Non-adiabatic losses in traveling-wave Stark deceleration
Particle trajectory simulation

Bachelor thesis

MARK BUISMAN
Research conducted at the Van Swinderen Institute
Under the supervision of Prof. dr. Steven Hoekstra & Dr. ir. Hans Beijers

Physics
UNIVERSITY OF GRONINGEN
Groningen, The Netherlands, July 5, 2017
Abstract
Traveling-wave Stark deceleration is a wonderful tool to slow down polar molecules. Once the molecules are slowed down, the molecules can be interrogated by means of spectroscopy and information can be extracted which might lead to new discoveries. Before that can happen, the deceleration process needs to be optimized and losses such as non-adiabatic transitions must be minimized. A computer simulation can help to assist, predict and analyze particle behaviour. The simulation which was previously developed has been extended with a new non-adiabatic transition mechanism based on energy difference between energy states. With the new loss mechanism in place, results have shown that the losses can have a great impact on the spatial particle distribution within the confinement zone.
Contents

1 Introduction 3
1.1 The Standard Model ........................................ 6
1.2 Matter-antimatter asymmetry .................................. 6
1.3 Violation of PT symmetry ...................................... 6
1.4 Motivation .................................................. 7

2 Theory 9
2.1 Rotational energy levels ...................................... 9
2.2 Degeneracy in energy levels ................................... 11
2.3 Stark-effect .................................................. 12
2.4 High-field and low-field seekers ............................. 14
2.5 After confinement ............................................. 14
2.6 Non-adiabatic transitions ..................................... 15

3 Simulation 17
3.1 The source distribution ....................................... 17
3.2 Time-of-flight profiles ........................................ 19
  3.2.1 Central peak ............................................. 20
  3.2.2 Distribution of arriving molecules ....................... 22
3.3 Properties of non-adiabatically lost molecules ............. 24
  3.3.1 Termination velocities .................................. 24
  3.3.2 Termination positions .................................. 25
  3.3.3 Starting velocities ....................................... 26
  3.3.4 Starting position ......................................... 27
  3.3.5 Termination energy difference ......................... 28
3.4 Counts per voltage amplitude .................................. 29
3.5 Counts per transition probability ............................ 30
3.6 Within the ‘danger zone’ .................................... 31
  3.6.1 Energy difference between rotational states .......... 31
  3.6.2 Electric field strength ................................. 32

4 Conclusion 33

5 Dankwoord 35

A Simulation manual 37
  A.1 Getting the simulation to work ............................ 37
  A.2 Changes and additions made ............................... 38
    A.2.1 Non-adiabatic transition mechanism .................. 39
  A.3 Peregrine high-performance cluster ....................... 40

References 43
1 Introduction

Nature supplies us with molecules of many different geometries and properties. If a molecule has on one side of the geometry negative charge and on the opposing side positive charge, the molecule forms two poles and is called a ‘polar molecule’. Two opposing charges that are spatially separated will form an electric dipole moment. In the case of polar molecules, this electric dipole moment is permanent and is subject to many ingenious applications in particle physics.

One of these applications is the guidance of polar molecules in a traveling wave potential. By exploiting the effect (Stark-effect) of an external electric field in the proximity of the polar molecule, the molecule can be ‘played’ with. The traveling-wave Stark decelerator deployed at the Van Swinderen Institute takes advantage of this and is able to guide, decelerate and accelerate strontium monofluoride (SrF) [1].

The Stark decelerator is a 4.5 meter long device that uses sets of ring-shaped electrodes to generate modulated electric fields. The modulation sequence is controlled in such a way that the gradient of the electric fields create three-dimensional potential wells that confine molecules both radially and longitudinally [2].

![Figure 1.1: The geometry of the setup create ‘wells’ of electric field minima to travel along the longitudinal direction. The color gradient indicates the electric field strength. The minimas are an important region as discussed in section 2.4](image)

In order to fill the potential wells, polar molecules need to be created. A solid tablet of strontium is targeted by a powerful laser. This happens in the presence of a sulfur hexafluoride gas (SF₆). The chemical reactions that occur during this process are responsible for the formation of polar strontium monofluoride. Pumps are used to insert the SrF gas into the decelerator region, where the electric fields will start to confine (or ‘trap’) the molecules. The process can be compared to a conveyor belt where goods are transported from A to B, only without the use of electric fields.
1. Introduction

Figure 1.2: An overview of the Stark decelerator and described processes. The skimmer makes sure that the ingoing package is trimmed. The valve opens when insertion of gas is required. At the end of the trajectory, the molecules are probed by a laser which induces fluorescence (excitement of the electronic state which releases photons upon relaxation to ground state). The intensity of photons is detected. From this a molecule count can be derived with appropriate timings. [1]

To be eligible for confinement, the molecule must be in the right quantum state (‘mood’). The right quantum state we refer to as the ‘low-field seeking (LFS)’ state. In the Stark decelerator it is of utmost importance for the molecules to remain in the low-field seeking state, as it is the state which is easy to focus throughout the decelerator [3]. If the molecule undergoes a quantum transition, and the transition leaves the molecule in an unwanted (high-field seeking) state, it will no longer be suited for confinement.

Transition of states happen all the time: before, during and after operation of the Stark decelerator. We are mainly interested in the transitions during guidance. It is of great interest to study these transitions so that they can be accounted for and possibly minimized. One cause of losses within the Stark-decelerator are the ‘non-adiabatic’ transitions, or sometimes referred to as ‘non-adiabatic spin-flips’. The word ‘adiabatic’ comes from the Greek word ‘adiabatos’ and stands for ‘passable; able to be passed through’ [4]. To maximize the amount of molecules that reach the end of the deceleration trajectory, we require the molecules to follow the changing field direction adiabatically. Unfortunately this is not always the case and a non-adiabatic transition takes place along the way.

A non-adiabatic loss typically happens within close proximity of the trap center, where the electric field strength is at its lowest. To make the analogy intuitive, imagine the electric dipole moment of the molecule as a vector. The vector points in the direction of the region where the electric field strength is at a minimum.

When the molecule gets too close to the trap center, and starts precessing at a high frequency, change of vector direction becomes very rapid. It can be said that the direction of the vector can not follow adiabatically. When this happens, the molecule is likely to transition into a high-field seeking state. This thesis will mainly be dedicated to the study of non-adiabatic losses, the added non-adiabatic loss mechanism...
to the simulation code, and the observations that result from the new simulations. Besides that, we will look at the bigger picture: what can be done with decelerated molecules, the Standard Model in physics and consequences of symmetry violations.

Figure 1.3: The trap region. The (electric dipole) vector points towards the center.
The Standard Model

The Standard Model is the physicists holy book. It is a model that has been pieced together for over 70 years, describing 3 fundamental forces (electromagnetic-, strong- and the weak force) and classification of all known elementary particles. However, the Standard Model is far from perfect and has some deficiencies: it fails to explain the origin of mass, the strong CP problem, neutrino oscillations, matter-antimatter asymmetry and the nature of dark matter and dark energy.

Matter-antimatter asymmetry

During very early stages of the universe, approximately $10^{-43}$ seconds after the Big Bang, particles and anti-particles were alive in equal proportion. In cosmology, this stage is referred to as the ‘Grand Unification Epoch (GUT)’. Three out of the four fundamental forces were unified as the electronuclear force.

When the temperature of the universe has lowered from $10^{32}$K to $10^{15}$K, approximately $10^{-10}$ seconds after the Big Bang, the electromagnetic and weak force are no longer unified and separate (‘Quark epoch’). After separation, quarks and anti-quarks start annihilating. A little later, most anti-matter has disappeared, with exception of the anti-matter locked up in mesons. Visible matter however, is still present. How could this have happened, when anti-matter and matter were present in equal proportion? Nature seems to give clear preference to keep visible matter and reject anti-matter. The Standard Model predicts that anti-matter and matter should have canceled each other out, leaving only energy.

The clear matter-antimatter asymmetry that we observe poses a mystery that needs to be solved. The violation of symmetry in P (parity)[5] and and CP (charge conjugation parity)[6] invariance were hints that matter-antimatter asymmetry may have been created dynamically by baryogenesis from a matter-antimatter symmetric initial state [7]. Bottom line, symmetries seem to break left and right.

Violation of PT symmetry

According to time-reversal (T) symmetry, all the known laws of physics must remain intact when time is reversed. Since it has already been shown that C, P and CP symmetry are being violated[5][6], it would not be a surprise if T symmetry is also violated. To find out, many precision measurements are being carried out. One of them being the search for a non-zero electric dipole moment (EDM) (i.e electron EDM).

In the ideal case, we can imagine the electron as a round billiard ball of negative charge. A tiny bump of extra charge is expected to be on top of the ball, if this is indeed the case, it would imply violation of T-symmetry.
1. Introduction

Figure 1.4: The electron (or billiard ball) with the electric dipole moment visualized as the grey vector pointing upwards. The black arrow indicates in which direction the electron spins. When time is reversed, this direction of spin is opposite and the bump of extra charge is still on the same pole. Since there is only one type of electron in the universe, one of these representations must not exist. This would imply that T-symmetry is broken since nature prefers one over the other [8].

It requires extreme precision to find this bump as it is at most $10^{-38}$ e cm [9] (electron charge centimeters). If we were to increase the size of the electron to the size of the solar system, the electron would be approximately the size of a grain of rice. Current experiments are not sensitive to probe the electron at this order of magnitude, but we are surely approaching it. A recent experiment at the University of Colorado has placed an upper bound on the eEDM of $10^{-28}$ e cm. This was obtained through electron spin resonance spectroscopy on hafnium monofluoride [10].

All in all beautiful prospects for the future, but before we are able to probe the eEDM, molecules must have been slowed down which brings us to battling the non-adiabatic losses in the deceleration process.

Motivation

On 30 September 2016, the Cold Molecule research group at the Van Swinderen institute published their report on deceleration of SrF molecules. They had successfully slowed down a supersonic beam of SrF to forward velocities of 120 m/s [1]. However, slight discrepancies were present between simulation and experimental results, as quoted:

“There are some slight but noticeable differences between simulations and experimental results that can be attributed to the systematic effects and mechanisms that are not included in the simulation code, which are: valve temperature stability during the measurements, imperfections of the waveforms, possible non-adiabatic losses or parametric heating mechanisms.”

To discover the effects and quantify the losses that are attributed to non-adiabatic transitions, the simulation required an additional loss mechanism.
1. Introduction
2

Theory

Rotational energy levels

A heteronuclear molecule has the molecular Hamiltonian $H_{mol}$. The molecular Hamiltonian is unperturbed in the case of no external electric/magnetic fields. This means that the energy levels are degenerate and only affected by the Coulomb interactions ($H_c$) between electrons and nuclei.

$$H_{mol} = H_c$$  \hspace{1cm} (2.1)

If we treat the molecule as a rigid rotor (a body that does not distort under the stress of rotation), the rotational energy levels can be extracted by solving the Schrödinger equation. However, using a classical approach, there is a much shorter way to get access to these energy levels:

The classical expression for the energy of a rotating body around an arbitrary axis ‘a’ is:

$$E_a = \frac{1}{2} I_a \omega_a^2$$  \hspace{1cm} (2.2)

where $\omega_a$ is the angular velocity and $I_a$ the moment of inertia about axis ‘a’.

If we then have a body which is free to rotate about three axes (x,y,z), the energy becomes:

$$E = \frac{1}{2} I_a \omega_a^2 + \frac{1}{2} I_b \omega_b^2 + \frac{1}{2} I_c \omega_c^2$$  \hspace{1cm} (2.3)

![Figure 2.1: A rigid rotator ($H_2O$) with three axes. About every axis there is a moment of inertia.](image)

The classical expression for angular momentum is $J_a = I_a \omega_a$. Plugging this into equation 2.3, we obtain:

$$E = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c}$$  \hspace{1cm} (2.4)
For linear rotor, the angular momentum around the principal axis is zero since rotation only occurs about an axis perpendicular to the array of atoms. Taking axis ‘c’ to be the principal axis, we can get rid of one term by setting $J_c = 0$. The moment of inertia of the remaining axes (‘a’ and ‘b’) are equal to each other due to symmetry ($I_a = I_b = I$). Applying these changes to eq. 2.4, we get:

$$E = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} = \frac{J_a^2 + J_b^2}{2I} = \frac{J^2}{2I}$$

We can now make the leap to the quantum mechanical expression by substituting in the quantized total angular momentum expression ($J^2 \rightarrow J(J + 1)\hbar^2$) where $\hbar$ is the reduced Planck constant:

$$E = J(J + 1)\frac{\hbar^2}{2I}$$

From eq. 2.6 we can find the final rotational energy levels of a linear rigid rotator. However, we cannot oversee that the angular momentum has a component ($M_j$) on the external laboratory fixed axis. Likewise, this component is also quantized and takes on values $M_j\hbar$ with permitted $M_j = 0, \pm 1, ..., \pm J$, leading to a total of $(2J + 1)$ values (see fig. 2.3). Later we will see that this component plays a crucial role when external electric fields come into play.

**Figure 2.2:** The total angular momentum ($J$) consists of the component $M_j$. In this figure, different permitted values of $M_j$ are shown and their effect on $J$ (a, b and c).

Given $J$ and $M_j$, we can fully specify the molecular state and the associated energy level(s). When a photon with sufficient energy is absorbed by the molecule, it can induce a transition of an electron. The transitions follow the selection rules which are specified as follows:

$$\Delta J = \pm 1 \quad \Delta M_j = 0, \pm 1$$

A transition with $\Delta J = +1$ corresponds to absorption and $\Delta J = -1$ to emission of a photon (with sufficient energy). The permitted values of $M_j$ and $J$ do not just pop up from thin air but arise from conservation of angular momentum.
Degeneracy in energy levels

Symmetry properties of a molecule cause degeneracy in energy levels, this is because the Hamiltonian is unperturbed and still invariant under a group of symmetry transformations. The energy levels seem to ‘stack’ up and are hardly distinguishable. To define degeneracy, we write in Dirac notation [11]:

\[ H_{mol} |E^{(0)}\rangle = E^{(0)} |E^{(0)}\rangle \]  \hspace{1cm} (2.8)

and the invariance of \( H_{mol} \) can be expressed by

\[ [H_{mol}, U(g)] = 0 \]  \hspace{1cm} (2.9)

where \( U(g) \) is an arbitrary unitary operator induced in the space of quantum mechanical states by a physical transformation ‘g’ (change to the symmetry). It can be said if above equation holds, that the operator ‘commutes’ with the Hamiltonian. Because of invariance of \( H_{mol} \), we get:

\[ H_{mol} (U(g) |E^{(0)}\rangle) = U(g) H_{mol} |E^{(0)}\rangle = U(g) E^{(0)} |E^{(0)}\rangle = E^{(0)} (U(g) |E^{(0)}\rangle) \]  \hspace{1cm} (2.10)

Again, \( U(g) |E^{(0)}\rangle \) is an eigenstate of \( H_{mol} \) with the same energy eigenvalue. If there are multiple energy eigenstates, but with identical energy eigenvalues, we call the levels ‘degenerate’. If there is only a single energy eigenstate (with one set of quantum numbers), it leads to one energy eigenvalue, which is ‘non-degenerate’. In all cases, the eigenstates must differ as imposed by the ‘Pauli Exclusion Principle’:

"Two or more identical fermions (particles with half-integer spin) cannot occupy
the same quantum state within a quantum system simultaneously."

In the degenerate case, the degeneracy can be broken by introducing an additional interaction which does not respect the symmetry of the molecule. With the additional interaction being the external electric field. We introduce the Stark effect, which is accompanied by the Stark Hamiltonian ‘\( H_s \).

**Stark-effect**

Since the molecular Hamiltonian (eq. 2.1) is now perturbed, we add the additional term ‘\( H_s \):

\[
H_{\text{mol}} = H_c + H_s \tag{2.11}
\]

When an external electric field (\( E \)) is switched on, electrons and nuclei in the molecule will experience a force \( F = qE \). In the case of a uniform electric field pointing from left to right, the electrons (negative charge) will be pulled to the left and the nuclei (positive charge) to the right. This will break the symmetry and cause energy levels to shift. To see to what extent this affects the energy levels, we need to look at the Stark Hamiltonian:

\[
H_s = -d \vec{E} = -d \vec{E} \cdot \hat{z} = -E d \cos \theta \tag{2.12}
\]

where \( d \) is the electric dipole moment and \( \theta \) the angle between the electric dipole vector and z-axis.

Using perturbation theory (chapter 6 in [12]), we can find first and second-order Stark shifts. The first-order Stark shift is:

\[
E_{J,M_j}^{(1)} = \langle H_s \rangle = - \langle \vec{d} \rangle \vec{E} \tag{2.13}
\]

In the case of SrF, the first-order Stark shift vanishes because of parity symmetry [12].

Next up, the quadratic Stark shift. From the second-order non-degenerate perturbation (also treated in [12]) we find:

\[
E_{J,M_j}^{(2)} = \sum_{J' = J \pm 1} \left| \frac{\langle J',M_j | H_s | J,M_j \rangle}{E_{J,M_j} - J'(J' - 1)} \right|^2 \tag{2.14}
\]

Substituting in eq. 2.6 for \( E_{J,M_j} \) and writing out \( H_s \), we obtain:

\[
E_{J,M_j}^{(2)} = \frac{\xi^2 d^2}{\hbar^2 / 2I} \sum_{J' = J \pm 1} \left| \frac{\langle J',M_j | \cos \theta | J,M_j \rangle}{J(J + 1) - J'(J' - 1)} \right|^2 \tag{2.15}
\]

Using the Clebsch-Gordan coefficients [12] for the two cases \( J' = J \pm 1 \) we solve \( \langle J',M_j | \cos \theta | J,M_j \rangle \) and arrive at the second-order energies:

\[
E_{J,M_j}^{(2)} = \xi^2 d^2 \left\{ \begin{array}{ll}
\frac{1}{2} \left[ \frac{(J-M_j)(J+M_j)}{J(J-1)(2J+1)} - \frac{(J-M_j+1)(J+M_j+1)}{J(J+1)(2J+1)(2J+3)} \right], & \text{if } J \geq 1 \\
-\frac{1}{6}, & \text{if } J = 0
\end{array} \right. \]

12
From above equation, we obtain the following energies for states \((J = 1, M = 0)\) and \((J = 1, M = 1)\), respectively. Important to notice are the opposite signs, which play an important role in classifying low and high-field seeking states.

\[
E_{1,0}^{(2)} = \frac{\mathcal{E}^2 d^2}{5\hbar^2 / I} \quad E_{1,1}^{(2)} = -\frac{\mathcal{E}^2 d^2}{10\hbar^2 / I}
\]  

(2.16)

The perturbation theory is an excellent tool to solve for the energy in the low-field strength region, in the higher-field region, not so much.

When we want to solve for the higher-field region \((E_{J,M_j}^{(2)} \gg E)\), we require full diagonalization of the Hamiltonian in order to solve the Schrödinger equation. This can be done by truncating the Hamiltonian, and finally diagonalizing by means of a numerical method. The energies resulting from this calculation are shown in fig. 2.4 (taken from [12]):

**Figure 2.4:** The energy levels in the high-field strength region of the electric field \((^2\Sigma\) state). The labels indicate the total angular momentum \(J\) and component \(M_j\), respectively.
High-field and low-field seekers

In an electric field, the molecule experiences a force (see fig. 2.5):

\[
F_s = -\nabla E_{J,M,J} \mathcal{E}
\]  

(2.17)

Using the energies we obtained in eq. 2.16, and plugging into above equation, we find two very useful properties of the states. Molecules in the (1,0) state, having a positive Stark shift, will feel a force towards the region where electric field strength is low. These molecules are called low-field seekers (LFS). On the other hand, molecules in the (1,1) states will experience a force away from the low-field region, towards the high-field. These are called high-field seekers (HFS). In general, any state which has a positive Stark shift could be identified as low-field seeking, and vice versa. From fig. 2.4, it can be seen that a (2,0) state would also be suited as a low-field seeking state.

Thus, by making smart use of electric fields, we can confine the molecules.

After confinement

The geometry the ring-modules has been set up in such a way that three-dimensional potential wells form. In these wells, electric field minima are present where the low-field seekers are looking for. Many of the molecules that have entered these wells, will remain in there, unless a loss occurs.

**Figure 2.5:** The molecule with longitudinal velocity \(v_{\text{molecule}}\) is trapped within the potential well. It experiences a force \(F_s\) towards the center of the trap where the strength of the electric field is at its lowest. Within the trap, the relative velocity of the molecule is \(v_{\text{relative}} = v_{\text{molecule}} - v_{\text{trap}}\). Figure taken from [12].

While the low-field seeking molecules are confined, they can be subtly ‘driven’ into submission by regulating the electric fields along the decelerator.
2. Theory

By regulating the electric-fields, or to be precise, the voltage on each consecutive ring/electrode, the potential-wells (or conveyor belt) can be decelerated, accelerated or guided. Guided means that neither acceleration nor deceleration occurs, but the well velocity remains constant. In total there are 4 modules, each containing a 2 sets of 168 electrodes. The 8 sets of electrodes are connected to 8 power amplifiers capable of amplifying ingoing voltage up to 5 kV. Per period of 8 rings, 2 potential wells can form [12].

If we move along in the inertial frame of reference of one potential well, the molecule will orbit around the trap center, this can be seen in fig. 2.6. The orbits depend on the initial position and momentum of the molecule when it enters the trap. Using the second law of Newton we find for the equations of motion [13]

\[
\begin{align*}
\frac{dx}{dt} &= v_x \\
\frac{dy}{dt} &= v_y \\
\frac{dz}{dt} &= v_z
\end{align*}
\]

\[
\begin{align*}
\frac{d^2x}{dt^2} &= -\frac{1}{m} \nabla E_E_x \\
\frac{d^2y}{dt^2} &= -\frac{1}{m} \nabla E_E_y \\
\frac{d^2z}{dt^2} &= -\frac{1}{m} \nabla E_E_z
\end{align*}
\] (2.19)

**Non-adiabatic transitions**

The molecules confined will have their electric dipole moment oriented by the electric field. The electric field minima will lead, and the dipole moment follows. In most cases they will remain in the same quantum state and adiabatically follow the minimum of the field as it travels along the longitudinal axis.

In some cases however, there exists a probability that the dipole moment can not follow adiabatically. When we define \( \vec{r} \) as the distance of the molecule to the field minima, it can be seen that the angular velocity (\( \vec{w} \)) increases drastically:

\[
\vec{w} = \frac{\vec{r} \times \vec{v}}{||\vec{r}||^2}
\] (2.20)

As the angular velocity increases, the change in orientation of the electric dipole moment will become very rapid. When the rate of change, given by \( \frac{v}{r} \), becomes larger than the energy splitting \( \Delta E \) between states, a non-adiabatic transition can occur [14].

\[
\frac{v}{r} > \Delta E \quad \text{‘Non-adiabatic transition condition’}
\]
Figure 2.6: Traces of 12 molecule orbits inside the inertial frame. Every subplot represents a molecule with different initial position and a non-zero angular momentum.
3
Simulation

The simulation that was previously developed [13][15] is capable of simulating particle trajectories in an electric potential. With the expansion of the new non-adiabatic transition mechanism, additional results have been produced. These will be explored in this section. The relevant simulation parameters are included in the figure captions.

The source distribution

After the laser ablation and expansion phase, the molecules temporarily exist in a cloud which we call the ‘source distribution’. The source distribution has very distinct properties which have a strong influence on the simulated time-of-flight profiles [13]. Attempts have been made to tweak the distribution to match the experimental parameters as close as possible. The positions and velocities have been drawn from a normal distribution and consist of:

- A longitudinal velocity (z) of 345 m/s with a FWHM of 6%
- A transverse velocity ranging from -2 to 2 m/s (truncated)
- A longitudinal position ranging from -3 to 3 mm (truncated)
- A transverse position ranging from -2 to 2 mm (truncated)

These properties apply to all simulation runs. Figures 3.1 and 3.2 show how these distributions look like.
3. Simulation

**Figure 3.1:** Heatmap of the initial distribution

![Heatmap](image1)

**Figure 3.2:** Histogram of the initial distribution

![Histograms](image2)
3. Simulation

**Time-of-flight profiles**

At the time of arrival in the detection chamber, the detection laser induces fluorescence in the molecule and the photons are detected by a photomultiplier tube. This signal is recorded and time of flight spectra can be made. In the simulation a distance is set, after which, when crossed by the molecule, will invoke a time reading. By accumulating a large amount of time readings, a histogram can be made which indicates how large the population of molecules is at the arrival time \( t_a \). A comparison has been made between experimental and simulation data which is shown in fig. 3.3.

![Figure 3.3](image)

**Figure 3.3**: Comparison between experimental and simulated time-of-flight profile of 500 000 molecules at \( V_0 = 4500\text{V} \) and a transition probability of 2%/dt. The central peak boundaries indicate the area in which the non-adiabatic effects can be studied.
Central peak

The central peak manifests itself within the indicated boundaries on fig. 3.3. The time of flight profiles are a good indicator for the study of non-adiabatic losses. When the non-adiabatic losses come into play, the internal structure of the central peak changes significantly, as shown in figure 3.4.

![Figure 3.4](image)

**Figure 3.4:** The change of internal structure due to non-adiabatic losses. Initial amount of $10^6$ molecules, voltage amplitude 4500V. A transition probability of 0% means that the mechanism is disabled and no non-adiabatic losses occur.
Increasing transition probability

When the transition probability per integration time-step is increased \( \frac{dt}{dt} \), the ‘well’ in the central peak steepens. This is a consequence of the transition mechanism favoring molecules with certain velocities as shown in fig. 3.8.

**Figure 3.5:** Change of internal structure as a function of increasing transition probability.
Distribution of arriving molecules

At the end of the trajectory the positions of the molecules are recorded. A heatmap of the spatial distribution is plotted in figure 3.6. This shows that when the loss mechanism is enabled, the losses occur mainly near the center of the trap, as predicted by theory (see section 2.6).

![Figure 3.6: A heatmap of the positions of 40000 accepted molecules. The positions were recorded at the end of the trajectory. The transition probability was set at 2%/dt. Red color indicates a high population, blue a low population.](image)

When the loss mechanism is disabled, the spatial distribution returns to a coherent shape (fig. 3.7).
**Figure 3.7:** A heatmap of the positions of 40000 accepted molecules. The positions were recorded at the end of the trajectory. The loss mechanism was disabled. Red color indicates a high population, blue a low population.
Properties of non-adiabatically lost molecules

The properties of molecules at the point of rejection are shown here.

Termination velocities

The ‘last known’ velocities before the loss mechanism has rejected the molecule are shown here. In the central packet, the mechanism has a clear preference to reject molecules with velocities of $345 \pm 1 \text{ m/s}$.

![Velocity distribution](image)

**Figure 3.8:** The termination velocities of 25000 molecules which were lost due to a non-adiabatic transition.
3. Simulation

**Termination positions**

The ‘last known’ positions of the molecules are shown here. The area covered can be defined as the ‘danger zone’ where most molecules are liquidated from the central packet. The positions at liquidation point are uniformly distributed over the ‘danger zone’. The area shows boundaries of 0.5 mm longitudinally and 1 mm in the transverse direction.

![Spatial distribution](image)

**Figure 3.9:** The termination positions of 25000 molecules which were lost due to a non-adiabatic transition.
3. Simulation

Starting velocities

The velocities of the lost molecules which they initially started with (close after laser ablation) are shown in fig. 3.10. The distribution resembles a Gaussian which is expected.

Figure 3.10: The starting velocities of 25000 non-adiabatically lost molecules.
Starting position

The starting positions of the non-adiabatically lost molecules (fig. 3.11) show no strange behavior.

Figure 3.11: The starting positions of 25000 molecules which were lost due to a non-adiabatic transition.
3. Simulation

Termination energy difference

The energy difference between the (1,0) and (1,1) state play an important role in the probability of a molecule transitioning. The energy difference between these states at the time of rejection are shown in fig. 3.12. From this we can see that the mechanism liquidates molecules with an energy difference between ~ 185 and ~ 1230.

![Figure 3.12: The energy difference at termination point.](image)

Figure 3.12: The energy difference at termination point.
Counts per voltage amplitude

The amount of molecules that are trapped are plotted as function of voltage amplitude (fig. 3.14). It can be seen that the trapped molecule population increases as voltage amplitude goes up, but there is a reversal in slope around 4.5. This is expected as the electric field strength is dependent on the voltage amplitude. An increasing field strength will induce a higher centrifugal force and hence a higher trapping strength. The reversal of slope occurs at the maximum of the SrF(1,0) energy curve, shown in fig. 2.4.

Figure 3.13: The number of trapped molecules as function of voltage amplitude. The transition probability was set at 0% (disabled).
Counts per transition probability

As the transition probability per timestep ($%/dt$) is increased, the amount of molecules trapped drops off significantly, converging to some value. The losses are too severe if the transition probability is set higher than $2%/dt$. It is suggested to stay within the $0$-$2\%$ region.

**Figure 3.14:** The number of trapped molecules as function of transition probability.
Within the ‘danger zone’

Within the ‘danger zone’, a number of phenomena happen which are interesting to look at.

Energy difference between rotational states

When the molecule enters the danger zone, it will be vulnerable to rejection. During these vulnerable times, the energy difference starts to oscillate, until the transition (or rejection) occurs. It can be seen that the energy difference decreases as the molecule penetrates into the danger zone (see fig. 3.15).

**Figure 3.15:** The energy difference of a vulnerable molecule in the danger zone as a function of time.
Electric field strength

At the time of rejection, the electric field strength is relatively small and ranges from 0 to 500 V/mm. The electric field strength at which the molecules are most vulnerable to rejection is surprisingly not at a minimum, but rather 400±30 V/mm (fig. 3.16).

Figure 3.16: The electric field strength the molecule experiences at the time of rejection from the central packet.
4 Conclusion

The simulation is able to make accurate predictions of particle behavior given the right parameters. The new expansion of the non-adiabatic loss mechanism to the simulation have shown that losses can have a greater impact than previously thought. It can be seen that, as predicted by the theory, the molecules are more vulnerable to a non-adiabatic transition within close proximity of the electric field minimum.

At the time of rejection:
- The electric field strength ranges from 0 to 500 V/mm with a maximum obtained at $\sim 400 \pm 30$ V/mm.
- The molecules are within a distance of $\sim 0.55$ mm longitudinally and $\sim 0.9$ mm transversely from the electric field strength minimum.
- The energy difference between the SrF(1,0) and SrF(1,1) state ranges from $\sim 187$ to $\sim 1229$ MHz.
- The longitudinal velocity of the molecules ranges from $\sim 339$ to $\sim 351$ m/s. This is a $\pm 6$ m/s difference from the mean velocity of 345 m/s.

The spatial distribution of molecules confined within the central packet are split up into two parts longitudinally when non-adiabatic effects are severe. The separation distance between the two parts is dependent on the transition probability. The separation distance gradually increases as transition probability is increased. This has consequences for the time-of-flight profile, altering the main signal.

Within the volatile region, where the molecule is considered for a non-adiabatic transition, the energy difference oscillates until the difference becomes too small and a transition occurs. The oscillations occur due to the orbiting nature of the molecule within the trap.

The transition probability parameter in the simulation should be kept below $\frac{2\%}{dt}$ in order to study the effects of the losses. Any probability above that will reject too many molecules.
4. Conclusion
Dankwoord

I would like to thank everyone at the Van Swinderen Institute (and the KVI in general) who I have been involved with. With all the smart minds around there was never a day wasted. The office culture has been a welcoming learning experience too: dealing with office water supply issues, not being able to flush the toilet after ‘you know’; interesting conversations during lunch, long discussions about types of tables, table sizes and the lack of chairs.

In no particular order,

Steven Hoekstra for giving me the opportunity and the freedom that I much needed to perform my thesis research; granting me access to the labs, and being available for council. I must say that I really appreciated the way we were involved in ongoing research and how we were welcomed. It felt functional.

Thank you Hans Beijers for being my second corrector.

Kevin Esajas for helping me out with the questions I had. Artem Zapara for giving me experimental datasets, teaching me Russian on the side, giving me all the necessary information about decelerator operation. спасибо.

Jeroen Muller for supplying me with additional information about the simulation. The very in-depth analysis in your thesis saved me alot of time. The code was easy on me while I gave it a rough beating. It sure accepts a lot of abuse.

Kees Steinebach, Rutger Hof and Hidde Makaske for discussions while they also performed/wrote their bachelor thesis, on different, but decelerator related matter.

The Center for Information Technology of the University of Groningen for their support and for providing access to the Peregrine high performance computing cluster.
5. Dankwoord
A

Simulation manual

Additional information about the simulation, besides the instructions given in [13], are listed here.

Getting the simulation to work

The simulation is build upon Python with a back-end that consists of C++ code. The back-end is mostly responsible for computational jobs such as integrating and evaluation of the electric fields based on the splines.

The requirements that must be met in order to run the simulation are:

- Python 2.7.12 must be installed
- GCC 5.1.0 compiler must be present
- Cython wrapper (for the C++ extension)
  Most Linux distributions already come equipped with Python 2.7.12, GCC 5.1.0 and Cython, if not, the Anaconda package can be installed that comes with these dependencies.
- The following python packages must be installed:
  - Numpy
  - Scipy
  - Joblib
  - PyTables
  - HDF5
  - Matplotlib

The Python packages can be installed through Python package manager ‘pip’. Pip comes with Python >= 2.7.12 by default. If this is not the case, it can be installed by following the instructions on: https://pip.pypa.io/en/stable/installing/.

Once ‘pip’ is installed, the dependencies can be installed by executing the following line in a terminal:

```
pip install --upgrade --user numpy scipy joblib matplotlib tables
```

If the requirements are met, the simulation code must be initialized by running the setup script. The setup script is the centre of all activity in building, distributing, and installing modules using the Distutils. The main purpose of the setup script is to describe your module distribution to the Distutils, so that the various commands that operate on your modules do the right thing. This makes sure the simulation knows where to find all the used packages.
A. Simulation manual

The setup script can be run by navigating to the ‘simulation’ folder and executing the following commands:

```
python setup.py build_ext inplace --force
python setup.py develop --user
```

After that, the simulation batch and plot scripts should work as intended. There should be sufficient disk space available as data files that are produced by batch scripts can easily reach 6 GB in size.

Changes and additions made

The integration process in ‘/simulation/src/cpp/integrate.cc’ keeps checks on the molecules in the check_acceptance function included in ‘/simulation/src/cpp/output.h’. If the non-adiabatic transition occurs, ‘acceptance_flag’ is set to 4 and returned.

If the user wants to include non-adiabatic losses in the time-of-flight batch simulations, an array in the batch script should be added with the adiabatic transition probabilities. For example, if the user desires testing a single transition probability, then:

```
nonadiab_transition_probs = [0.02]
```

For 4 different transition probabilities:

```
nonadiab_transition_probs = [0.02 , 0.05 , 0.5]
```

The simulation will execute 4 runs, each with a different transition probability. This allows for parallel computing, in case the Peregrine cluster is used. For instructions on how to make the batch scripts parallel I would like to refer to [13].

The array should be added as an argument in the ‘grid_runs(...)’ function in the batch script. For example:

```
files = grid_runs(..., nonadiab_probs=nonadiab_transition_probs)
```

By default, if no transition probability is supplied, the simulation will automatically set the transition probability to 0 (the transition mechanism is disabled). After this, the batch script can be executed. All requested data will be written to a ‘*.h5’ file.
If one wishes to read out the '.h5' files for plotting, the non-adiabatic specific parameters can be found by addressing the runs data tables. For example, if we wish to find the transition probability of the run, and the amount of non-adiabatically rejected molecules:

```python
#Open the produced file by the batch script
with open_file('tofs.h5') as f:

    # Iterate over each consecutive run.
    # If 4 transition probabilities were defined in the array, 
    # we will have 4 runs
    for run in f.root.data.batch:

        # Request the probability of the run
        transition_prob = run._v_attrs.nonadiab_prob

        # Request the amount of lost molecules
        rejected = run._v_attrs.rejected_nonadiab

        print 'Lost:', rejected
        print 'Probability:', transition_prob
```

To get an overview of the table structure, and where to find specific data, one could print the file contents:

```python
with open_file('tofs.h5') as f:
    print f
```

**Non-adiabatic transition mechanism**

The ‘check_acceptance(...)’ function in the C++ core has been expanded to include the non-adiabatic transition mechanism. In pseudo-code the mechanism can be described as follows:

```python
if (transition_prob != 0){
    if (field_strength < 450){
        dE = energy level difference

        if ((vel/d) > dE){
            rnd = generated random (0−1)

            if (rnd < transition_prob){
                reject molecule
            }
        }
    }
}
```

where ‘vel’ is the velocity of the molecule and ‘d’ the distance between trap center and molecule. The mechanism is checked every timestep, hence, the transition probability of the molecule should be defined as probability per timestep (%/dt).
Peregrine high-performance cluster

If the user has access to the Peregrine cluster, the cluster can be reached through ‘ssh’. For example:

\[
\text{ssh sxxxxxxx@peregrine.hpc.rug.nl}
\]

Once logged in, the simulation source code can be retrieved through ‘wget’ or cloning a git repository (git clone <address>). Since the peregrine work environment is not yet equipped with the necessary requirements (see section A.1), we need to load these. To load the necessary requirements on Peregrine, we can use:

\[
\text{module load Python/2.7.12 − foss − 2016a}
\]

\[
\text{module load GCC/5.1.0}
\]

\[
\text{module load git}
\]

Then, by executing the same commands as described in section A.1, we can run the scripts as usual.

To execute a batch script which is parallelized, a job can be requested. This can be done by submitting a bash script (*.sh) containing the necessary commands. To make a bash script, execute:

\[
# creates a shell script
touch job.sh
# grant permissions to make it executable
chmod +755 job.sh
\]

The instructions should be written inside the bash script. Open the shell script by typing 'nano job.sh'. Once opened, instructions can be set, for example:

\[
#!/bin/bash
#SBATCH --job-name=tof
#SBATCH --output=time_of_flight.txt
#SBATCH --nodes=5
#SBATCH --ntasks=10
#SBATCH --ntasks-per-node=2
#SBATCH --cpus-per-task=2
#SBATCH --time=10:00:00
#SBATCH --mem-per-cpu=2000

module load Python/3.5.1 − foss − 2016a
module load GCC/5.1.0
cd /home/sxxxxxxx/simulation/batch_scripts
python ./time_of_flight.py
\]

This will execute 10 tasks on 5 nodes with 2 available CPU cores for each node. For example, if we were to execute a time-of-flight batch script with 10 different transition probabilities like so:

\[
\text{transition_prob} = [0, 0.01, 0.02, \ldots, 1]
\]
then there will be 1 task dedicated to each time-of-flight simulation with 1 of the transition probability defined in the array. Parallelized, there would be 10 time-of-flight simulations going on, on 5 nodes. Each executing 2 tasks (time-of-flight simulations).

After the job instructions have been described, and the bash script file is saved it can be submitted to the job system:

```
# send in the job
sbatch job.sh
```

It can take considerable time before resources have been allocated to execute the job, this depends on requested resources and efficiency ranking. Users acquire a good efficiency ranking if their job fits well within the set time-limit and puts the CPUs to good use (CPU walltime). During rush-hour (17:00 or on Fridays) resource allocation can also take a long time.

While the job is running, output can be read by executing:

```
# track output realtime
tail -f time_of_flight.txt
```

Once finished, the produced (*.h5) file can be transferred for analysis by using ‘sshfs’ or ‘rsync’.
References