The accumulated signal over 100 ms of the delay line detectors as seen on an oscilloscope for multi-photon ionization of CF\(_3\)I. The arrival of the electron, the ringing due to the high voltage switching and the arrival of various ions are clearly visible.

Before the laser interaction, the voltages are set to electron extraction mode \( V_1 = 0 \text{ V}, V_2 = -525 \text{ V}, V_3 = -385 \text{ V}, V_4 = -270 \text{ V} \) and electrons are detected in the first 200 ns after the laser interaction. Thereafter, the voltages are switched in about 50-70 ns (Behlke HV switches)
to detect ionic fragments. The ions need significant impact energy \((\geq 1000 \text{ eV})\) to be detected by the MCP with high efficiency\(^{22}\). Therefore the voltages are typically switched to \(V_1 = +750 \text{ V}, V_2 = +1500 \text{ V}, V_3 = +2000 \text{ V}, V_4 = -270 \text{ V}\). After 20-30 \(\mu\text{s}\), sufficiently long after all masses of interest have reached the detector, the voltages are switched back in about 10 \(\mu\text{s}\) to the values for electron extraction mode. Thus when the next laser pulse arrives the setup is ready for electron detection. The switching of the charged particle lenses causes ringing on the delay-line detector, indicated in Fig. 2.3C. However, this does not interfere with the experiment as its time of occurrence (between 0.2 and 1.5 \(\mu\text{s}\)) is after the electron hit and before the arrival of most ions. These settings enable the detection of electrons with kinetic energy up to 3 eV and ions with a kinetic energy up to 2 eV. A more elaborate description of the whole operation is given in chapter 5 and in Ref. 18.

Each detector consists of a chevron micro-channel plate (MCP) assembly (Photonics, 40 mm active diameter, 5 \(\mu\text{m}\) pore size) backed by a position and time sensitive particle delay line detectors (Roentdek, large anode DLD-40X\(^8\)). The delay line detector, schematically shown in Fig. 2.4, consists of two wires; one for the \(x\)-coordinate and one for the \(y\)-coordinate. The delay line detector records both the arrival time and the angle resolved position of the particle. A detailed report on the operation of the delay line detector can be found here\(^{18,23}\).

In short, when a charged particle hits the MCP, it induces an avalanche of electrons in the MCP pore which results in an electron cloud exiting the MCP. This electron cloud is accelerated towards the delay line detector where it hits the wires of the delay line at a certain position. The induced signal travels to the ends of the wires where it is collected and processed by a differential amplifier (Roentdek, ATR-19\(^8\)), followed by a commercial 8-channel TDC, short for time-to-digital converter (Roentdek, HPTDC\(^8\)).

The time difference between the two signals pulses at the end of each wire is proportional to the position on the detector. For example, hitting the detector like indicated in Fig. 2.4 will lead to a huge time difference in the \(y\)-coordinate, while the time-difference in the other wire will be approximately zero. Regardless of where the electron cloud hits the delay line detector, the time sum of the two signals pulses of each coordinate delay-line wire is the constant \((x_1+x_2 = y_1+y_2 = \text{constant})\). However, the signal processing is triggered by the laser, and therefore the time difference of the trigger time and the time sum is a direct measurement.
of the flight time of the particles and can be used to determine the TOF of the ions.

The time-to-digital converter has a resolution of $25 \text{ ps}^8$. The position on the delay line can be calculated using the time to position factor of $1.9 \text{ ns/mm}$. To measure the TOF of the electrons with higher accuracy, the arrival time of the MCP pick-up pulse is coupled to a time-to-analogue converter (Becker & Hickl, SPC-130$^{24}$). The time-to-analogue converter can be considered as a linear voltage ramp generator, which is started by the MCP pick-up signal. Once started, the ramp voltage increases linearly until it is stopped with an experimental trigger pulse from a fast photodiode. The signal is only processed when both the start and the stop pulse arrive inside the measurement window; in other words the time-to-analogue converter is only triggered in case of an event. The measurement window is typically set to $3.34 \text{ ns}$ and in this window the arrival time of the electrons is determined with a resolution of $(3.34 \text{ ns}/4096=) 0.8 \text{ ps}$. Applying our typical electron imaging voltages, the maximum difference in arrival time for electrons with kinetic energy of $E_{\text{kin}} = 0.5 \text{ eV}$ is about $600 \text{ ps}$. This difference increases to approximately $1.2 \text{ ns}$ for photoelectrons with kinetic energy of $2 \text{ eV}$.

The photoelectron angular distribution can be directly extracted from the full electron velocity sphere without Abel inversion by slicing the sphere. This is illustrated in Fig. 2.5. This is possible due to sub-picosecond resolution in measuring the electron arrival times. The electrons arriving in the central time-slice (containing the center of the sphere and symmetry axis, e.g. laser polarisation or k-vector) essentially contains the entire angular distribution information. This method of slicing through the center also works when there are two or more velocity distributions nested one inside the other due to various ionization channels and appearance energies. While Abel inversion has to incorporate the projection of these nested spheres onto the same 2D-plane and then resolve the nested distributions, the central time-slice shows all the velocity distributions and their angular distributions.

While a simple slicing strategy is to take all electrons events between $t_c-\delta t$ and $t_c+\delta t$, it can however cause more events in the central part than at the outer radius as the solid angle subtended by electrons at the outer radius is smaller than those closer to center. As a consequence, the central part could be more intense than it actually is. To avoid this problem and to preserve the solid angle of scattering in such a slicing scheme, we chose to slice in terms of angle of ejection.
Figure 2.4: left) Detector unit consisting of the MCP and under the MCP the delay line detector. right) Schematic representation of the delay line detector. The electron cloud exiting of the back of the MCP hits the delay line and subsequently pulses of electrons will travel to the 4 ends of the wires. The position in the x,y-plane is determined by the time difference between the pulses at the end of each wire; i.e. \( x = x_1 - x_2 \) and \( y = y_1 - y_2 \). The time-of-flight of the event is given by the time sum \( t = x_1 + x_2 = y_1 + y_2 \) with respect to a starting trigger.

Figure 2.5: The principle of time-slicing. The top row shows a measured 3D-momentum distribution in the plane parallel to the detector, the bottom row shows the same distribution in a plane perpendicular to the detector. From left-to-right: non-sliced image, time-sliced image (60°), time-sliced image (10°). The velocity distribution gets sharper as the time-slice is reduced. This is a consequence of the projection of a 3D-distribution onto a 2D-surface.
In other words, the procedure of 'time slicing' is actually 'solid angle slicing' - again facilitated by the superior time resolution of the electron recording.

The best obtainable resolutions of the coincidence imaging machine are $\Delta E/E = 3.5\%$ for electrons and $\Delta m/m = 2 \cdot \Delta t/t = 1/2000$ for ions\textsuperscript{18}.

### 2.2.3 Coincidence Imaging on a single detector

Recently, we have reported on a new simplified setup for velocity map photoelectron-photoion coincidence imaging using only a single particle detector\textsuperscript{25}. In this setup both photoelectrons and photoions are extracted towards the same micro-channel-plate delay line detector by fast switching of the high voltages on the ion optics. This single detector setup retains essentially all the features of a standard two-detector coincidence imaging setup viz. the high spatial resolution for electron and ion imaging, while only slightly decreasing the ion TOF mass resolution. The setup is described in details in chapter 5.

### 2.3 Calibration of the electron and the ion detector

To obtain the 3D-momentum of a charged particle, the electron and ion detector have to be calibrated. After laser ionization, energy conservation dictates that the produced charged particle(s) can have a maximum value for the sum of the kinetic energy of the electron and the atomic fragments, according to

$$n \cdot E_{\text{photon}} - E_{\text{Appearance}} = E_{k,\text{ion}} + E_{k,\text{neutral}} + E_{k,\text{el}} + E_{\text{internal}}$$  (2.1)

#### 2.3.1 Calibration of electron detector

The simplest method to calibrate the electron detector is to ionize Xe atoms at 400 nm and near 520 nm. The obtained photoelectron images and the corresponding kinetic energy spectra are shown in Fig. 2.6. For this ionization, Eq 2.1 simplifies to
Figure 2.6: Single color ionization of Xe atoms at 400 nm (top) and 520 nm (bottom). The photoelectron image (left) and the corresponding kinetic energy distribution (right).

\[ n \cdot E_{\text{photon}} - E_{\text{Appearance}} \approx E_{k,\text{el}} \]  

and the kinetic energy of the photoelectron equals the total photon energy minus the ionization energy. The simplicity of the calibration relies on the spin-orbit coupled ionic states of Xe(\(2P_{3/2}\)) and Xe(\(2P_{1/2}\)), which are separated by 1.31 eV in energy.

Multiphoton ionization of Xe near 520 nm yields 4 photoelectron peaks; two peaks result from 6-photon ionization, whereas the two higher energy peaks are coming from 7-photon ionization. For both processes the distance between the peaks is exactly 1.31 eV and therefore this spectrum is perfectly suitable to calibrate the electron detector. Four-photon ionization at 400 nm results in photoelectrons with 0.27 eV kinetic energy and this peak is used to check the previous calibration. The experimentally observed Full-Width-Half-Maximum (FWHM) of the electron peak is 42 meV for the multi-photon excitation process at 400 nm, while it is 233 meV for the excitation process near 520 nm. This difference is explained by the typical bandwidth of the femtosecond laser pulses, which is about 19 meV at 400 nm and 91 meV at 520 nm. Due to the finite width of the femtosecond laser pulses, the expected widths are FWHM.
\[
\sqrt{(4 \cdot 19^2)} = 38 \text{ meV} \quad \text{and} \quad \text{FWHM} = \sqrt{(6 \cdot 91^2)} = 223 \text{ meV}
\]
for the multi-photon excitation at 400 nm and near 520 nm, respectively.

### 2.3.2 Calibration of ion detector

The calibration of the ion detector is slightly more complicated. Multi-photon excitation of an atom will not be sufficient, because the produced ions will have zero kinetic energy. Therefore a molecule has to be used and as a consequence Eq 2.1 can not be simplified and \( E_{k,\text{ion}} \), \( E_{k,\text{neutral}} \) and \( E_{\text{internal}} \) have to be measured. However, in a photon-induced dissociative ionization process, conservation of linear momentum determines that the ionic and neutral fragment have an equal momentum but opposite direction, i.e. \( m_i v_i = -m_n v_n \). The total kinetic energy of this process can be expressed as

\[
E_{k,\text{total}} = E_{k,\text{ion}} + E_{k,\text{neutral}} = \frac{1}{2} m_i v_i^2 + \frac{1}{2} m_n v_n^2 = \frac{1}{2} m_i v_i^2 \cdot (1 + \frac{m_i}{m_n}) \tag{2.3}
\]

Under the assumption that the internal energy can be neglected, i.e. all the excess is converted into kinetic energy, Eq 2.1 can be rewritten to

\[
n \cdot E_{\text{photon}} - E_{\text{Appearance}} - E_{k,\text{el}} \approx E_{k,\text{total}} = \frac{1}{2} m_i v_i^2 \cdot (1 + \frac{m_i}{m_n}) \tag{2.4}
\]

where \( v_i \) is the only unknown quantity and can be measured by the ion detector. The delay line detector measures the full three-dimensional momentum distribution of the ion, that is the position in the plane of the detector (x- and y-direction) and the TOF (z-direction). The measured coordinates are a projection of the velocity vectors \((v_x, v_y, v_z)\) in the lab frame, see Fig. 2.7. The following relation is used to convert the lab frame coordinates into the momentum coordinates

\[
v_x = c_x \cdot x \quad \quad v_y = c_y \cdot y \quad \quad v_z = c_z \cdot \Delta t \tag{2.5}
\]

where \( \Delta t = \text{TOF}_{\text{measured}} - t_{\text{offset}} \) represents the initial velocity of the ion parallel to the TOF direction and \( t_{\text{offset}} \) is the mean TOF of the ion. All lab frame coordinates are proportional to the mass of the ion, the
initial velocity parallel to the coordinate direction and the inverse of the extraction field (E).

\[ x \propto \frac{mv_x}{qE} \quad \quad y \propto \frac{mv_y}{qE} \quad \quad \Delta t \propto \frac{mv_z}{qE} \] (2.6)

**Figure 2.7:** Schematic overview of the fragment detection. An ion fragment with initial momentum (v) is formed at the interaction region. The momentum in the plane of the detector (v<sub>x</sub> and v<sub>y</sub>) is projected on the detector (x- and y-coordinate) by velocity map imaging. The momentum parallel to the time-of-flight direction (v<sub>z</sub>) is transferred into a small time difference (\(\Delta t\)) with respect to the mean time-of-flight (\(t_0\)) of the ion fragment. The lab frame coordinates (x, y and \(\Delta t\)) are used to extract the initial momentum coordinates (v<sub>x</sub>, v<sub>y</sub> and v<sub>z</sub>).

**Figure 2.8:** Photoelectron-photoion energy correlation plot for the non-scaled ion detector (left) and using a scaling vector (right) to match the ion kinetic energy to the maximum available energy of the dissociation process (green line).
In order to obtain the correct velocity vector, the values of $c_x$, $c_y$ and $c_z$ have to be determined. The application of the velocity map condition dictates $c_x = c_y$. Since the image should be spherical, the value of $c_z$ can be empirically chosen to yield $v_{x,max} = v_{y,max} = v_{z,max}$. The resulting coordinates are still given in TDC units and have to be converted into units of energy, for example eV. This can be done by plotting the energy correlation plot, wherein the kinetic energy of the electron is displayed as a function of the kinetic energy of the coincident ion. The maximum excess energy of a given process yields a diagonal line in the correlation plot. Presuming that the electron detector is already calibrated, the ion detector can be calibrated by multiplying $v_{ion,max}$ with a scaling vector, see Fig. 2.8. For example, single-color 400 nm photodissociation can be used to calibrate the ion detector.

## 2.4 Molecular Beam: Continuous vs. Pulsed Expansion

A homebuilt high-repetition rate (up to 5 kHz) cantilever piezo valve has been incorporated into the coincidence imaging machine. The details of the valve have been discussed in full elsewhere\textsuperscript{20,21}. The incorporation of the piezo valve allows the use of a continuous beam or a pulsed beam. The utilization of pulsed molecular beams can strongly reduce the pumping requirements of the experimental apparatus. Moreover, an increase in the number density, narrowing of the velocity distribution and cooling of the internal state distribution in the gas pulse can be achieved using pulsed molecular beams\textsuperscript{26–31}.

Some of these consequences (for example internal temperature, speed ratio etc) of working with a pulsed beam are discussed in this section. First the influence of the carrier gas on the ion yield and ion resolution will be discussed, followed by the influence of the backing pressure.

### 2.4.1 Carrier gas: Gas pulse duration

The influence of the carrier gas on the total ion yield as a function of the time delay between the drive pulse of the piezo and the crossing time of the femtosecond laser pulse with the gas pulse is presented in Fig. 2.9 and Table 2.1.
The curves show the total ion yield measured in single-color 400 nm ionization of 2% NO seeded in different carrier gases: Argon, Neon and Helium, respectively. Each point is obtained by measuring the amount of NO ions inside a well defined area of the detector during 10,000 laser shots. For each measurement the opening time of the piezo cantilever valve was kept at 25 µs, the backing pressure at 3 bar and the distance from the piezo valve to the interaction region was 45 cm. The opening time of the piezo valve with respect to the laser beam was scanned in steps of 5 µs. As can be seen from Fig. 2.9 and Table 2.1 the carrier gas changes the flow velocity of the gas pulse and the spread of the gas pulse in time. The spread of the gas pulse increases with increasing mass of the carrier gas, while the flow velocity of the gas pulse decreases with increasing mass of the carrier gas. The smaller spread at higher speed of the gas pulse is an indication of a decrease in internal temperature of the gas mixture. The amount of NO-clusters was non-existing to negligible for seeding in Argon as well as Neon. However, for seeding in Helium at 3 bar backing pressure, approximately 1.5% of the total ion yield was corresponding to \((\text{NO})_2^+\). To obtain gas mixtures with low internal energy while avoiding clusters seeding with Neon is preferred for our coincidence imaging machine.

### 2.4.2 Backing Pressure: Speed ratio

Fig. 2.10 shows the ion images of a seeded beam of 1.4% Xe in Ne measured for a continuous expansion at 1 bar backing pressure and pulsed expansion (1 kHz) at backing pressures of 4 and 7 bar. The images were measured at the top of the gas pulse distribution of time. In each case, an area of 7.36x7.36 mm² around the position where the Xe⁺ ion hits the delay line detector was selected. The displacement of the ion image with respect to the background image together with the fitted Full-Width-Half-Maximum (FWHM) distribution along the laser and molecular beam direction are given in Table 2.2.

As can clearly be observed, the continuous beam has a much more elongated spot along the molecular beam direction compared to the pulsed expansions. This shows directly that the pulsed molecular beams have a more narrow velocity distribution. The distribution along the laser direction is independent of the expansion mode and is determined by the laser focus and the diameter of skimmers that skim the molecular beam before it enters the detection chamber.
Table 2.1: The maxima and Full-Width-Half-Maximum (FWHM) distribution of the gas pulses as shown in Fig. 2.9 together with the calculated flow velocity of the gas pulse. The distance from the piezo valve to the interaction region is 45 cm.

<table>
<thead>
<tr>
<th></th>
<th>$t_{max}$ (µs)</th>
<th>FWHM (µs)</th>
<th>$v$ (m/s)</th>
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<tbody>
<tr>
<td>2% NO in Ar</td>
<td>853.6</td>
<td>269.6</td>
<td>542.9</td>
</tr>
<tr>
<td>2% NO in Ne</td>
<td>570.1</td>
<td>105.5</td>
<td>789.3</td>
</tr>
<tr>
<td>2% NO in He</td>
<td>299.6</td>
<td>44.4</td>
<td>1502.0</td>
</tr>
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Figure 2.9: The total ion yield, measured in single-color 400 nm ionization of 2% NO in different carrier gases: Argon (black), Neon (red) and Helium (yellow) respectively. The backing pressure of the piezo valve was set to 3 bar for all carrier gases. Each point is obtained by measuring the amount of NO$^+$-ions inside a well defined area of the detector during 10,000 laser shots. The dots display the measured data points, the solid line is a Gaussian fit. For each measurement the opening time of the piezo cantilever valve was kept at 25 µs. The opening time of the piezo valve with respect to the laser beam is displayed on the x-axis. A higher Piezo Valve - Laser delay corresponds to a lower flow velocity of the molecular beam. The distance from the piezo valve to the interaction region is 45 cm. The spread of the gas pulse increases with increasing mass of the carrier gas, while the flow velocity of the gas pulse decreases with increasing mass of the carrier gas. More details can be found in Table 2.1.

Furthermore, the pulsed molecular beams have a higher flow velocity than the continuous beam as can be seen from the shifts of the center of the ion spots in Table 2.2. The speed ratio (S) of the gas beams can be calculated according to $^{30,32}$
\[
\frac{dV}{dv} = 2\sqrt{\ln 2} \cdot \frac{x}{dx}
\]

(2.7)

where \( v \) is the flow velocity, \( dv \) the FWHM distribution in the direction of the molecular beam, \( x \) the displacement and \( dx \) the FWHM of the molecular beam in the direction of the molecular beam.

The speed ratio is linked to the final translational parallel temperature for a three-dimensional expansion of an ideal gas\textsuperscript{31,32} by

\[
T = T_0 \cdot \left(1 + \frac{2}{5}S^2\right)^{-1}
\]

(2.8)

where \( T_0 \) is the stagnation temperature at the piezo valve and is assumed to be 298 K. The best speed ratio of 29.0 is obtained for the pulsed beam at 7 bar backing pressure, which corresponds to a velocity distribution with a velocity spread of \( dv/v = 6.2\% \). The measured speed ratio of the pulsed expansion at 4 bar is 28.4, while the continuous beam only achieves a speed ratio of 8.8, which is a factor of 3.5 worse than the speed ratio measured for the pulsed expansions. The final translational temperature for the pulsed molecular beams is 0.9 K and this is one order of magnitude lower than for the continuous expansion.

Recapitulating, the pulsed expansion narrows the velocity distribution and cools the internal state distribution better than in the continuous expansion. Moreover the pulsed expansion reduces the gas consumption during the experiments and allows the use of lighter carrier gases and/or higher backing pressures without overloading the turbo pumps.

**Table 2.2:** Presentation of the displacement of the ion image with respect to the background ion image \((x)\), the FWHM of the distribution along the molecular beam and the laser beam direction, the speed ratio and the translational temperature of the three ion images shown in Fig. 2.10. The speed ratio and translational temperature are calculated using Eq 2.7 and Eq 2.8, respectively.

<table>
<thead>
<tr>
<th></th>
<th>( x )</th>
<th>FWHM\textsubscript{mol}</th>
<th>FWHM\textsubscript{laser}</th>
<th>Speed ratio</th>
<th>Temp (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Continuous, 1 Bar</td>
<td>8.27</td>
<td>1.564</td>
<td>0.940</td>
<td>8.8</td>
<td>9.4</td>
</tr>
<tr>
<td>Pulsed, 4 Bar</td>
<td>9.27</td>
<td>0.544</td>
<td>1.053</td>
<td>28.4</td>
<td>0.9</td>
</tr>
<tr>
<td>Pulsed, 7 Bar</td>
<td>9.24</td>
<td>0.530</td>
<td>1.050</td>
<td>29.0</td>
<td>0.9</td>
</tr>
</tbody>
</table>
Figure 2.10: Ion images and their distributions along the molecular beam and laser directions of a seeded beam of 1.4% Xe in Ne measured for a continuous expansion at 1 bar backing pressure (black curve) and pulsed expansion at backing pressures of 4 bar (red curve) and 7 bar (yellow curve). A detector region of 7.36mmx7.36mm is selected for each ion image. For representation purpose the ion images have been displaced in the horizontal as well as in the vertical direction. For each of the three ion images the displacement of the ion image with respect to the background ion image, the fitted distributions, the speed ratio and the translational temperature is given in Table 2.2.
References