Stark deceleration to produce cold SO₂ molecules.

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1. Introduction

In the recent years, the topic of cold molecules has gained a remarkable interest. As a number of techniques of cooling, trapping, and manipulating atoms have emerged, the new fields also have opened research on cold molecules. The attempt was taken to implement with molecules all techniques known to be successful for the atoms. Some of the cooling methods as laser cooling were not successful due to the complex nature of the energy levels of the molecules. The controlled transitions between ultra cold atomic and molecular phases are especially interesting for quantum chemistry of the predissociation effect [1].

SO₂ is an ideal candidate for this kind of research as the spectroscopic parameters of its ground level and some of the electronic excited levels are precisely known. Especially interesting is the electronically excited state $\tilde{C}^{-1}B_2$ which predissociates into SO and O [2]. As it was observed that the energy levels near to dissociation can be effectively populated, so fragments can be created with low energy exceed. As the number of the predissociation channels after laser excitation is low the fragmentation of the SO₂ into cold SO and O is a state-to-state defined reaction [1].

In order to use the low excess energy for the fragmentation it is important first to obtain a cloud of the cold SO₂. Exactly for this purpose the method of Stark deceleration is applied. According to calculations [3] a number of 340 deceleration stages is needed to decelerate SO₂ to a stand still. That large number of stages is needed because of the relatively high mass of the SO₂ even though it has a relatively high dipole moment (in the ground state) equal $\mu_b(\tilde{X})=1,633 D$ [4]. There are three SO₂ vibrational bands of $\tilde{C}^{-1}B_2$ state, (1,4,2), (3,1,2) and (5,1,0) known to posses energies overlapping with vibrational levels v=0,1,2 of the SO and O in the ground state. For the purpose of this work the band (1,4,2) was found to be the most convenient to use [5].

2. Theoretical background

Realization of the idea to decelerate molecules starts with its attribute of being polar. If the particular molecule's positive and negative charge centers do not overlap, then the molecule possesses a non-zero dipole moment $\vec{\mu}$. Polar molecules experience within an electric field the effect of splitting and shifting their energy levels, named after its discoverer the Stark effect. Dependence of the energy levels on the electric field strength makes the molecule experiencing a force when placed in an electric field gradient. That behavior is a cornerstone for guiding and focusing molecules with the use of time independent electric fields, and finally decelerating them with use of time dependent electric fields. With an appropriate setup of a static electric multipole it is possible to curve the molecules' trajectories corresponding to the behavior of the light beam put through the glass lens. Moving a particle which is exposed to an electric field gradient parallel to its trajectory, will transfer part of its kinetic energy into the potential energy of the Stark effect. Abrupt, non-adiabatic removal of the electric field makes the induced stark shift to disappear without gaining back the kinetic energy of molecule. By appropriate switching of the electric field through the track of the molecule it is possible to expose the molecule almost constantly to the gradient of electric field and efficiently remove its kinetic energy. The number of cycles needed to bring the molecule to the still stand depends on the starting kinetic energy of the molecule, Stark shift and electric field applied. In order to provide starting conditions for deceleration as good as possible the initial kinetic energy of the particles was limited and supersonic beam expansion technique by using of heavy carrier gas and cooled a nozzle.

2.1. SO₂ rotational theory

Basically SO₂ by the location of its nuclei can be treated as an even-armed triangle, and follows the C_{2v} symmetry, that is a group consisting of single rotation of 180 degrees on X axis (see drawing 1), and two plane symmetries on the XY and XZ planes. As the nuclear framework of the molecules does not change due to the symmetry operations,



Drawing 1: Symmetry group C_{2v} components.

the Coulomb potential of the nuclei remains also constant, which means, that the potential energy of the molecule is invariant with respect to all symmetry operations. It is also easy to find that the mean kinetic energy of the electrons in a given electronic state will remain also unchanged as it is determined by the nuclear configuration. As tri-atomic molecule, as SO2 has exactly three normal modes of vibrations (see drawing 2) it is to be observed that none of the symmetry operations of C_{2v} symmetry group change center of the mass of the molecule. It is to be noticed that vector lengths presented on the drawing 2 are not in scale.



Drawing 2: Three normal modes of vibration in tri-atomic molecule ($C_{2\nu}$ symmetry) according to the Table 1.

Despite the fact that electron density distribution is conserved by symmetry operations of the molecule, the wavefunctions of the states can change. From the requirement that $|\psi|^2$ should remain the same one obtains the nondegenerate states of $\psi(x,y,z)$ due to its single-valuedness of, as (right arrow remarks symmetry transformation)

$$|\Psi|^2 \to |\Psi|^2 \quad |\Psi| \to \pm \Psi \quad . \tag{1}$$

On the basis of the representation theory the symmetry group can be assigned a set of linearly independent matrices operating on the vector space, that correspond to the symmetry operations contained in the symmetry group. If the space spread on these matrices contains no invariant subspaces, then these matrices constitute a basis of irreducible representation. The traces of these matrices are called characters of the representation, and as in case of the SO₂ all the matrices are one dimensional and have character value of 1 for symmetric, and -1 for antisymmetric transformations (see table 1).

C _{2v}	E	C ₂ (x)	σ _v (xy)	σ' _ν (xz)	components	symmetry type
Γ ₁	1	1	1	1	T _x	A ₁
Γ2	1	1	-1	-1	R _x	A ₂
Гз	1	-1	1	-1	T _y , R _z	B ₁
Γ_4	1	-1	-1	1	T_z , R_y	B ₂

Table 1: Table of characters for $C_{2\nu}$ symmetry group, with translation transformations marked as T, and rotation transformations marked as R.

The SO₂ molecule is almost an asymmetric top with prolate character. For the purpose of the quantum mechanical description, it can be described with use of following

Hamiltonian:

$$H_{rot} = \frac{1}{\hbar^2} \cdot (A J_x^2 + B J_y^2 + C J_z^2) \quad ,$$
 (2)

where $J_x J_y J_z$ are angular momentum values, and rotational constants are represented by:

$$A = \frac{\hbar^2}{2 \cdot I_x}$$
, $B = \frac{\hbar^2}{2 \cdot I_y}$, $C = \frac{\hbar^2}{2 \cdot I_z}$ with $I_x I_y I_z$ representing moments of inertia of given axes.

In the particular case of the asymmetric top the rotational constants satisfy A > B > C, contrary to the case of symmetric top, where two of the constants are equal. Constant A is equal B in case of oblate top, and constant B is equal C in case of prolate top.

For the symmetric top the projection of J on the molecule axis is a good quantum number, that is not the case of asymmetric top. Introducing angular momentum ladder operators of the locale molecules system (m):

$$J_{m}^{+} = (J_{x} + iJ_{y}) \quad J_{m}^{-} = (J_{x} - iJ_{y})$$
(3)

it is possible to describe the Hamiltonian of the asymmetric top in the form, which directly shows the influence of asymmetry (prolate case)

$$H_{rot} = \frac{1}{\hbar^2} \cdot \left[(B+C) \vec{J}^2 + (2A-B-C) \vec{J}_z^2 + \frac{1}{2} (B-C) \left[(J_m^+)^2 + (J_m^-)^2 \right] \right] \quad . \tag{4}$$

The matrix elements of H_{rot} can be represented in the basis of symmetric top $|kJM\rangle$, where

$$|KJM\rangle = [\frac{2J+1}{8\pi^2}]D'_{Mk}(\phi, \theta, \chi)$$
(5)

k is a projection of the the angular momentum J on the molecule axis, and , \vec{J}^2 , \vec{J}^2_z , $(\vec{J}^+_m)^2$, $(\vec{J}^-_m)^2$, are defined by

$$\langle KJM | J^{2} | KJM \rangle = J(J+1)\hbar^{2} \langle KJM | J_{z}^{2} | KJM \rangle = K^{2}\hbar^{2}$$

$$\langle (k-2)JM | (J_{m}^{*})^{2} | kJM \rangle = \{ [J(J+1) - (K-1)(K-2)] \cdot [J(J+1) - K(K-1)] \}^{\frac{1}{2}}\hbar^{2}$$

$$\langle (k+2)JM | (J_{m}^{*})^{2} | kJM \rangle = \{ [J(J+1) - (K+1)(K+2)] \cdot [J(J+1) - K(K-1)] \}^{\frac{1}{2}}\hbar^{2}$$
(6)

From equation (6) it is apparent that H_{rot} has non-vanishing matrix elements for states with equal J, M, and the difference in K equal to zero or \pm 2. As the Hamilton matrix splits into J blocks, and every block contains 2J+1 identical sub blocks for every M, the symmetric top wavefunctions can be presented as follows:

$$|\pm, KJM>=\frac{1}{\sqrt{2}}(|KJM>\pm(-1)^{J}|(-K)JM>)$$
, (7)

with exception for K=0

$$|(-1)^{J}, 0 JM > = |0JM >$$
, (8)

The sub-blocks of H_{rot} are diagonal, and split into submatrices representing four irreducible representations of the symmetry group D_2 corresponding the ellipsoid of inertia. The reason for that is that there are no nonvanishing elements between wavefunctions even and odd K, or between wavefunctions with + and functions with -. The resulting four blocks are named E^+ , E^- , O^+ , O^- for even (E), odd (O) and with + or - wavefunction symmetry, respectively. Accordingly the symmetries of the D_2 group are: E, B_x , B_y , B_z , with symmetry operators as **E** (identity) and **C**_{2(x,y,z)}. The symmetry of the wavefunction is to be described by the projection at the prolate (z axis) or oblate (y axis) with the appropriate quantum number of K = K_z, or K_+ = K_y. The characters of D_2 symmetry are presented in table 2.

Symmetry	wavef. symm.	K ₊	K.	Е	C ₂ (Z)	C ₂ (x)	C ₂ (y)	block name
А	+	е	е	1	1	1	1	E+
B _x	-	е	0	1	1	-1	-1	E.
Bz	+	0	0	1	-1	1	-1	O⁺
By	-	0	е	1	-1	-1	1	0 ⁻

Table 2: Table of the characters of the rotation group D₂

The degree of the top asymmetry is described by:

$$\kappa = (2\mathbf{B} - A - C)/(A - C) \quad . \tag{9}$$

where the border values of κ are 1 for oblate and -1 for prolate top, leaving space for -1 < κ < 1 for the asymmetric top. The wavefunction of the asymmetric top can be constructed with positive values of K₊ and K quantum numbers, representing projection of

the J on the molecular axis of the oblate or prolate top respectively. The complete wavefunction of the asymmetric top consists of the superposition of the wavefunctions of symmetric top in the following manner:

$$|K_{L}K_{+}JM\rangle = \sum a_{K}^{J\pm} |\pm, KJM\rangle$$
, (10)

with + for K_+ and K_- even and - for K_+ and K_- odd respectively. Although J and it's projection M are good quantum numbers in the field free conditions, the complete description of the rotational wavefunction can be described with use of K_+ and K_- quantum numbers.

The total wavefunction of the molecule the is composed of four components, that is:

$$\Psi = \Psi_{el} \Psi_{vib} \Psi_{rot} \Psi_{nucl} , \qquad (11)$$

electronic, vibrational, rotational and nuclei wavefunctions, for the particular case of SO₂ which contains two oxygen atoms, it can be limited to use the first three only, as the oxygen atoms (being bosons with nuclear spin zero) enforce the wavefunction to be symmetric for the nuclei exchange:

$$\Psi_{bon} = \Psi_{el} \Psi_{vib} \Psi_{rot} \quad . \tag{12}.$$

In order to determine rotational wavefunction symmetry on the exchange of the oxygen atoms one needs to find symmetry of the vibrational wavefunctions only. The exchange of the oxygen atoms in SO₂ is represented as composition of the rotation over the axis x for 180°, (C₂(x)) and reflection on the plane σ'_v ($\sigma'_v(xz)$). The electronic wavefunction is symmetric under these transformations for state $\tilde{X}^{-1}A_1$, and anti-symmetric for state $\tilde{C}^{-1}B_2$. Then the only cases left are the case of even number of excitation quanta in the asymmetric vibrational mode of $\tilde{X}^{-1}A_1$ with irreducible representations of E⁺ and O⁺,

and for state $\tilde{C}^{-1}B_2$ with irreducible representations E⁻ O⁻. In case of odd number of excitation quanta the behavior is exactly contrary.

Due to the symmetry reasons, in case of the electronic ground state $\tilde{X}^{-1}A_1$ only an excitation of state with an even number of vibrational quanta is possible in the asymmetric vibration. Following that in case of SO₂, in the electronic and vibrational ground state only states with K₊+K₋ even exist.

2.2. Stark effect theory

The Stark effect is the splitting of spectral lines of the polar molecules due to the presence of an external static electric field. The polar molecules are defined as those which have the centers of the positive and native charge distribution spatially separated, and though have an (permanent) electrical dipole moment.



Drawing 3: Simplified view of the electric dipole of the polar molecule.

The Stark effect is the electric analogue of the Zeeman effect where a spectral line is split into several components due to the presence of a magnetic field.

In the SO₂ molecule the dipole moment for ground state $\tilde{X}^{-1}A_1$ was found to be equal $\mu_x(\tilde{X}) = 1$ 1,63305(4) D [4], and for the excited state $\tilde{C}^{-1}B_2 \ \mu_x(\tilde{C}) =$ 1,99(6) D [5]. Where $\mu_x(\tilde{X})$ has a meaning of the permanent dipole for state \tilde{X} measured in the molecule fixed system in direction x (see drawing 1). In the external electric field \vec{E} the Hamiltonian is gets additional component:

$$H_{st} = -\vec{\mu} \cdot \vec{E} \quad , \tag{14}.$$

It is essential to realize that the dipole moment of the molecule ($\vec{\mu}$) is expressed in the molecule fixed system and the electric field (\vec{E}) is represented with respect to the external system of coordinates. In order to calculate matrix elements of H_{st}, the rotation matrix D, from the space fixed to the molecule fixed system, is to be applied. With this the matrix matrix elements of H_{st} follow:

$$< K_{-}'K_{+}'J'M'|H_{St}|K_{-}K_{+}JM >$$

$$= -\sum_{p} < K_{-}'K_{+}'J'M'|\mu_{p}D_{p0}E_{0}|K_{-}K_{+}JM >$$

$$= -E_{0}\sum_{pKK'}\mu_{p}a_{K'}^{J'\pm'}a_{K}^{J\pm} < \pm ', K'J'M'|D_{p0}|\pm , KJM >$$

$$= -E_{0}\sum_{pKK'}(-1)^{K'-M'}\mu_{p}a_{K'}^{J'\pm'}a_{K}^{J\pm}\sqrt{(2J+1)} \times \sqrt{(2J'+1)} \begin{pmatrix}J' & 1 & J\\ -M' & 0 & M \end{pmatrix} \begin{pmatrix}J' & 1 & J\\ -K' & p & K \end{pmatrix}$$

$$(15)$$

where the 3J symbols are resolved by Edmonds [6].

2.2. Stark effect theory

Only two of four irreducible representations (E⁺, E⁻, O⁺, O⁻) can be coupled with H_{st}. The equation 15 shows that the Stark effect is mixing various rotational levels with different J, and only its projection on the quantization axis (defined by the external electric field) - remains a good quantum number. As the SO₂ molecule possesses the permanent dipole moment in the direction of the axis x, it experiences the quadratic Stark effect and it is dependent only on the value of M, not on it's sign. In order to find the shift of the energy levels one has to diagonalize the Hamiltonian with appropriate matrix elements substituted. The dimension of this matrix is dependent on the maximal J value (from thereon referenced as J_{max}). In principle coupling exists for all the values of J, but practical calculations for J_{max} equal 15 have shown sufficient compliance with experimental results for all energy levels relevant for the purpose of this thesis. The mixing coefficients $c_{JK,K_{-}}^{J'M}(E)$ are found from the eigenvectors of the H_{st} + H_{rot}, and these allow to write the field dependent wavefunctions as:

$$|K'_{K'_{+}}J'ME\rangle = \sum_{J} c_{JK_{+}K_{+}}^{J'M}(E)|K'_{K'_{+}}J'M\rangle$$
(16)

It still appears to be reasonable to describe field dependent quantum states with the field free quantum numbers, even if these lose their meaning in the field exposed system, because electric field shifted levels are adiabatically connected to the field-free levels.

The method described above was implemented in the Fortran program named StarkAsymRot [5]. With the use of this program it was possible to calculate shifts and splittings of the energy levels for the vibrational levels of the ground state X. The Dependency of the stark energy shifts on the electric field strength is shown on the chart 1 bellow. Vibrational states were labeled using notation like J_{K+K-} .



Chart 1: Stark energy shifts dependency on the electric field, for the first four rotational levels of the vibrational ground state of SO₂.

It is to be noticed, that depending on the M, J, K₊, K. quantum numbers some of the states are experiencing positive Stark effect, others negative. Exposure of the particle in the state showing negative Stark effect will cause a force directed into the the region of the high electric field. This kind of particles, from now on, will be called high-field seekers. On the other hand, particles experiencing positive Stark effect in the presence of electric field will be pushed into the direction of the low field (low field seekers). The Rotational state M=0, 1_{11} will be of special interest there, as the positive Stark effect is strongly pronounced in the range of electric field intensities available for the experiment.

2.3. Idea of particle deceleration with the use of the Stark effect.

The particular application of the Stark energy shifts of SO₂ molecules is to transfer kinetic energy of the moving molecule into the potential energy of the Stark effect. The force experienced by the particle in an electric field is utilized for the purpose of SO₂ decelerator in two ways. The application of the static electric field with field gradient orthogonal to the particle trajectory can be used as a method of deflecting or focusing of the particles. In the particular case of the electric n-pole configuration it may serve as a lens applicable for a selected state [5]. In the other situation, when particle is exposed to the electric field increasing in the direction of the particle's flight, the particle will be slowed down. Appropriate application of switching electric field can make the particle to

experience periodic electric field slopes, and therefore have its kinetic energy transfered into Stark energy, which is removed from the system during a rapid shutdown of the electric field.

A system providing such switched electric field conditions needs to operate with the pair of grounded electrodes, and pair of the electrodes with high potential difference. In the moment when the particle approaches the high field of the powered electrodes (loosing part of its kinetic energy on its way), the electric configuration of the electrodes can be changed that high voltage is applied now to the electrodes that were previously grounded, and grounding those which were under high voltage before. A schematic sketch of this operation is presented on the drawing 4. By repeating this switching process several of times, the particle is exposed to periodically raising electric field.



Drawing 4: Two step scheme of the switched Stark decelerator operation.

The crucial element for the switching process is the so called phase angle of the

switching event. The phase angle defines the position of the particle between the high potential and grounded electrodes, as pictured on the drawing 5. The phase angle is anchored by the 90° line which is to be put exactly in the position of the high potential electrodes, and 0° line being put exactly between grounded and high potential electrodes.



decelerator's switching event.

Particularly by selecting a switching phase angle of zero degrees, the particle will be exposed to varying potential which finally does not influence the particle's kinetic energy. This is due to the fact that all the kinetic energy transfered to the Stark energy during the climb of the potential is given back on the way down of the decreasing slope. The extreme cases of $\pm 90^{\circ}$ switching angles expose the particle to the potential which is the most efficient in decelerating (+90°) or accelerating (-90°) particles, but offer extremely small phase-space acceptance and due to that very limited number of particles decelerated [5].

The moving particle located at the position defined by the phase angle in the moment of switching is the so called synchronous molecule. In the case of properly adjusted switching pattern parameters, that is switching timing adopted to the available electric field strength, and starting kinetic energy of the molecules, the synchronous molecule is repetitively hitting precisely the switching event in the distance corresponding to the selected switching phase angle. Nevertheless as the decelerator operates on a continuous beam of a molecules, not on a single molecule, only a very small number of particles will be positioned precisely where synchronous molecule should be during the first switching event. This fact raises the question of the so called phase acceptance of the decelerator [5] which defines a range of phase angle values of the particles that will be able to follow the switching pattern and eventually get decelerated.

Following the idea of the molecules' trajectory deflection the decelerator can be operated with constant voltage applied to all the electrodes at once in order to obtain a guiding effect. With so called guiding regime molecules are just passing through all the decelerator stages without altering their forward velocities. This behavior can be found useful for determining velocity distribution of the particles in a molecular beam.

3. Experimental setup

The apparatus used in this experiment is a development and refinement of all the experiences gathered in previous iteration of the project driven by Christian Lisdat and Sebastian Jung (IQO Uni-Hannover). The former decelerator construction consisted of the molecular beam section (directly imported into new construction), the exapole lens (also directly imported) and 140 staged decelerator that allowed decrease of the SO₂ particles' kinetic energy up to 42% [5].

3.1. Vacuum system

The ultra high vacuum conditions for the purpose of the experiment were delivered in two chambers separated by a wall, with use of three turbo molecular pumps letting the system reach vacuum level of $2 \cdot 10^{-9}$ mbar. The separation of the decelerator and nozzle chambers allowed efficient removal of the large amount of gas skimmed by the molecular beam skimmer, saving high voltage exposed elements from potential discharge, as the nozzle chamber's vacuum level was going down during nozzle operation to the level of 10^{-5} mbar. Sketch of the decelerator's vacuum chambers is presented on the drawing 6.

The exhaust of the turbo molecular pump evacuating the nozzle chamber was let through the cold trap in order to condensate poisonous and corrosive SO_2 in the liquid nitrogen temperature conditions, before reaching the pre-vacuum pump. The corrosive influence of the SO_2 to the turbo molecular pump bearing was limited by use of argon as a purge gas. Cold trap and purge gas were applied only to the pumps operating on the nozzle chamber, as that was the place where the vast majority of the particles produced by the nozzle was stopped by the beam skimmer and evacuated.



3.2. Laser system used

The molecular fluorescence in the experiment was excited by two staged laser setup. Frequency doubled, tunable dye laser (commercial Lambda Physik construction FL3002) operated with Coumarin 120 (420-470 nm) dye and pumped by the Xenon-Fluoride (352 nm) pulsed excimer laser (Lambda Physik ComPex 102). The obtained UV maximum pulse power reached up to 0.5 mJ and was tunable within the range of eight wave numbers around the central value of 45710.44 cm⁻¹ (218.7684 nm) corresponding to SO₂ 2(1,2)-1(1,1) transition ($\tilde{X}^{-1}A_1$ to $\tilde{C}^{-1}B_2$). The beam power applicable for the purpose of detection was ranging between 120 and 200 µJ per pulse (10 Hz operation). The radius of the laser beam leaving the dye laser was 300 µm.

The vacuum system was equipped with two interaction zones of the molecular beam with laser beams. First one is placed in the nozzle chamber just 13 mm after the nozzle throat, the second one at the end of decelerator in the decelerator chamber in the distance of 1795 mm from the nozzle. The second interaction zone was equipped with a sophisticated stray light elimination tube (see drawing 6) holding a set of stray (and ambient) light reducing cones, and a mirror+lens configuration to pick up as much SO₂ fluorescence as possible [5].

Due of the unstable power characteristics of the dye laser there was a photo diode for beam power measurement applied at the end of the beam path through the system for the first interaction zone. The measured laser beam intensity served as a reference for analysis of the fluorescence signal intensity.

For the purpose of high time and spatial resolution the original laser beam size in the 2^{nd} interaction zone (estimated to be ~1mm) had to be decreased with the by a collimating lenses setup. The obtained beam radius of ~500 µm, and ~250 µm allowed observation of the internal structure of decelerated molecule bunches. For the detailed investigation on the laser beam size please refer to the chapter 4.5.

3.3. Molecular beam techniques used

Translationally cold molecular beam formation is a fundamental part of the experiment. The nozzle chamber of the apparatus was equipped with a modified magnetcoil-type nozzle (originally General Valve Series 9), followed by the conical beam skimmer. The nozzle to skimmer distance, and skimmer size were experimentally adjusted to optimize supersonic beam expansion conditions [5]. In order to obtain preliminary low longitudinal beam velocity, SO₂ vapor was mixed with the noble (argon/xenon) gas as for carrier. The relatively high atomic mass of the carrier gas acted as a buffer for the kinetic energy of SO₂ molecules. For low beam velocity and good fluorescence intensity, SO₂ to carrier gas ratio was found to be 5% of concentration. In addition to this technique the nozzle itself was cooled down (-60 C⁰) by liquid nitrogen, which effected in additional reduction of the overall kinetic energy of the SO₂ particles resulting in the average beam velocity of about 300 m/s in the case of Xenon.

3.3.1. Supersonic beam expansion technique.

The expansion of the gas mixture into the vacuum causes the beam to experience adiabatic cooling by expansion [7]. The supersonic speed of the beam expansion, under decreasing density and similar velocity of the molecules in vacuum dramatically decreases number of molecule collisions in the gas. The reduced number of collisions taking place in the beam can be divided into:

• central elastic that exchange kinetic energy between particles in the direction of the beam,

• noncentral elastic that cause both collision partners to leave the beam and eventually to be removed by the skimmer together with the rest of particles propagating out of the axis,

• non-elastic that transform energy of the rot-vibrational degrees of freedom into translational energy, effectively cooling internal energy of the molecule.

The schematic sketch of the particles expanding by the supersonic beam is presented on the drawing 7.



Drawing 7: Supersonic beam expansion sketch

As internal energy of the gas decreases, the enthalpy is conserved and given by:

$$\frac{f}{2}kT_{0} + \frac{p_{0}V}{N} = \frac{1}{2}mv^{2} + (\Delta E_{trans} + E_{rot} + E_{vib})$$
(17)

where, T_0 and p_0 are temperature and pressure of the gas, f is a number of degrees of freedom of gas particle, N as number of particles, and ΔE_{trans} is a relative kinetic energy of the particle in the moving frame with velocity v. Due to the fact that collision cross-sections for the rotation-translation energy transfer are smaller than elastic collision cross-section, and vibration-translation transfer is even smaller than those during adiabatic cooling thermodynamical equilibrium is not kept, following relation $T_{trans} < T_{rot} < T_{vib}$ can be expected. As this process reduces significantly ΔE_{trans} , E_{rot} , and E_{vib} , practically all the

kinetic energy of the particle is contained in the kinetic energy ($\frac{1}{2}mv^2$).

For the purpose of this experiment, SO_2 vapor was mixed with one of the noble gases (Argon/Xenon) serving as a carrier gas. The heavy collision partner for SO_2 molecules serves as a kinetic energy buffer, and practically determines the velocity after the supersonic beam expansion.

The molecule density *n* which stays constant during the beam expansion through the decelerator, can be obtained from following equation:

$$n = n_0 \left(\frac{T}{T_0}\right)^{\frac{1}{1-\gamma}},$$
 (18)

where T_0 is the temperature, and n_0 is a particle density before expansion, and γ is the adiabatic coefficient dependent on the number of the degrees of freedom of the gas

particles:

$$\gamma = \frac{f+2}{f}$$

For the particular case of SO₂, which is a tri-atomic molecule, the value of γ was taken to be 5/3. Typically, the working mixture contained 5% of the SO₂ in Xenon and was cooled down before expansion to T₀=-60 C⁰, with p₀=0.4 bar. T was found to be equal 3 K^o (please refer to the section 4.2). With the use of *P*=*nkT*, the calculated particle density before expansion (n₀) was 8,2[·]10¹⁷ molecules per cubic centimeter, and density of 2,8[·]10¹⁵ molecules per cubic centimeter after the expansion.

3.4. Focusing the molecular beam by high voltage hexapole lens.

In order to increase the number of particles entering decelerator, the molecular beam that has left the nozzle and passed through the skimmer, was focused with use of hexapole lens. The hexapole lens is basically a six electrode system which creates a cylindrically symmetric electric field with the field strength described by following equation: [5]

$$E(r) = \frac{3}{2} \cdot \frac{U_0}{r_0} \cdot \left(\frac{r}{r_0}\right)^2 , \qquad (19)$$

where r_0 is the inner radius of the hexapole, U_0 is the potential difference between hexapole electrodes, with which the force acting on a molecule with linear Stark effect placed in the lens was linearly dependent on the distance from the lens axis. The hexapole lens was optimized for the molecules in quantum state 1(1,1) |M|=0 traveling with velocity of 300 m/s, to obtain high particle flux to the decelerator inlet. The applied voltage difference between hexapole electrodes was equal 24 kV, and was constructed asymmetrically of -11 kV and +13 kV due to the fact that higher voltages were less problem prone for the positive polarity. Additionally to ease entrance of the particles to the decelerator, the deceleration switching sequence was preceded with switching on the first decelerator stage for a period of time that could guide incoming particles into the decelerator.

3.5. Stark decelerator

The major mechanical modifications of the system are connected with the electrode bars mounting. First of all the new system length was increased to 1.97 meter, which significantly rose the expectations on the system stiffness. The electrode mounting bars consist now of two elements connected with a cylindrical junction that helps to adjust electrodes' plain perfectly.

The lateral alignment of the electrodes' plain was possible to be tuned with custom made isolator holders (drawings 8 and 9) that allowed to bend the electrode holding bar in three points of support. The inter electrode spacing adjustment (between electrodes of opposing polarities) was performed with the use of a rectangular block of appropriate dimension made of soft metal (copper), which was least harmful for the electrodes' surface.



The stiffness of the mounted electrode bars was secured by the full aluminum pipe housing. The mounted system was moved into the ultra high vacuum chamber on a custom made rail system centered with respect to the chamber's axis.

3.5.1. HV exposed surfaces fineness

The design condition of having electric field gradient in order of 150 kV/cm and switched operation at +/- 10.0 kV has pushed the cleanness requirements very high. The decelerator apparatus was manufactured for the sake of rigidity of stainless steel. The

parts which are most exposed to the high electric field, are of course the electrodes themselves and these were machined and polished by the external company (Beutter). All other parts (including electrode handling bars, insulator holders, pendulum stage mounting elements) were hand polished with use of widely available metal polishing agents.

3.5.2. Smooth high voltage feedthroughs

Preliminary tests of the high voltage treatment to the apparatus have shown a major difficulty coming from the high current leaks at the moment of having no electrodes mounted yet. Short investigation of that point has revealed that high voltage connections to the decelerator are extremely sensitive on having sharp edges or peaks. The experience has shown that so called electron spray effect is more likely to occur for negative polarity than for positive. The new system of plug-like connectors was designed and implemented, which resulted in no more current leaks due to the vacuum feedthroughs.

3.5.3. High voltage conditioning practice

In order to ensure secure behavior of the high voltage elements under switching conditions, a procedure of conditioning was applied. The procedure is performed by stepwise increase of the voltage applied to decelerator bars, while measuring the current flowing through the decelerator, to shutdown the voltage in case of excessive current flowing through. The stepping procedure started with the voltage of 6 kV for mono-polar, and 4 kV for bi-polar configurations, which was increased by 1kV in time periods of 10 minutes. Reaching the limit of 125% of the preliminary operation voltage (10 kV), the step size was reduced to 0.5 kV, and time periods prolonged to 20 minutes. 25% excess over the operational voltage was taken in order to have a safety limit for the switched operation. High voltage was provided to the decelerator bars through 100 M Ω resistors in order to limit possible current flow to values that can not be harmful to the decelerator's electrodes. Practice has shown, that due to remaining the dust inside vacuum chamber, the conditioning current can rise up to few micro amperes for times shorter than few seconds, during which electric discharge efficiently burns the impurity. High voltage conditioning was to be applied for the apparatus each time the decelerator chamber was

3.5. Stark decelerator

exposed to air. Occasionally the current drain between opposing electrode bars was checked in order to ensure electric safety of experiment. Practice has shown, that electrode bars posses different characteristics for positive and negative potential. As long as there are no geometrical constraints on the assignment of the polarities to electrode holding bars (as far as opposite electrodes posses opposite polarities), polarity selection was made the way that was fitting the best characteristics (no current drains) of given electrode bars.

The complete conditioning procedure consisted of following steps

• three electrodes grounded, positive or negative potential applied to fourth electrode, repeated consecutively for all four electrode bars, up to 125% of desired operational voltage (10 kV),

• bi-polar conditioning, with one pair of electrodes having high voltage applied (positive and negative polarities), and other pair grounded. Up to the 125% of operational voltage (10 kV),

• electrodes pair conditioning for guiding, having both positive, or both negative electrode pairs powered, with other pair grounded, up to the guiding voltage of 3.5 kV,

• bi-polar bar pairs conditioning for guiding, two negative, against two positive bars, up to guiding voltage of 3.5 kV.

Since the hexapole electrodes are exposed to a constant potential, conditioning of these was performed with the same stepping as for decelerator electrodes, following mono-polar and then bi-polar pattern.

The condition of the decelerator's switching system was controlled by observing the average current drain (<10 mA) from the HV power supplies during switched operation of complete burst containing 163 switching events with 10 Hz repetition rate.

3.5.4. High voltage switching problems and solutions

The switching system, based on Behlke Electronic HTS 151-03-GSM switches was supplied with the high voltage by two ISEG LPS 300W power supplies, connected through

45 k Ω resistor to the large, charge buffering capacitors (1µF). A loading resistor was added between the power supply and capacitor in order to prevent the voltage stabilization system of the power supply from experiencing rapid potential fluctuations on the capacitors during the switching. A 100 M Ω resistor shortcutting the capacitor itself served as a discharge circuit, as charge on the capacitor could possibly remain there for a long time, being potentially dangerous. Appropriate operation of this discharge resistor was checked by observing current drain level from the active power supply while switches were idling. Lack of this current could be an indication of potentially dangerous malfunction of the system. The idle state of the switching apparatus was designed that electrode bars were cut short to the ground. The switched state indicated connection between the capacitor, through 1 k Ω resistor, switch, and 0.5 k Ω resistor to the electrode holding bars, as presented on the drawing 10. The set of high power (50 W) resistors was applied in order to limit the peak current during charging. Resistances of 1 k Ω and 0.5 k Ω resistors were adjusted to optimize heat emission on the elements, as the loading charge of the electrode bar was transferred only once during the cycle through the 1 k Ω resistor, instead of two times for the 0.5 k Ω resistor. Great care had to be taken on any indication of increasing current drain of HV power supply, as possible inter-electrode discharge inside the decelerator chamber could be destructive for electrodes and HV switches.



Drawing 10: HV Switching circuit tree.

The experimental setup utilizes a single HV power supply to support two switching circuits of the same polarity but switched in the different plane (horizontal/vertical - see drawing 11). There was a need of installing an additional shortcut that bridged capacitors of the same polarity, as the 45 k Ω resistors were found to hold excessive current at the moment of switching. Responsible for that was the rapid potential drop occurring on one of the capacitors, which was balanced by the charge of the other one through two 45 k Ω resistors.

Future plans include installation of separated power supplies for each switching circuit in order to provide truly separated operation.



Drawing 11: Symmetric HV switching circuit tree supporting two switches of the same polarity.

Trigger signals for the switching were provided by TTL-like steering supplied from the computer driven pattern generator through the set of opto-couplers. In order to ensure RF pickup reduction, and HV safety, switches were equipped with well shielded additional circuits, that handled increased driving voltage (9 instead of TTL 5V), and appropriate logic negation for negative polarity switches, to make electrode bars grounded when the decelerator was idling or in case of no signal cable connected.



Drawing 12: Positive and negative high voltage switching logic schemes.

In order to protect the system from the distribution of the high voltage breakdown on the switches through the power supplying connections each switch was supported with the separated power supply.

3.6. Data acquisition setup

The data acquisition system consists of a set of modules triggered by the computer driven digital input/output interface called pattern generator (National Instruments

PCI-6534), and an universal analog/digital input/output register (National Instruments PCI-6014). These provide the following input and outputs, as presented on the drawing 13:

• Nozzle driver triggered by TTL signal from pattern generator, with manually preselected molecular pulse length (250-350 μ s) on the nozzle driver,

• Photo diode laser power measurement subsystem, built with use of box-car integrator, triggered simultaneously with excimer laser, and read out by the input/output analog register,

• Four independent triggers, each driving one switch supplying electrodes holding bar with positive or negative voltage respectively,

• Single logical input of four OR gates connecting the fault-out signals from four switches,

- Single trigger for the transient recorder,
- Single trigger for the excimer laser,
- Single trigger for the dye laser tunning step, with ACK signal read out,

• Read out line for the voltage slope provided by the dye laser for the rough monitoring of the frequency scan,

• RS-232C connection to the standalone wave meter (HighFinesse WS-7)



Drawing 13: Triggering and data acquisition scheme.

The most simple type of measurement in the first interaction zone of the apparatus involved only nozzle triggering and firing laser after the time needed for the molecules to travel the distance of 13 mm between nozzle and skimmer. By tunning the time delay between nozzle and laser trigger the time dependence of the SO_2 particle density was measured, just next to the nozzle throat. This type of measurement was named 1st interaction zone time scan.

Measurements performed in the 1^{st} interaction zone allowed the observation of the complete molecular beam produced by the nozzle, precise measurement of its length, and spectroscopy scans to determine the population distribution in the SO₂ molecules.

The track of the molecules reaching 2nd interaction zone follows through the the beam skimmer, hexapole lens, and decelerator electrodes. Basically measurements in the 2nd interaction zone could be divided into so called guiding regime, and switched regime measurements. While operating in guiding regime, a constant voltage of 3 kV was applied to all the electrode bars (with appropriate polarity respectively). The guiding potential allowed low field seeking molecules to be focused and guided through the decelerator, which has resulted in the number of particles arriving to the 2nd interaction zone, to be high enough for fluorescence detection. By tunning of the time delay between nozzle and

3.6. Data acquisition setup

detection laser trigger, it was possible to measure time-of-flight spectra of molecular beam. By comparing TOF gathered in 1st and and 2nd interaction zone one can calculate the average velocity, and velocity spread of the molecular pulse. The velocity spread is clearly visible in the 2nd interaction because of its placement in distance of almost 2 meters from the nozzle (compared with only 13mm for 1st interaction zone).

The fluorescence signal picked up by the photo multiplier tube, and amplified by high frequency operational amplifier (Hamamatsu C5594), was fed into the digital transient recorder (Tektronix RTD 720A). Digitized with resolution of 16bit, data was transmitted into the NI digital i/o register controlled with use of LabView data acquisition program.

For the sake of the spectroscopic measurements a connection with computerized wave meter was established to read out the precise wavelength of the laser at the moment of the measurement. After a preselected number of measurements at a given wavelength, the dye laser driver was triggered to perform step and progress with a different laser frequency.

It has to be mentioned that the repetition rate for the subsequent measurements was set to 10 Hz, which was suitable frequency for the excimer laser operation, and a delivered reasonable number of measurement samples.

3.6.1. Signal processing with use of software

The digitized fluorescence signal arriving at the i/o register was processed by the iterating program (LabView script). The 500ns long sample containing signal coming from laser stray light and from fluorescence was integrated in order to produce the single value interpreted as the signal intensity. In order to improve the signal-to-noise ratio following methods were applied:

• signal integration starting point can be shifted farther, reducing influence of the laser induced stray light, and emphasizing fluorescence, which occurs later,

• value of the fluorescence signal integration can be normalized with use of photo diode signal reading as a reference,

preselected number of measurements can be averaged

Measurement results were stored in column/row structured text file to ease reading data into processing applications. (Microcal Origin 6.1)

3.7. Auxiliary software used.

Following programs developed before were used to support the measurement:

• Spektrum_AsymRot - simulation of the asymmetric top model described in the chapter 2.1, resulting in calculation of molecular transition frequencies,

• TimeOfFLight - simple simulation of the molecular beam propagation through the decelerator, that allowed to find out appropriate average velocity, and temperature of the Gaussian velocity distribution in molecular beam,

• SchaltzeitenEinfach - program used to establish appropriate HV switching pattern for given synchronous molecule velocity, switching phase, and decelerator voltage,

• StarkDec (9) - single dimensional Monte-Carlo method based simulation of the experimental setup used for precise prediction of time of flight for decelerated particles,

• StarkDec (8) - three dimensional version of the model mentioned before, taking into account transversal movement of the particles in decelerator,

• TofMittelung - model of the molecules' fluorescence detection in the interaction zone, effectively folding Gaussian laser beam shape, of the given radius with the discrete function (produced by StarkDec) of the molecules arrival into the interaction zone.

4. Results

Basically following goals of the measurements performed with the described decelerator were envisaged:

• proof of the agreement between simulated (with StarkDec) time-of-flight spectra and measured time-of-flight for decelerated molecular bunches, with three switching phase angles of 40, 55 and 65 degrees,

- proof of the state selectivity of the decelerator,
- investigation on the fine structure of the decelerated molecular bunch,
- attempt to obtain cold SO₂ molecules.

Following paragraphs will address each of these goals.

4.1. Signal-to-noise level considerations

The experiment was actually burdened with the number of noise sources lowering overall signal-to-noise ratio. Most important of these, with remedies used, follow:

• instability of the detection (UV laser) beam power due to the instable dye laser behavior in range of about 40% of average laser power. Photodiode was used to read out instantaneous laser power for the purpose of results normalization. But measurements with and with and without the normalization enabled has shown that it does not improve the signal-to-noise ratio,

• possible saturation of the fluorescence that could cause dramatic increase of the effective laser beam diameter resulting in reduced measurement resolution.

4.2. Time-of-flight spectra in first and second interaction zone

Following the procedure described in paragraph 3.6 time-of-flight measurements of in the 1st and 2nd interaction zone were performed, results of these are presented on following charts. The curve presented on the chart 2 shows florescence from a 260 µs long (full width at half maximum) molecular pulse. On the other hand curve on the chart 3 presents the same molecular beam, observed in the second interaction zone, after passing through the decelerator operating in the guiding regime (3 kV). The laser wavelength was adjusted to 451710.44 cm⁻¹, which corresponds to the the 2(1,2) - 1(1,1) transition ($\tilde{X}^{-1}A_1 \rightarrow \tilde{C}^{-1}B_2$), exactly the same which is latter used to observe decelerated molecule bunches.



Chart 2: Time scan of 1st interaction zone.

Chart 3: Time scan of 2nd interaction zone together with simulation result

measurement model

The red curve, overlaid with the measurement on the chart 3 shows the modeled TOF distribution for the molecular pulse pictured on previous chart, with an average velocity of the Gaussian distribution found to be 300 m/s and its longitudinal temperature of 3 K^o (which are typical values for the system). The measurement conditions were equal for recordings on charts 2 and 3, nozzle temperature down to -60 C^o and SO₂ mixture pressure adjusted to 0.4 bar over the vacuum level.

What is to be seen on the chart 2 is that molecular bunch produced by the pulsed nozzle has steep bunch edges and fairly flat particle distribution inside the package. The time-of-flight scale zero point was adjusted in the middle of the molecular pulse. This convention is kept all through the TOF spectra presented from there on. Experimental curve pictured on the chart 3 directly shows the molecular bunch after traveling the distance of almost two meters through the decelerator have spread due to the velocity molecules' velocity distribution. Average velocity and longitudinal temperature of the velocity distribution fitted with the TimeOfFlight program served as starting parameters for further simulations with StarkDec(8) and StarkDec(9) programs.

4.3. Appearance of the decelerated molecule bunches in the second interaction zone.

Having already determined the particle velocity distribution in the molecular beam, chosen synchronous molecule velocity, switching phase, and switching voltage, one can

proceed with the generation of the appropriate switching pattern. The important fact to notice is that the synchronous molecule velocity does not have to coincide with the average velocity of the particles in molecular beam (see paragraph 2.3). Making use of a lower synchronous molecule velocity one can select particles with lower starting kinetic energy, compromising signal strength due to reduced population.



Chart 4: Gaussian velocity distribution in the molecular beam leaving the nozzle.

For the particular case considered already in paragraph 4.2 and pictured on the chart 4. An average velocity of the distribution found to be 300 m/s, selecting synchronous velocity of 285 m/s would result in the degradation of the available particle population by 25%.

Chart 5 presents a view composed of three measurements of decelerated molecules for specified deceleration angles, showing apparent influence of the switching angle on the particles' time-of-flight.



Chart 5: Composition of the decelerated molecules on the common time scale.

The measurement results were overlapped with the data obtained by three dimensional simulation performed with use of StarkDec (8). Chart 5 shows in detail that the obtained time-of-flight spectra for all three phase angles are perfectly consistent with with simulation on the matter of decelerated bunches arrival timing. As the absolute value of time-of-flight of SO_2 particle through the decelerator is burdened with a number of experimentally determined offsets, so one can not directly judge if the modeled and measured TOF fits precisely. Collecting three TOF for different switching phase angles and overlapping them with simulated data shows a fairly good fit of both arrival time and fluorescence intensity. One can infer from that StarkDec(8) model (with its input data) well reproduced SO_2 deceleration conditions.

It has to be noted that the intensity inconsistence for the last decelerated bunches (rightmost) is caused by the molecular burst being slightly longer in reality than the value

specified for the simulation.

The end velocity of the synchronous molecule arriving to the 2nd interaction zone is strictly connected to the HV switching pattern applied during the experiment, but that's not the case for molecules arriving in bunches other than synchronous. Particularly those arriving in earlier bunches missed last decelerator switching events and due to that have higher end velocity, than synchronous molecules have. That behavior is well pictured on the chart 6.



Chart 6: Phase-space diagram of decelerated molecules, 65°, starting velocity 300m/s, deceleration voltage 10kV.

Molecular bunches arriving after the synchronous molecule have the same end velocity as synchronous bunch. This is caused by the fact that molecules in these bunches have missed first switching events which means that at the moment of entering the decelerator (later than synchronous molecule), they must have been slower than synchronous molecule to fit HV switching pattern and eventually get decelerated. Bunches arriving latter than synchronous bunch have decreased population of the molecules because of the lower population of molecules slower than synchronous one in the molecular beam (see chart 4). Second reason for the lower population is that these late bunches have to travel longer path to reach interaction zone and due to that are more spread. Planed solution of this problem is to add a number of switching events with phase

angle zero at the end of deceleration switching pattern. This will not influence velocity of the molecules in this bunches, but just keep them together until 2nd interaction zone (see chapter 2.3).

The good signal-to-noise ratio for the TOF scan in chart 12, captured with phase angle of 65° gave also promising perspective for the deceleration with higher phase angles to obtain particles at very low velocities (<50 m/s), close to the standstill (see chapter 4.8).

4.4. Simulation of 3D molecules tracking

In order to obtain a detailed view on the behavior of the molecules in the decelerator a 3 dimensional tracking simulation was used (StarkDec (8)). Chart 7 presents a simulated phase-space diagram of the particles arriving at the 2nd interaction zone, tracked for the starting synchronous velocity of 300 m/s, switching phase angle of 40°, and deceleration voltage of 10 kV. It is clearly visible on the chart 7 that a large number of particles with TOF between 5.5 and 7.5 ms arrives to the 2nd interaction zone not being decelerated but just guided. Only a relatively small number of particles with TOF in the range between 7.5 and 8 ms is decelerated and bunched, and these will be of the experimental interest. Chart 8 presents phase-space data from chart 7 processed with use of TofMittelung (see chapter 3.7) in order to obtain simulated TOF spectra.



Chart 7: Overall phase space diagram containing all molecules arriving at 2nd interaction zone.

Chart 8: Overall space diagram converted to intensity diagram.

By taking very close look on the single decelerated molecules bunch from the chart 7 one

can find that molecules create in a phase-space a closed shape resulting from the phase acceptance of the decelerator (chart 9). Use of single dimensional particle tracking results in homogeneous distribution of molecules in the bunch, as pictured on the chart 9. Three dimensional molecule tracking in decelerator which takes into account transversal movement (chart 10), reveals unstable regions inside the shape of decelerated bunch [8].



Chart 9: Phase-space diagram of the 1D simulated synchronous molecule bunch decelerated from starting velocity of 300 m/s, switching phase of 40° and deceleration voltage of 10 kV.

Chart 10: Phase-space diagram of the 3D simulated synchronous molecule bunch decelerated from starting velocity of 300 m/s, switching phase of 40° and deceleration voltage of 10 kV.

That behavior gives a reason for the fine structure of molecular bunches to be observed with TOF scan of appropriate resolution (discussed in detail in paragraph 4.5). Chart 11 presents result of the TOF simulation of the same molecular bunch as presented in phase-space in chart 10 with various laser beam diameters applied. Significant difference in the TOF signal is visible between 1 mm and 0.5 mm laser beam diameter. Fluorescence dip appearing in the simulated data (chart 11) at 7,69 ms was a point of interest for the measurements presented on the chart 12. Three curves on the chart 12 represent three time scanning step sizes, of 20, 2 and 0.2 μ s respectively. It is to be noticed that TOF scan with step size of 0.2 μ s in given circumstances (0.5 mm laser beam) according to the table 3 does not result in resolution increased over 2 μ s step scan as laser beam limits effective resolution (please refer to the chapter 4.5). The 0.2 μ s scan is presented on the chart 12 ropes of reference with 2 μ s step scan.



Chart 11: Zoom in of the single bunch of decelerated molecules for various laser beam sizes. Chart 12: Experimental curves for the single bunch of decelerated molecules.

The attempt to resolve the fine structure of this particular bunch with laser beam diameter of 0.5 mm did not produced in satisfactory result. It is expected time resolution of the time-scan might have been reduced by the fluorescence saturation which caused effective broadening of the interaction intersection of the detection laser with molecular beam.

Consistence of the three dimensionally modeled data with experiment was to be proven on the ground of the fluorescence intensity comparison between main (non-decelerated) bunch and decelerated molecular bunches. Two curves visible on the chart 13 present the modeled (lower plot) and experimental (upper plot) data of the deceleration with starting velocity equal 300m/s, switching phase angle equal 55° and deceleration voltage of 10 kV. Upper curve was shifted vertically for the sake of clarity.



Chart 13: Combined time-of-flight scans of the main molecular bunch, and decelerated molecules' bunches for deceleration of molecules with synchronous starting velocity equal 300m/s, switching phase 55° and deceleration voltage of 10 kV.

It is to be noticed that experimental (upper) curve on the chart 13 contains an additional molecular bunch at the beginning (to the left) of the train of the bunches which does not have corresponding bunch on the simulated (lower curve). The contrary situation occurs for the last bunch (to the right) which is only weakly represented on the experimental curve. The reason for this behavior is that in the simulation the decelerator switching begins in the moment when exactly half of the molecular pulse. In this particular experimental case the switching started later and affected the beam which was more than in a half inside the decelerator. Described inconsistency is not negating overall consistency of simulated and measured data as it does not influence time of flight of decelerated particles neither timing of the synchronous molecule nor intensity of the decelerated bunches excluding first (left-most) and last (right-most) one.

4.5. Considerations on the influence of the detection laser beam size.

One of the critical parameters determining the time resolution of the experimental apparatus is the size of the detection laser beam. This is due to the fact that the width of the laser beam intersecting the molecular beam in the interaction zone determines the spatial region corresponding to a TOF window of particles being detected. Use of the cylindrical lenses is preferred as a linear laser beam shape of the laser eases overlapping the molecular beam in the interaction zone, which would not be the case for the spherically collimated beam.

		Laser beam diameter [mm]			
Phase angle [deg]	End Velocity [m/s]	2,00	1,00	0,50	0,25
40	193	10,36	5,18	2,59	1,30
55	157	12,74	6,37	3,18	1,59
65	116	17,24	8,62	4,31	2,16

Table 3: Time scanning resolution [μ s] for given end velocities and laser beam diameters with starting synchronous particle velocity of 300 m/s and high voltage of 10 kV

Table 3 shows calculated end velocities of the decelerated particles of the quantum state 1(1,1) M=|0| with starting synchronous molecule velocity of 300 m/s and switching voltage of 10 kV. The grayed fields represent achievable measurement resolution in µs for the detection laser beam diameter. For the purpose of the increase of the timescan resolution, the telescope consisting of two lenses was built. A preliminary beam diameter of 2 mm was successfully reduced to 1 mm and even further by an iris, down to 0.5 mm. The iris was set just before the telescope lens stopping of the non Gaussian beam rays, that might have caused undesirable stray light in the interaction zone.

Laser beam size was measured with use of sharp barrier (razor blade) mounted to the micrometric stage and laser power meter. As blade was stepwise moved into the laser beam the laser power meter readings were recorded. For the purpose of measurement laser beam was reflected out of it's normal path (through the 2^{nd} interaction zone) the way that razor blade could be put in exactly the distance from the telescope equal to the distance between telescope and 2^{nd} interaction zone. The purpose of this setup was to reproduce precisely laser beam shape in the 2^{nd} interaction zone exactly in the place where razor blade was mounted. Scan presented on the chart 14 started with razor blade put far out of the beam and followed in steps of 100 µm. With use of non-linear fit method the differential of curve from chart 14 was fitted to the Gaussian distribution function defined by:

$$y = y_0 - A * \exp\left(\frac{-2 * (x - x_0)^2}{w^2}\right)$$
.

Curves presented on the chart 15 show a differential (black) and Gaussian fit of the laser beam intensity. Non-linear fit have found the value of w (beam radius) to be equal \sim 0.26 mm.



Chart 14: Manual sharp blade scan through the laser Chart 15: Differential of the sharp blade scan curve beam (250µm) for laser beam (250µm)

Knowing the detection laser beam diameter allowed also to apply it for the TofMittelung program and to obtain a detailed view on the structure of a single decelerated molecular bunch. Chart 16 presents the result of 3D modeling of molecules with starting velocity of 300 m/s, switching phase angle of 40°, and deceleration voltage of 10 kV, treated with three different detection laser beam sizes. It is important to notice, that relative fluorescence intensity is expected to go down with decrease of the laser beam size, due to decrease of the interaction volume. As expected, the smaller laser beam size has revealed fine structure of the molecule bunches.



Chart 16: Combined chart of the intensity of modeled decelerated bunches for various laser beam sizes.

4.6. State selectivity of the decelerator

The first quantum state discrimination occurring in the decelerator happens already at the beginning, that is in the hexapole. The hexapole lens being optimized for the given low field seeking state (1(1,1), |M|=0 for the purpose of this experiment) efficiently defocuses high field seeking states or even make them to crash into the electrodes due to non-fitting Stark shift of the state. Further on the switching pattern for SO₂ deceleration is also calculated for the specified Stark shift characteristic for the given quantum state. Due to phase space acceptance of the switching pattern it is possible to effectively decelerate more than one quantum state with close values of the Stark shifts. In case of SO₂ the other source of low field seeking molecules is the quantum state 2(1,1) |M|=2 (see chart 1), which gives a contribution to the broad line at 45709.00 cm⁻¹ and weak line at

45711.22 cm⁻¹ (see chart 18).



Chart 17: Frequency scan of the 1st interaction zone.

Chart 18: Frequency scan of the decelerated bunch in 2^{nd} interaction zone.

Chart 17 presents an assigned spectrum measured in the 1st interaction zone of the apparatus. It contains transitions from all the populated quantum states in the molecular beam leaving the nozzle. The assignment was done with the use of the table presented in Appendix A containing transition wavelengths calculated with the use of AsymStarkRot (see paragraph 3.7) program based on the rotational structure theory presented in chapter 2.1 and applying appropriate rotational constants (also see appendix A)

Chart 18 presents the same type of measurement performed in the 2^{nd} interaction zone, with the experimental timing adjusted to hit the maximum intensity of the decelerated molecule bunch with TOF value of 8.583 ms (for 300m/s synchronous molecule starting velocity, 55° switching phase angle). The lower line repeats the curve presented on the chart 17, for the sake of reference. As expected, the decelerated bunch of molecules, consists mostly of the particles in state 1(1,1) (|M|=0), with addition of the molecules arriving in the state 2(1,1) (|M|=2) that are not really decelerated, but just guided through and by chance have the same TOF as decelerated molecules.

4.7. Decelerator's internal electric field considerations

An additional effort on simulation was done in order to research the case in which the electric field strength inside the decelerator does not fit the value expected from the applied high voltage, and designed inter-electrode distance. The reason for such fault could lie either in imprecise mechanical adjustment of the decelerator electrodes spacing, or degradation of the voltage due to discharge of the buffering capacitors during continuous switching. Simulations were performed for the starting synchronous velocity of 305 m/s with switching phase angle of 40° and defined switching pattern voltage of 10 kV. As long as the deceleration switching pattern was generated for the voltage of 10 kV, the simulations were run with actual deceleration voltages inconsistent (set to 9 kV and 11 kV) with the switching pattern. Curves plotted on the chart 19 show a definite influence of the applied voltage on the simulated fine structure of the molecular bunches. The task of showing compliance of this simulated results with measurements remains open.



Chart 19: Zoom in of two simulated, decelerated bunches with starting velocity of 305 m/s, switching phase angle of 40° and defined switching pattern for voltage of 10kV, with three actual deceleration voltages applied.

4.8. SO₂ deceleration close to the standstill.

By having three tunable parameters of the decelerator, it was possible to find out starting velocity, switching phase angle, and HV level required to bring synchronous molecule to the velocity of 50 m/s. Results were gathered in the Table 4.

	switching voltages					
starting velocity [m/s]	10 kV	10.5 kV	11 kV	12 kV	12.5 kV	
300	75.9	71.4	66.3	58.7	55.6	
295	74.3	68.2	63.5	56.6	53.6	
290	70.1	65.2	61.5	54.5	51.8	
285	67.3	62.6	58.8	52.6	50.0	
280	64.5	60.2	56.6	50.7	48.2	

Table 4: Switching phase angles [deg] for given starting velocities and switching voltages specified to decelerate molecules down to 50 m/s.

Being limited for the time of writing this thesis to deceleration voltage of 10 kV the conditions of deceleration were taken as following: 285 m/s starting velocity (see paragraph 4.4) and switching phase of 67.3°. Measurement of TOF for these conditions (presented as the lower curve on the chart 20) resulted in poor signal-to-noise ratio, but has shown very good time overlap with the simulated data (upper curve on the same chart). It is important to notice that the central, and the most pronounced molecular bunch (with TOF of 11,9 ms) on the chart 20 is the synchronous bunch. The effect of spreading of the bunches described in the paragraph 4.4 is very clearly visible on the bunches following the synchronous bunch.



Chart 20: Time-of-flight spectra of decelerated bunches for synchronous starting velocity of 285 m/s, switching phase angle of 67.3° and deceleration voltage of 10 kV.

This result gives a big promise on the accomplishment of more efficient deceleration

with use of higher deceleration voltage and lower switching phase angle which will increase phase acceptance of the deceleration and eventually effect in higher number of slowed down particles.

5. Conclusions and outlook

The results presented int this work cover the construction and successful startup of the stark decelerator with the largest number of the deceleration stages (available in the moment of writing this thesis). Numerous improvements in the mechanical setup of the decelerator were performed. The supersonic beam expansion of SO₂ mixture with carrier gas (Xenon) was demonstrated to produce a molecular beam with a narrow Gaussian velocity distribution. The deceleration, starting at velocity of 285 m/s, with the deceleration voltage of 10kV, was shown to reach 50m/s. By further increase of the operating voltage to 12.5 kV it is believed to obtain cold SO₂ molecules with end velocity below 30 m/s which is low enough to allow efficient trapping. The quantum state selectivity of the decelerator was demonstrated for the low-field seeking states. Consistence of the time-of-flight measurements to the 3D molecule tracking simulations was shown with respect to the synchronization and intensity of the fluorescence signal.

Gathered results provide tools to further investigation of the quantum chemistry, ultra cold molecules and interactions of the molecule fragments.

6. Appendix A

List of the SO₂ transition lines observable in the molecular beam calculated with use of Spektrum_AsymRot program with following input parameters specification:

```
SO2 Grundzustand nach JMS 201 1 2000, 300 Szankowski
0
45494.12
                    upper Te
                     unit Tv
0.344173886
cm-1
    2.027354198
                                                0.29352651
                     0.0000000000
0.0000000000
                                         0.0000000000
    0.0000000000
                                                                   lower DJ,DJK,DK
    0.0000000000
                                               lower dJ,dK

        0.000000000
        0.00000000

        0.000000000
        0.00000000

        0.000000000
        0.00000000

                                        0.000000000 0.000000000
0.0000000000 lower hJ,
                                                                                      lower HJ,HJK,HKJ,HK
                                                                lower hJ,hJK,hK
    1.1357 0.33850.2608
                                  upper A,B,C
    lower DJ,DJK,DK
                                               lower dJ,dK

        0.000000000
        0.00000000

        0.0000000000
        0.000000000

        0.0000000000
        0.000000000

                                        0.000000000 0.000000000
                                                                                      lower HJ,HJK,HKJ,HK
                                         0.000000000
                                                                 lower hJ,hJK,hK
cm-1
                    unit of A,B,C
cm-1
                    unit of output
20
                    Max J to be calculated
f
                    list of term energies
f
                    output of eigenvectors of rotational matrix
                  dipole, type
1.63305, a
2
                    rotational Temperature
.0005
                    intensity threshold 0 = all
                    output of spectrum
t
45475,45500,2000,.03 from, to, steps, linewidth
cm-1
                    unit of 'from' and 'to'
f
                    weights from external file (IntensExt.dat)
3
                    column used as weight
4
                    column with quantum numbers
```

Wavenumber [cm-1]	Relative intensity [1]	Transition
45710.5552	0.1532	1(0,1)-0(0,0)
45709.0872	0.1179	1(1,0)-1(1,1)
45710.4412	0.1179	2(1,2)-1(1,1)
45708.6432	0.1768	1(0,1)-2(0,2)
45712.0439	0.2651	3(0,3)-2(0,2)
45706.5725	0.0412	2(2,1)-2(2,0)
45708.6130	0.0206	3(2,1)-2(2,0)
45707.7105	0.0793	1(1,0)-2(1,1)
45709.0645	0.0441	2(1,2)-2(1,1)
45711.1192	0.1410	3(1,2)-2(1,1)
45704.6605	0.0119	2(2,1)-3(2,2)
45706.7011	0.0166	3(2,1)-3(2,2)
45709.4217	0.0214	4(2,3)-3(2,2)
45707.3800	0.0868	2(1,2)-3(1,3)
45709.4347	0.0190	3(1,2)-3(1,3)
45712.1300	0.1221	4(1,4)-3(1,3)
45702.4144	0.0032	3(3,0)-3(3,1)
45707.5958	0.0981	3(0,3)-4(0,4)
45713.7169	0.1227	5(0,5)-4(0,4)
45704.1343	0.0102	3(2,1)-4(2,2)
45706.8549	0.0061	4(2,3)-4(2,2)
45710.2560	0.0143	5(2,3)-4(2,2)
45706.4810	0.0522	3(1,2)-4(1,3)
45709.1764	0.0063	4(1,4)-4(1,3)
45712.6166	0.0668	5(1,4)-4(1,3)
45703.6857	0.0057	4(2,3)-5(2,4)
45711.1674	0.0073	6(2,5)-5(2,4)
45706.6256	0.0321	4(1,4)-5(1,5)
45714.0899	0.0390	6(1,6)-5(1,5)
45706.7634	0.0198	5(0,5)-6(0,6)
45715.6047	0.0231	7(0,7)-6(0,6)
45712.0305	0.0028	7(2,5)-6(2,4)
45705.3379	0.0100	5(1,4)-6(1,5)
45714.2003	0.0117	7(1,6)-6(1,5)
45706.1514	0.0047	6(1,6)-7(1,7)
45716.3298	0.0054	8(1,8)-7(1,7)

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Declaration

Hereby i declare that the following diploma work I have prepared independently with exclusive use of the referenced bibliography.

Hannover 31 May 2007