Astatine and Yttrium Resonant Ionization Laser Spectroscopy

by

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#### Abstract

Providing intense, contamination-free beams of rare isotopes to experiments is a challenging task. At isotope separator on-line facilities such as ISAC at TRIUMF, the choice of production target and ion source are key to the successful beam delivery. Due to their element-selectivity, high efficiency and versatility, resonant ionization laser ion sources (RILIS) gain increasingly in importance.

The spectroscopic data available are typically incomplete in the region of excitedand autoionizing atomic states. In order to find the most efficient ionization scheme for a particular element, further spectroscopy is often required. The development of efficient laser resonant ionization schemes for yttrium and astatine is presented in this thesis.

For yttrium, two ionization schemes with comparable relative intensities were found. Since for astatine, only two transitions were known, the focus was to provide data on atomic energy levels using resonance ionization spectroscopy. Altogether 41 previously unknown astatine energy levels were found.

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## 1. Introduction

The optical spectrum of an atom provides important information about its atomic structure and certain nuclear ground state properties of its individual isotopes. Of the 118 known elements, optical spectra are mostly known for those with atomic number  $Z \leq 100$  [Sew03]. One of the few exceptions is astatine, atomic number Z = 85, first discovered by D. C. Corson et al. in 1940 [CMS40] by bombarding <sup>208</sup>Bi with  $\alpha$  particles. All astatine isotopes are radioactive; the <sup>210</sup>At isotope has the longest half-life,  $\tau = 8.3$  h [JLS49]. Despite these limitations, McLaughlin managed to perform astatine spectroscopy using a 1000 W Hanovia hydrogen-discharge tube on a sample of <sup>210</sup>At in a vapor cell [McL64]. He found two transitions from the ground state into the first excited states at 44549.3 cm<sup>-1</sup> and 46233.6 cm<sup>-1</sup><sup>1</sup>. The focus of the work described in this thesis is to look for other resonant transitions which may serve as a basis for further spectroscopic studies of atomic and nuclear properties of astatine.

The measurements were performed at TRIUMF's Isotope Separator and Accelerator (ISAC) facility which specializes in producing intense radioactive or rare isotope

<sup>&</sup>lt;sup>1</sup>The wavenumber  $\tilde{\nu} \text{ [ cm}^{-1} \text{]}$  is a common unit to express energies in atomic spectra (1 cm<sup>-1</sup> = 123 µeV = 30 GHz = 1 cm).

beams (RIB). These are produced by bombarding target materials with protons of 500 MeV energy and up to 100 µA intensity. The heaviest target material available until recently has been tantalum, where isotopes up to a mass of A = 178 u could be produced. Since September 2009 the ISAC operating licence allows the use of actinides as target materials. With uranium compounds as target material, the accessible isotopes have been extended to higher masses such as A = 232 u and neutron-rich ones. Hence, it is also possible with this technique to produce isotope beams of the desired astatine atoms.

The spectroscopy was carried out at TRIUMF's Resonant Ionization Laser Ion Source (TRILIS). TRILIS is one of three different on-line ion source types currently available at TRIUMF, which are necessary to guide and to accelerate the requested isotopes from the target to the respective experiment. TRILIS uses resonant ionization techniques in which a valence electron is stepwise resonantly excited above the ionization potential. Since the excitation process is unique for every element, this ion source is elementally selective. TRILIS only operates solid state laser systems consisting of ns-pulsed titanium-doped sapphire (Ti:Sa) lasers. The classical on-line RILIS in operation at ISOLDE-CERN [Klu85] used dye lasers until 2011 [RMM<sup>+</sup>11], and as a result, the most efficient ionization schemes tested are available for the dye laser spectrum in the ultraviolet (UV) to visible optical spectrum (VIS). However, the emission spectrum of Ti:Sa crystals is located in the near infrared spectrum. By frequency conversion using nonlinear crystals, wavelengths in the UV and blue regions can be reached. Due to the different wavelength ranges, ionization schemata applicable for dye laser systems are not necessarily applicable to Ti:Sa laser-based laser systems. Within the Ti:Sa RIS network consisting of TRILIS at TRIUMF, LARISSA at the University of Mainz, IGISOL at Jyväskylä, and the ORNL-RILIS in Oakridge, excitation schemes for 44 elements have been successfully tested. Figure 1.1 indicates the 17 radioactive species (of the 44) which have been ionized by TRILIS thus far and delivered to users at TRIUMF.

The efficiency of an ionization scheme depends greatly on the ionizing step, which can be either nonresonant into the continuum or resonant into a Rydberg or autoionizing state. Resonant transitions have higher transition probabilities and are therefore more promising for higher yield ionization schemes. However, these transitions are mainly unknown for most elements. To look for energy levels around the ionization potential, a laser ion source test stand, including an oven to evaporate samples of stable isotope elements and a mass-separator, was developed in 2010, as a part of the dissertation of J. P. Lavoie [Lav10]. Consequently, ionization schemes can be tested off-line without requiring radioactive species or disrupting RIB delivery to experiments.

The technique used to look for resonances around the ionization potential in stable isotopes can be applied to look for energy levels in astatine. In preparation for the astatine spectroscopy in which available radioactive ion beam time is limited, the development of an efficient excitation scheme has been performed on yttrium in order to familiarize ourselves with the equipment and spectroscopy technique. Yttrium had been chosen since it was requested by an approved high-priority experiment at TRIUMF using collinear spectroscopy techniques for the determination of nuclear charge radii.

Group																	
1A				TRIUMF	- RILIS	isotope:	s on-lin∈	C)	status	3: 05/201	5						8A 18
_	Ē			tested 7	TiSa las	er schei	mes		status	:: 01/201:	0						<sup>∠</sup> He
Hydro	gen 2A 2			(TiSa n	etwork:	Mainz, T	RIUMF, (	GANIL, H	IRIBF, JY	FL, ISOLE	Ű.	3A <mark>13</mark>	4A 14	5A 15	6A 16	7A 17	Helium
e	Li <sup>4</sup> Be											5 B	° C	Z	8	9	10 Ne
Lithiu	ım Beryllium			Ti:Sa las	er ioniză	ation sch	iemes on	ı paper (t	theory)			Boron	Carbon	Nitrogen	Oxygen	Fluorine	Neon
11	Va <sup>12</sup> Mg						Ĺ	88 				13 AI	<sup>14</sup> Si	<sup>15</sup> P	<sup>16</sup> S	17 CI	<sup>18</sup> Ar
Sodiu	im Magnesium	n 3B <mark>3</mark>	4B 4	5B 5	6B 6	78 7	8	6	10	1B 11	2B 12	Aluminum	Silicon	Phosphorus	Sulfur	Chlorine	Argon
19	K <sup>20</sup> Ca	1 <sup>21</sup> Sc	22 Ti	23 V	<sup>24</sup> CI	25 Mr	1 <sup>26</sup> Fe	27 CC	D 28 N	<sup>29</sup> Cu	<sup>30</sup> Zn	<sup>31</sup> Ga	<sup>32</sup> Ge	<sup>33</sup> As	<sup>34</sup> Se	<sup>35</sup> Br	<sup>36</sup> Kr
Potass	ium Calcium	Scandium	Titanium	Vanadium	Chromiur	m Mangane	se Iron	Cobalt	Nickel	Copper	Zinc	Gallium	Germanium	Arsenic	Selenium	Bromine	Krypton
37 F	tb <sup>38</sup> Sr	<sup>39</sup> Y	40 Zr	41 NC	42 MC	A 43 TC	<sup>44</sup> RL	I 45 R	1 46 PC	47 Ag	<sup>48</sup> Cd	<sup>49</sup> In	<sup>50</sup> Sn	51 Sb	<sup>52</sup> Te	53	<sup>54</sup> Xe
Rubidi	ium Strontium	r Yttrium	Zirconium	Niobium	Molybdenui	[98] Technetiur	n Rutheniun	n Rhodiun	n Palladium	Silver	Cadmium	Indium	μ	Antimony	Tellurium	lodine	Xenon
55 C	Ss <sup>56</sup> Ba	57-71 *	72 Hf	73 Ta	74 V	/ <sup>75</sup> R€	50 92 j	5 77 Ir	<ul> <li>78 Pt</li> </ul>	<sup>79</sup> Au	<sup>80</sup> Hg	<sup>81</sup> TI	<sup>82</sup> Pb	<sup>83</sup> Bi	<sup>84</sup> PO	<sup>85</sup> At	<sup>s6</sup> Rn
Cesiu	mBarium		Hafnium	Tantalum	Tungsten	Rhenium	Osmium	Iridium	Platinum	Gold	Mercury	Thallium	Lead	Bismuth	[209] Polonium	[210] Astatine	[222] Radon
87	-r <sup>88</sup> Ra	89-103 **	104 Rf	105 Db	106 SG	1 107 BF	108 HS	109 M1	t 110 Ds	III Rg	112	113	114	115			
[225 Franci	l] [226] um Radium		[261] Rutherfordiun	[262] Dubnium	[266] Seaborgiur	n Bohrium	[277] Hassium	[268] Meitneriur	[281] m Darmstadtiu	[272] mRoentgenium	[285] Ununbium	[284]	[289]	[288]	1 SUBL	-assen TRI LIS sta	atus: 05/2012
								ľ									
		*	57 La	<sup>58</sup> Ce	59 PI	< 60 N	d ₀ Pn	1 <sup>62</sup> Sm	n <sup>63</sup> Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	mT ®	$dY^{07}$	71 Lu
			Lanthanum	Cerium	Praseodymiu	m Neodymiu	[145] m Promethiu	m Samariur	n Europium	n Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium
		*	<sup>89</sup> Ac	<sup>90</sup> Th	<sup>91</sup> P2	1 <sup>92</sup> L	J 93 NG	0 94 PU	I <sup>95</sup> Am	n <sup>%</sup> Cm	<sup>97</sup> BK	98 Cf	<sup>99</sup> Es	<sup>100</sup> Fm	101 Md	102 NO	<sup>103</sup> Lr
			[227] Actinium	232.0381 Thorium	231.0359 Protactiniu	238.0289 m Uranium	Neptuniur	n Plutoniur	m [243] Thericium	[247] Curium	[247] Berkelium	[251] Californium	[252] Einsteinium	[257] Fermium	[258] Mendelevium	[259] Nobelium	[262] Lawrencium

Figure 1.1.: Elements accessible with Ti:Sa laser excitation schemes. The elements indicated in green have been ionized by TRILIS and provided as RIB to experiments on-line at TRIUMF. The elements assigned in blue have been tested within the Ti:Sa RIS network, and for the elements highlighted in grey, transitions suitable for Ti:Sa based ionization schemes are available but have not yet been tested as such.

#### 1. Introduction

This thesis is segmented into six chapters. The first chapter gives the motivation for the Ti:Sa-laser-based resonant ionization spectroscopy at TRIUMF, with a focus on the study of the atomic structure of astatine via its hitherto unknown optical spectrum. Chapter 2 explains the physical background necessary to be able to draw conclusions from the measured spectra and compares ionization schemes developed prior to this work for their possible efficiency. In Chapter 3, the all-solid-state laser system used at TRILIS is introduced. The ionization scheme development for yttrium, comparing different nonresonant and resonant ionization schemes is described in Chapter 4. The knowledge gained from this previous ionization scheme development is applied to the spectroscopy performed on radioactive isotopes of astatine as described in Chapter 5. As a conclusion, all obtained results are presented in Chapter 6.

## 2. Resonant ionization spectroscopy

Resonant ionization spectroscopy is based on the stepwise resonant excitation of a valence electron into the continuum. A typical excitation scheme consists of one or two resonant transitions before ionization. The criteria required for resonant transitions are described in Section 2.1. The ionizing step can either be realized resonantly via a transition into an autoionizing or Rydberg state, or nonresonantly. All three methods are discussed in Section 2.2. Since the energies required to fulfil a resonant transition into an excited state are element-specific, this ionization process is element-selective. With resonant laser ionization, ionization efficiencies of up to 20-40% can be reached [Klu85]. The parameters required from the laser system to ensure an efficient ionization are outlined in Section 2.3.

## 2.1. Selection of resonant excitation steps

In databases such as the Atomic Spectra Database from NIST [RKRT11] or the Atomic Spectral Line Database of R.L. Kurucz [SHEK], a wealth of spectral lines and levels are listed for a large fraction of the elements in the periodic table. The databases contain in general:

- wavelengths
- energy levels
- electron configurations or term schemes
- Einstein coefficients  $A_{ki}$  or oscillator strengths  $f_{ik}$

but are in most cases incomplete.

### 2.1.1. Transition probability

The optical spectrum of an element depends on the energy differences between any state  $|k\rangle$  and  $|i\rangle$  of a valence electron. The frequency  $\nu_{ik}$  is given by

$$h\nu_{ik} = |E_i - E_k| \,. \tag{2.1}$$

By measuring an absorption or emission spectrum of an element, it can be seen that the intensities of the spectral lines are not equal to each other. The intensity of a line depends on the probability P of a photon being absorbed or emitted by an electron. In practice these transition probabilities can be expressed by different physical observables where the most common ones are discussed in what follows.

#### **Einstein coefficients**

Since electrons can only stay in an excited state for certain time  $\tau^{-1}$  before they decay into other lower lying states, one distinguishes between spontaneous and induced

 $<sup>{}^{1}</sup>N(t) = N(0) \cdot e^{-t/\tau}$  in which N is the excited state population at the time t and  $\tau$  is the radiative lifetime.

transitions. The induced transitions depend on the number of available photons at the required frequency  $n(\nu)$ . For that reason, the transition probabilities of these transitions are proportional to the spectral energy density  $\rho(\nu) = n(\nu) \cdot h\nu$ . They are given as

$$P_{ik} = B_{ik} \cdot \rho(\nu)$$
 for absorption, (2.2)

$$P_{ki} = B_{ki} \cdot \rho(\nu)$$
 for stimulated emission and (2.3)

$$P_{ki} = A_{ki}$$
 for spontanous emission, (2.4)

where the constants  $B_{ik}$ ,  $B_{ki}$  and  $A_{ki}$  are the so-called Einstein coefficients of the respective transition. For resonant laser ionization, the probability for absorption is mainly of interest. In the above mentioned databases, typically the Einstein coefficient for spontaneous emission is listed as an indicator for transition strength. The Einstein coefficients themselves can easily be converted into each other using the following relations [Dem06]

$$B_{ki} = \frac{g_i}{g_k} B_{ik} \tag{2.5}$$

$$A_{ki} = \frac{8\pi h\nu^3}{c^3} B_{ki} , \qquad (2.6)$$

in which  $g_i = 2J_i + 1$  and  $g_k = 2J_k + 1$  are the statistical weights and total angular momentum J (further described in Section 2.1.2) of the corresponding states.

A characteristic value for a strong transition would be  $A_{ki} = 10^8 \text{ s}^{-1}$ . The lifetime of state  $|k\rangle$  for a two level system the inverse of this coefficient. In general, various



Figure 2.1.: Interaction of radiation with matter described by the three Einstein coefficients for absorption, stimulated emission, and spontaneous emission. Absorption and stimulated emission are induced interactions and require resonant photons that couple the states  $|i\rangle$  and  $|k\rangle$ . For stimulated emission the emitted photon has the same properties in terms of energy and coherence as the incident; in contrast, spontaneous emission is a random process.

transitions into lower lying states are possible; thus the lifetime of the state  $|k\rangle$  is defined as

$$\tau_k = (\sum_i A_{ki})^{-1} \,. \tag{2.7}$$

For a state with strong transition probabilities, the lifetime is therefore on the order of  $\tau_k \sim 10^{-8}$  s.

#### **Oscillator strength**

In the classical electromagnetic approach to absorption and emission, a damped harmonic oscillator is stimulated by an oscillating electric field  $E = E_0 e^{i\omega t}$  along the *x*-direction. The resultant equation of motion is

$$\ddot{x} + \gamma \dot{x} + \omega_0^2 x = \frac{e}{m} E_0 \mathrm{e}^{i\omega_{ik}t} \,, \tag{2.8}$$

where  $\gamma$  is the damping coefficient which is inversely proportional to the lifetime  $\tau_k$ , and  $\omega_0$ , e, and m are the eigenfrequency, charge and mass of the electron. The energy losses introduced by the damping correspond to the emitted radiation [Dem07].

Since more than one transition is possible from an excited state  $|k\rangle$ , the fraction of electrons decaying to a specific state  $|i\rangle$  is expressed by the dimensionless number  $f_{ki}$ called the oscillator strength or f-value. That means, for summing up the oscillator strengths for all possible states  $|i\rangle$  from a specific state  $|k\rangle$ , one obtains the overall number of involved electrons N

$$\sum_{i} f_{ki} = N . (2.9)$$

This relation is called the Thomas-Reiche-Kuhn sum rule, where the oscillator strength for emission  $f_{ki}$  is defined as negative and the oscillator strength for absorption  $f_{ik}$  is positive. The relation

$$g_k f_{ik} = -g_i f_{ki} \tag{2.10}$$

follows. For a system with just one electron, it can be seen that  $|f| \leq 1$ . The connection between the Einstein coefficient  $A_{ki}$  and the absorption oscillator strength  $f_{ik}$  is given as

$$A_{ki} = \frac{2\pi e^2}{mc\epsilon_0 \lambda^2} \frac{g_i}{g_k} f_{ik} . \qquad (2.11)$$

Other common parameters to express transition strength and their relationship can be found in [Hil02].

## 2.1.2. Selection rules

The resonances observed in an absorption or emission spectrum not only depend on the energy conservation as described in Equation (2.1) but also on the conservation of momentum and certain symmetry properties of the wave functions  $\Psi_i$  and  $\Psi_k$  of the electron. From the quantum mechanical derivation of Equations (2.2) to (2.4), it can also be shown that the Einstein coefficients are proportional to the square of the dipole matrix element

$$D_{ik} = e \int \Psi_i^* \vec{r} \Psi_k dV , \qquad (2.12)$$

in which  $\vec{r}$  is the position vector of the electron [Dem06]. The Einstein coefficient e.g. for absorption can therefore be expressed as

$$B_{ik} = \frac{2}{3} \frac{\pi^2 e^2}{\epsilon_0 h^2} |D_{ik}|^2 \,. \tag{2.13}$$

It is obvious that a transition from state the  $\Psi_i$  to state  $\Psi_k$  and vice versa (because  $D_{ik} = D_{ki}$ ) is only possible if the integral in Equation (2.12) does not vanish. The requirements resulting from this condition are called selection rules for dipole transitions and are described in what follows.

#### Parity selection rule

Without knowing how the wave functions  $\Psi_i$  and  $\Psi_k$  look in detail, the first selection rule can be derived by taking a closer look at its symmetry. Under the transformation  $\vec{r} \rightarrow -\vec{r}$ , symmetric wave functions revert to themselves as symmetric,

$$\Psi(\vec{r}) = \Psi(-\vec{r}), \qquad (2.14)$$

while asymmetric wave functions are,

$$\Psi(\vec{r}) = -\Psi(-\vec{r})$$
. (2.15)

From this symmetry, one ascribes even parity to symmetric wave functions and odd parity to asymmetric wave functions. An example of an even and odd parity function is shown in Figure 2.2. As the dipole operator  $e \cdot r$  is odd, the integral of an odd wave



Figure 2.2.: Examples of wave functions with even and with odd parity. When the wave function is reflected (dashed line) about x = 0, the even parity function is converted into itself while the odd parity function is transformed into a function with the same magnitude but opposite sign.

function with symmetric boundaries is zero. Thus it can be seen from Equation (2.12), that the dipole matrix element only does not vanish if  $\Psi_i$  and  $\Psi_k$  have different parities [HWB05].

#### Orbital and spin quantum number selection rules

Hydrogen is the simplest atom, and its wave function can therefore be exactly calculated. The parity of its wave functions is  $(-1)^l$  where l is the orbital quantum number. In order to fulfill the dipole transition condition that the wave functions must have different parities, the quantum number l has to differ by an odd number. Since the photon introduces an angular momentum of  $\pm\hbar$ , the first selection rule is set to

$$\Delta l = \pm 1 . \tag{2.16}$$

Since the dipole operator does not operate on the electron spin the latter remains unaffected:

$$\Delta s = 0. \tag{2.17}$$

#### Many-electron systems

The above mentioned selection rules apply strongly only for light elements where the spin-orbit coupling is weak. For heavier elements the electron spin and orbital angular momentum first couple to a total angular momentum  $\vec{j} = \vec{l} + \vec{s}$ . In these systems, transitions between different multiplets are possible even though they are typically weaker. These transitions are called intercombination lines.

For these atoms, the most interesting quantum number is the total angular momentum J. Depending on the mass of the nucleus, J is treated differently. The two extremes are spin-orbit coupling and j - j coupling.

The spin-orbit coupling is valid for light elements; here,  $\vec{J} = \vec{L} + \vec{S}$  where  $\vec{L} = \sum_i \vec{l_i}$ and  $\vec{S} = \sum_i \vec{s_i}$ . For these elements, Equations (2.16) and (2.17) are also valid for the total spin S and total orbital momentum L. From these rules it can be seen that the selection rule for the total angular momentum J is

$$\Delta J = 0, \pm 1 \qquad \text{but} \qquad J = 0 \not\rightarrow J = 0, \qquad (2.18)$$

since only the magnitude of S in Equation (2.17) is important, not the direction.

In order to more quickly see whether a transition is allowed, the electron configuration of an energy level is typically given in the so-called spectroscopic notation

$$^{2S+1}L_J$$
 (2.19)

where the term 2S + 1 describes the multiplicity or the number of fine structure components of the level and L is expressed in capital letters as follows: S(L = 0), P(L = 1), D(L = 2), F(L = 3), and so on. Sometimes the parity of the wave function is assigned the small letter "o" for odd on the upper right side.

In the case of heavy elements, the spin s and orbital momentum l of each electron couple first to a single total angular momentum  $j_i$ . The total angular momentum of the atom is then formed by  $\vec{J} = \sum_i \vec{j}_i$ . Even though the L-S coupling is no longer valid for these elements, the electron configuration is often still expressed as shown in Equation (2.19). It should be noted that Equations (2.16) and (2.17) cannot be applied any more in this case. The only significant selection rule is then Equation (2.18).

#### 2.1.3. Thermal population

To obtain resonant laser ionization, the atoms have to exist in a gas-phase. At the LIS test stand, this is done by evaporating a sample of stable isotopes in an oven. Radioactive isotopes are produced by impinging up to 100  $\mu$ A of protons at 500 MeV on a target material, dumping as much as 50 kW of power on the target. For both

cases the ionization takes place in a hot environment. Consequently, low lying atomic levels at energies  $\ll 9000 \text{ cm}^{-1}$  [KFM03] may be significantly populated such that it can be of interest to look for excitation schemes starting from one of these levels rather than from the ground state at  $E_0 = 0 \text{ cm}^{-1}$ . In a thermal equilibrium, the population probability  $P(E_i)$  can be described by the Boltzmann distribution

$$P(E_i) \propto g_i \mathrm{e}^{\frac{-E_i}{k_B T}}, \qquad i = 0, 1, 2...$$
 (2.20)

in which  $g_i = 2J_i + 1$  is the statistical weight of each energy level  $E_i$ ,  $k_B$  is the Boltzmann constant, and T is the absolute temperature of the ionization region. A list of elements which are more likely to have reduced ground state population is given in [KFM03].

The ground states of both yttrium and astatine elements treated in this thesis are doublets. The fine structure splitting of astatine is so far not known. As the splitting in the halogens increases with mass, and for Br and I it is already (with 3685 cm<sup>-1</sup> and 7603 cm<sup>-1</sup> respectively) too high to be considered for significant thermal population, it is expected that this trend is similar for astatine. The two levels of yttrium are separated by 530.36 cm<sup>-1</sup> where  $J_0 = 3/2$  and  $J_1 = 5/2$ ; the population probability of both states with regard to the ionizer temperature is shown in Figure 2.3. At room temperature, 90% of the electrons are in the ground state, whereas at the temperature region in which the isotopes are produced, both the ground state and the low lying excited state are approximately equally populated.



Figure 2.3.: Thermal population of low lying atomic energy levels in yttrium. While at room temperature 90% of the electrons are in the ground state at  $0 \text{ cm}^{-1}$ , for an operation temperature at  $\approx 2000 \text{ K}$  both low lying energy levels are equally populated.

## 2.2. Ionization process

After selecting the resonant steps to excite the electron into a higher energy level, the final ionizing step has to be chosen. This can be realized by three different methods:

- nonresonant ionization into the continuum
- resonant ionization into an autoionizing state above the ionization potential
- field or far infrared ionization via a resonant transition into a high lying Rydberg state

illustrated in Figure 2.4, which will be further discussed in detail in the following sections.

#### 2.2.1. Nonresonant ionization

The simplest way of ionizing an atom is via nonresonant ionization. The only condition which has to be fulfilled is that the photon energy of the ionization laser  $h\nu_I$  has to be larger than the energy difference between the excited state  $E_k$  and the ionization potential IP:

$$h\nu_I > IP - E_k \,. \tag{2.21}$$

In many cases, the photon energy of one of the excitation steps can be used. Although the wavelength of the ionization laser is not as critical as that for resonant transitions, the ionization probability  $P_I$  is still not independent of it. The ionization probability for photoionization is given by

$$P_I = \sigma_I \cdot n(\nu) \tag{2.22}$$



Figure 2.4.: Ionization processes for laser resonant excitation schemes. The number of resonant excitation steps before ionization can vary from element to element. The ionization step is usually the rate-limiting process and therefore requires special attention. Moreover, for most elements the knowledge of the autoionizing state spectrum is limited, despite the often observed large transition strengths.

where  $\sigma_I$  is the ionization cross-section, and  $n(\nu)$  is the photon flux [Dem08b]. By deriving the ionization cross-section for hydrogen-like atoms using Born's approximation which is only valid for high photon energies, it can be seen that the ionization probability is proportional to  $\sigma_I \propto (h\nu)^{-7/2}$  [HS07] and largest if the photon energies match exactly the energy difference in Equation (2.21).

The typical ionization cross-sections for nonresonant ionization with  $\sigma_I \sim 10^{-17}\text{-}10^{-19} \text{ cm}^2$  [AL72, Dem08b] are rather low. In order to achieve maximal ionization, the electrons located in the excited state have to be ionized before they decay, which can be obtained for  $P_I > A_{ki}$ . For an excitation scheme with two resonant steps, the lifetime of the highest excited energy level is in most cases  $\tau \approx 10^{-7}$  s. It follows that the photon flux for maximum nonresonant ionization in the best case is

$$n(\nu) > \frac{A_{ki}}{\sigma_I} = 10^{24} \text{ cm}^{-2} \text{s}^{-1}$$
 (2.23)

For the Ti:Sa laser system running at 800 nm with a pulse length of 50 ns and a repetition rate 10 kHz focused to a spot size of 3 mm, the laser would have to deliver an output power of  $P_{out} > 8.7$  W. Since the output power available from the Ti:Sa lasers is around 2–3 W, at TRILIS typically a specific high-power ionization laser with good beam profile<sup>2</sup> introduced in Section 3.3 is used for this purpose.

 $<sup>^2\</sup>mathrm{TEM}_{00}$  and  $M^2<1.2$ 

## 2.2.2. Ionization of Rydberg states

As already discovered in 1885 by Balmer for the example of hydrogen [Bal85], the density of energy levels increases as the IP is approached. These highly excited energy levels are called Rydberg states, and their binding energies are given by

$$E = -\frac{Ry}{(n-\delta)^2}, \qquad (2.24)$$

where Ry is the element-specific Rydberg constant, n is the principal quantum number and  $\delta$  is the quantum defect. The quantum defect is a shielding constant and is a measure of how much the Rydberg electron interacts with the nucleus. For hydrogen, the quantum defect is defined as  $\delta = 0$  [Dem06]. Since the probability for the electron being found in the nucleus decreases with increasing orbital quantum number l and decreasing atomic number Z,  $\delta$  depends strongly on these parameters and increases with increasing probability [HS07].

As the energy difference from the IP decreases for highly excited Rydberg states, low energies such as provided by thermal photons, collisions with other atoms or an external electric field can be enough to ionize the atom. The closer the excited electron gets to the IP, the more easily it will be ionized. However, since the wave functions of the neighbouring states have a rather small overlap, the lifetime of a Rydberg can be extremely long, as much 1 s [HWB05], which decreases the transition probability as shown in Equation (2.7). In order to use the Rydberg state as an ionizing step, a compromise has to be found between good ionization and good transition probabilities. A typical Rydberg series is shown in Figure 2.5. It can be



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seen that the states of interest have a principal quantum number n = 10 to 40. The ionization cross-sections for these levels are around  $\sigma_I = 10^{-12}$  cm<sup>2</sup> [WBG+05] which means approximately five magnitudes higher than nonresonant ionization. During the spectroscopy on calcium, in which this Rydberg series was measured, it was possible to saturate a Rydberg transition with around 500 mW of laser power.

### 2.2.3. Autoionizing states

So far it is assumed that absorption of photons for multi-step excitation is performed by just one electron, the valence electron, while the rest remain in their ground states. However, for atoms with multiple electrons it is also possible that two electrons can be excited simultaneously. Once the electrons are excited, both electrons can either decay by emitting two photons, or one of the electrons can transfer its excitation energy to the second excited electron which can lift it above the ionization potential. The later process is called autoionization [HS07].

A characteristic of this resonances is its asymmetric lineshape, known as a Fano-Beutler profile. This arises from a special kind of interference between the nonresonant and multi-electron-excitation ionization [Fan61, HS07]. Autoionizing states typically have extremely short lifetimes on the order of  $10^{-13}$  s [Con98] which leads to natural linewidths  $\Delta \nu > 1600$  GHz. Typical ionization cross-sections for autoionizing states are between  $\sigma_I = 10^{-16} - 10^{-15}$  cm<sup>2</sup>. For selected resonances, cross-sections up to  $\sigma_I =$  $10^{-12}$  cm<sup>2</sup> have also been measured [BNBW03].

## 2.2.4. Surface ionization

Under certain circumstances, atoms can be ionized if they come in contact with hot surfaces. This effect can be used for positive as well as negative ion production and is known as surface ionization. Since ISAC is designed to produce positive ions, only the first case will be considered further. At thermal equilibrium, the degree of ionization  $\alpha$  is defined as the ratio of the number of ions  $n_i$  to the number of neutral atoms  $n_0$ :

$$\alpha = \frac{n_i}{n_0} = \frac{g_i}{g_0} e^{\frac{W - IP}{k_B T}} .$$
 (2.25)

Equation (2.25) is called the Saha-Langmuir equation [LK25], where  $g_0$  and  $g_i$  are the respective statistical weights of the atom and the ion, W is the work function of the hot cavity material, IP is the ionization potential of the first ion,  $k_B$  is the Boltzmann constant and T is the absolute temperature of the cavity. The ionization efficiency is given by [Kir96]:

$$\eta_{SI} = \frac{\alpha}{1+\alpha}.\tag{2.26}$$

This ionization method is the simplest way to efficiently ionize elements with low ionization potentials such as the alkali metals. In order to increase the efficiency, the source should be operated at high temperatures, and materials with high work functions should be used. The typical ionizer material at TRIUMF is rhenium, with a work function of W = 5.0 eV. The ionization efficiency at T = 2000 K for a selection of elements is shown in Figure 2.6.

The hot cavity is not only used as an ionizer, but also as a transfer tube for the ions from the target to the extraction electrodes. If the laser ion source is used, this





is also the region of ionization. However, for laser ion source applications the effect of surface ionization is undesired since it compromises the laser ion source biggest advantage of element selectivity. Especially in a radioactive environment where the number of available isotopes is highest, the amount of surface ion contamination can be significant.

In order to produce a contamination-free laser ion beam, a new ion source design is currently under construction. In this design, the hot cavity ionizer tube will be replaced by a radio frequency quadrupole which guides the ions with less contact and therefore reduces surface ionization. First tests of this design are described in [Lav10].

## 2.3. Linewidth

As already discussed in Section 2.1, an electron exists in an excited state  $E_k$  for just an average time  $\tau$ , which can vary from a few tenth of ns for strong transitions up to several years for highly forbidden transitions. For that reason, due to the uncertainty principle

$$\Delta E \tau \ge \frac{h}{2\pi}$$
 with  $\Delta E = h \Delta \nu$ , (2.27)

light absorbed or emitted from an atom will always have a minimum linewidth  $\Delta \nu$ which is defined by the full width at half maximum (FWHM). This linewidth  $\Delta \nu \geq \frac{1}{2\pi\tau}$  is called the natural linewidth. Since the lifetime of an excited state is the same for all atoms in an ensemble, the line broadening is homogeneous, which leads to a Lorentzian line profile. However, measuring an energy level with a precision of close to its natural limit requires some experimental effort [Dem08b, HS07]. In general, additional broadening mechanisms are involved in the measurement. The broadening mechanisms of relevance for the here applied experimental setup will be described in the following sections.

### 2.3.1. Doppler broadening

The light absorbed by an atom moving relative to the light source with velocity  $\vec{v}$  is shifted from its eigenfrequency  $\nu_0$  depending on its direction. For an atom moving in z direction with  $v = (0, 0, v_z)$ , the light absorbed by the atom in the nonrelativistic case is given by

$$\nu = \nu_0 \left( 1 + \frac{v_z}{c} \right) \,. \tag{2.28}$$

This frequency shift is caused due to the Doppler effect. Light absorbed by an atom moving towards the source is shifted to a shorter wavelength, while an atom moving away from the source absorbs light shifted to a longer wavelength.

The atoms to be ionized in the discussed experiments are in a low-pressure gas phase in which the atoms move according to the Maxwell-Boltzmann velocity distribution, which is given by:

$$n(v) = \sqrt{\frac{2}{\pi} \left(\frac{m}{k_B T}\right)^3} \cdot v^2 \cdot e^{-\frac{mv^2}{2k_B T}}, \qquad (2.29)$$

where m is the mass of the atoms,  $k_B$  is the Boltzmann constant and T is the absolute temperature of the ensemble. Since the intensity distribution  $I(\nu)$  of the absorbed light is proportional to the velocity distribution n(v) of the atoms, it can be seen in Figure 2.7 that the intensity spread is larger for lighter atoms.


Figure 2.7.: Maxwell-Boltzmann-velocity-distribution for particles at constant temperature with the atomic weight M = 9 u, 89 u and 199 u. This velocity distribution is responsible for the observed Doppler-broadened linewidths in laser resonance ionization spectroscopy.

By substituting Equation (2.28) in Equation (2.29), the intensity distribution can be expressed as

$$I(\nu) = I(\nu_0) \cdot e^{\left(\frac{\nu - \nu_0}{\nu_0} \frac{c}{v_p}\right)^2},$$
(2.30)

where  $v_p = \sqrt{2k_BT/m}$  is the velocity with highest probability. It can be seen that this function behaves like a Gaussian. From this, the linewidth of the peak can be derived as:

$$\Delta \nu_D = \frac{\nu_0}{c} \sqrt{\frac{8k_B T \ln 2}{m}} \,. \tag{2.31}$$

In order to simplify this expression, the Avogadro constant  $N_A$  can be introduced [Dem08a] which allows m to be replaced by the atomic weight

 $M = mN_A$ , and  $k_B$  can be replaced by the gas constant  $R = k_B N_A$ . Equation (2.31) can then be written as:

$$\Delta \nu_D = \frac{\nu_0}{c} \sqrt{\frac{8RT \ln 2}{M}} = 7.16 \cdot 10^{-7} \nu_0 \sqrt{\frac{T}{M}} \left[ \text{ s}^{-1} \right] .$$
 (2.32)

In the example of the first transition in yttrium, the Doppler broadening should be calculated. The temperature of the atomic vapor is typically around T = 2000 K. Taking the first transition in yttrium shown in Figure 4.8,  $\nu_0 = 827.7$  THz. The existing stable isotope in yttrium is M=89. It follows that the Doppler width for this transition is  $\Delta \nu_D = 2.8$  GHz. As a comparison, the natural linewidth of this transition is  $\Delta \nu_n = A_{ki}/2\pi = 37.2$  MHz. The Doppler width is therefore about two orders of magnitude larger than the natural linewidth.

# 2.3.2. Saturation broadening

Due to the high light intensities available with lasers, a further broadening mechanism has to be taken into account, which is caused by the change of the population distribution of the atomic levels [Dem08a]. The population of a two level system can be expressed by the rate equation

$$\frac{\mathrm{d}N_1}{\mathrm{d}t} = -\frac{\mathrm{d}N_2}{\mathrm{d}t} = -PN_1 - R_1N_1 + PN_2 + R_2N_2.$$
(2.33)

where P describes the absorption and emission probabilities due to the laser-stimulated processes given in Equations (2.2) and (2.3) assuming that the two levels are not degenerated, and  $R_i$  is the relaxation probability. For the stationary case  $dN_1/dt = 0$ with  $N = N_1 + N_2$ , and the population of the lowest level can be written as

$$N_1 = \frac{P + R_2}{2P + R_1 + R_2} \,. \tag{2.34}$$

For high intensities, the stimulated processes dominate the relaxation probabilities and  $P \gg R_i$ . As a result, the populations of  $N_1$  and  $N_2$  equalize, and it is said that the transition is saturated. In the other extreme with no external radiation incidence P = 0, and the two levels are in thermal equilibrium as given in Equation (2.20). In this case, the population densities can be expressed as

$$N_{10} = N \frac{R_2}{R_1 + R_2} \tag{2.35}$$

$$N_{20} = N \frac{R_1}{R_1 + R_2} \,. \tag{2.36}$$

By combining the last three equations, the difference  $\Delta N = N_1 - N_2$  between the level populations is given by

$$\Delta N = \frac{\Delta N_0}{1 + 2P/(R_1 + R_2)} = \frac{\Delta N_0}{1 + S}$$
(2.37)

where  $S = 2P/(R_1 + R_2)$  is called the saturation parameter. Since for optical transitions  $\Delta E$  in Equation (2.20) is too large to populate  $N_{20}$ ,  $R_1$  can be neglected and  $R_2 = A_{ik}$ . From Equations (2.2) and (2.6), S can be also written as

$$S = \frac{g_k}{g_i} \frac{\lambda^3 I(\nu)}{h\pi c A_{ki}} = \frac{I}{I_{sat}}$$
(2.38)

where  $I(\nu)$  is the laser intensity and

$$I_{sat} = \frac{g_i}{g_k} \frac{h\pi c A_{21}}{\lambda^3} \tag{2.39}$$

is the intensity in which the transition is saturated [Mes08].

As mentioned in Section 2.3, the light absorbed in an optical transition has a Lorentzian line shape. Since S depends mainly on the absorption probability  $P(\nu)$ , the saturation parameter follows a Lorentzian shape, too. Driving a transition into saturation, leads to a line profile which is broadened by a factor [Dem08a]:

$$\Delta \nu_S = \Delta \nu \sqrt{1+S} \,. \tag{2.40}$$

If the incident light intensity equals the saturation intensity, the line is therefore broadened by a factor of  $\sqrt{2}$ .

# 3. Laser System

One of the requirements a laser system has to fulfill for operation at laser ion sources is a large tuning range in order to access resonances for as many elements as possible. The strongest transitions of the first excitation step for most elements are in the UV to blue region, while the second excitation step often lies in the VIS to NIR. Common lasers with wide tuning ranges are dye lasers, which cover a wavelength range from the UV to NIR by switching between different dyes. These lasers were used at the first laser ion source in operation at ISOLDE CERN [Klu85, KFM03]. The lasers used at TRILIS, described in Section 3.1, are titanium-doped sapphire (Ti:Sa) lasers which lase in the NIR region. Shorter wavelengths from the UV to blue region can be reached by frequency conversion, further discussed in Section 3.2. The missing gap, the visible spectrum, may either be covered with a combined system of dye and Ti:Sa lasers [RMM+11, MNB+05], or partly (584 nm to 672 nm) with the frequencydoubled light of a Cr:Forsterite laser [Rot09]. In addition to the Ti:Sa lasers, TRILIS operates a high-power Nd:YVO<sub>4</sub> laser (Section 3.3) for higher efficiency of nonresonant ionization.

# 3.1. Titanium sapphire laser

Titanium-doped sapphire (Ti:Sa) crystals are the most widely used, tunable, solid state laser mediums. They consist of corundum crystals  $(Al_2O_3)$  in which 0.1 atomic percent of the  $Al^{3+}$  are replaced by  $Ti^{3+}$  ions, which are responsible for the characteristic wide emission spectrum from 600–1100 nm [Mou86]. The emission peak is at 780 nm with a FWHM of about 180 nm [Koe06]. The absorption spectrum is between 400–650 nm with a peak at 488 nm [Mou86]. Due to an overlap of the emission and absorption spectra and their wide tails, the tuning range in laser operation is between 680-1000 nm.

A pump source for the Ti:Sa lasers at TRIUMF is realized by a frequency-doubled Nd:YAG laser<sup>1</sup> emitting a wavelength of 532 nm. It provides 50 W of laser power which can be divided between the maximum four lasers on the table.

The resonator design of TRILIS Ti:Sa lasers, as shown in Figure 3.1, is based on a Ti:Sa laser developed at Mainz University [Hor03], which is optimized for operating conditions at on-line, ISOL<sup>2</sup> type, radioactive ion beam facilities i.e. pulsed operation to make use of the high pulse peak power, at repetition rates of 10 kHz and higher to match the duty cycle. It is a linear, Z-shaped resonator, with two resonator mirrors of curvature of R = 75 mm in whose centre the Ti:Sa laser is located and two end mirrors at the end of parallel arms orientated at 36.2° to the resonator arm. This angle is chosen to compensate for the astigmatism introduced by the Brewster angles [Hec01] on the Ti:Sa crystal and reduces reflection losses on its surfaces. In order to

 $<sup>^1 \</sup>rm LEE~LPD~100~MPQ$ 

<sup>&</sup>lt;sup>2</sup>Isotope Separator On-Line



- (b)
- Figure 3.1.: Schematic drawing (a) and photograph (b) of a birefringent filter-tuned Ti:Sa laser. The photograph shows an intracavity doubled birefringent filter-tuned Ti:Sa laser. In addition to the typical laser setup, a doubling crystal and a dichroic mirror are placed inside the resonantor, which leads to a better beam profile and longer crystal lifetime than external doubling.

better match the pump mode with the resonator mode, the focus is set to the far crystal surface. In the original design, the focus was set to the front of the crystal whereas in the new designs two different crystal positions can be chosen from. The advantage of having the focus on the back side is that the laser can be pumped harder without damaging the crystal.

All mirrors except the output coupler have a reflectivity near 100% at their centre wavelength, whereas the resonator mirrors have an additional anti-reflection coating for 532 nm in order to minimize the pump beam transmission losses. Since the TRILIS laser system runs in pulsed operation with a repetition rate of 10 kHz, the output coupler has a reflectivity of 70–80 %.

The advantage of pulsed laser systems is the availability of high peak intensities and linewidths in the 0.6–7 GHz region. High laser intensities are required to saturate weak excitation steps and for frequency conversion in nonlinear crystals needed to reach wavelengths in the blue and UV spectra. The typical average power the TRILIS Ti:Sa lasers provide at 10 W pump power is between 1–2.5 W at a pulse length of about 40 ns [Alb07].

Since for resonant ionization the laser pulses have to reach the ionization region simultaneously, each laser can be equipped with a Pockels cell. The Pockels cell is based on the electro-optical effect, and consists of a nonlinear crystal (KDP) which converts linear polarized laser light to circular polarized under application of a voltage of 1.5–6 kV. Due to the change of polarization, additional losses are introduced associated with the resonator which spoils the resonator Q-factor. By turning off the voltage, the crystal becomes transparent and the conversion can be accessed again [Str01]. If the time lag between two pulses is short, the synchronization can be realized passively by either adjusting the pump power, or changing the Ti:Sa crystal position in one of the resonators. The closer the focus is located to the front crystal surface, the earlier the laser starts lasing.

For laser ion source operation, a laser linewidth which fits the Doppler broadened spectrum best is desirable in order to excite atoms of all velocity classes. Typical Doppler broadened linewidths for a source temperature of 2000 °C are between 1–4 GHz. If the laser is used to scan over a resonance in order to look for possible detail, a narrow laser linewidth is desirable, since the resulting measured linewidth  $\Delta \nu_R$  is always a convolution of the laser linewidth  $\Delta \nu_L$  and natural atomic linewidth  $\Delta \nu_R$ :

$$\Delta \nu_R = \sqrt{\Delta \nu_L^2 + \Delta \nu_A^2} \,. \tag{3.1}$$

However, the linewidth of a plain resonator is typically several THz wide, resulting from the emission spectrum of the gain medium and the reflection curves of the resonator mirrors. In order to reach the required linewidth, additional wavelengthselective elements are placed in the resonator. At TRILIS, two different ways for wavelength selection are applied, which are described hereafter.

## 3.1.1. Birefringent filter tuned laser

The common method for wavelength selection in the TRILIS Ti:Sa-laser is the combined use of a birefringent filter (BRF) and an etalon. The features of this laser are its long time frequency stability [BAD<sup>+</sup>12], narrow linewidths, and high laser intensities of 1–3 W average power at 10 W pump power due to the minor losses introduced.

### **Birefringent Filter**

The BRFs<sup>3</sup> mostly used in TRILIS lasers consist of four birefringent crystal plates with thickness ratios of 1:4:8:15 and a base thickness of 0.5 mm. Linear polarized light passing through the birefringent plate is divided into an ordinary and an extraordinary beam, travelling in the material with different velocities  $v_o = c/n_o$  for the ordinary beam and  $v_{eo} = c/n_{eo}$  for the extraordinary beam. Both beams are polarized perpendicular to each other. If the two beams have a phase difference

$$\delta \neq 2m\pi$$
 with  $m = 1, 2, 3...$  (3.2)

after passing through the plate, the resulting beam is elliptically polarized. Since in the resonator all surfaces which are not mirrors are chosen as Brewster surfaces in order to reduce reflection losses, beams which are not p-polarized are suppressed. Wavelengths  $\lambda$  passing through the filter

$$\lambda = \frac{\Delta n \cdot d}{m} \qquad \text{with} \qquad m = 1, 2, 3 \dots \tag{3.3}$$

therefore depend on the difference between the indexes of refraction  $\Delta n = n_o - n_{eo}$ and the thickness d of the thinnest plate. Since the extraordinary index of refraction  $n_{eo}$  depends on the angle  $\alpha$  between the direction of propagation and the optical axis shown in Figure 3.2, the wavelength can be selected by rotating the optical axis of the crystal around the direction of propagation of the light. Since the resulting transmission curve, shown in Figure 3.3, is the product of the transmission curve of

<sup>&</sup>lt;sup>3</sup>VLOC BFU38.1-1T4T8T15T





Figure 3.2.: Index ellipsoid for birefringent materials. The extraordinary index of refraction is dependent on the angle  $\alpha$  between the direction of propagation and the optical axis.

each plate, the thinnest plate is responsible for the free spectral range (FSR) of the filter, i.e., the spectral distance between two transmission peaks. The thickest plate is crucial for the laser linewidth. In order to prevent the laser from running on two wavelengths simultaneously, a large FSR has to be chosen. However, as shown in Equation (3.3), the condition for transmission is valid for several wavelengths at a time. For that reason it is important, particularly if wavelengths beyond the emission maximum are required, to choose mirrors which suppress lasing in the maximum. The further away from maximum the chosen wavelength is, the narrower the reflectivity of the mirror has to be.

The laser linewidth reachable with BRF has been measured to be  $\Delta \nu \approx 100$  GHz [Hor03] which is, for most cases, too wide for efficient excitation. In order to narrow the linewidth further, an etalon can be added.



Figure 3.3.: Transmission curves of the TRILIS four plate birefringent filter where the plates have a thickness ratio of 1:4:8:15. The final transmission (bottom panel) is the product of the individual plate transmission curves (upper panels). The free spectral range is defined by the thinnest plate and the linewidth by the thickest.

### Fabry-Pérot etalon

A solid Fabry-Pérot etalon is basically a thin glass plate of thickness d and partly reflecting coatings with reflectivity R on each surface. Due to interference effects, only wavelengths which are integer multiples of its thickness can be transmitted. In order to change the wavelength, the etalon can be tilted by an angle  $\beta$ , which increases the path length that the light travels in the material. Since the linewidth provided by the BRF is  $\Delta \nu \approx 100$  GHz, the FSR of the etalon should be larger in order to prevent the laser from running in multiple spectral modes. Similar to the FSR of the BRF, the etalon's FSR also depends on its optical thickness:

$$FSR = \frac{c}{2nd} \,. \tag{3.4}$$

It follows that an etalon, consisting of fused silica (n = 1.45), should have a maximum thickness of

$$d = \frac{c}{2 \cdot 1.45 \cdot 100 \text{ GHz}} = 1 \text{ mm}.$$
 (3.5)

The linewidth of the light transmitted depends on the number of partial beams it can interfere with. This number is described by the Finesse F of the etalon, regulated by its reflectivity

$$F = \frac{\pi\sqrt{R}}{1-R} \,. \tag{3.6}$$

The better the reflectivity, the larger the finesse. The actual linewidth is given by the ratio of the FSR to the finesse

$$\Delta \nu = \frac{FSR}{F} \,. \tag{3.7}$$

With these laser linewidths  $\Delta \nu < 1$  GHz can be reached; however, it typically operates at about 3 GHz. This linewidth is in a comfortable range, as it matches well with the Doppler-limited absorption profile of the atoms in the hot ionization region of the on-line target ion source.

### 3.1.2. Grating-tuned laser

Even though the birefringent filter tuned laser has impressively good frequency stability and high output power, scanning the wavelength range of a couple of nm with this laser is tedious and labour intensive. For that reason, another laser has been developed [Tei09], which is continuously and effortlessly tunable over almost the entire emission spectrum. The resonator design shown in Figure 3.4 is based on the BRF-tuned laser in which the wavelength selective elements have been removed, and the high reflector is replaced by a gold coated diffraction grating with a blaze angle [Hec01] of  $\alpha_{Blaze} = 26.7^{\circ}$  and a grating constant of G = 1800 grooves/mm<sup>4</sup>.

When monochromatic light is incident upon a grating under an angle  $\alpha$ , it is diffracted at the surface, and clear intensity maxima are observable at a diffraction angle  $\beta$  depending on the wavelength of the light as shown in

$$d(\sin \alpha + \sin \beta) = m\lambda$$
 with  $m = 1, 2, 3...$  (3.8)

where d is the groove spacing. In order to use a diffraction grating as a wavelengthselective element, two different configurations are common. The first is called the Littman/Metcalf [LM78] configuration in which the grating is mounted under a fixed

 $<sup>^4</sup>$ Newport 53999ZD02-290R



Figure 3.4.: Schematic drawing (a) and photograph (b) of the prototype grating-tuned Ti:Sa in Littrow configuration. Visible are the Pockels cell for pulse synchronization, the Ti:Sa crystal, the four anamorphic prism beam expander and the ruled, blazed diffraction grating.

angle  $\alpha > 80^{\circ}$ , and the wavelength is selected by an additional mirror rotating around the grating in order to reflect the selected wavelength back. The second method is called the Littrow/Hänsch [Hän72] configuration. Here the required wavelength is directly diffracted back in to the resonator by rotating the grating. Equation (3.8) simplifies then to

$$2d\sin\alpha = m\lambda,\tag{3.9}$$

since the angle of incidence and the diffraction angle are equal in this case. Due to the fact that the Littman/Metcalf configuration requires an additional mirror, making the setup more complex, the Littrow/Hänsch configuration was chosen.

In order to rotate the grating, it is mounted on a rotary stage<sup>5</sup> controlled with a LabView program optimized for spectroscopic application [Grü12], which has a maximum resolution of 0.87 µrad. This leads to a tuning accuracy of 0.5 GHz.

The spectral resolution  $R = \nu/\Delta\nu$ , however, depends on the number of illuminated grooves. For that reason and since the damage threshold of metal coated ruled gratings is rather low [BBD+95], the beam is expanded in front of the grating. The most robust and compact way for one dimensional beam expansion is the use of anamorphic prism pairs [HKW75]. With four prisms made of SF11, a beam expansion of

 $<sup>^5\</sup>mathrm{Aerotech}$  ADRS-100

 $17 \times$  could be reached by choosing an angle of incidence in the low reflection losses region around the Brewster angle

$$\alpha_B = \arctan n_{SF11}(800 \text{ nm}) \tag{3.10}$$

$$= \arctan 1.77 \tag{3.11}$$

$$= 60.5^{\circ}$$
. (3.12)

The linewidth of this laser has been measured to  $\Delta \nu \approx 6.5 \text{ GHz} \text{ [TBC+10]}$ .

Since the grating is the only wavelength-selective element in this resonator which has a strong wavelength suppression, a set of broad band mirrors has been chosen. As a result, the continuous tuning range is theoretically only limited by the emission spectrum of the Ti:Sa crystal. However, since the losses introduced by the grating are higher than for the BRF, the tuning range is limited to 700–950 nm at output powers of 0.5–1.6 W at 10 W pump power, although wavelengths from 685–1005 nm have been measured by changing mirror sets. Due to the high losses, wavelength selection happens after only one round trip in the resonator, and the grating-tuned laser typically fires earlier than the BRF-tuned lasers. While the BRF-tuned lasers can also be passively synchronized, a Pockels cell is mandatory for the grating-tuned laser as it is designed for scanning over large wavelength regions.

# 3.2. Harmonic frequency generation

Since the strongest first excitation steps of atoms are typically in the blue to UV spectrum, a frequency conversion of the fundamental of the Ti:Sa-lasers is necessary. This frequency conversion is realized by nonlinear polarization effects in optical nonlinear crystals [Dem08a]. In this way, two monochromatic waves at frequencies  $\nu_1$  and  $\nu_2$ can be converted into a third wave with frequency  $\nu_3 = \nu_1 + \nu_2$ . Typical crystal materials used at TRILIS are  $\beta$ -barium-borate (BBO) which is known for its high damage threshold [Dem08a], bismuth-borate (BiBO) for its high conversion efficiency, and lithium-triborate (LBO) for its good beam profile due to its small walk-off angle<sup>67</sup>. The phase matching for these crystals is realized by adjusting the tilting angle.

The easiest case of frequency conversion is frequency-doubling in which two photons of the same beam can be converted into one photon with twice their energy. In this way, wavelengths between 345–495 nm are reachable. By frequency-tripling, a combination of the doubled and the fundamental light; and frequency-quadrupling, where the fundamental is doubled twice, the wavelength spectrum can be extended to 330–210 nm.

In order to realize frequency conversion in nonlinear crystals, high electric field intensities are required. Since TRILIS uses pulsed lasers, the peak intensity of a single pulse is high enough that the frequency can be converted by only one pass through the crystal. For that reason, it is sufficient to focus the laser on the crystal surface. A good beam profile (TEM<sub>00</sub>) [Hec01] is mandatory. Depending on which nonlinear crystal is used, the beam profile may have an elliptic shape, which can be compensated for by introducing a set of cylindrical lenses.

Another possibility for frequency-doubling is to place the crystal inside the laser cavity. Due to the high intra cavity intensity, no focusing is necessary, which protects

<sup>&</sup>lt;sup>6</sup>as specified by the manufacturer www.crystech.com

<sup>&</sup>lt;sup>7</sup>separation between ordinary and extraordinary waves in nonlinear crystals

the crystal. For intra cavity doubling, the output coupler can be replaced with a high reflector for the fundamental, which is also highly transparent for the blue light. Since the crystal emits light in both directions in the resonator, the blue output power can be increased by placing a dielectric mirror behind the crystal. The advantages of intra cavity doubling compared to external doubling are therefore high output powers, better beam profiles and longer crystal life times.

# 3.3. Ionizing laser

As shown in Section 2.2.1, the power necessary to saturate a nonresonant transition is about 9 W, which cannot be provided by the common Ti:Sa lasers. Since for many elements no efficient resonant ionization step is known, nonresonant ionization is the most common and reliable method of ionization. For that reason, a diode-pumped Nd-doped vanadate (Nd:YVO<sub>4</sub>) laser <sup>8</sup> completes the TRILIS laser system. In addition to its fundamental which provides 13 W at 1064 nm, a frequency-doubling unit is available which provides 6.7 W at 532 nm. Since in most cases the energy difference from the second excitation step to the ionization potential is considerable large, the frequency-doubled variety is the mostly used one. The advantages of using the nonresonant ionization laser instead of the pump laser are that it can be individually synchronized with the Ti:Sa lasers, it has good beam quality of TEM<sub>00</sub>,  $M^2 < 1.2$ [Spe02], which leads to higher intensities at the focus, and it has a similar pulse length as Ti:Sa lasers.

 $<sup>^{8}</sup>$ Spectra-Physics YHP40

# 4. Yttrium ionization scheme development

The main task of TRILIS is to deliver clean isotope beams to nuclear physics experiments using the ISAC facility. In order to increase the TRILIS yields, efficient laser excitation and ionization schemes are required. Where stable isotopes exist, these laser ionization schemes can be tested off-line. The existing laser off-line lab is equipped with a laser system similar to the one used in the on-line laser lab as described in Chapter 3, and a laser ion source test stand is located in the adjacent room. The latter is further described in Section 4.1.1. In preparation for the astatine experiment S1237, an efficient excitation scheme for yttrium was developed in order to become familiar with the equipment and experimental technique.

An yttrium-isotope beam is requested for the approved high priority nuclear structure experiment S1326, in which the nuclear spin moments and mean-square charge radii of yttrium and Sr isotopes shall be measured using collinear laser spectroscopy techniques. Measurements of these nuclear properties for the elements with proton numbers Z = 36-42 have already been extensively performed for neutron rich isotopes [CF10]. For neutron numbers  $N \approx 60$ , a sudden onset of deformation has been observed by measuring the mean-square charge radius, which was largest for yttrium [CGA<sup>+</sup>07]. A similar phenomenon is expected for isotopes with Z = N, which is why neutron-deficient isotopes are now of interest.

# 4.1. Experimental setup

### 4.1.1. Laser ion source test stand

As the on-line target ion source is in essence reserved for physics experiments requiring radioactive isotopes and only very limited beam development time is available, a LIS test stand was designed in the course of J.P. Lavoie's dissertation [Lav10]. At this test stand, laser excitation schemes of elements are developed using stable isotopes, and improved new designs of surface, laser and RFQ - laser ion sources are tested off-line. Since its completion in May 2009, different excitation schemes for Ga, Al, Ca, Sb and Sc have been successfully tested.

The LIS test stand consists of two o-ring and ConFlat-sealed vacuum chambers which can be pumped on with two scroll pumps<sup>1</sup> for rough vacuum and two turbo molecular pumps<sup>2</sup> for a vacuum down to  $10^{-7}$  Torr. The larger vacuum chamber contains a standard ISAC surface ion source module including extraction optics which simulates the conditions for on-line operation and allows direct transfer of obtained results to on-line applications. The smaller chamber contains the ion beam transport

<sup>&</sup>lt;sup>1</sup>Varian Tri Scroll 300

 $<sup>^2</sup>$  Varian V1001, 1000 l/s and Varian V501, 500 l/s

optics, diagnostic tools and a compact **Q**uadrupole **M**ass **S**pectrometer  $(QMS)^3$  for mass separation. The two vacuum chambers can be separated by a gate valve which allows work on the ion source, e.g., exchanging the sample, while the rest of the LIS test stand remains under vacuum. A schematic drawing of the LIS test stand is shown in Figure 4.1.



Figure 4.1.: Schematic drawing of the LIS test stand. The requested element is placed in a crucible and vaporized. In the ionizer tube atoms are ionized by resonant laser ionization. Through different steering and focussing optics the ion beam is transported to a QMS where it then can be mass-selectively detected. Both the ion source region and the QMS region can be operated at a potential of up to 30 kV.

For off-line experiments, the target container is replaced by a crucible which can be filled with a sample of the required element. This crucible is resistively heated by a tantalum filament connected to a 60 A, 20 V power supply. Crucible operating con-

 $<sup>^3\</sup>mathrm{EXTREL}$  QMS MAX-300 with a 3/4" rod system a length of 30 cm, operating at 1.02 MHz radio frequency

ditions vary greatly from element to element. Obtaining the desired vapor pressure of the source material within the crucible is one of the intricate operations in the LIS stand operation. Further improvements and changes in the crucible design are forthcoming. The atom vapor effusing out of the crucible can be ionized in a hot ionizer cavity. This ionizer is a 3 mm diameter and 40 mm long tantalum tube, identical to the ionizer tube used on-line, which can be resistively heated by a current of 300 A. On-line typically 235–240 A are used to ensure long target life time of approximately four weeks. The corresponding temperature dependencies for the filament and the ionizer tube are shown in Figure 4.2.



Figure 4.2.: Temperature of the filament and ionizer as functions of the heating current. This measurement was taken during the LIS test stand characterization using a two color digital pyrometer<sup>4</sup>. The ionizer temperature was measured inside the tube [Lav10].

Ions produced in the ionizer tube are created at a potential of 10–35 keV and extracted to ground potential through the extraction and ground electrodes. The beam transport from the ionization region to the QMS is realized via a set of einzel lenses, a 90° spherical deflector, and a set of horizontal and vertical steerers in front of each einzel lens. The three einzel lenses focus the beam both in the  $90^{\circ}$  spherical deflector and the decelerating and injection optics into the QMS. In order to guarantee maximal transmission along the 3.4 m long flight path, beam diagnostics are located before and after the deflector. The diagnostic tools are: a Faraday cup for beam intensity determination, and a wire scanner in order to measure the transverse beam profile. Additional skimmer plates are located between the einzel lens system to define the ground plane and beam losses. As opposed to on-line operation, where a mass separator magnet is used, the mass separation is realized with a QMS which has the advantage of a more compact setup and the ability to perform rapid mass scans. In addition, it is possible to monitor several masses quasi-simultaneously by rapidly switching between QMS mass settings. The possible scan region of the QMS for singly ionized ions is 2–300 u. For acceptable mass resolution, the beam has to be decelerated to <50 eV. The deceleration optics are based on the design used at the TITAN<sup>5</sup> radio frequency quadrupole beam cooler and buncher, where the ions from the ISAC beam are stopped and cooled inside a gas-filled environment [SBDD07]. Ions passing the QMS are detected with either an electron multiplier for beam intensities lower than  $10^6$  cps or a Faraday cup at higher beam intensities.

The entire LIS test stand, excluding the QMS which is controlled by the EXTRELprovided control and data analysis software MERLIN, is operated by the Experimental **P**hysics and Industrial Control System (EPICS) [EPI]. The corresponding vacuum and ion optics control pages are shown in Figure 4.3. The software-provided

 $<sup>{}^{5}</sup>$ TRIUMF's Ion Trap for Atomic and Nuclear Science

strip tool, in which all implemented device values can be plotted as a function of time, is also used for LIS test stand basic data acquisition.

The lasers access the LIS test stand through a viewport window consisting of UV grade fused silica with excellent optical transmission throughout the entire required wavelength region from 200–2000 nm, and propagate to the ionization region through a 7.9 mm hole in the 90° spherical deflector. The window is mounted on a precision port alignment mount<sup>6</sup> which allows it to be tilted up to 2°. The  $\sim 4\%$  reflection from the window is used as a reference for spatial overlap and focussing. For this reason, a laser-sensitive ceramic disk<sup>7</sup> is placed about 2 m from the window on the laser table, the same distance as that from the window to the ionization region. The laser spot is monitored with a CCD-camera on the viewing disk. Directly behind the viewport window, an additional gate valve is located which can act as a laser shutter and also allows to protect the laser viewport against the evaporation source from being coated on the vacuum side whenever lasers are not in use.

### 4.1.2. Laser beam transport

The off-line laser laboratory is equipped with two permanently installed BRF- and one grating-tuned Ti:Sa laser. For nonresonant ionization, a high-power frequencydoubled Nd:YVO<sub>4</sub><sup>8</sup> laser is used, that matches the repetition rate and the temporal pulse width of the Ti:Sa lasers. For all excitation schemes in yttrium, the first excitation step was realized by an internally frequency-doubled Ti:Sa laser, whereas the

<sup>&</sup>lt;sup>6</sup>MDC PAT-2 precision port aligner

<sup>&</sup>lt;sup>7</sup>Kentek VSPOT-IR

<sup>&</sup>lt;sup>8</sup>Spectra-Physics YHP40



# 4. Yttrium ionization scheme development

(a) vacuum page

LUS OPTICS 1	
USS (C3)A         ent         in         1.466+12.A         USS (C3)A           C3         LISS (C3)A         ent         6 V           LISS (C3)A         2e-68.A         6 V	IDS01         IDS02           Image: Second secon
LISSY2         Sec0.0 //	
Inscrete	Instrum         environment         fill         environment         fill         Instrum         environment         fill         environment         environment         fill         environment         environment         environment         environment         fill         environment
	ISSNE         -2e-87 €           105 501         °         200         10500         173 ∨         106 ∨         0         204         1000           11         105 ∨         °         7         100         15 ∨         115 ∨
US HYDRASS         00000 V         #           PYS on         PYS off         Reconfig PYS         Save/Restore         Host/Frev           Soder         LtS Heating         LtS Velage Raup         Host of the set           Soder         LtS Velage Raup         Host of the set         Host of the set	Lissol         38-88 Å           URI         977e-13 Å         USIGPTIA           USIGN         38-80 Å         USIGPTIA           USIGN         977e-13 Å         USIGPTIA

(b) optic page horizintal section

(c) optics page vertical section



second BRF laser was used in its fundamental in order to excite into a second excitation state or autoionizing resonance. In order to achieve a smaller beam focus in the ionization region, the laser beam is expanded by a factor of 2.5. For expansion, Galilean telescopes are applied (i.e., a combination of concave and convex lenses) having the advantage of a more compact setup without an intermediate focus which, as the high-powered pulsed lasers can create a plasma when focussed in air, could adversely affect the spatial beam quality. Afterwards, the two fundamental-wavelength Ti:Sa lasers are overlapped using a polarizer beam splitter cube<sup>9</sup>. Due to the particular orientation of the Brewster surfaces inside the laser cavities, all TRILIS Ti:Sa lasers are p-polarized. For the use of a polarizer beam splitter cube, the polarization of one of the lasers must be rotated 90°, which is realized with a rotatable  $\lambda/2$ -plate. Applying another rotatable  $\lambda/2$ -plate for both lasers allows to continuously adjust the laser beam intensity used, without introducing beam steering, which can be profitable for saturation measurements.

All laser beams are overlapped with dichroic mirrors which have an antireflection coating for the passing wavelengths on their backs. Care has to be taken that the mirrors are sorted by wavelength such that the longest wavelength passes through the most mirrors. The final beam transport into the LIS test stand is realized by total reflection in an uncoated, UV-graded fused silica prism. The combined laser beams are focused by an uncoated 5 m focal length lens located directly in front of the prism. A schematic drawing of the laser setup is shown in Figure 4.4.

<sup>&</sup>lt;sup>9</sup>CVI PBSH-670-980-100



4. Yttrium ionization scheme development

Figure 4.4.: Schematic off-line laser beam transport setup.

In order to monitor the wavelength of each laser and the temporal overlap, the leakage of the Ti:Sa laser's high reflector is coupled into a 90/10 fibre coupler where the 90% goes to the fibre switch of the wavemeter<sup>10</sup> and the remaining 10% goes to a photo diode whose signal is monitored on an oscilloscope. Wavelength monitoring is served by a high precision wavemeter, which is calibrated with a frequency-stabilized HeNe laser<sup>11</sup>.

 $<sup>^{10}\</sup>mathrm{HighFinesse}$  WS6 — Fitzeau type wavelength meter with four port fiber switch

 $<sup>^{11}\</sup>mathrm{Melles}$  Griot Model 05 STP 901 — polarized stabilized He-Ne laser

# 4.2. Experimental procedure

The laser excitation schemes for yttrium reported prior to this work were either realized with a dye laser system at ISOLDE [FMF<sup>+</sup>05] or a mixed laser system consisting of Ti:Sa and dye lasers at IGISOL [KMK<sup>+</sup>08]. The most promising excitation schemes from both groups are shown in Figure 4.5. Since TRILIS operates an all-solid-state laser system, these excitation schemes are not necessarily sufficient.



Figure 4.5.: Excitation schemes rated as most efficient. Where IGISOL uses both second excited states and ionizes nonresonant with respect to the other step, ISOLDE just uses the 662.5 nm step and ionizes nonresonant with their pump laser.

# 4.2.1. Sample preparation and first ion signal

A sample of about  $10^{17}$  atoms was prepared by adding  $\approx 10 \text{ µl}$  of yttrium solution<sup>12</sup> on a 1 cm×1 cm titanium foil. This was placed in an oven for about 10 min at 100 °C in order to dry it out. Afterwards the foil was folded several times until it was small

 $<sup>^{12}{\</sup>rm AAS}$  standard solution, Specpure<sup>®</sup>, yttrium 1000 µg/ml Y<sub>2</sub>O<sub>3</sub> in 5% HNO<sub>3</sub>

enough to fit in the crucible. The titanium foil was simply used as support material (its common use as reduction material, as discussed in detail in [Die00] for the example of calcium atomization, is not applicable in the case of yttrium, since  $Y_2O_3$  as present available in the solution, is resistant against reduction with titanium).

The standard beam energy for excitation scheme tests was 10 keV, whereas on-line typically 20–50 keV are applied. Since the beam energy typically stays the same for all laser ionization scheme tests, an older ion optics tuning file<sup>13</sup> was loaded and used. Yttrium's only stable isotope is at mass 89 u. Since there are no other stable isotopes at this mass and the next closest isotope ionized by surface ionization, <sup>87</sup>Rb, is too far away to be present in the tail, a pure yttrium isotope beam is expected, once resonant laser ionization is achieved.

For the first tests, the excitation scheme tested at IGISOL in Jyväskylä [KMK<sup>+</sup>08] was applied because the surface ionization efficiency was expected to be too low for detection. However, even with lasers, the crucible filament heated up to maximum current at 55 A and the ionizer tube to the maximum 250 A, no ions could be detected. Since at 55 A on the filament, the crucible itself did not become hot enough to vaporize the yttrium, the crucible and the filament were removed and the sample was placed directly in the ionizer tube. The disadvantage of this method is that the overall efficiency is reduced because the ions can escape in both directions from the ionizer tube. Nevertheless, with this setup laser-ionized yttrium ions were detected right away at an ionizer current of 150 A, corresponding to a temperature of  $\approx 1170$  °C.

 $<sup>^{13}10~\</sup>mathrm{kV}\mathchar`-Ga-3nov09\mathchar`-2.snap$ 



Figure 4.6.: Different experimental arrangements for sample atomization (a) cold filament and crucible (b) ionizer tube with sample.

current, the temperature was increased until an approximately stable signal could be detected. This temperature was reached at about 210 A. All further measurements were performed at this temperature unless otherwise noted. It turns out that this method of introducing the sample allows to take advantage of the excellent high temperature and rather uniform temperature distribution of the transfer tube set up. This allows for very reproducible sample evaporation and vapor pressure control.

### 4.2.2. Excitation scheme development

Although there is already a lot of information known about the atomic structure of yttrium [RKRT11, SHEK], most transitions listed are classified in the visible wavelength region and are therefore better suitable for dye laser systems. In order to find the most efficient excitation scheme out of the listed 50 ground state transitions, the 6 most promising with respect to their accessibility with Ti:Sa lasers and their transition probabilities were chosen (see Table 4.1). It has to be taken into account that the

ground state is split into two fine structure states. At a temperature of  $\approx 1600$  °C, both states are equally populated (Figure 2.3). For that reason, excitation from both states should be considered when trying to obtain high ionization efficiency.

	length and transition probability. Since both the ground state and the						
low lying state at 530 $\rm cm^{-1}$ are equally populated, transitions from bo							
states were considered [SHEK].							
ser. no.	$E_0$	configuration	$E_1$	configuration	$\lambda_{vac}$	$A_{ki}$	
	$[\mathrm{cm}^{-1}]$		$[\mathrm{cm}^{-1}]$		[nm]	$[ s^{-1} ]$	
1	0	$4\mathrm{d}5\mathrm{s}^2$ a $^2\mathrm{D}_{3/2}$	24131.25	$4d5p y {}^{2}D_{3/2}$	414.400	$1.58\cdot 10^8$	
2	0	$4d5s^2 a {}^2D_{3/2}$	24518.75	$4d5p y {}^{2}F_{5/2}$	407.851	$1.11\cdot 10^8$	
3	530.36	$4d5s^2 a {}^2D_{5/2}$	24746.57	$4d5p y {}^{2}D_{5/2}$	412.947	$1.56\cdot 10^8$	
4	530.36	$4d5s^2 a {}^2D_{5/2}$	24899.63	$4d5p y {}^{2}F_{7/2}$	410.353	$1.27\cdot 10^8$	
5	0	$4d5s^2 a {}^2D_{3/2}$	27824.65	$4d5p \ge {}^{2}P_{1/2}$	359.394	$2.41\cdot 10^8$	
6	530.36	$4d5s^2 a {}^2D_{5/2}$	28139.65	$4d5p \ x \ ^{2}P_{3/2}$	362.197	$2.34\cdot 10^8$	

Table 4.1.: 6 most promising first excitation steps in vttrium chosen by their wavelength and transition probability. Since both the ground state and the h

### Second excitation steps in yttrium

Even though there are several possible second excitation steps listed, in most cases no information about their transition probability is known. By scanning the grating laser on top of each first excitation step, a peliminary assessment of the efficiency of each excitation scheme can be given by comparing the height of each peak in the obtained ion current signal. For nonresonant ionization, 6.8 W of 532 nm light is available from the frequency-doubled nonresonant ionization laser. As the ion current varied over time, in order to compare the different ionization schemes with each other, frequent ion current measurements of previously measured ionization schemes were made. All ion currents shown in Figure 4.7 are relative intensities.



### 4. Yttrium ionization scheme development

Altogether, 20 energy levels have been observed corresponding to 43 different excitation schemes listed in Table 4.2. Of these levels, one new at 40910.4 cm<sup>-1</sup> was seen in the scans from two different first excitation steps. Furthermore it was possible to assign the *J*-value for the 41853.2 cm<sup>-1</sup> level, since it was seen both from the  ${}^{2}P_{1/2}$ and  ${}^{2}P_{3/2}$  in addition to the  ${}^{2}D_{5/2}$  state at CERN [FMF<sup>+</sup>05]. For that reason, the *J*-value for this level can only be J = 3/2. All measured levels for the second excitation steps, their electron configuration if known, and the corresponding references, are listed in Table 4.2. The uncertainty for the unknown level is estimated from the variance of both level positions in the spectra shown in Figure 4.7. For all other energy levels the literature value is given.

For nonresonance ionization, the strongest resonance in Figure 4.7 provides the strongest ion signal. The corresponding ionization scheme is depicted in Figure 4.8. In addition to the peak height, the saturation power of each excitation step can also give some indication about the quality of the excitation scheme. As shown in Section 2.3.2, if saturation is achieved, in the ideal two level model case, the populations of both energy levels are equal and higher laser power does not necessarily increase the ion current. In order to measure the saturation power, the laser power is stepwise reduced from its maximum either with a neutral density filter wheel placed in the expanded beam, or if available, by changing the polarization of the laser with the rotatable  $\lambda/2$ -plate in front of the polarizer beam splitter cube. The advantage of the latter method is that it provides smooth power attenuation without the introduction of steering or beam focusing effects. While the saturation power for one step is measured, the other lasers remain at their maximum powers.

$E_2$	configuration	first excitation step	reference
$[{\rm cm}^{-1}]$		(Table $4.1$ )	
36420.1	$4s6s f {}^{2}D_{3/2}$	1,2,3	[RKRT11, SHEK]
36431.2	$4s6s f {}^{2}D_{5/2}$	$1,\!3,\!4$	[RKRT11, SHEK]
36859.0	3/2	$1,\!2,\!3$	[PN86]
37074.2	$4s6s {}^{2}D_{5/2}$	$1,\!3,\!4$	[RKRT11, SHEK]
37524.5	5/2	$2,\!3,\!4$	[PN86]
37549.0	3/2	$1,\!2,\!3,\!4$	[PN86]
38159.0	5/2	$1,\!2,\!3,\!4$	[PN86]
38411.8	$4d^{3} {}^{2}F_{7/2}$	$2,\!3,\!4$	[SHEK]
39446.3	$4s5d^2 e {}^4F_{3/2}$	5	[RKRT11, SHEK]
39553.0	?	5	$[FMF^+05]$
40287.5	?	$^{5,6}$	$[FMF^+05]$
40307.7	?	5	$[FMF^+05]$
40454.8	?	6	$[FMF^+05]$
40517.0	$4s5d f {}^{4}P_{5/2}$	6	[RKRT11, SHEK]
40910.4(1)	?	$^{5,6}$	
41422.7	3/2	6	$[PN86, FMF^+05]$
41660.7	3/2	$^{5,6}$	$[PN86, FMF^+05]$
41669.4	5/2	6	$[PN86, FMF^+05]$
41853.2	3/2	$^{5,6}$	$[FMF^+05]$
41879.7	?	$^{5,6}$	$[FMF^+05]$

Table 4.2.: All second excitation steps in yttrium investigated as part of this thesis.

In order to obtain the saturation power, the ion current dependence of the laser power is fitted by the following equation [Got11]

$$I = a \frac{P_L/P_{sat}}{1 + P_L/P_{sat}} + bP_L \tag{4.1}$$

where  $P_L$  is the available laser power,  $P_{sat}$  is the power necessary to reach saturation, and a and b are constants. The first term describes the behaviour of the ion current in saturation of a resonant transition, while the second term adds a linear dependence caused by possible nonresonant ionization.



Figure 4.8.: Best ionization scheme for yttrium with Ti:Sa lasers and nonresonant ionization.

The saturation curves of the best excitation scheme for nonresonant ionization are shown in Figure 4.9, and the saturation and available power of each step are listed in Table 4.3. The first two excitation steps are well saturated. The nonresonant step shows an exponential dependence where a linear dependence would be expected. This observation is an indication that the nonresonant step not only ionizes the atoms
but also helps in vaporizing the sample that was introduced directly into the transfer/ionizer tube. The ionization laser was operating the entire time at its maximum power of 6.8 W.



Figure 4.9.: Saturation of transitions in the most efficient, nonresonantly ionized yttrium excitation scheme. All resonant excitations steps are saturated.

	$\begin{bmatrix} P_{sat} \\ [ mW ] \end{bmatrix}$	$\begin{array}{c} P_{max} \\ [ mW] \end{array}$
first excitation step (362.197 nm)	$2.5 \pm 1.0$	180
second excitation step $(739.177 \text{ nm})$	$32.7{\pm}0.7$	1210
nonresonant ionization $(532 \text{ nm})$	n/a	6800

Table 4.3.: Saturation and available laser power for the most efficient nonresonant ionization scheme in yttrium.

#### Autoionizing steps in yttrium

In general, ionization via a Rydberg or autoionizing state shows cross sections that are typically 1–2 orders of magnitude larger than those for nonresonant ionization processes. For excitation schemes applied at TRILIS, this is for example the case for Be [Seb99] and Mg [LBD<sup>+</sup>09]. For that reason, fundamental wavelength scans from selected second excitation steps have been performed starting from chosen energy levels:

- $36420.6 \text{ cm}^{-1}$ ,  $37549.0 \text{ cm}^{-1}$  and  $38159.0 \text{ cm}^{-1}$  from  $24131.3 \text{ cm}^{-1}$  as the first excitation step.
- 39553.0 cm<sup>-1</sup> and 41660.7 cm<sup>-1</sup> from 27824.7 cm<sup>-1</sup> as the first excitation step (no resonances seen).
- 41669.3 cm<sup>-1</sup> from 28139.6 cm<sup>-1</sup> as the first excitation step (no resonances seen).

A significant improvement in comparison to the nonresonant ionization was observed for the scans from the  $37549.0 \text{ cm}^{-1}$  and  $38159.0 \text{ cm}^{-1}$  levels. The enhancement for the first case is in fact 5.6 times better, as shown in Figure 4.10. For the other two scans, the strongest resonances were comparable to the nonresonant ionization.

The excitation schemes chosen for the scans in Figure 4.10 were selected in chronological order. In the course of the experiment it was observed that certain resonances were stronger using a different first excitation step. Assuming that all resonant steps are saturated, and the efficiencies of the ionizing steps are independent of the first two excitation steps, the relative intensities for nonresonant ionization and ionization via an autoionizing step were multiplied in order to assess which wavelength combinations were the most promising. As a result, three excitation schemes were found which could be more efficient than the nonresonant ionization discussed above. The three schemes are shown in Figure 4.11.

**Ionization schemes I and II** both have the same second excited state of 38159.0 cm<sup>-1</sup>, but with different first excitation steps. Figure 4.12a and 4.12b are detailed views of the two strongest resonances from this state. Of the two schemes, the best ionization was observed for the resonance at  $\lambda = 735.5$  nm, which corresponds to a total energy of 51431.2(1) cm<sup>-1</sup> and has a linewidth of  $\Delta \nu = 236(7)$  GHz. The second autoionizing state has a total energy of 51109.5(3) cm<sup>-1</sup>, and with  $\Delta \nu = 604(17)$  GHz is even broader than the first one.

Although the first two schemes were the most promising with theoretical enhancements of 1.33 and 1.17, subsequent evaluation showed that, compared with their nonresonant schemes, these schemes provided ion currents with about an order of magnitude lower intensity. However, in both cases the highest ion currents were measured by adding the nonresonant step on top of the autoionizing step even though



Figure 4.10.: Autoionizing states in yttrium measured from the four prior detected second excitation steps. The intensity is normalized to the previously measured intensity for nonresonant ionization.



Figure 4.11.: Three most promising ionization schemes into autoionizing states for yttrium, selected by combining the most efficient excitation schemes for nonresonant ionization and multiplied by the corresponding enhancement going into an autoionizing state.



Figure 4.12.: Detailed views of the two strongest autoionizing states from scans starting at the  $38159 \text{ cm}^{-1}$  level. The ion current is normalized to the corresponding nonresonant ionization.

there was no influence of the temporal overlap for the nonresonant step observed. When all four lasers were added, it was possible to detune the nonresonant ionization laser by 1 µs, without changing the ion current. This behaviour confirms the observation during the saturation measurement in Figure 4.9c that the nonresonant laser also helped to vaporize the yttrium in the ionizer tube.

In order to investigate this phenomenon further, all three ionizing methods were compared while increasing the temperature of the ionizer, as shown in Figure 4.13. An intensity plateau has been noticed for all curves at around 230 A. In addition, a small temporal dependence for the nonresonant step has also been noticed again when all lasers are applied. Whereas above this plateau the ion current for the autoionizing step yields are approximately equal to the nonresonant step in Scheme I, the autoionizing step in scheme II yields even higher intensities than the nonresonant step.



Figure 4.13.: Temperature dependence of the ionization efficiency for nonresonant ionization, resonant ionization into an autoionizing state and the combination of both for ionization scheme I and II.

For that reason, the saturation curve for the autoionizing step was measured twice for scheme II, once at a heating current of 210 A and once at 245 A. Where the saturation curve at a heater current of 210 A shows a purely linear dependence, at 245 A the autoionizing step starts to show the expected behaviour. The saturation curves for both schemes are shown in Figure 4.14 and Figure 4.15. The saturation and available power of each step are listed in Table 4.4. The maximum power of the nonresonant step is again 6.8 W.



Figure 4.14.: Saturation curves for ionization scheme I.



Figure 4.15.: Saturation curves for ionization scheme II.

0 1	v			
	$\operatorname{scheme}$	Ι	scheme II	
	$P_{sat}$	$P_{max}$	$P_{sat}$	$P_{max}$
	[ mW ]	[ mW]	[ mW]	[mW]
first excitation step	$13.7 {\pm} 6.9$	240	$8.7 {\pm} 4.4$	260
second excitation step	$6.4 \pm 3.9$	1300	$53.2 \pm 9.7$	1230
autoionizing step	$435.9 {\pm} 107.7$	1200	$137.0 \pm 56.6 @ 245 A$	1030

Table 4.4.: Saturation and available power for ionization scheme I and II using autoionizing steps in yttrium.

**Scheme III** Unlike Schemes I and II where the assumption was made that the efficiency of the autoionizing step is independent of how the second excitation state is populated, the enhancement of Scheme III can be directly scaled from the previously collected data. The first excitation step is the same which was already used for the excitation schemes at IGISOL and ISOLDE. The transition to the second excitation state at 37549.4 cm<sup>-1</sup> is one of the transitions that has not been measured before. Figure 4.16 shows detailed views of the regions of interest of the corresponding scan in Figure 4.11. For all further measurements the autoionizing state C1 from Table 4.5 is used.

Table 4.5.: Level position, wavelength and enhancement of autoionizing states compared to nonresonant ionization using 37550 cm<sup>-1</sup> as the second excited state. The uncertainty results from the standard error of the Gaussian fit function.

	total energy $[ \text{ cm}^{-1} ]$	wavelength [ nm]	maximum height [a.u.]
A1	50292.15(3)	784.742(2)	3.3
Β1	51081.33(6)	739.000(3)	3.8
B2	51095.90(4)	738.207(2)	3.9
B3	51105.80(5)	737.661(3)	3.1
B4	51131.80(3)	736.251(2)	3.4
C1	51412.82(3)	721.323(2)	4.7
C2	51426.62(4)	720.600(2)	2.9
C3	51459.15(5)	718.919(3)	2.7

This excitation scheme yields a relative intensity of 0.81. Nevertheless, adding the nonresonant step to this scheme increases the ion current by a factor of 2.1, leading to an enhancement of 1.73 in comparison to the nonresonant scheme discussed above, and would therefore be the best excitation scheme so far.



Figure 4.16.: Detailed views of the three strongest autoionizing states from the  $37550 \text{ cm}^{-1}$  level.

While measuring the saturation power of each step (Figure 4.17 and Table 4.6), it was observed that the first excitation step could not be saturated with the available power. However, the saturation power for the first excitation step has not been measured with the excitation scheme discussed in this paragraph but rather, the first experiments with a weaker second excitation step to the 36420.6 cm<sup>-1</sup> level and a nonresonant ionization step. Since the first excited state will be emptied faster by applying a second excitation step with a strong transition probability, it is indeed possible that the saturation power varies with the applied excitation scheme even though no appreciable difference, especially for the first excitation step, has been noticed in previous experiments. Due to the fact that at operating temperature both ground states are equally populated and the transition probabilities of the first excitation steps in Scheme I, II and III are about the same, a saturation power of  $P_{sat} \approx 10$  mW is expected. The second excitation step as well as the step into the autoionizing state are fully saturated.

Table 4.6.: Saturation and available power for all excitation steps in ionization scheme III in yttrium.

	$P_{sat}$ mW	$P_{max}$ mW
first excitation step	n/a	200
second excitation step	$36.5 {\pm} 2.1$	1450
autoionizing step	$41.0 \pm 3.6$	1190



(a) saturation first excitation step (b) saturation second excitation step



(c) saturation autoionizing step

Figure 4.17.: Saturation curves for all excitation steps in ionization scheme III (414.400 nm + 745.268 nm + 721.344 nm). Except for the first excitation step all further resonances are saturated.

# 4.3. Transferring results to on-line operation

The excitation scheme that delivers the highest ion current requires the frequencydoubled, nonresonant ionization laser for nonresonant ionization. Over the course of the measurements it was observed that this laser not only results in the ionization of the atoms but also in vaporizing the sample. This helps to explain the exponential saturation behaviour and the temporal independence when a resonant ionization step is added.

The vaporizing effect of the laser can be explained due to the fact that the original design of the test stand was modified such that the crucible and filament were removed and the sample was placed directly in the ionizer. For that reason the lasers directly interact with the sample itself and not just the atomic vapour as desired. The effect of the nonresonant ionization laser on the copper heat shield can be seen in Figure 4.18; the shield acts as a beam dump when the source is operated without a crucible. Over two weeks of operation, a significant amount of the heat shield ablated within a submillimeter diameter area caused by the nonresonant ionization laser even though its focus was set to the centre of the ionizer tube. It is clear that the sample material could be affected by the laser light.

In on-line operation since the lasers only interact with the isotopes produced radiogenically, a different behaviour of the nonresonant ionization step is expected. Furthermore, even if the exponential power dependence of the nonresonant ionization step could be measured on-line as well, its influence could be significantly lower than measured off-line since for the on-line beam transport more optical elements are involved and thereby higher losses are introduced.

#### 4. Yttrium ionization scheme development



Figure 4.18.: A small hole is drilled by the nonresonant ionization laser in the heat shield after two weeks of operation.

The ionization efficiency could be increased by using the fundamental of the nonresonant ionization laser at  $\lambda = 1064$  nm, since the photon energy required for nonresonant ionization in this scheme corresponds to a wavelength  $\lambda < 1179$  nm, as shown in Figure 4.8. This increase of ionization efficiency can be understood by two reasons. First, the ionization cross section increases as the photon energy gets closer to the energy difference between the excited state and the ionization potential, as described in Section 2.2.1. Second, the output power available by operating the nonresonant ionization laser at its fundamental wavelength is with 13 W approximately doubled.

The overall laser enhancement for laser ionization is defined as the ratio of ions produced by laser-ionization  $I_l$  to the entire measured ion current  $I_e$  [FS73]

$$\nu = \frac{I_l}{I_e} \,. \tag{4.2}$$

In order to determine this value the ion current is measured once with all lasers resonant and once with a detuned first excitation step on the Faraday cup in front of the QMS. That way the thermal effects introduced from the lasers are the same in both cases. However, due to the copper ablation on the heat shield, the background is too large for the influence of the first step to be seen. A measurement on the channeltron behind the mass filter was not possible, since the surface ionization of yttrium is too low to be detected and it is the only stable isotope at this mass. In order to determine which excitation scheme is really the best, both the ones shown in Figure 4.8 and Scheme III in Figure 4.11 should be tested under on-line conditions.

In both cases, the ionization efficiency could be increased by a factor of two by adding an additional first excitation step to the scheme in order to also excite the electrons from the ground state or low lying excited state. The wavelength required for the nonresonant scheme would be  $\lambda_1 = 355.370$  nm which has a transition probability of  $A_{ki} = 2.3 \cdot 10^7 \text{s}^{-1}$  and for Scheme III  $\lambda_1 = 423.713$  nm which has a transition probability of  $A_{ki} = 3.0 \cdot 10^7 \text{s}^{-1}$ . Since the saturation power depends linearly on the transition probability as shown in Equation (2.39), the power required in order to saturate these transitions would be about one order of magnitude higher.

# 5. Resonant ionization spectroscopy of astatine

Astatine, atomic number 85, is the heaviest naturally occurring halogen. It was first investigated in 1940 at the Radiation Laboratories of the University of California by bombarding <sup>209</sup>Bi, the only stable bismuth isotope, with 32 MeV  $\alpha$  particles [CMS40]. The resulting isotope was <sup>211</sup>At which has a half-life of  $\tau = 7.5$  h. In 1943, first evidence of the natural occurrence of this element was shown by looking at the decay products of certain Ra, Th and Ac isotopes [KB43, KB44]. In this way, <sup>218</sup>At, <sup>215</sup>At and later <sup>217</sup>At and <sup>219</sup>At were investigated as decay products of <sup>235</sup>U, <sup>238</sup>U and <sup>237</sup>Np. Due to the short half-lives of these isotopes,  $\tau = 1.5$  s, 0.1 ms, 32.3 ms and 56 s, respectively [Lun02], astatine is the least abundant element on earth. The isotope with the highest possibility to occur is <sup>217</sup>At resulting from the <sup>237</sup>Np decay chain.

So far, a total of 30 radioactive astatine isotopes from mass A = 193-223 [Lun02], as shown in Figure 5.1, have been found. The longest-lived isotope <sup>210</sup>At has a half-life of  $\tau = 8.3$  h [JLS49].





Due to the difficult and inefficient production process and short half-lives, very little information about the physical and chemical properties of astatine exists. A detailed description of the individual isotopes and chemical properties identified via tracer analysis can be found in [RDDW88]. Similar to iodine, astatine shows a metallic and halogen behaviour.

Most physical properties of astatine are only estimated by extrapolation from the other halogens. This, among others, is a case for the importance of measuring spectroscopic values such as the first ionization potential and fine structure splitting of the ground state. Via extrapolation and different approximation methods, the ionization potential can be estimated to a value between 8.3 eV and 10.1 eV [FS50, MW06, CLD10].

Since for all halogens only one electron is missing to fill up the outer shells, the electron configuration for the ground state is  $[Xe]4f^{14}5d^{10}6s^26p^5$ . From the spectroscopic term  ${}^{2}P^{o}_{3/2}$  it can be seen that the ground state is a doublet where the fine structure splitting is estimated to 2.4 eV – 3.4 eV [MW06, CLD10, Fri11].

Like all other physical properties, the optical spectrum of astatine is practically unknown. The only successful experiment to find resonant transitions in <sup>210</sup>At was performed in 1964 using absorption spectroscopy techniques [McL64]. Their range of measurements was between 210 nm and 300 nm. In this region, two absorption lines at 224.471 nm and 216.292 nm were found. By extrapolation from the known energy levels of the other halogens, the two observed absorption lines were assigned to ground state transitions of the  $6p^47s$   $^4P_{5/2}$  level for the 224 nm line and  $6p^47s$   $^4P_{3/2}$  level for the 216 nm line.

The task of this thesis is to look for further optical transitions in astatine using resonant ionization laser spectroscopy at TRIUMF's ISAC facility with regard to rendering assistance in finding more precise values for the ionization potential and fine structure splitting, getting a better understanding of the atomic and nuclear properties of astatine, and finding an efficient ionization scheme. The ionization scheme is requested by a number of experiments, among others for a radon electric dipole moment experiment which requires a pure beam of excited <sup>223</sup>Rn isotopes, <sup>223</sup>Rn being a decay product of <sup>223</sup>At.

## 5.1. Experimental setup

#### 5.1.1. Radioactive ion beam production and transport at ISAC

Radioactive ion beams (RIB) at TRIUMF are produced by bombarding a target material with a high energy proton beam. The proton beam is produced by accelerating  $H^-$  ions in TRIUMF's main cyclotron. When the ions have the required intensity, typically around 500 MeV, the two electrons can be removed by means of a thin graphite stripper foil (typically 2.5–4.5 mg/cm<sup>2</sup>). Since the hydrogen ion changes its charge, it also changes its direction of movement and can thereby be ejected to the beam line supplying the ISAC target stations. The proton beams can have varying intensities as needed of up to 100 µA, which is the target station intensity limit, dictated by the shielding installed.

ISAC has two target stations, named after their cardinal directions east and west, which are alternatively operated for two to four weeks at a time. This is approximately the time needed for a used target to cool down and be replaced by a new one. Due to the long operation time, continuous RIB production can be achieved. Furthermore, with the continuous proton driver beam also a continuous beam of radioactive ions can be extracted.

The target itself is a 20 cm long and 19 mm diameter tantalum tube placed along the proton beam. The target container is filled with thin foils of the respective target material [Bri07]. So far, targets consisting of Si, Ti, Zr, Nb, Ta and since September 2009 also U, have been used. These elements are used typically in refractory form, either elemental or as compounds. The possibility for the use of uranium as a target material extended the isotope production to heavy elements like At, Rn, Fr and Ac, and to the neutron rich side of the lighter elements. For the astatine spectroscopy discussed in this chapter, an UC<sub>x</sub> target has been used which was either bombarded with a proton intensity of 2  $\mu$ A or 10  $\mu$ A, depending on the time of the experiment, and the valid licensing limit for maximum proton beam intensity and integrated irradiation.

By resistively heating the target container to about 1500 °C, the spallation, fragmentation and fission products are helped to diffuse and effuse out of the target material into the transfer tube connected at the upper centre of the container perpendicular to the proton beam. In order to be able to manipulate the radioactive isotopes, they have to be ionized. For this purpose, different ion sources, e.g.

- hot surface ion source
- resonant ionization laser ion source (TRILIS)

• forced electron beam induced arc discharge (FEBIAD) ion source

can be used. The first two are of relevance for this thesis as the resonant ionization laser ion source makes use of the surface ion source's transfer/ionizer tube as the ionization volume for laser ionization.

The 40 mm long and 3 mm diameter hot transfer tube also operates as a surface ion source, and during the measurement of astatine, is responsible for possible background. As several different experiments are run during the operation time of one target, typically both ion sources, surface and RILIS are required; a thin rhenium foil is placed at the tip of the tube in order to improve the surface ionization efficiency [BAD<sup>+</sup>12]. As shown in Figure 2.6, this source is only efficient at the % level of ionization efficiency for alkali metals and some of the lanthanide elements. The laser ion source is especially of interest for ionization of the elements with an ionization potential above 5 eV and below 13 eV. For other elements the FEBIAD<sup>1</sup> is used.

After ionization of the isotopes, they are guided via steering, focussing, and accelerating elements to a mass separation system. The latter consists of a low resolution mass separator, also functioning as a switchyard between target stations, and the high resolution mass separator, with a mass dispersion of 394 mm, enough to be isotopeselective, and the main mass separator magnet with a mass dispersion of 2250 mm leading to some isobaric selectivity [Bri06]. The requested isotope can then be sent to the experiment, but the first stop is usually the yield station. Here the yield of the requested isotope can be determined by implanting the isotope beam on a metallic tape for a selected time, and measuring its  $\alpha$ ,  $\beta$ , and  $\gamma$  decay afterwards. Most of the

 $<sup>^1{\</sup>bf F} {\rm orced}$  Electron Beam Induced Arc Discharge ion source

astatine isotopes are  $\alpha$  emitters. The  $\alpha$  particles can be detected with two windowless Si PIN photo diodes<sup>2</sup> with dimensions  $10 \times 10$  mm.

Along the way from the target station to the experiments, several diagnostic tools like Faraday cups and channeltrons are located. For astatine spectroscopy, the ion current on channeltrons  $CEM19^3$  and  $CEM20^4$  has been monitored. CEM19 is located just below the yield station in the vertical beamline between the mass separator and experimental areas; and CEM20 directly after the mass separator, as shown in Figure 5.2. For all experiments performed in 2011 and later, it is possible to add a beam attenuator of a factor 10 or 100 in order to protect the channeltrons. If not otherwise noted, all measurements implemented at CEM19 used the  $10 \times$  attenuator.

#### 5.1.2. TRILIS laser beam transport

The TRILIS Laser laboratory for on-line operation is equipped with three BRFtuned Ti:Sa lasers for ion source operation, one grating-tuned Ti:Sa laser for spectroscopy purposes, one ionization laser for nonresonant ionization, and two frequencytripling/quadrupling units. The Ti:Sa lasers are pumped with one frequency-doubled Nd:YAG laser. All of these components are discussed in detail in Chapter 3.

The laboratory is located on the floor of the experimental area in the ISAC I hall and therefore two levels above the target stations, as shown in Figure 5.2. This has the advantage that all operational parts of this ion source are away from any radiation. In order to get the laser light to the ionization area which is the transfer tube at the

 $<sup>^2\</sup>mathrm{Hamamatsu}$ S<br/>3590-02

 $<sup>^3\</sup>mathrm{Dr.Sjuts}$  Optotechnik Model KBL 10RS

<sup>&</sup>lt;sup>4</sup>PHOTONIS USA MAGNUM 5903



Figure 5.2.: ISAC target hall and experimental area [TRI12]. The proton beam coming form TRIUMF's cyclotron is stopped in one of two target stations. The rare isotopes produced by the protons interacting with the target material diffuse into a ion source where they are ionized. After mass separation, the requested isotopes are sent to the experiment. For diagnostics, several channeltrons and Faraday cups are located along the beam line. The location of the two channeltrons CEM19 and CEM20 of interest for the astatine spectroscopy experiment are marked in this picture.

target container, all lasers with similar wavelengths are combined on the laser table and transported via dielectric mirrors down to the mass separator area. Depending on which target station is in use, the lasers are transported to one of two laser tables where the focussing lenses are located and the beams are overlapped using dichroic mirrors. The lasers access the ionization region via a fused silica vacuum window located at the preliminary separator.

A reflection of the window acts as a reference if all lasers are focussed and overlapped in the source. Alternatively to the entrance window reflection, a separate 4% beam splitter is located at the last accessible point before the lasers enter the preliminary separator. In both cases the reference spot is monitored via a camera on a ceramic disc<sup>5</sup>. The disc is placed at the same distance to the window or beam splitter as these are to the transfer tube, about 8-10 m depending on the set up.

Due to the natural divergence of a laser beam and the long transport path from the on-line laser laboratory to the ionization region of about 20 m, the lasers have to be focused in order to match the laser diameter with the transfer tube diameter of 3 mm. For that reason, the laser beams are expanded with a telescope in the laser laboratory as explained in Section 4.1.2, and focused with the already mentioned lens on the laser table in the mass separator area. A more detailed description of the laser beam transport can be found in [Mei12].

 $<sup>^5\</sup>mathrm{Kentek}$  ViewIt-IR

## 5.2. Experimental results

The astatine spectroscopy is a collaboration project between RILIS ISOLDE at CERN and TRILIS at TRIUMF. In this thesis only the results measured at TRIUMF will be discussed. At TRIUMF, the astatine spectroscopy was performed mainly for the isotope <sup>199</sup>At chosen because of its convenient, short half-life of 7.2 s, little contamination due to no isobaric contamination from surface ions, and good production rates. The decay chain of <sup>199</sup>At is shown in Figure 5.3.

#### 5.2.1. First excitation step confirmation

The only existing spectroscopic data about astatine are two transitions, one at 216 nm and one at 224 nm, measured by absorption spectroscopy methods in 1964 [McL64]. During an experiment in November 2010 at CERN, these two lines were confirmed by resonant laser ionization spectroscopy methods, and the transition at 216 nm was found to be the stronger one as predicted [CLD10].

This stronger transition was chosen first in order to look for further energy levels. After spectral accuracy and temporal overlap, spatial overlap is an important factor in order to laser-ionize an isotope. A nonresonant excitation scheme consisting of the known resonant step and a nonresonant was chosen to create the first laser ionization signal at TRIUMF and set the spatial reference point. At that time the ionization potential was still estimated to be 9.5 eV [FS50]; therefore, a photon energy  $E_{photon} > 3.77$  eV would be required for nonresonant ionization. This corresponds to a wavelength  $\lambda < 329$  nm which, with Ti:Sa lasers, can only be realized by the frequency-tripling of the fundamental. This process only leads to laser powers of about

			Fr 199	Fr 200	Fr 201	Fr 202	Fr 203	Fr 204	Fr 205	Fr 206
			16 ms	24 ms	48 ms	290 ms	550 ms	1.7 s	3.92 s	16 s
Rn 195	Rn 196	Rn 197	Rn 198	Rn 199	Rn 200	Rn 201	Rn 202	Rn 203	Rn 204	Rn 205
6 ms	3 ms	65 ms	57 ms	620 ms	1.03 s	7 s	9.94 s	43.5 s	1.24 min	2.8 min
At 194	At 195	At 196	At 197	At 198	At 199	At 200	At 201	At 202	At 203	At 204
40 ms	328 ms	253 ms	350 ms	4.2 s	7.2 s	43.2 s	1.417 min	3.067 min	7.4 min	9.2 min
Po 193	Po 194	Po 195	Po 196	Po 197	Po 198	Po 199	Po 200	Po 201	Po 202	Po 203
420 ms	392 ms	4.64 s	5.56 s	6 5	1.77 min	5.48 min	11.5 min	15.3 min	44.7 min	36.7 min
Bi 192	Bi 193	Bi 194	Bi 195	Bi 196	Bi 197	Bi 198	Bi 199	Bi 200	Bi 201	Bi 202
34.6 s	1.117 min	1.583 min	3.05 mir	5.1 min	9.3 min	10.3 min	27 min	36.4 min	1.8 h	1.72 h
РЬ 191	РЬ 192	РЬ 193	РЬ 194	РЬ 195	РЬ 196	РЬ 197	РЬ 198	РЬ 199	РЬ 200	РЬ 201
1.33 min	3.5 min	5 min	12 min	15 mip	37 min	8 min	2.4 h	1.5 h	21.5 h	9.4 h
TI 190	TI 191	TI 192	TI 193	TI 194	TI 195	TI 196	TI 197	TI 198	TI 199	TI 200
2.6 min	20 min	9.6 min	21.8 min	33 min	1.16 b	1.84 h	2.84 h	5.3 h	7.42 h	1.088 d
Hg 189	Hg 190	Hg 191	Hg 192	Hg 193	Hg 194	Hg 195	Hg 196	Hg 197	Hg 198	Hg 199
7.6 min	20 min	49 min	4.85 h	3.8 h	444.3 a	9.9 h	2.502E18 a	2.692 d	stabil	stabil
Au 188	Au 189	Au 190	Au 191	Au 192	Au 193	Au 194	Au 195	Au 196	Au 197	Au 198
8.84 min	28 <i>7</i> min	42.8 min	3.18 h	4.94 h	17.65 h	1.584 d	186.1	6.183 d	stabil	2.694 d
Pt 187	Pt 188	Pt 189	Pt 190	Pt 191	Pt 192	Pt 193	Pt 194	Pt 195	Pt 196	Pt 197
2.35 h	10.2 d	10.87 h	6.504E11 a	2.802 d	stabil	50.03 a	stabil	stabil	stabil	19.89 h
lr 186	lr 187	lr 188	lr 189	lr 190	lr 191	lr 192	lr 193	Ir 194	lr 195	lr 196
16.64 h	10.5 h	1.729 d	13.2 d	12 d	stabil	73.82 d	stabil	19.3 h	2.5 h	52 s
0s 185	Os 186	Os 187	Os 188	Os 189	Os 190	Os 191	Os 192	Os 193	Os 194	Os 195
93.8 d	2.001E15 a	stabil	stabil	stabil	stabil	15.3 d	stabil	1.255 d	6.004 a	6.5 min

Figure 5.3.: Decay Chain of <sup>199</sup>At. The main branch is marked in bold. 89% of the <sup>199</sup>At isotopes decay by  $\alpha$  particle emission into <sup>195</sup>Bi, 11% decay by  $\beta^+$  emission into <sup>199</sup>Po [Nuk11].

100 mW, not enough for nonresonant ionization as shown in Section 2.2.1. Instead, the frequency-doubled ionization laser is externally frequency-doubled by focussing the laser with a lens<sup>6</sup> into a BBO-crystal, resulting in a wavelength of 266 nm with a conversion efficiency of  $24 \pm 2\%$  as shown in Figure 5.4. For nonresonant ionization, the quadrupled nonresonant ionization laser is typically operated at 600 mW



Figure 5.4.: Available laser power of the frequency-quadrupled nonresonant ionization laser. The conversion efficiency from 532 nm to 266 nm is  $24 \pm 2\%$ .

The wavelength for the first excitation step is realized by first intra-cavity doubling the fundamental wavelength of 865 nm, and then externally doubling the resulting blue light. That way, a linewidth of 1.5 GHz in the fundamental can be reached corresponding to an actual linewidth of 3 GHz using Equation (3.1). The available laser power for the first excitation step is 70 mW.

The first At ion signal at TRIUMF could be seen on CEM20 as shown in Table 5.1. Figure 5.5 shows the two ground state transitions with their saturation curves mea- $\overline{{}^6r = 77.3 \text{ mm AR coating for 532 nm}}$ 

Table 5.1.: First astatine ion signal at TRIUMF using a two step excitation scheme with a nonresonant ionization step.

	Ion signal on CEM20 [kcps]
All lasers blocked	26
Quadrupled nonresonant ionization laser	83
216 nm and nonresonant ionization laser	94

sured with one of the excitation schemes discovered and described in Section 5.2.2. For the measurement of the transition to the 44549 cm<sup>-1</sup> level, the laser power of the first step has been reduced to 2 mW in order to reduce power broadening effects. The result is listed in Table 5.2.

Table 5.2.: Energy level and saturation power of the two known ground state transitions in astatine.

total energy ${\rm cm}^{-1}$	saturation power mW
$46233.7 \\ 44549.2$	$21(12) \\ 11(1)$

### 5.2.2. Second excitation steps from the 46233.7 cm<sup>-1</sup> level

Prior to the experiment, some theoretical values for energy levels were determined by [CLD10, Fri11]. Since these data have an uncertainty of about 1000 cm<sup>-1</sup> and the grating laser has a linewidth of about  $\Delta \nu = 0.2$  cm<sup>-1</sup>, there is only a hint as to where a density of energy levels can be expected. In Figure 5.6, the theoretical values in comparison to the scan region of the grating-tuned Ti:Sa laser starting from the two known levels are presented.



(a) wavelength scan for the 216 nm transition.



(b) saturation curve for the 216 nm transition, using the 795 nm transition as the second excitation step and the nonresonant ionization laser at 532 nm for nonresonant ionization.



(c) wavelength scan for the 224 nm transition. The laser power has been reduced to 2 mW in order to reduce power broadening.



(d) saturation curve for the 224 nm transition, using the 786 nm transition as the second excitation step and the nonresonant ionization laser at 532 nm for nonresonant ionization.

Figure 5.5.: Wavelength scans and saturation curves for first excitation steps of <sup>199</sup>At.



Figure 5.6.: Theoretically determined energy levels of astatine calculated by [Fri11, CLD10] on the left compared with the Ti:Sa scan region starting from the two known transitions on the right.

Since for nonresonant ionization, adding to the first excitation step the lowest reachable wavelength of the grating-tuned Ti:Sa laser, a photon energy of  $E_{photon} >$ 2.23 eV is sufficient, the frequency-doubled ionization laser at 532 nm was used. In order to look for new energy levels, the grating-tuned Ti:Sa laser and the nonresonant ionization laser were spatially overlapped with the UV of the first excitation step on the previously defined reference spot. In order to reduce statistical errors, during the scan of the grating-tuned Ti:Sa laser, its wavelength was simultaneously monitored by two wavemeters<sup>7</sup>, which were calibrated with a frequency-stabilized HeNe laser<sup>8</sup>. By scanning the grating tuned Ti:Sa laser from 930 nm to 715 nm, three second excitation steps were found, which are shown in Figure 5.7.



Figure 5.7.: Second excitation steps scan from the  $46233.7 \text{ cm}^{-1}$  level. The ionizing step is realized by the frequency doubled nonresonant ionization laser.

Due to the half-life of <sup>199</sup>At of  $\tau = 7.2$  s, an additional asymmetric broadening is introduced, caused by the decay of the At-ions on the channeltron. This is demonstrated in Figure 5.8 which shows a detailed view of one of the peaks in Figure 5.7.

 $<sup>^7\</sup>mathrm{HighFinesse}$  WaveMeter Ångstrom WS/6 and WS/7

<sup>&</sup>lt;sup>8</sup>Spectra-Physics Model 117A

The exponential decay is towards higher energies since this was the scan direction of the laser.



Figure 5.8.: Detailed view of one of the resonances shown in Figure 5.7. The tail to higher energies is caused by the radioactive decay of the ions on the channeltron.

In order to determine more precisely the centre of the resonance, the laser may be scanned in both directions, so that way the peak has a symmetric shape and can more easily be fitted, or it can be detected at the yield station. In this case the wavelength of the laser is varied stepwise, where for every step a separate yield measurement has been taken.

In order to measure the yield of <sup>199</sup>At, the isotope beam is implanted on a metallic tape for 5 s. Afterwards, the beam is deflected onto a Faraday cup<sup>9</sup> in the mass separator area while the emitted  $\alpha$  particles are detected for 10 s at a photodiode. Next, the contaminated spot on the tape is moved behind lead shielding and the procedure is repeated 20 times. A typical  $\alpha$  spectrum for a measurement at <sup>199</sup>At is shown in Figure 5.9. As shown in Figure 5.3, not all of the <sup>199</sup>At isotopes decay by  $\alpha$  emission; 11% decay by  $\beta^+$  emission into <sup>199</sup>Po which is also an  $\alpha$  emitter. These

 $<sup>^9\</sup>mathrm{IIS}\mathrm{:FC2}$  collection station behind the kicker



Figure 5.9.: <sup>199</sup>At  $\alpha$  spectrum where the peak at 6643 keV belongs to <sup>199</sup>At, the peak at 5952 keV to <sup>199</sup>Po and at 6059 keV to <sup>199m</sup>Po. The peak at 6466 keV is not listed in any database and deserves further investigation, as it could stem from an astatine decay.

 $\alpha$  lines can be found in the spectrum shown in Figure 5.9 and could also be used for determining the astatine yield. The peak at 6466 keV is unassigned. In the plots shown in Figures 5.5 and 5.10, not the actual yields but rather the counted events in the respective  $\alpha$  emission peak have been plotted. Since the  $\alpha$  counts in the unassigned peak correlates exactly to these of the astatine and polonium, it can be followed that it is directly caused by the decay of <sup>199</sup>At and not due to any contamination on the tape. The results of the fits in Figure 5.10 are listed in Table 5.3. From the excited states, which can be reached by from more than one energy level, it can be seen that the level positions in astatine can be given with an uncertainty of  $\pm 1$  cm<sup>-1</sup>.



Figure 5.10.: Wavelength scans and saturation curves of second excitation steps in astatine using the 46233.7 cm<sup>-1</sup> transition as the first excitation step. The wavelength scans have been measured at the yield station by plotting not the actual yields, but the events in the respective  $\alpha$  emission peaks.

Table 5.3.: Energy position and saturation curves of second excitation steps in astatine measured from the 216 nm transitions and using the frequencydoubled nonresonant ionization laser for nonresonant ionization.

total energy	saturation power
$\mathrm{cm}^{-1}$	$\mathrm{mW}$
57157.1(10)	170(23)
57277.0(10)	31.2(95)
58805.3(10)	111(44)

## 5.2.3. Second excitation steps from the 44549.2 cm<sup>-1</sup> level

For the next undertaking, second excitation steps were looked for, starting from the  $44549.2 \text{ cm}^{-1}$  energy level. As a starting point, it was checked if there are any allowed transitions from this energy level to the previous one found, listed in Table 5.3. An overlap has been seen for two of these levels, one to the 57157.1 cm<sup>-1</sup> level and one to the 58805.3 cm<sup>-1</sup> level.

In order to look for more possible transitions, a wide wavelength scan has been performed. Meanwhile at CERN, the first ionization potential was determined to 9.30(1) eV [Ghy11]. Having that in mind, it can be seen that for nonresonant ionization a laser with a wavelength  $\lambda < 504$  nm is necessary. Therefore, in addition to the frequency-doubled nonresonant ionization laser, a frequency-doubled Ti:Sa-laser has been added. As a comparison to a known resonance achieved that way, an ion current of 18 kcps could be achieved by ionization with the nonresonant ionization laser and 3 kcps by ionizing with the blue light of the Ti:Sa laser, all with a background of 1.7 kcps and measured at CEM19. The entire scan is shown in Figure 5.11. In addition to the already known energy levels, one further level at 57267.8 cm<sup>-1</sup> is



Figure 5.11.: Second excitation steps from the 44549.2 cm<sup>-1</sup> level using a frequencydoubled Ti:Sa laser and the frequency-doubled nonresonant ionization laser for ionization. Since the grating-tuned Ti:Sa could not operate with this setup at 701 nm, this peak has been measured separately with a BRF-tuned Ti:Sa laser.

observed. The transition to the  $58805.3 \text{ cm}^{-1}$  level is not shown on this scan since, with 701.45 nm, it is at the edge of the emission spectrum of the Ti:Sa crystal and could not therefore be reached with the grating-tuned Ti:Sa laser in this set up. This transition has been verified using a BRF-tuned Ti:Sa laser.

As not all energy levels can be reached from both first excitation steps, it is possible to assign preliminary J-values to the energy levels of four second excitation steps found so far. Since the level at 57267.8 cm<sup>-1</sup> can just be measured from the  ${}^{4}P_{5/2}$ state, it is likely that this level has a J = 7/2 value. Similarly, the 57277.0 cm<sup>-1</sup> state can be assigned to a J = 1/2 value. The two energy levels reachable from both first excitation steps can either be J = 3/2 or J = 5/2.

Detailed views of all three resonances can be found in Figure 5.12. They were measured by detecting the ion current on CEM19 while scanning the laser in both
directions in order to detect a symmetrical peak. Since the resulting peak is a convolution of a Gaussian and two adjoining exponential functions, no conventional fit function could be used. However, the only interest in fitting the peak is to find its centre. For that reason, optionally a Gaussian or Lorentzian was used for fitting, depending on which function led to the better residual.

#### 5.2.4. Second excitation steps in the blue wavelength region

During the course of a B.Eng. project [Que12], a system has been developed which gives the opportunity to perform a continuous frequency-doubled wavelength scan. For this purpose a BBO-crystal has been mounted on a rotary stage as shown in Figure 5.13, since at TRILIS the phase matching has been realized by angular adjustment of the crystal. At the beginning of the scan, a calibration file has to be created in which the motor position of the rotary stage for the highest output power is noted for four to five corresponding fundamental wavelengths. The parameters resulting from performing a second-order polynomial fit to these data are inserted into a Lab-View program. By reading in the fundamental wavelength from the wavemeter, the program is able to rotate the crystal, tracking the wavelength so that a continuous scan is possible.

This system is not yet sophisticated, and the scanning process is therefore still time consuming. Several crystal changes would be necessary for scanning the whole available wavelength region. Since the available on-line beam time was limited, only short scans have been performed for both first excitation steps.



(c) Wavelength scan of the peak at  $58805 \text{ cm}^{-1}$ 

Figure 5.12.: Wavelength scans of second excitation steps in astatine using the 44549.2 cm<sup>-1</sup> transition as the first excitation step. The detailed scans were taken by scanning the grating laser slowly in both directions and detecting the ion signal on CEM19.

#### 5. Resonant ionization spectroscopy of astatine



Figure 5.13.: Set up for continuous blue scans. The grating-tuned Ti:Sa laser is externally frequency-doubled by focusing the light into a BBO crystal mounted on a motorized rotary stage.

By scanning the frequency-doubled Ti:Sa laser, energy levels can be reached which are just below the ionization potential. As a result, small photon energies of  $\lambda <$ 1100 nm are enough for nonresonant ionization. For that purpose, the Ti:Sa laser light in its fundamental has been added. At the beginning of the scan, the laser used for nonresonant ionization has been set to one of the resonances shown in Figures 5.7 and 5.11 in order to look for second excitation steps and autoionizing states simultaneously. For this setup, the astatine isotopes are always ionized, leading to a constantly high and noisy background signal which makes it difficult to find the actual resonances. As a consequence, the scan was repeated with the fundamental Ti:Sa laser detuned. The resulting scans are shown in Figure 5.14.

Ground state transitions of most elements are typically in the blue to UV region. Therefore it could be possible to ionize one of the isobars at mass A = 199 by



Figure 5.14.: Blue wavelength scans for both first excitation steps using the fundamental wavelength of the Ti:Sa laser for nonresonant ionization. In order to prove that the observed resonances belong to astatine, the first step has been detuned. By this means, one of the measured resonances was assigned to thallium.

using the first excitation step of astatine as an ionizing step or performing twophoton ionization. In order to eliminate this possibility, for every observed resonance the resonance signal was tested to see whether it disappeared when detuning the wavelength of the first excitation step. That way, it was possible to assign four out of the five found resonances to astatine. The resonance at 72711 cm<sup>-1</sup>, shown in Figure 5.14, is a transition in thallium from the  ${}^{2}P_{1/2}$  ground state to the  ${}^{2}S_{1/2}$  state of 377.679 nm. Detailed views of the four blue transitions in astatine are shown in Figure 5.15. As a summary, all second excitation schemes found so far are listed in Figure 5.16. Since the ground state of astatine has odd parity, the wave function for all of these eight new states must be an odd wave function, too. As the scans in the blue wavelength region do not overlap, it is not possible to assign any *J*-value to these energy levels.



Figure 5.15.: Detailed scans of second excitation steps in the blue region.



Figure 5.16.: Overview of all observed second excitation steps in a statine. The most likely J assignments, as deduced from the third excitation step spectra are noted in bold. Note that all wavelengths in this thesis are vacuum wavelengths.

#### 5.2.5. Third excitation steps

In order to look for further energy levels from all four states found by scanning the fundamental wavelength of the grating-tuned Ti:Sa laser, a wide wavelength scan was performed. Since a similar energy region is scanned to that for the blue wavelength, the photon energy necessary for nonresonant ionization is  $E_{photon} > 0.9$  eV. As a consequence, for these scans, no additional laser for nonresonant ionization needed to be added. A possible resonance can either be ionized by absorbing a photon from the second excitation wavelength or from the scanning laser.

An overview of all observed resonances is shown in Figure 5.17. Due to the fact that the data collection for this graph has been performed during different experimental runs, with different experimental parameters e.g. different excitation schemes, proton currents and attenuators, no definite conclusion about the relative transition strengths can be made from comparing the respective peak heights.

In addition to the previously discussed ten new transitions and eight energy levels, 45 transitions to 33 new energy levels have been found. A list of these levels is given in Table 5.4.

By taking a closer look at the distribution of the transitions to the different energy levels, it is possible to better specify the *J*-values of the four second excitation steps. First, it can be seen that there is no overlap between the energy levels reached from the 57267.8 cm<sup>-1</sup> level and the 57276.7 cm<sup>-1</sup> level. It follows that the previous assignment of J = 7/2 and J = 1/2 respectively is correct. Since the overlap of energy levels found by scans from the J = 1/2 level is larger with these levels found by scans from the 58805.0 cm<sup>-1</sup> level than with the 57157.1 cm<sup>-1</sup> and the other way around from



Figure 5.17.: Third excitation steps in astatine measured from all red second excitation steps using the corresponding second excitation step for nonresonant ionization.

the J = 7/2 level, it is most likely that the 58805.0 cm<sup>-1</sup> level has a J = 3/2 value and the 57157.1 cm<sup>-1</sup> level has a J = 5/2 value.

Assuming that these J-values are correct, for a few of the new energy levels a possible J-value can be assigned; these are listed in the last column in Table 5.4.

### 5.3. Outlook

The bulk of the spectroscopy done on astatine focused on getting a better understanding of the heretofore absolutely unknown atomic structure of this element. So far, 55 transitions to 41 new energy levels were found in addition to the two ground state transitions found in 1964 [McL64]. The scans for transitions below the ionization potential reachable within the fundamental wavelength range of the Ti:Sa laser are completed. First tests have been performed with continuous scans of frequencydoubled Ti:Sa lasers where altogether four transitions could be found. These scans were mainly considered a proof of principle for this scanning technique. Based on the density of even parity states in this energy region, an extensive scan for odd parity states is worthwhile as soon as the possibility for frequency-doubled continuous scans is improved.

However, these experiments are performed with TRIUMF's laser ion source whose primary duty is to deliver contamination-free radioactive ion beams to nuclear physics experiments. Where for example <sup>223</sup>At is requested by a Rn EDM experiment, different excitation schemes have to be compared as a next step in order to find the most efficient one. A direct comparison between the measurements taken so far is not possible since the data have been collected during three different experiments spread over

total energy $E$	57157.1	57267.8	57276.7	58805.0	possible J
$(  {\rm cm}^{-1})$	3/2  or  5/2	7/2	1/2	3/2  or  5/2	
68253.8(10)	$\square$				
68469.3(10)	$\square$				
68778.7(10)			Ø		$1/2  { m or}  3/2$
69179.5(10)	$\checkmark$				
69505.7(10)			Ø		$1/2  { m or}  3/2$
69969.0(10)	Ø	Ń			$5/2  { m or}  7/2$
70036.5(10)	$\checkmark$	$\checkmark$		$\checkmark$	5/2
70048.4(10)	Ø		Ø	$\checkmark$	3/2
70059.7(10)		$\checkmark$			
70076.4(10)			$\square$	Ø	$1/2  { m or}  3/2$
70130.0(10)	Ń	$\square$			$5/2  { m or}  7/2$
70303.7(10)			$\square$	Ø	$1/2  { m or}  3/2$
70431.7(10)	$\checkmark$		$\square$	Ń	3/2
70467.9(10)	$\checkmark$			Ń	3/2  or  5/2
70745.0(10)	$\checkmark$			Ń	$3/2  { m or}  5/2$
70754.9(10)			$\square$		$1/2  { m or}  3/2$
71515.0(10)				$\checkmark$	
71548.7(10)				Ń	
71657.3(10)				Ń	
71668.2(10)				$\checkmark$	
71677.3(10)				$\checkmark$	
71721.0(10)				$\checkmark$	
71883.3(10)				$\square$	
71925.5(10)				Ŵ	
72095.3(10)				Ø	
72097.9(10)				\ ل	
72149.9(10)				Ø	
72627.3(10)				Ø	
72744.5(10)				Ø	
72765.9(10)				Ø	
72797.5(10)				Ń	
72906.7(10)				Ø	
72907.8(10)				Ń	

Table 5.4.: Energy position of third excitation steps in astatine with respect from which second excitation state they have been excited and their possible J-value assignments.

a time period between December 2010 and December 2011. For all these experiments, different proton currents, detectors with attenuators, and ionization lasers have been used. Using the excitation scheme with two resonance steps to the 46234 cm<sup>-1</sup> and the 58805 cm<sup>-1</sup> levels and the frequency-doubled nonresonant ionization laser at 6 W, an ion signal of 140 kcps has been detected. When this is compared in Table 5.1 to the excitation scheme with only one resonant step and the quadrupled nonresonant ionization laser, which results in an ion current of 94 kcps, an improvement of the ion signal by a factor of 1.5. has been made. Furthermore, fundamental wavelength scans can also be taken in order to look for autoionizing states which could increase the ionization efficiency compared to nonresonant ionization.

#### 5.3.1. Optical isotope shift

All measurements described so far have been performed for the isotope <sup>199</sup>At due to its convenient short half-life and low to nonexistent contamination through surface ionized francium isotopes. Switching between different isotopes can cause a shift in the location of the energy levels due to the change in mass and the size of the nucleus; this is explained in detail in [Kin84]. This so-called optical isotope shift in this mass region is typically on the order of a few hundred MHz/u and is therefore, with the lasers used for laser ionization having a linewidth of  $\approx 3$  GHz, only of relevance when considering a large mass change between the isotopes. For the example of beryllium, an isotope shift of  $\approx 8$  GHz has be observed in switching between <sup>9</sup>Be and <sup>10</sup>Be [Seb99]. Therefore, knowing the magnitude of the expected isotope shift is important information in looking for isotopes with low production rates. In order to obtain some information about the isotope shift for astatine, the first excitation step of 216 nm was measured for different isotopes, as shown in Figure 5.18. It is possible to determine an isotope shift for this transition to  $\approx 1.4 \text{ GHz} \pm 0.1 \text{ GHz}/\text{u}$ 



Figure 5.18.: Optical isotope shift in astatine for 216 nm transition.

(this can just be taken as an estimation since the optical isotope shift does not proceed linear). In addition to increasing the ionization efficiency for isotopes far away from the production maximum, the isotope shift gives important information about the nuclear ground state properties of the isotope. In general, the isotope shift is a combination of two effects, the mass shift and field shift, and for heavy isotopes the field shift is the dominant effect. The measured isotope shifts directly correlate with the mean square radius  $\delta \langle r^2 \rangle$  of the nuclear charge distribution. This information is especially of interest for isotopes around <sup>211</sup>At due to its closed neutron shell, which is also close to the double magic number isotope <sup>208</sup>Pb as described in [KBG<sup>+</sup>91] for the example of polonium. In order to perform more precise measurements, a laser with narrow linewidth and Doppler-free spectroscopy techniques would be necessary.

#### 5.3.2. Hyperfine structure

Further information about the nuclear ground state of an isotope discerned from its optical spectra are the nuclear magnetic moment and its nuclear spin, which is directly related to the hyperfine structure splitting of a transition. The hyperfine structure is caused by the coupling between the total angular momentum of the valence electron J and the spin of the nucleus I. Whereas for light and medium mass nuclei the hyperfine structure typically cannot be resolved with lasers which have a linewidth of a few GHz such as these used during this experiment, this is different in the heavy mass region (e.g. Pb, Po, Bi). However, despite the Doppler and power broadening and the wide laser linewidth during the measurements, a few lines could be observed which show a clear hint of a structure in them. The lines of interest are listed in Figure 5.19. The resonances in Figures 5.19d to 5.19f only show a double peak structure in the spectrum detected by plotting the  $\alpha$  events in the <sup>199</sup>Po peaks.



Figure 5.19.: Observed structure in astatine, for different isotopes and excitation schemes, where the scanned transition is in bold.

## 6. Summary

This thesis mainly divides into two parts:

- the ionization scheme development on yttrium for laser ion source applications
- in-source resonant ionization spectroscopy on astatine.

For yttrium, different excitation schemes have been tested and compared. For this purpose, several long wavelength scans using the grating-tuned Ti:Sa laser have been performed. As a result, 43 transitions to 14 energy levels were measured, which were mostly absent from the common databases. One of these missing transitions was identified as the strongest for nonresonant ionization.

Since resonant ionization was proposed to be more efficient than nonresonant ionization due to its higher cross section, additional scans were performed in order to look for autoionizing or Rydberg states. No significant Rydberg series could be measured. However, several promising autoionizing states were detected; two with an enhancement by a factor of 5 compared to their corresponding nonresonant ionization schemes. Comparing the best resonant and nonresonant ionization schemes, both deliver approximately the same results. Nevertheless, by measuring the saturation curves of each step, it was observed that the high-power ionization laser introduces further effects helping in the evaporation and hence ionization of yttrium by heating the ionizer tube of the test stand. Since these heating effects are reduced in online operation, no clear statement could be made as to which of the two ionization schemes, resonant or nonresonant, performs best in on-line operation.

The main purpose of this thesis is the spectroscopy at astatine, one of few elements where very little physical and chemical information is known due to its low production rates, short half-lives and difficulty of production. At TRIUMF it became possible with the permission from the governing body in December 2010 to use  $UC_x$  as a target material, allowing the creation of rare isotope beams of astatine.

At the beginning of this thesis only the two ground state transitions had been confirmed, from which systematic long wavelength scans were performed. That way, four second excitation steps belonging to one quadruplet in the infrared spectrum could be measured where, due to further measurements, a clear assignment of their J-value was possible.

Based on these four excitation steps, further scans were performed whereby 45 further transitions to 33 new energy levels were detected. As proof a principle, a method was tested by which it is possible to realize continuous scans in the blue wavelength region. That way four additional resonances belonging to astatine could be assigned. As a result a total number of 55 new transitions to 41 energy levels were detected whereby the scans in the energy regions accessible with the fundamental wavelength of the Ti:Sa are completed.

The first hints of a hyperfine splitting could be seen in individual states. Also, measurements to determine the optical isotope shift have been performed.

# A. Theoretical determined energy levels and transitions in astatine

Table A.1.: Theoretical values by Chang et al. [CLD10]. In the literature both oscillator strength for the length and the velocity gauge are listed. However, here only the values for the length gauge are give since only these are of interest for dipole transitions [Sta71].

transition	energy	f-value
$[6s^{2}6p^{2}_{1/2}6p^{2}_{3/2}7s_{1/2}]_{5/2} \rightarrow [6s^{2}6p^{2}_{1/2}6p^{3}_{3/2}]_{3/2}$	44510	$1.73 \cdot 10^{-1}$
$[6s^{2}6p_{1/2}^{}6p_{3/2}^{\dot{3}}7s_{1/2}]_{5/2} \rightarrow [6s^{2}6p_{1/2}^{}6p_{3/2}^{}]_{3/2}$	72060	$1.38\cdot 10^{-2}$
$[6s^{2}6p^{2}_{1/2}6p^{2}_{3/2}7s_{1/2}]_{3/2} \rightarrow [6s^{2}6p^{2}_{1/2}6p^{3}_{3/2}]_{3/2}$	45570	$8.25 \cdot 10^{-1}$
$[6s^{2}6p_{1/2}^{3}6p_{3/2}^{3}7s_{1/2}]_{3/2} \rightarrow [6s^{2}6p_{1/2}^{2}6p_{3/2}^{3'}]_{3/2}$	66780	$1.5\cdot10^{-1}$
$[6s^{2}6p_{1/2}6p_{3/2}^{3'}7s_{1/2}]_{3/2} \rightarrow [6s^{2}6p_{1/2}^{2'}6p_{3/2}^{3'}]_{3/2}$	71270	$0.97\cdot10^{-2}$
$[6s^{2}6p^{2}_{1/2}6p^{3'}_{3/2}7s_{1/2}]_{1/2} \rightarrow [6s^{2}6p^{2'}_{1/2}6p^{3'}_{3/2}]_{3/2}$	68140	$0.85\cdot10^{-1}$
$[6s^{2}6p_{1/2}^{3}6p_{3/2}^{3}7s_{1/2}]_{1/2} \rightarrow [6s^{2}6p_{1/2}^{2}6p_{3/2}^{3}]_{3/2}$	71730	$043\cdot 10^{-4}$
$[6s^{2}6p^{2}_{1/2}6p^{2'}_{3/2}7s_{1/2}]_{1/2} \rightarrow [6s^{2}6p^{2'}_{1/2}6p^{3'}_{3/2}]_{1/2}$	45300	$2.49\cdot10^{-1}$
$[6s^{2}6p_{1/2}^{3}6p_{3/2}^{3}7s_{1/2}]_{1/2} \rightarrow [6s^{2}6p_{1/2}^{2}6p_{3/2}^{3'}]_{1/2}$	49610	$7.87\cdot 10^{-3}$
$[6s^{2}6p^{2}_{1/2}6p^{2'}_{3/2}7s_{1/2}]_{3/2} \rightarrow [6s^{2}6p^{2'}_{1/2}6p^{3'}_{3/2}]_{1/2}$	22730	$3.49\cdot10^{-3}$
$[6s^{2}6p_{1/2}^{3}6p_{3/2}^{3}7s_{1/2}]_{3/2} \rightarrow [6s^{2}6p_{1/2}^{2}6p_{3/2}^{3}]_{1/2}$	43930	$1.58 \cdot 10^{-2}$
$[6s^{2}6p_{1/2}6p_{3/2}^{3}7s_{1/2}]_{3/2} \rightarrow [6s^{2}6p_{1/2}^{2}6p_{3/2}^{3}]_{1/2}$	48530	$1.02 \cdot 10^{-1}$

Energy Level [ $\rm cm^{-1}$ ]	$\operatorname{configuration}$	Parity	$\operatorname{comments}$
0	$6p^{5} {}^{2}P_{3/2}$	odd	ground state
19141	${}^{2}\mathrm{P}_{1/2}$	odd	-
44999	$\mathrm{J}{=}7^{'}/2$	even	
45075	$6p^47s \ ^4P_{5/2}$	even	experimental value 44549 [McL64]
45159	$\mathrm{J}{=}3/2$	even	
45299	$6d{+}7s J{=}1/2$	even	
45895	$J{=}7/2$	even	
46181	$J{=}1/2$	even	
46623	$6 p^4 7 s \ ^4 P_{3/2}$	even	experimental value 46233 [McL64]
47060	$J{=}5/2$	even	
47711	$J{=}5/2$	even	
48175	$J{=}3/2$	even	
53578	$6 p^4 7 p J = 3/2$	$\operatorname{odd}$	
53630	$J{=}5/2$	odd	
57396	$J{=}5/2$	odd	experimental value 57157 [Chapter 5]
57417	$J{=}7/2$	odd	experimental value 57268 [Chapter 5]
57434	$J{=}1/2$	odd	experimental value $57277$ [Chapter 5]
57684	J=3/2	odd	experimental value 58805 [Chapter 5]
55746	$6p^{4}6d J{=}3/2$	even	
55967	$J{=}5/2$	even	
57797	$J{=}1/2$	even	
63637	$6 p^4 7 p J = 1/2$	odd	
67493	J=3/2	odd	
67608	$6p^{4}6d J{=}1/2$	even	
68112	$J{=}7/2$	even	
68250	$J{=}3/2$	even	
68852	$J{=}5/2$	even	
68912	$J{=}5/2$	even	
69470	$J{=}3/2$	even	
70557	J=3/2	even	

Table A.2.: Theoretical values by Fritzsche [Fri11].

## Bibliography

- [AL72] R. V. Ambartzumian and V. S. Letokhov. Selective two-step (STS) photoionization of atoms and photodissociation of molecules by laser radiation. Appl. Opt., 11(2):354–358, 1972.
- [Alb07] D. Albers. Design, Assembly and Characterization of a Double-Sided-Pumped, High Repetition Rate Titanium Sapphire Laser System. Diplomarbeit, Fachhochschule Oldenburg Ostfriesland Wilhelmshaven, 2007.
- [BAD<sup>+</sup>12] P. G. Bricault, F. Ames, M. Dombsky, F. Labrecque, J. Lassen, A. Mjos, G. Minor, and A. Teigelhoefer. Recent developments of the ion sources at Tri University Meson Factory/Isotope Seperator and ACcelerator Facility. *Rev. Sci. Instrum.*, 83:02A914, 2012.
- [Bal85] J. J. Balmer. Notizen über die Spectrallinien des Wasserstoffs. Ann. Phys., 261:80-87, 1885.
- [BBD+95] R. D. Boyd, J. A. Britten, D. E. Decker, B. W. Shore, B. C. Stuart, M. D. Perry, and L. Li. High-efficiency metallic diffraction gratings for laser applications. Appl. Opt., 34(10):1697-1706, 1995.
- [BNBW03] B. Bushaw, W. Nörtershäuser, K. Blaum, and K. Wendt. Studies of narrow autoionizing resonances in gadolinium. Spectrochim. Acta, Part B, 58:1083-1095, 2003.
- [Bri06] P. Bricault. Status report of the radioactive ion beam production at TRIUMF. *Review of Scientific Instruments*, 77:03A710, 2006.
- [Bri07] P. Bricault. ISAC-I and ISAC-II: Present status and future perspectives. Eur. Phys. J. - Spec. Top., 150:227–232, 2007.
- [CF10] B. Cheal and K. T. Flanagan. Progress in laser spectroscopy at radioactive ion beam facilities. J. Phys. G: Nucl. Part. Phys., 37(11):113101, 2010.

- [CGA<sup>+</sup>07] B. Cheal, M.D. Gardner, M. Avgoulea, J. Billowes, M.L. Bissell, P. Campbell, T. Eronen, K.T. Flanagan, D.H. Forest, J. Huikari, A. Jokinen, B.A. Marsh, I.D. Moore, A. Nieminen, H. Penttilä, S. Rinta-Antila, B. Tordoff, G. Tungate, and J. Äystä. The shape transition in the neutron-rich yttrium isotopes and isomers. *Phys. Lett. B*, 645(2-3):133-137, 2007.
- [CLD10] Z. Chang, J. Li, and C. Dong. Ionization Potentials, Electron Affinities, Resonance Excitation Energies, Oscillator Strengths, And Ionic Radii of Element Uus (Z = 117) and Astatine. J. Phys. Chem., 114(51):13388– 13394, 2010.
- [CMS40] D. C. Corson, M. R. MacKenzie, and E. Segre. Artificially Radioactive Element 85. *Phys. Rev.*, 58:672–678, 1940.
- [Con98] J. P. Connerade. *Highly Excited Atoms*. Cambridge University Press, 1998.
- [Dem06] W. Demtröder. Atoms, Molecules and Photons: An Introduction to Atomic -, Molecular- and Quantum Physics. Springer, Berlin, 1 edition, 2006.
- [Dem07] W. Demtröder. Laserspektroskopie: Grundlagen und Techniken. Springer, Berlin, 5., erweiterte und neubearbeitete auflage. edition, 2007. German.
- [Dem08a] W. Demtröder. Laser Spectroscopy: Vol. 1: Basic Principles. Springer, 4th edition, 2008.
- [Dem08b] W. Demtröder. Laser Spectroscopy: Vol. 2: Experimental Techniques. Springer, 4th edition, 2008.
- [Die00] S. Diel. Entwicklung eines analytischen Messprozesses zur selektiven Ultraspurenbestimmung von 41Ca mit der Lasermassenspektrometrie. Diplomarbeit, Johannes Gutenberg-Universität Mainz, 2000. German.
- [EPI] EPICS. Argonne National Laboratory. http://www.aps.anl.gov/epics.
- [Fan61] U. Fano. Effects of Configuration Interaction on Intensities and Phase Shifts. Phys. Rev., 124:1866, 1961.
- [FMF<sup>+</sup>05] V. N. Fedosseev, B. A. Marsh, D. V. Fedorov, U. Köster, and E. Tengborn. Ionization scheme development at the ISOLDE RILIS. *Hyperfine Interact.*, pages 15–27, 2005.

- [Fri11] S. Fritzsche. private communication (e-mail), May 2011.
- [FS50] W. Finkelnburg and F. Stern. Electron Screening and Ionization Potentials of Neutral and Singly Ionized Atoms. *Phys.l Rev.*, 77(2):303–303, 1950.
- [FS73] J. H. Freeman and G. Sidenius. The technology and chemistry of heavy ion sources. Nucl. Instrum. Methods, 107(3):477 – 492, 1973.
- [Ghy11] L. Ghys. Inverstigation of the atomic properties of At with resonant laser ionization in order to develop pure radioactive ion beams. Master's thesis, Katholieke Universiteit Leuven, 2011.
- [Got11] T. Gottwald. Studium hochkomplexer atomarer Spektren mittels Methoden der Laserresonanzionisation. PhD thesis, Johannes Gutenberg-Universität, 2011. German.
- [Grü12] J. Grüneisen. Grating tuned Titanium Sapphire laser system controls with LabVIEW 8.6. Bachelor thesis, Hochschule Emden-Leer, 2012.
- [Hec01] Eugene Hecht. Optics. Addison Wesley, 4 edition, August 2001.
- [Hil02] R. C. Hilborn. Einstein coefficients, cross sections, f values, dipole moments, and all that. arXiv:physics/0202029, 2002. Am. J. Phys. 50, 982-986 (1982).
- [HKW75] D. C. Hanna, P. A. Kärkkäinen, and R. Wyatt. A simple beam expander for frequency narrowing of dye lasers. Opt. Quantum. Electron., 7(2):115– 119, 1975.
- [Hän72] T. W. Hänsch. Repetitively Pulsed Tunable Dye Laser for High Resolution Spectroscopy. *Appl. Opt.*, 11(4):895–899, 1972.
- [Hor03] R. E. Horn. Aufbau einers Systems gepulster, abstimmbarer Festkörperlaser zum Einsatz in der Resonanzionisations-Massenspektrometrie. PhD thesis, Johannes Gutenberg-Universität Mainz, 2003. German.
- [HS07] I. V. Hertel and C.-P. Schulz. Atome, Moleküle und optische Physik 1: Atomphysik und Grundlagen der Spektroskopie. Springer, Berlin, 1 edition, 2007. German.

- [HWB05] H. Haken, H. C. Wolf, and W. D. Brewer. The Physics of Atoms and Quanta: Introduction to Experiments and Theory. Springer-Verlag, enlarged 7th edition, 2005.
- [JLS49] G. L. Johnson, R. F. Leininger, and E. Segrel. Chemical Properties of Astatine. I. J. Chem. Phys., 17(1):1, 1949.
- [KB43] B. Karlik and T. Bernert. Eine neue natürliche alpha-Strahlung. Naturwissenschaften, 31:298–299, 1943. German.
- [KB44] B. Karlik and T. Bernert. Das Element 85 in den natürlichen Zerfallsreihen. Z. Phys., 123(1-2):51-72, 1944. German.
- [KBG<sup>+</sup>91] D. Kowalewska, K. Bekk, S. Göring, A. Hanser, W. Kälber, G. Meisel, and H. Rebel. Isotope shifts and hyperfine structure in polonium isotopes by atomic-beam laser spectroscopy. *Phys. Rev. A*, 44:R1442–R1445, Aug 1991.
- [KFM03] U. Köster, V. N. Fedoseyev, and V. I. Mishin. Resonant laser ionization of radioactive atoms. *Spectrochim. Acta, Part B*, 58(6):1047–1068, 2003.
- [Kin84] W.H. King. Isotope Shifts in Atomic Spectra. Springer, 1 edition, May 1984.
- [Kir96] R. Kirchner. Ion sources for radioactive beams and related problems. *Rev. Sci. Instrum.*, 67(3):928–933, 1996.
- [Klu85] Laser ion sources, 1985.
- [KMK<sup>+</sup>08] T. Kessler, I. D. Moore, Y. Kudryavtsev, K. Perajarvi, A. Popov, P. Ronkanen, T. Sonoda, B. Tordoff, K. D. A. Wendt, and J. Aysto. Off-line studies of the laser ionization of yttrium at the IGISOL facility. *Nucl. Instrum. Methods Phys. Res., Sect. B*, 266(4):681–700, 2008.
- [Koe06] W. Koechner. Solid-State Laser Engineering. Springer, 6th, rev. and updated ed. edition, 2006.
- [Lav10] J.-P. Lavoie. Production of pure ion beams by Laser ionization and a fast release RFQ. PhD thesis, Université Laval Québec, 2010.
- [LBD<sup>+</sup>09] J. Lassen, P. Bricault, M. Dombsky, J. P. Lavoie, M. Gillner, T. Gottwald, F. Hellbusch, A. Teigelhoefer, A. Voss, and K. D. A. Wendt. Laser

Ion Source Operation at the TRIUMF Radioactive Ion Beam Facility. 1104:9–15, 2009. 4th International Conference on Laset Probing, Nagoya, JAPAN, OCT 06-10, 2008.

- [LK25] I. Langmuir and K. H. Kingdon. Thermionic Effects Caused by Vapours of Alkali Metals. Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character, 107(741):pp. 61-79, 1925.
- [LM78] M.G. Littman and H.J. Metcalf. Spectrally narrow pulsed dye laser without beam expander. *Appl. Opt.*, 17:2224–2227, 1978.
- [Lun02] LBNL Isotopes Project Nuclear Data Dissemination Home Page. http://ie.lbl.gov/toi.html, Retrieved March 11 2002.
- [McL64] R. McLaughlin. Absorption Spectrum of Astatine. J. Opt. Soc. Am. B, 54:965–967, 1964.
- [Mei12] J. Meissner. Laserbeam Transport for Laser Ion Sources. Diplomarbeit, Hochschule Emden-Leer, 2012. in preparation.
- [Mes08] D. Meschede. *Optik, Licht und Laser.* Vieweg+Teubner, 3., durchgesehene Auflage edition, 2008. German.
- [MGK<sup>+</sup>06] M. Miyabe, C. Geppert, M. Kato, M. Oba, I. Wakaida, K. Watanabe, and K. D. A. Wendt. Determination of ionization potential of calcium by high-resolution resonance ionization spectroscopy. J. Phys. Soc. Jpn., 75(3), 2006.
- [MNB<sup>+</sup>05] I. D. Moore, A. Nieminen, J. Billowes, P. Campbell, C. Geppert, A. Jokinen, T. Kessler, B. A. Marsh, H. Penttilä, S. Rinta-Antila, B. Tordoff, K. Wendt, and Äystö J. Development of a laser ion source at IGISOL. J. Phys. G: Nucl. Part. Phys., 31:1499–1502, 2005.
- [Mou86] P. F. Moulton. Spectroscopic and laser characteristics of Ti: A12 03. J. Opt. Soc. Am. B, 3(1):125, 1986.
- [MW06] A. V. Mitin and van C. Wüllen. Two-component relativistic densityfunctional calculations of the dimers of the halogens from bromine through element 117 using effective core potential and all-electron methods. J. Chem. Phys., 124:064305, 2006.

- [Nuk11] Nuklliddatenv2.7. http://www.marcoschwarz-online.de/einsteinsagt/download-nukliddaten/, 2011. Freeware Program.
- [PN86] Ronald E. Pitts and G. H. Newson. Shock tube measurements of Y I and Y II oscillator strengths. J. Quant. Spectros. Radiat. Transfer, 35(5):383– 399, 1986.
- [Que12] T. Quenzel. Frequency doubled TiSa laser with automated scan. Bachelor thesis, Hochschule Emden-Leer, 2012. in preparation.
- [RDDW88] T. J. Ruth, M. Dombsky, J. M. D'Auria, and T. E. Ward. The radiochemistry of astatine. Office of Scientific and Technical Information, United States Department of Energy, 1988.
- [RKRT11] Y. Ralchenko, A. Kramida, J. Reader, and NIST ASD Team. NIST Atomic Spectra Database (version 4.1), [Online]. Available: http://physics.nist.gov/asd, 2011. National Institute of Standards and Technology, Gaithersburg, MD.
- [RMM<sup>+</sup>11] S. Rothe, B. A. Marsh, C. Mattolat, V. N. Fedosseev, and K. Wendt. A complementary laser system for ISOLDE RILIS. J. Phys. Conference Series, 312(5):052020, 2011.
- [Rot09] S. Rothe. Aufbau eines Chrom:Forsterit-Lasers und Resonanzionisationsspektroskopie an Strontium, Titan, Nickel, Scandium und Silicium. Diplomarbeit, Johannes Gutenberg-Universität Mainz, 2009. German.
- [SBDD07] M. Smith, L. Blomeley, P. Delheij, and J. Dilling. First Tests of the TITAN Digital RFQ Beam Cooler and Buncher. Hyperfine Interact., 173:171–180, 2007.
- [Seb99] V. Sebastian. Laserionisation und Laserionenquelle an ISOLDE/CERN. PhD thesis, Johannes Gutenberg-Universität Mainz, 1999. German.
- [Sew03] M. Sewtz. Optische Spektroskopie an Fermium (Z=100). PhD thesis, Johannes Gutenberg-Universität in Mainz, 2003.
- [SHEK] P. L. Smith, C. Heise, J. R. Esmond, and R. L. Kurucz. Atomic spectral line database from CD-ROM 23 of R. L. Kurucz. Available:http://www.cfa.harvard.edu/amp/ampdata/kurucz23/sekur.html.
- [Spe02] Spectra-Physics. Navigator II Fiber-Coupled, Diode- Pumped, Q -Switched Laser Series YHP70 and YHP40, 2002. Manual.

- [Sta71] A. F. Starace. Length and Velocity Formulas in Approximate Oscillator -Strength Calculations. *Phys. Rev. A*, 3:1242–1245, 1971.
- [Str01] B. Struve. Laser, Grundlagen Komponenten Technik. Verlag Technik Berlin, 2001. German.
- [TBC<sup>+</sup>10] A. Teigelhöfer, P. Bricault, O. Chachkova, M. Gillner, J. Lassen, J.P. Lavoie, R. Li, J. Meißner, W. Neu, and K.D.A. Wendt. Grating tuned Ti: Sa laser for in-source spectroscopy of Rydberg and autoionizing states. *Hyperfine Interact.*, 196:161–168, 2010.
- [Tei09] A. Teigelhöfer. Development and characterization of a continuously tunable titanium-sapphire laser. Diplomarbeit, Fachhochschule Oldenburg Ostfriesland Wilhelmshaven, 2009.
- [TRI12] TRIUMF. private communication, 2012.
- [WBG<sup>+</sup>05] K. D. A. Wendt, K. Blaum, C. Geppert, P. Müller, W. Nörtershäuser, A. Schmitt, P. Schumann, N. Trautmann, and B. A. Bushaw. Laser based techniques for ultra trace isotope production, spectroscopy and detection. *Hyperfine Interact.*, 162(1):147–157, 2005.