



Diploma thesis

First Laser Raman measurements with tritium for KATRIN and studies of systematic effects of the LARA-setup

Magnus Schlösser



FIRST LASER RAMAN MEASUREMENTS WITH TRITIUM FOR KATRIN AND STUDIES OF SYSTEMATIC EFFECTS OF THE LARA-SETUP

Magnus Schlösser

Diplomarbeit

bei Prof. Dr. G. Drexlin Institut für experimentelle Kernphysik, Fakultät für Physik, Universität Karlsruhe

> Korreferent Prof. Dr. H.H. Telle Department of Physics, Swansea University (Wales)

an der Fakultät für Physik der Universität Karlsruhe

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Erklärung

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> Magnus Schlösser Eggenstein-Leopoldshafen, den 14. Oktober 2009

Zusammenfassung

Das **Ka**rlsruhe **Tr**itium Neutrino (KATRIN) Experiment untersucht das β -Spektrum von Tritium in der Nähe des Endpunkts von 18,6 keV, woraus die Ruhemasse des Elektronantineutrinos bestimmt wird. Die Messungen werden mit einer fensterlosen, molekularen, gasförmigen Tritiumquelle hoher Luminosität und einem hochauflösenden elektrostatischen Filter mit einer Energieauflösung von $\Delta E = 0,93 \,\text{eV}$ durchgeführt.

KATRIN strebt eine Sensitivität von $0.2 \,\mathrm{eV/c^2}$ für die modellunabhängige Bestimmung der Neutrinomasse an. Dies kann nur erreicht werden, indem sowohl die statistischen als auch die systematischen Fehler der Observablen m^2 unterhalb von $0.017 \,\mathrm{eV^2/c^4}$ liegen. Der statistische Fehler wird hierbei nach einer Messzeit von ca. drei Jahren erreicht. Die Reduzierung systematischer Unsicherheiten wird zum einen durch die Stabilisierung der einzelnen Untersysteme auf dem Promille Level als auch durch die Überwachung der relevanten, experimentellen Parameter erreicht (z.B. Einspeisungsrate in die Quelle, Feldstärke der Führungsmagneten, Spektrometer Retardierungsspannung,...).

Der Parameter ε_T gibt die isotopische Reinheit des Tritiumgases an, das in die Quelle injiziert wird. Eine Änderung der Gaszusammensetzung bewirkt vor allem eine Änderung der Zählrate der β -Elektronen am Hauptdetektor. Des weiteren treten gasartabhängige, systematische Effekte in der Quelle auf. Beispiele hierfür sind die Streuung von β -Elektronen an Restgasmolekülen oder die Wahrscheinlichkeitsverteilung der Endzustände in denen sich das Molekül mit Tochterkern nach dem Zerfall befinden kann.

Eine konstante und hohe isotopische Reinheit $\varepsilon_T > 95\%$ soll durch das Entfernen von Verunreinigungen aus dem geschlossenen Tritiumkreislauf von KATRIN und durch die Einspeisung von reinem Tritium erreicht werden. Die Zusammensetzung dieser Gasmischung wird in-line durch Laser Raman Spektroskopie mit einer Präzision von 0.1% überwacht.

Im Rahmen dieser Arbeit wurde die Leistungsfähigkeit des Laser Raman Systems untersucht, das in den Jahren zwischen 2005 und 2007 von R. Lewis entwickelt wurde [Lew07]. Dazu wurden zum ersten Mal im TLK¹ und bei KATRIN Laser Raman Messungen an tritiumhaltigen Gasproben durchgeführt. Desweiteren wurden ausführliche Studien bezüglich systematischer Effekte durchgeführt und ein erster Schritt in Richtung quantitativer Analyse getan. Neben diesen Mess- und Analysearbeiten wurden der optische Aufbau, sowie das Gehäuse teilweise verändert. Es wurden Schaltungen und Massnahmen für den sicheren (Langzeit-) Betrieb entwickelt und installiert, sowie Software für die automatische Datenaufnahme und Auswertung programmiert.

Im Folgenden ist ein kurzer Überblick über die Kapitel gegeben (ausführliche Darstellungen und Zitate befinden sich im englischen Haupttext):

 $^{^{1}}TLK$ =Tritiumlabor Karlsruhe

1. Einleitung Im Universium gibt es ca. 10^9 mal mehr Neutrinos als Baryonen und trotzdem ist das Wissen über Neutrinos vergleichsweise jung. In den 30er Jahren wurde das Neutrino zum ersten Mal von Wolfgang Pauli postuliert, um die Form des Energiespektrums beim β -Zerfall zu erklären. Nachgewiesen wurde es allerdings erst 1956 von F. Reines und C. Cowan. Im Standardmodell der Teilchenphysik gilt das Neutrino als masselos. Allerdings gab es durch Messungen des solaren Neutrinosflusses bereits im Jahre 1968 erste Hinweise auf Neutrino-Oszillationen. Bei diesen Oszillationen wandelt sich ein Neutrino-Flavor in einen anderen um, wobei dieser Prozess nur für massebehaftete Neutrinos möglich ist.

Für die Messungen der Neutrinomasse gibt es indirekte Methoden, die stark modellabhängig sind, und direkte Methoden, wobei nur kinematische Variablen verwendet werden. Die Bestimmung der Masse anhand des kinematischen Endpunkts des Tritium- β -Zerfalls ist der modellunabhängige Ansatz den KATRIN verfolgt.

2. Das KATRIN-Experiment Bisherige Tritiumzerfallsexperimente in Mainz ([Kra05]) und Troitsk ([Lob03]) konnten eine Obergrenze für die Neutrinomasse von $2, 0 \text{ eV}/\text{c}^2$ bestimmen [PDG08]. Das Nachfolgerexperiment KATRIN zielt dabei auf eine bisher unreichte Sensitivität von $0, 2 \text{ eV}/\text{c}^2$ für die Masse des Neutrinos. Das Messprinzip beruht, wie bei den beiden Vorgängerexperimenten, auf der Verwendung des sogenannten MAC-E Filters, wobei ein integrierendes, elektrostatisches Spektrometer (Energiefilter) mit dem Prinzip der magnetischen adiabatischen Kollimation² eingesetzt wird. Das Experiment wird im Forschungszentrum Karlsruhe (jetzt Teil des Karlsruher Institut für Technologie (KIT)) von einer internationalen Kollaboration aufgebaut. Die tritiumführenden Systeme befinden dabei im Tritiumlabor Karlsruhe (TLK) an dem diese Arbeit durchgeführt wurde.

3. Der (Laser) Raman Effekt Der Raman-Effekt beschreibt die inelastische Streuung von Licht an Molekülen. Dabei wird die Wellenlänge des gestreuten Lichts verschoben, da ein Teil der Photonenenergie in Rotations- und/oder Vibrationsanregungen des Moleküls transferiert wird. Durch die fortschreitende Entwicklung von Lasern als Lichtquelle in den 1960er Jahren, hatte sich die Laser Raman Spektroskopie im Bereich quantitativer Spektroskopie etabliert.

Nur eins von ungefähr 10^7 einfallenden Photonen streut inelastisch an einem Molekül. Daher ist Laser Raman Spektroskopie eine Technik mit einer vergleichsweisen schwachen Intensität. Dennoch bietet sie einige Vorteile: (1) die Abdeckung eines weiten Spektralbereichs, wie für die Wasserstoffisotopologe H₂, HD, D₂, HT, DT und T₂ notwendig; (2) die Detektion von homopolaren Molekülen ohne permanentes Dipolmoment (wie O₂ oder T₂); (3) die Messung kann kontaktfrei und zerstörungsfrei durchgeführt werden und (4) die Messung kann in einen verfahrenstechnischen Prozess eingebaut werden. Daher ist Laser Raman Spektroskopie für KATRIN ein exzellentes Instrument zur Bestimmung der isotopischen Reinheit ε_T .

4. Der Aufbau des Systems Folgende Anforderungen hat KATRIN gegenüber dem Laser Raman System:

 $^{^{2}\}mathrm{MAC}\text{-}\mathrm{E}=\mathbf{M}\mathrm{agnetic}\ \mathbf{A}\mathrm{diabatic}\ \mathbf{C}\mathrm{ollimation}+\mathbf{E}\mathrm{nergy}\ \mathrm{Filter}$

- Nachweisgrenze für Wasserstoffisotopologe geringer als 0,1 mbar bei einem Gesamtdruck von ca. 100 mbar.
- Reproduzierbarkeit der Signale mit einer Präzision von < 0.1% in weniger als 250 s bei 100 mbar.
- Stabilität des optischen Aufbaus und der aktiven Elemente wie Laser und CCD-Detektor innerhalb einer KATRIN Messphase von 60 Tagen
- Tritiumkompatibilität durch ultrahoch-vakuumdichte Gasprobenzellen (d.h. Leckrate $< 10^{-9}$ mbarls⁻¹), die sich in einer zweiten Sicherheitshülle befinden (für Aktivitäten $> 10^{10}$ Bq).

Allerdings ist kein kommerzielles System vorhanden, das diesen Anforderungen genügt. Aus diesem Grund wurde ein entsprechendes Laser Raman Systems (LARA) selbst entwickelt, dessen Aufbau in Abbbildung 1 gezeigt ist.

Ein 532 nm Laser mit einer Ausgangsleistung von bis zu 5 W liefert monochromatisches Licht. Dieses Licht wird in die Laser Raman Zelle fokussiert, in der es an den Molekülen der Probe streut. Das gestreute Licht wird durch eine Linsenkombination auf ein Glasfaserbündel abgebildet durch das das Streulicht in das Spektrometer transportiert wird. Hier schneidet zunächst ein Filter die Wellenlängen < 532 nm ab, um Streulicht an der Anregungslinie des Lasers zu unterdrücken. Das Gitter im Spektrometer zerlegt anschließend das gefilterte Licht anhand der Wellenlänge. Dieses Spektrum wird schließlich mit einer CCD Kamera detektiert.

Nachdem die Rohdaten von der CCD Kamera aufgenommen wurden, müssen diese Daten durch Software aufgearbeitet werden, damit eine quantitative Analyse schließlich möglich ist. Darunter fallen Korrekturen von Abbildungsfehlern durch das Linsenspektrometer, das Entfernen von Ereignissen, die durch kosmische Strahlung erzeugt wurden, und die Wellenlängenkalibration.

5. Erste Laser Raman Messungen an Tritium im TLK Bevor erste Messungen mit Tritium im Tritiumlabor Karlsruhe (TLK) möglich waren, mussten einige Vorarbeiten erledigt werden. Dazu wurde das Gehäuse des Aufbaus modifiziert und dabei eine Verbindung zum Abluftsystem des TLK hergestellt, um bei eventueller Tritiumfreisetzung die Kontamination durch Absaugen zu minimieren. Desweiteren wurden die vorhandenen LARA-Zellen erfolgreich auf Tritiumkompatibilität überprüft.

Danach wurden mehr als 7 Proben mit allen Wasserstoffisotopologen hergestellt und nacheinander gemessen. Darunter waren Proben mit Reinstoffen und Mischungen. Ein Spektrum, worin alle sechs Wasserstoffisotopologe enthalten sind, ist in Abbildung 2 gezeigt. Darüber hinaus wurden in allen Spektren Beiträge zum Untergrund verschiedener Art festgestellt. Die verschiedenen Beträge der Zelle können deutlich im Spektrum einer evakuierten Zelle beobachtet werden, wie in Abb. 2 (rechts) gezeigt ist.

Des weitern konnte eine Nachweisgrenze von 0.015 mbar (3σ) in 1000 s bei 5 W bestimmt werden.



Figure 1: Aufsicht auf den LARA Aufbau. Das Bild zeigt die wesentlichen Komponenten des LARA-systems: Laser, LARA-Zelle, Glasfaser, Spektrometer und CCD Detektor. Eine kurze Beschreibung des Funktionsprinzip befindet sich im Text.



Figure 2: (Links): Raman Spektrum mit allen 6 Wasserstoffisotopologen und (rechts): Spektrum einer evakuierten Zelle. Beide Spektren wurden mit 5 W Laserleistung und einer Belichtungszeit von 1000 s aufgenommen. Das linke Schaubild zeigt einen Spektrumsausschnitt mit allen 6 Wasserstoffisotopologen der Probe. Im rechten Bild wird das volle Spektrum einer evakuierten Zelle gezeigt. Dabei fallen zwei Features auf: (1) Raman-Linien von SiO₂ aus dem die Zellfenster bestehen und (2) Fluoreszenz-Hintergrund der sich weit in das Spektrum zieht.

6. Untersuchungen systematischer Effekte im Laser Raman System In diesem Kapitel wurden viele Fragstellungen untersucht, die sich aus dem Vorherigen ergeben haben. Darunter fallen der Einfluss der Zellposition, der Laserleistung und thermischen Effekten auf Signalintensität und Fluoreszenz-Hintergrund der Zelle.

Der wichtigste Teil betrifft Langzeitmessungen, bei denen sich das System über einen Zeitraum von ein paar Tagen bis zu einer Woche im kontinuierlichem Messbetrieb befand.

Hierbei wurde festgestellt, dass der Fluoreszenz-Hintergrund in der Zelle nicht konstant ist, sondern mit der Zeit zunimmt. Der Grund dafür wird in der Bildung von laser-induzierten Farbzentren im Quarzglas gesehen. Die dadurch gesteigerte Absorption führt wiederum zu einer verstärkten Emission von Fluoreszenzlicht.

In einigen Langzeitmessungen wurde eine Reduktion der Raman-Intensitäten von bis zu -22% beobachtet. Dies kann dadurch erklärt werden, dass der Laserstrahl zu einem gewissen Teil aus dem Fokus der Sammeloptik wandert und somit das Streulicht nur noch teilweise auf die Glasfaser fällt. Diese 'beam-pointing' Instabilität kann durch Temperaturfluktuationen der Laserkopfgrundplatte entstehen.

Schließlich wurde die Präzision der absoluten und relativen Intensitäten aller Messungen experimentell aus den Schwankungen der Intensitäten bestimmt. Die beste absolute Präzision $2\sigma/I = 0.16$ % wurde in einer Probe mit 985 mbar / 250 s bestimmt. Die Präzision der relativen Intensitäten ist im Allgemeinen beinahe um den Faktor 2 besser, da hierbei die Fluktuation der Laserleistung nicht eingeht. Die Extrapolation für die Präzision einer Probe mit Druckbedingungen etwas unterhalb derer von KATRIN (103, 4 mbar) zeigt, dass die KATRIN Bedingung von 0.1 % erfüllt werden kann.

Die abschließende Bestimmung der erwarteten Präzision aus theoretischen Überlegungen in Einbeziehung der Rauschquellen zeigt eine gute Übereinstimmungen mit den Messungen. Die Fehlerquellen der Messung sind also verstanden, wobei die Bestimmung der Baseline im Spektrum die größte Fehlerquelle darstellt.

7. Quantitative Analyse Als Methode für die Quantifizierung der Probenbestandteile aus dem Ramanspektrum bietet sich das sogenannte 'Indirect hard modeling' (IHM) an, das in einigen Punkten den klassischen Zugängen wie CLS³ oder PLS⁴ überlegen ist [Kri08].

Im Prinzip wird dabei ein spektrales Modell aus mehreren parameterisierten Komponenten erstellt, welches z.B. auf einem theoretischen Modell beruht. Dieses Modell wird dann durch Optimierung der Parameter an die gemessenen Spektren gefittet. In einem zweiten Kalibrier-Modell wird anschließend die Zusammensetzung der Probe bestimmt. Da gerade für Wasserstoff-Isotopologe solche Modelle mit ausreichender Genauigkeit erzeugt werden können, ist dies eine vorteilhafte Methode für KATRIN.

Erste Versuche zeigen, dass die Präzision der relativen Intensitäten mithilfe dieser Methode gesteigert werden kann. In der betrachteten Messreihe wurde die Präzision von 0,28% auf 0,18% verbessert. Hierbei ist die Verbesserung vorallem auf die genauere Baseline-Erkennung zurückzuführen. Allerdings zeigen sich beim Peakfitting geringe Abweichungen von der tatsächlichen Linienform. Der Grund dafür ist, dass die Modellfunktion (Pseudo-Voigtfunktion) des IHM die Abbildung der Spektrometereingangsschlitzes auf die CCD nur

³CLS=classical least squares

⁴PLS=partial least squares

unzureichend beschreibt, und dass die Abbildungsfehler des Linsenspektrometer nicht vollständig korrigiert wurden, sodass dadurch eine leichte Verzerrung besteht. Dies muss für die zukünftige Verwendung berücksichtigt werden. Des weitern muss das volle theoretische Modell erstellt werden.

8. Zusammenfassung und Ausblick Zusammenfassend für diese Arbeit lässt sich sagen, dass die Anforderungen des KATRIN Experiments an das Laser Raman System erfüllt werden können. Es wurden ausserdem verschiedene weitere Einflüsse des Lasers und der Zellfenster festgestellt, die sich negativ auf die Langzeitstabilität auswirken können. Dazu müssen weitere Untersuchungen angestellt werden.

Messungen mit hohen Tritiumanteilen und KATRIN ähnlichen Drücken waren im Rahmen dieser Arbeit nicht möglich. Als nächster Schritt werden in einem geschlossenen Kreislauf Messungen durchgeführt, wie sie später bei KATRIN stattfinden werden.

Die Sensitivität des Systems kann mit einigen Erweiterungen nur noch geringfügig gesteigert werden. Eine Steigerung von mehreren Größenordnungen, um weitaus geringere Bestandteile in kürzen Zeiten detektieren zukönnen, kann also mit Standard Raman Spektroskopie nicht erreicht werden. Hier sind daher Techniken wie SRS⁵ oder CARS⁶ notwendig, bei denen die Raman Emission durch weitere Lichtquellen stimuliert wird.

⁵SRS=Stimulated Raman scattering

 $^{^6\}mathrm{CARS}{=}\mathrm{Coherent}$ anti-Stokes Raman scattering

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Chapter 1

Introduction

The present work focuses on Laser Raman spectroscopy as an analytic method for the KATRIN¹ experiment, a next-generation tritium β -decay experiment for the determination of the neutrino mass by kinematic means. This chapter gives a short introduction to neutrinos and the measurement of their masses.

Postulation and discovery of the neutrino Historically, the first hints for the existence of the neutrino were provided by the study of β -decay. From the process $n \to p^+ + e^$ one expects a discrete energy spectrum of the emitted β electrons. However, the energy spectrum measured is continuous which is in contradiction to energy conservation [Sch97].

W. Pauli postulated the neutrino² in 1930 to solve this problem. By the emission of the (anti-)neutrino in the neutron decay process

$$n \to p^+ + e^- + \overline{\nu_e} \tag{1.1}$$

it is possible to distribute the decay energy among two particles which then allows to describe the shape of the electron spectrum (see section 2.1.1). The particle new is required to be uncharged to conserve charge and it has to be a spin 1/2 particle like the electron to conserve angular momentum.

More than 25 years passed until the neutrino was finally discovered by Reines and Cowan [Rei56]. They placed an experiment for anti-neutrino detection in the proximity of a nuclear fission reactor which provides a strong anti-neutrino source from β -decay. The detection was enabled by observation of the inverse β -decay reaction

$$\overline{\nu_e} + p^+ \to e^+ + n. \tag{1.2}$$

The reaction above was indicated by delayed coincidence of a positron with the annihilation radiation and the gamma photons from the excited state of a Cd nucleus following neutron capture ([Sch97]).

¹KATRIN= \mathbf{Ka} rlsruhe \mathbf{Tri} tium \mathbf{N} eutrino experiment

 $^{^{2}}$ Pauli's original notation was *neutron*. Later the name *neutrino* was introduced by Fermi, after Chadwick discovered the neutron in 1932 [Sch97].

Table 1.1: Leptons and anti-partners The 6 fundamental leptons of the Standard Model, their electric charge (Q), the lepton number (L) and interactions are summarized in this table. Each fermion has a the corresponding anti-particle with opposite lepton number and charge.

| Generation | | Electric | Lepton | Interaction | |
|--------------------|------------------------|-----------------------|--------|-------------|-----------------------|
| 1 | 2 | 3 | charge | number | |
| ν_e | $ u_{\mu}$ | $\nu_{	au}$ | 0 | +1 | weak |
| e^- | ν^{-} | $	au^-$ | -1 | +1 | weak, electromagnetic |
| $\overline{\nu_e}$ | $\overline{\nu_{\mu}}$ | $\overline{ u_{	au}}$ | 0 | -1 | weak |
| e^+ | ν^+ | τ^+ | +1 | -1 | weak, electromagnetic |

Neutrinos in the Standard Model (SM) Table 1.1 shows the overview over the six leptons and their anti-partners in the Standard Model (SM) of particle physics. For every charged lepton (electron, muon and tau) an uncharged lepton of the same flavor (electron neutrino, muon neutrino, tau neutrino) exists. As well, an anti-neutrino exists for each corresponding anti-particle, such as the positron. The reason why an *anti*-neutrino appears in equation (1.1) is related to the conversation of lepton number. The electron generated in the β -decay has lepton number L = +1, hence the other particle generated needs to have L = -1 and thus an electron *anti*-neutrino $\overline{\nu_e}$ is required.

Neutrinos are regarded as mass-less particles in the Standard Model.

Neutrino oscillations For a long time the vanishing neutrino rest mass was confirmed by experimental data. This changed until neutrino oscillations were discovered in 1998, a process which is only possible if neutrinos are massive particles.

A neutrino of the specific flavor α created in a weak interaction process is today described as a superposition of neutrino mass eigenstates [PDG08]:

$$|\nu_{\alpha}\rangle = \sum_{i} U_{\alpha i}^{*} |\nu_{i}\rangle \tag{1.3}$$

where U is the unitarian neutrino mixing matrix. The neutrino flavor change process $\nu_{\alpha} \rightarrow \nu_{\beta}$ arises while neutrinos are propagating in vacuum. Quantum mechanical time evolution, the factor $\exp(-im_i\tau_i)$ arises with m_i as the mass of ν_i and τ_i as the elapsed time during propagation. This term can be re-written as $m_i\tau_i = E_it - p_iL$, where L is the distance between neutrino source and detector, t the time of travel and E_i/p_i are energy/momentum of the ν_i component. Finally, the probability of a $\nu_{\alpha} \rightarrow \nu_{\beta}$ can be written as [PDG08]:

$$P(\nu_{\alpha} \to \nu_{\beta}) = \sin^2 2\theta \sin^2 [1.27\Delta m^2 (L/E)]$$
(1.4)

where θ is referred to as the mixing angle and L is given in dimensional units of km and E in GeV. When neutrinos travel through matter (e.g. Sun, Earth, ...), the propagation can be modified significantly by matter effect (MSW effect) which results in a modified oscillation probability [Wol78].

The neutrino flux of from the Sun has been measured by several experiments such as Homestake [Dav68], GALLEX [Ans92], SAGE [Abd94], (Super-)Kamiokande [Hos06, Hir89] or SNO [Ahm01]. The measured fluxes show a neutrino deficit compared to the expected flux from the Standard Solar Model [Bah06]. In this case the detection reaction is a charged current (CC) reaction, which is sensitive to the neutrino flavor, selecting on the ν_e fraction of the solar ν 's.

The SNO-experiment was also sensitive to neutral currents (NC) mediated by a Z^0 boson and elastic scattering (ES) [Ahm01]. This allowed the detection of all three neutrino flavors. The SNO results indicated a non-electron flavor component in the total flux of solar ⁸B. The explanation to this phenomenon is that matter-enhanced neutrino oscillations transform the original flavor into a different flavor (e.g. $\nu_e \rightarrow \nu_{\mu}$).

Neutrino oscillations have also been successfully investigated at neutrinos from nuclear reactors (e.g. KamLAND [Egu03]) and from particle accelerators (e.g. K2K [Ali05], MI-NOS [Mic06])

The latest results for the squared mass differences obtained from neutrino oscillation experiments are listed in [PDG08].

For the case of oscillations of atmospheric neutrinos $\nu_{\mu} \rightarrow \nu_{\tau}$, the mass splitting Δm^2 is in the range:

$$1.9 \cdot 10^{-3} \text{eV}^2/\text{c}^4 < \Delta m_{\text{atmos}}^2 < 3.0 \cdot 10^{-3} \text{eV}^2/\text{c}^4 \tag{1.5}$$

While for oscillations of solar neutrinos $\nu_e \rightarrow \nu_{\mu,\tau}$, they are confined to the interval:

$$7.7 \cdot 10^{-5} \mathrm{eV}^2/\mathrm{c}^4 < \Delta m_{\mathrm{solar}}^2 < 8.3 \cdot 10^{-5} \mathrm{eV}^2/\mathrm{c}^4$$
(1.6)

These results however only allow to access the mass differences of the various neutrino flavors. Accordingly, the absolute mass scale cannot be determined by oscillation experiments. In principle, two mass scenarios are possible, as presented in figure 1.1:

- a) Hierarchical neutrino masses: The neutrino masses m_i are small compared to the mass differences Δm_{ij}^2 ($m_1 \ll m_2 \ll m_3$). This scheme could be of an inverted hierarchy type, too.
- b) Quasi-degenerate neutrino masses: All neutrinos have approximately the same mass $(m_1 \approx m_2 \approx m_3)$

Role of massive neutrinos

1. Particle Physics

In the Standard Model (SM) charged fermions acquire their mass by the Yukawa couplings of the left-handed weak isospin fermion doublet (e.g. (ν_L, e_L)) to the Higgs doublet (Φ^+, Φ^0) and a right handed fermion singlet (e.g. (e_R)) [Ott08]. In the SM, no right-handed neutrino and no left-handed anti-neutrino singlet exists, resulting in a vanishing neutrino mass. The introduction of these singlets would need a Yukawa coupling which is about 6 orders of magnitudes smaller compared to charged fermions. Therefore this mechanism is rather unlikely. The experimental evidence of a neutrino mass is therefore seen as the first evidence for physics beyond the Standard Model.



Figure 1.1: Neutrino mass scenarios. Shown are the values of the neutrino mass eigenstates m_1, m_2 and m_3 as a function of the lightest mass eigenstate m_1 . In case of a quasi-degeneracy of the neutrino masses ($m_1 \approx m_2 \approx m_3$), the mass of the lightest neutrino defines the fundamental mass scale of all three flavors. The hierarchical scenario requires m_1 to be very light and the differences Δm_{solar} and Δm_{atmos} to be greater in comparison to m_1 . [KAT05]

A large group of theories, which explore the origin of neutrino mass, make use of the so-called See-Saw mechanism to generate mass for Majorana³ neutrinos. In the type I See-Saw mechanism the small neutrino masses can by explained by introducing a heavy right-handed Majorana neutrino [Moh02]. In principle, the heavier the right-handed neutrino is, the lighter the left-handed neutrino becomes. Other models require a Higgs triplet which couples directly to the light neutrinos [Moh02].

The experimental results on the absolute neutrino mass scale and the hierarchy will help to validate specific theories of neutrino mass generation. The problem is crucial for the fermion mass generation in general.

2. Cosmology

The abundance of neutrinos in the universe is higher by about a factor of 1 billion compared to other massive particles. Therefore neutrinos have an impact on many different aspects of cosmology. In the evolution of large scales structures (LSS) they have played an important role as neutrino hot dark matter ν HDM. That means that

 $^{^{3}\}mathrm{A}$ Majorana neutrino is particle and anti-particle at the same time in constrast to Dirac neutrinos.



Figure 1.2: Cosmological matter density and neutrino masses. The neutrino mass contribution Ω_{ν} is compared to the other matter densities (dark energy, cold dark matter and baryons). The allowed ν HDM contribution Ω_{ν} is bound by experimental data. The lower bound results from oscillation data of atmospheric ν 's. The upper bound is given by the results from current tritium β -decay experiments and studies of structure formation. KATRIN will investigate the parameter space $\Omega_{\nu} > 0.01$, where relic neutrinos would play a significant role in the evolution of large scale structures. (from [Eic09], accord. to [KAT05])

the massive relic neutrinos were relativistic when decoupling⁴ from matter in the early universe. ν HDM freely streams out from gravitational potential wells formed by cold dark matter (CDM) and baryons. This effects slows the growth of density fluctuations [Han04]. The neutrino density Ω_{ν} depends on the sum of the neutrino masses [Kom09]

$$\Omega_{\nu}h^2 = \sum m_{\nu}/94 \,\mathrm{eV} \tag{1.7}$$

whereby h is the Hubble-constant. This correlation is shown in figure 1.2. The neutrino density is limited by experiments to the interval $0.001 < \Omega_{\nu} < 0.15$. The upper bound is given by the tritium β -decay experiments [PDG08] and the lower bound arises from the Δm^2 -scale determined by atmospheric neutrino oscillations [Abe06]. KATRIN will measure the neutrino mass with a sensitivity of 0.2 eV (90 % C.L.) which corresponds to a neutrino contribution of $\Omega_{\nu} = 0.01$. Therefore KATRIN will significantly constrain the role of ν HDM in structure formation by a model independent method.

Experimental determination of absolute neutrino mass scale The different methods to determine neutrino masses can be divided into two groups of experiments.

⁴Decoupling occurs at a temperature of about $k_B T_{\text{decouple}} = 1 - 2 \text{ MeV}$ shortly before e^-e^+ annihilation into the CMBR photons.

- Indirect methods are very sensitive to neutrino masses, however, their results are model-dependent.
- **Direct methods** do not rely on further assumptions on the neutrino mass type or models. They make use of the relativistic energy momentum relation

$$E^2 = p^2 c^2 + m^2 c^4 \tag{1.8}$$

where E is the total energy, p the momentum, c the speed of light and m the rest mass. In these models only the conservation of energy and momentum is assumed. ([KAT05], [Ott08]).

Indirect methods

• Neutrino masses from cosmology

The non-statistical fluctuations of the cosmic microwave background (CMB) have been mapped with great accuracy by the WMAP satellite experiment [Kom09]. It represents the structure of the early universe about 380,000 years after the Big Bang. The observed fluctuation pattern of the background radiation temperature is expanded into spherical harmonics up to the power $l \approx 1000$. These temperature variations correspond to fluctuations of matter density in the early universe. The positions and amplitudes of maxima and minima in the power spectrum allow to deduce cosmological parameters like the total mass density $\Omega_{\rm tot}$, dark energy density Ω_{Λ} , matter density $\Omega_{\rm m}$, baryonic matter density $\Omega_{\rm b}$ and neutrino density Ω_{ν} .

The upper limit for the sum of the neutrino masses determined by the WMAP data alone is [Kom09]

$$\sum m_{\nu} < 1.3 \,\text{eV}/c^2 \quad (95 \,\% \,\text{C.L.}). \tag{1.9}$$

If the data are combined with distance information from type Ia supernovae (SN) and the Baryon Acoustic Oscillation (BAO) [Per07] in the distribution of galaxies, the neutrino mass limits can be tightened. With these additional constraints, the upper limit on the neutrino mass is given as [Kom09]

$$\sum m_{\nu} < 0.67 \,\text{eV}/c^2 \quad (95 \,\% \,\text{C.L.}). \tag{1.10}$$

However, it should be noted that these results are strongly model dependent.

• Neutrino mass from neutrinoless double β decay

The search for the neutrinoless double β decay $(0\nu\beta\beta)$ relies on physics beyond the Standard Model, as the process would violate the conservation of lepton number [Ott08], [Sch97]. For the neutrinoless double decay to happen, the neutrino needs to be a Majorana particle.

$$(A, Z) \to (A, Z+2) + 2e^- + 0\nu$$
 (1.11)

In that case a neutrino is emitted at vertex I (right-handed $\bar{\nu}_R$) and absorbed at vertex II (left-handed ν_L), which is only possible if $\nu = \bar{\nu} = \nu^M$ and $\nu_L = \bar{\nu}_L$ ($\nu_R = \bar{\nu}_R$).

Massive neutrinos are required for this spin flip. Therefore, $0\nu\beta\beta$ experiments are sensitive to the so-called effective neutrino mass m_{ee}

$$m_{ee} = \left| \sum_{j=1}^{3} U_{ej}^2 m_j \right|$$
(1.12)

where U_{ej} are complex elements from the neutrino mixing matrix which include Majorana phases (thus m_{ee} can differ from the true mass scale). The signature of this decay is the emission of two electrons whose energy add up to the total decay energy Q because of the absence of neutrinos. The half-time $T_{1/2}^{0\nu}$ of this process is connected to the Majorana mass (e.g. in [Cho07])

$$\frac{1}{T_{1/2}^{0\nu}} = G^{0\nu} |M_{\text{had}}|^2 m_{ee}^2$$
(1.13)

where $M_{\rm had}$ is the nuclear matrix element and $G^{0\nu}$ is a phase space factor. The highest sensitivity on m_{ee} was achieved by the Heidelberg-Moscow-Experiment by the investigation of the ⁷⁶Ge decay. A Majorana mass was published with a 4.2σ evidence for the $0\nu\beta\beta$ process [Kla04]

$$T_{1/2}^{0\nu} = (0.69 - 4.18) \cdot 10^{25} \,\text{years}$$
 (1.14)

$$m_{ee} = (0.24 - 0.58) \,\mathrm{eV}/c^2 \tag{1.15}$$

However, this result is discussed highly controversially in the community and new $0\nu\beta\beta$ experiments are being developed such as GERDA [Sch05], Majorana [Aal05], Cuore [Ped08] and EXO [Aki05].

Direct methods This type of experiments makes use of kinematic variables only.

• Time-of-flight studies of supernova neutrinos

Astrophysics offers neutrino sources which could provide a neutrino time-of-flight measurement [Ott08], [Sch97]. In particular, type II supernovas are extremely bright neutrino sources. They involve massive stars with several solar masses. When the nuclear fusion generates nuclei with $A \approx 52 - 56$, the core of the star can no longer resist the gravitational force of the outer shells and collapses to a neutron star. In the formation of the neutron star, neutrinos are generated by the following reactions

$$e^- + p^+ \to n + \nu_e \tag{1.16}$$

$$e^- + e^+ \to \nu_i + \bar{\nu}_i \tag{1.17}$$

Neutrinos carry away about 99 % of the gravitational energy. The rebouncing matter shockwave hits the outer shell of the star and ignites the supernova explosion via neutrino heating. The duration of the neutrino emission from the mechanisms given in equations (1.16) and (1.17) lasts about 10 s. The neutrinos cannot escape the core without scattering because [Sch97] the forming neutron star is so dense⁵, that it

 $[\]overline{{}^5 \ \rho \sim 2 \cdot 10^{11} \mathrm{g/cm}^3}$

is opaque even for neutrinos. The shape of the neutrino pulse is determined by the neutron star formation process. Therefore the derived ν -masses are model dependent.

In 1987, a burst of neutrinos which arrived from the supernova 1987A in the Large Magellanic Cloud was detected in underground detectors in Baksan, Caucas [Ale88], the Morton Thiokol mine, Ohio [Bra88] and the Kamioka mine, Japan [Hir88]. The time-of-flight T_{ν} of a neutrino with mass m_{ν} , velocity v_{ν} and energy E_{ν} from the source (time of emission t_0 , distance $L = 1.5 \cdot 10^{18}$ km) to the detector (time of detection t) [Sch97] is given by:

$$T_{\nu} = t - t_0 = \frac{L}{v_{\nu}} = \frac{L}{c} \frac{E_{\nu}}{\sqrt{E_{\nu}^2 - m_{\nu}^2 c^4}} \approx \frac{L}{c} \left(1 + \frac{m_{\nu}^2 c^4}{2E_{\nu}^2}\right)$$
(1.18)

Two neutrinos with different energies $E_{\nu,1} > E_{\nu,2}$ thus arrive at the Earth in a time span $\Delta t = t_2 - t_1$

$$\Delta t = t_2 - t_1 = \Delta t_0 + \frac{Lm_{\nu}^2 c^4}{2c} \left(\frac{1}{E_{\nu,2}^2} - \frac{1}{E_{\nu,1}^2}\right)$$
(1.19)

 Δt_0 is an unknown parameter which regards the time of emission. All calculations for m_{ν} are thus model dependent, since an assumption of Δt_0 is needed.

A detailed analysis by Loredo and Lamb identifies an upper limit of the neutrino mass [Lor02] of:

$$m_{\nu_e} < 5.7 \,\mathrm{eV}/c^2 \ (95 \,\% \,\mathrm{C.L.})$$
 (1.20)

• Studies of kinematics of the weak decays

The mass of the electron neutrino ν_e is generally investigated by analyzing β decays.

One possibility is the use of cryogenic bolometers which are β source and detector at the same time. Suitable for this technique is the isotope ¹⁸⁷Re, which has the lowest known transition energy $E_0 \approx 2.5$ keV. The current upper limit for the neutrino mass from the ¹⁸⁷Re micro-calorimeter array (Milano) is [Sis04]

$$m_{\nu_e} < 15 \,\mathrm{eV/c^2}.$$
 (1.21)

The expected sensitivity in the future experiment MARE-I will be about $2 \,\mathrm{eV/c^2}$ [Sis07].

One group of experiments has achieved the most sensitive upper limits on the neutrino mass by investigating the β decay of tritium. In these experiments the energy spectrum of the decay electrons from the tritium β decay

$$T \rightarrow {}^{3}\text{He}^{+} + e^{-} + \bar{\nu}_{e} \qquad (1.22)$$

is analyzed near the endpoint of about 18.6 keV. The experimental method and the setup will be explained in detail in the following chapter. The combined analysis of the data from the experiments in Mainz and Troitsk is published as [PDG08]

$$m_{\nu} < 2.0 \,\mathrm{eV/c^2} \ (95 \,\% \,\mathrm{C.L.}).$$
 (1.23)

KATRIN will be the successor experiment with an increased sensitivity of $0.2 \,\mathrm{eV/c^2}$ which will be achieved by the use of a strong gaseous tritium source and a high resolution spectrometer for the energy analysis.

The projected sensitivity can only be reached by the significant reduction of systematic errors compared to Mainz and Troitsk, therefore precise monitor systems are required which measure the relevant parameters on the 0.1% level.

In the scope of this thesis the Laser Raman system is studied in detail which will determine the tritium gas composition before injection into the source. After modifications on the hardware and the acquisition software were completed, the system was ready for first measurements with tritium for KATRIN. Furthermore the long term performance in regard to signal stability and systematic effects has been checked in numerous measurements. The results show that the KATRIN requirements can be met by the actual setup.

This thesis is structured in the following way: First, tritium β decay experiments in general and the KATRIN experiment in particular are introduced in chapter 2. In chapter 3 the basic principles of the (Laser) Raman effect are presented. Chapter 4 describes the actual experimental setup of Laser Raman system. The results obtained in first tritium measurements are shown in chapter 5. In chapter 6 the investigations of systematic effects (e.g. stability) within the Laser Raman system are presented. First experiences with an approach to quantitative analysis are reported in chapter 7. A summary of the KATRIN relevant results and an outlook on future activities at this domain conclude this work with chapter 8.

CHAPTER 1. INTRODUCTION

Chapter 2

The KATRIN experiment

This chapter gives an overview on the tritium β -decay experiment KATRIN. The aim of KATRIN is to determine the anti-neutrino mass with a sensitivity of $0.2 \text{ eV}/c^2$. The chapter is structured as follows: section 2.1 gives an introduction into the physics of tritium β -decay experiments, section 2.2 describes the KATRIN experiment in an overview and the following four sections explain the main components of KATRIN. The chapter closes with a discussion on the sensitivity and systematic uncertainties of the KATRIN measurements (section 2.7). The chapter is mainly based on the KATRIN design report [KAT05].

2.1 Tritium β -decay experiments

2.1.1 Tritium β -decay

The most sensitive direct searches for the electron neutrino mass up to now are based on the investigation of the electron spectrum of tritium β -decay

$$T \rightarrow {}^{3}\text{He}^{+} + e^{-} + \bar{\nu}_{e} \qquad (2.1)$$

The electron energy spectrum of the tritium β -decay for an electron neutrino with mass $m_{\bar{\nu}_e}$ can be calculated from Fermi's Golden Rule: (according to [Wei03], speed of light reintroduced)

$$\frac{d^2N}{dtdE} = C \times F(E, Z+1)p(E+m_ec^2)(E_0-E)\sqrt{(E_0-E)^2 - m_{\bar{\nu}_e}^2c^4}\Theta(E_0-E-m_{\bar{\nu}_e}c^2)$$
(2.2)

 E, m_e and p are the kinetic energy, mass and momentum of the electron. E_0 corresponds to the maximal electron energy for $m_v = 0$ (endpoint energy). F(E, Z + 1) is the Fermi function, taking into account the Coulomb interaction of the outgoing electron in the final state. The heaviside-function ensures energy conservation. The constant C is given by

$$C = \frac{G_F^2}{2\pi^3 \hbar^7 c^5} \cos^2 \theta_C |M_{\text{had}}^2|.$$
(2.3)

Here G_F is the Fermi constant, θ_C is the Cabibbo angle and M_{had} is the hadronic matrix element for tritium. Equation (2.2) is only valid for infinitely heavy nuclei. In the case of



Figure 2.1: The electron energy spectrum of tritium β -decay (a) Complete β -spectrum. (b) Shape of the curve near the kinematic endpoint of about $E_0 = 18.6$ keV plotted for a vanishing neutrino mass $m_{\nu} = 0$ eV and for a neutrino mass $m_{\nu} = 1$ eV. The shade area corresponds to a fraction of $2 \cdot 10^{-13}$ of all tritium β -decays.

a decaying atom or molecule, the possible excitation of the shell electron in the forming ${}^{3}\text{He}^{+}$ -ion has to be taken into account. Therefore, the energy spectrum is a weighted sum of single spectra with different endpoint energies:

$$\frac{d^2 N}{dt dE} = C \times F(E, Z+1) p(E+m_e c^2) \\ \times \sum_i W_i (E_i - E) \sqrt{(E_i - E)^2 - m_{\bar{\nu}_e}^2 c^4} \Theta(E_i - E - m_{\bar{\nu}_e} c^2) \quad (2.4)$$

 W_i is the probability that the electrons remain in an excited state with the excitation energy V_i . The endpoint energies of decays in the excited states are $E_i = E_0 - V_i$. Rotation and vibration are possible excitations at the decay of molecular tritium.

The Fermi function F(E, Z + 1) and the matrix element M_{had} are independent of $m_{\bar{\nu}_e}$. In addition, M_{had} is independent of E, since the tritium β -decay is super-allowed.

A non-vanishing neutrino mass only influences the shape of the spectrum near the endpoint as shown in figure 2.1. This region is used in the fit analysis for the determination of the observable $m_{\tilde{\nu}_e}^2$. From this it follows that tritium β -decay experiments need a strong source for high count rates as well as a spectrometer with a sub-eV resolution to enable the determination of the neutrino mass in the sub-eV region.

2.1.2 Principle of the MAC-E Filter

A new type of electrostatic filter was introduced at the former neutrino-mass experiments in Mainz and Troitsk, the so-called MAC-E-filter¹. It is combines high luminosity and low background with a high energy resolution ([Wei99], [Lob99])

Figure 2.2 illustrates the main features of the MAC-E-Filter. Decay electrons starting from the tritium source are guided along the magnetic field lines on cyclotron tracks to the detector with an accepted solid angle of up to 2π . The lowest magnetic field in is the middle of the MAC-E filter (analysis plane). The magnetic gradient force transforms most of the cyclotron energy E_{\perp} into longitudinal energy E_{\parallel} . The variation of the magnetic

 $^{^1\}mathbf{M} \mathrm{agnetic}\ \mathbf{A} \mathrm{diabatic}\ \mathbf{C} \mathrm{ollimation}$ with an $\mathbf{E} \mathrm{lectrostatic}\ \mathrm{Filter}$



Figure 2.2: Principle of MAC-E Filter (a) Two superconducting solenoids produce an inhomogeneous magnetic guiding field B. β -electrons are starting from the source located in a solenoid into the forward hemisphere. They are guided magnetically on a cyclotron motion along the magnetic field lines in direction of the spectrometer. The accepted angle is up to 2π depending on B_S . The magnetic field drops by many orders of magnitude on the way to the analysis plane in the middle of the spectrometer. The magnetic gradient transforms the cyclotron motion in the longitudinal direction as shown in (b). The energy analysis is done by an electrostatic retarding potential U_0 which is applied via a set of cylindrical electrodes. According to [KAT05].

field during one cyclotron circulation is slow which ensures an adiabatic transformation of the momentum vector. The magnetic moment remains $constant^2$

$$\mu = \frac{E_{\perp}}{B} = \text{const.} \tag{2.5}$$

Cylindrical electrodes form an electrostatic retarding potential. The MAC-E-filter acts as an integrating high-energy pass filter: only electrons with energies higher than eU_0 are able to pass the analysis plane and are collimated onto the detector. The relative sharpness of this filter follows from equation (2.5):

$$\frac{\Delta E}{E} = \frac{B_{\min}}{B_{\max}} \tag{2.6}$$

where B_{\min} is the magnetic field in the analysis plane and B_{\max} is the maximum magnetic field at a point between source and detector. At the KATRIN spectrometer setup the maximum magnetic field is between detector and spectrometer end.

 $^{^2 {\}rm For}$ relativistic particles $(\gamma+1) \cdot E_\perp/B$ is the adiabatic invariant of motion

The electrostatic retarding potential $U_0 = U_{\rm MS} - U_{\rm WGTS}$ is set by a change of either the retarding voltage $U_{\rm MS}$ at the spectrometer or $U_{\rm WGTS}$ at the source. Varying U_0 allows to measure the beta spectrum in an integrating mode.

2.1.3 Results of the Mainz and the Troitsk experiment

Both experiments used spectrometers of the MAC-E-filter type, but quite different types of tritium sources. Therefore the systematic uncertainties are different.

The Mainz experiment included a spectrometer with a diameter of 1 m and a quenchedcondensed molecular tritium source which had its main uncertainties in solid state effects like inelastic β -electron scattering within the T₂ film, excitation of neighbors and selfcharging. The final result is ([Kra05])

$$m_{\nu}^2 = -0.6 \pm 2.2_{\text{stat}} \pm 2.1_{\text{sys}} \,\mathrm{eV}^2/\mathrm{c}^4$$
 (2.7)

$$m_{\nu} < 2.3 \,\mathrm{eV/c^2} \ (95 \,\% \,\mathrm{C.L.})$$
 (2.8)

The Troitsk experiment used a spectrometer with a diameter of 1.2 m and a windowless gaseous tritium source. The final result including a spectral anomaly near the endpoint is $([\text{Lob99}]^3)$:

$$m_{\nu}^2 = -1.9 \pm 3.4_{\rm stat} \pm 2.2_{\rm sys} \,{\rm eV}^2/{\rm c}^4$$
 (2.9)

which corresponds to an upper limit on the neutrino mass of

$$m_{\nu} < 2.5 \,\mathrm{eV/c^2} \ (95 \,\% \,\mathrm{C.L.}).$$
 (2.10)

The sensitivity limit of both experiments is reached. New data will not improve the sensitivity on m_{ν} significantly since the systematical uncertainties of both experiments cannot be suppressed further enough. Sub-eV sensitivity can only be reached with a new generation of tritium β -decay experiments.

2.2 KATRIN - an experimental overview

The results from Mainz and Troitsk, equations (2.10) and (2.8), were used for a combined analysis by the Particle Data Group. This led to an upper limit for the neutrino mass of [PDG08]:

$$m_{\nu} < 2.0 \,\mathrm{eV/c^2} \ (95 \,\% \,\mathrm{C.L.}).$$
 (2.11)

KATRIN is a new tritium β -decay experiment which aims to determine the neutrino mass from tritium β -decay with a sensitivity of $0.2 \,\mathrm{eV/c^2}$

The main requirements for the new experiment are ([KAT05]):

 $m_{\nu}^2 = -2.3 \pm 2.5 \pm 2.0 \,\mathrm{eV}^2/\mathrm{c}^4 \rightarrow m_{\nu} < 2.05 \,\mathrm{eV}/\mathrm{c}^2 \ (95 \,\% \,\mathrm{C.L.})$

³New limits from Troitsk were published in [Lob03]. :

This result wasn't published as refereed journal article, thus it is not considered by the Particle Data Group [PDG08]


Figure 2.3: The setup of the KATRIN experiment (a) Calibration & monitoring system (CMS), (b) Windowless gaseous tritium source (WGTS), (c) Differential pumping section (DPS), (d) Cryogenic pumping section (CPS), (e) Pre-spectrometer, (f) Main spectrometer, (g) Electron detector.

- High signal rate in the endpoint region. The strength of the tritium source has to be a factor of 100 higher compared to the predecessor experiments in Troitsk and Mainz.
- High energy resolution of the spectrometer $\Delta E < 1 \, \text{eV}$
- Reduction of the background rate near the endpoint down to $< 1\,\mathrm{mHz}$
- Increase of measurement time to minimize the statistical errors by a factor of 100
- Reduction of the systematic uncertainties on $m_{\nu}^2 c^4$ by a factor a 100 to aim a equality of statistical and systematic errors

The overview on the KATRIN setup is shown in 2.3. The main four components are

- 1. The high luminosity tritium source for the beta electrons.
- 2. The transport section (DPS&CPS) guiding electrons and reducing the tritium flux.
- 3. The spectrometer acting as an energy filter.
- 4. The detector to count the electrons.

The KATRIN experiment is sited at the Forschungszentrum Karlsruhe (FZK), which offers all infrastructure for this large-scale project. Source and transport section are housed in the Tritium Laboratory Karlsruhe (TLK) which has the license for the handling of 40 g of tritium [Pen00]. The TLK has more than 15 years experience in tritium processing technology and provides the relevant infrastructure for KATRIN. One of the safety concepts is the use of secondary containments surrounding each tritium primary system which prevents a contamination of the laboratory in case of leakage. The realization of this containments is done by double wall pipes or glove boxes. Figure 2.4 gives a view into the TLK.

2.3 The tritium source

KATRIN uses a windowless gaseous tritium source (WGTS) which is suited for long-term measurements as it offers highest luminosity and smaller systematic uncertainties than a quenched condensed one.



Figure 2.4: View into the Tritium Laboratory Karlsruhe (TLK). In the front: A worker is accessing the primary tritium system via a glove box which acts as safety enclosure.

The strength of the WGTS is given by the product of source area A_s , column density ρd and tritium purity ε_T

$$N(T_2) = A_s \cdot \rho d \cdot \varepsilon_T \tag{2.12}$$

The main source requirements are ([KAT05]):

- The column density $\rho d = 5 \times 10^{17}$ molecules/cm² has be stable on a 0.1%-level.
- The isotopic purity has be $\varepsilon_T > 95 \%$. A detailed discussion on the required stability and the related systematic uncertainties is found in the last section of this chapter (2.7).
- The resulting total decay rate is $9.5 \cdot 10^{10}$ Bq in the volume within by magnetic flux tube (191 T cm²).
- The temperature of the beam line is set to 27-30 K to minimize Doppler-broadening from thermal influx.

The WGTS is substantially a 10 m long tube with an inner diameter of 90 mm as shown in figure 2.5. At its ends the differential pumping sections DPS1-R and DPS1-F are mounted. The tritium is injected in the middle of the tube through more than 250 holes. The molecules stream freely from the middle to both ends of the tube where they are pumped away. Thereby a stable gas density profile is formed along the source tube (*top* of figure 2.5). The daily tritium throughput is 40 g which is only possible at the TLK which has both, the license and the experience to perform such a challenging task. The required injection rate is q = 1.853 mbar l/s with a stability $\delta q/q \leq 0.1$ %.

The required stability of the tritium column density needs (a) a stable injection, (b) a stable tube temperature and (c) a stable pumping at the end, all at the level 0.1%. This can be achieved in a controlled closed loop operation as shown in the blockdiagram of figure 2.6. The Inner Loop has to provide the stable tritium injection and the high and



Figure 2.5: WGTS principle of function. *Bottom*: tritium injection and differential pumping at the WGTS tube. *Top*: schematic density profile. (According to [KAT05])



Figure 2.6: Block diagram of tritium related parts of KATRIN. Tritium is injected in the middle of the WGTS tube and pumped out at its ends. The major part of the tritium is reinserted to the control system for T_2 injection (Inner Loop). About 1% is redirect into the TLK tritium recovery and isotope separation system for purification (Outer Loop). Tritium from the transport section is transferred to Outer Loop and TLK tritium retention system. (According to [KAT05])



Figure 2.7: Simplified flow diagram of Inner Loop and source. Tritium gas is fed through a capillary with known conductivity to the central injection chamber of the source. The WGTS buffer vessel with controlled pressure and temperature keeps the injection rate of q = 1.853 mbar l/s constant. The operation pressure is about 10 mbar. This vessel is fed by the pure T₂ buffer vessel at ≈ 130 mbar. The purity of the gas is monitored between both vessels by the Laser Raman system. The pure T₂ buffer vessel is fed with the circulated gas from the source. Before, it is cleaned by a palladium membrane filter (permeator) permeable only for hydrogen isotopologues. The outer loop provides fresh tritium batches from the TLK Isotope Separation System ISS and ensures the recovery and purification of gaseous waste. The whole system is built into the ISS glove box.

stable tritium purity together with the Outer Loop. The principle of function is explained by the Inner Loop flow diagram in figure 2.7.

The source is placed within super-conducting solenoids forming a guiding magnetic field at 3.6 T. The constant temperature of the beam tube is provided by a boiling liquid neon cryostat which allows a stable operation at a level of $\pm 3 \text{ mK}$ [Gro09].

2.4 The transport section

The transport section adiabatically guides the β -decay electrons by super-conducting magnets from the source to the spectrometers. At the same time the flow rate of tritium molecules and ions has to be suppressed by many orders of magnitude.

The maximum allowed tritium flow rate into the pre-spectrometer should be less than 10^{-14} mbar l/s to limit the increase of background caused by decay of tritium molecules in the spectrometers to 10^{-3} counts/s. The reduction by a factor of 10^{14} is achieved by two separate pumping systems. The first suppression is provided by the DPS2-F by differential arranged turbo molecular pumps ([Zol09]) as shown in figure 2.6. A tilt of 20° within the beam tube reduces the effect of molecular beaming and ensures the pumping efficiency.

The tritium flow is reduced to $\approx 10^{-7}$ mbar l/s. The DPS2-F also houses electric dipole units which deflect ions by $\vec{E} \times \vec{B}$ -drift from the beam line and neutralizes them ([Rei09a]). Otherwise, these ions would follow the magnetic field lines and would generate background processes in the spectrometers.

Further reduction is provided by the cryogenic pumping section (CPS). The remaining traces of tritium are trapped on liquid helium cold surfaces. The surface is covered with condensed argon snow which acts as cryosorbent for better trapping. The feasibility of the required reduction of 10^7 has been successfully demonstrated at the TRAP experiment at the TLK ([Stu07],[Eic08],[Eic09]). The total reduction of the tritium flux by both systems is about 14 orders of magnitude.

2.5 The electrostatic spectrometers

KATRIN will use a tandem-spectrometer system consisting of two MAC-E-filters (see figure 2.8).

The pre-spectrometer: The electrons guided by the transport section first reach the pre-spectrometer. It is a cylindrical tank with a length of l = 3.38 m and an inner diameter of d = 1.68 m suitable for XHV⁴ conditions. The energy resolution is $\Delta E \leq 100$ eV. The retarding potential of this filter is foreseen to be set to 300 V lower than the endpoint. In this configuration the electron flux into the main spectrometer is reduced from > 10¹⁰ to $\sim 10^4$ electrons per second. This should reduce the ionization of residual gas molecules in the main spectrometer which can cause background events ([KAT05]).

The main spectrometer: The key component of KATRIN's energy analysis is the main spectrometer. It is similar to the pre-spectrometer but much larger in the dimensions. The overall length is 23.3 m and the diameter about 10 m. The magnetic field configuration is asymmetric with B = 4.5 T at the front end and the maximum field $B_{\text{max}} = 6$ T at the rear ends of the tank generated by superconducting solenoids ([Wan09]). This field drops in the analysis plane down to 0.3 mT, which means an energy resolution of $\Delta E = 0.93$ eV.

The high-voltage $(-18.5\cdots - 18.7 \text{ keV})$ is applied to the spectrometer tank. A more negative potential is applied to an inner wire-electrode system which minimizes the background from electrons from the tank walls [Pra10].

Additional air coils are built around the spectrometer vessel for fine forming of the magnetic field in the analysis plane [Wan09] and for earth magnetic field compensation [Rei09b].

2.6 The detector

All electrons passing the retarding potential in the analysis plane of the main spectrometer will be re-accelerated to the former energy. These electrons are collimated by the increasing magnetic field and hit the main detector which counts the transmitted β electrons. The

⁴XHV=eXtreme High Vacuum $p \le 10^{-11}$ mbar



Figure 2.8: The tandem-spectrometer of KATRIN. Sketched are pre- and main spectrometer and the magnet field configuration. The plotted field lines don't represent the real field configuration which is asymmetric due to the different *B*-field at the entrance and exit of the main spectrometer. (According to [KAT05]).

detector is a segmented silicon PIN diode. The design energy resolution is $\Delta E < 600 \text{ eV}$ for 18.6 keV electrons which is sufficient for background discrimination. In figure 2.9 the segmentation of the detector is shown. The spatial resolution by single pixels allows the detection and investigation of inhomogeneities in source or spectrometer.

The detector can handle high count rates ($\sim 100 \text{ kHz}$) for calibration down to low count rates ($\sim 1 \text{ mHz}$) during neutrino-mass measurement. This means that the intrinsic background has to be suppressed under 1 mHz by active and passive shielding.



Figure 2.9: Main detector. The detector is segmented in 148 pixel with equal areas. Manufacturer: Canberra/Belgium (2007). [Doe08]

2.7 Remarks on sensitivity and systematic uncertainties

The count rate at the detector is directly dependent on the β -activity.

$$N \sim \rho d \cdot \varepsilon_T \tag{2.13}$$

Therefore changes in column density ρd and isotopic purity ε_T have to be monitored precisely during the scanning interval at a specific retarding voltage. The precision of

these measurements directly contributes to the systematic uncertainties of the measurement points of the β -spectrum.

Isotopic purity ε_T means the relative number of T atoms in the mixture of all six hydrogen isotopologues (H₂, HD, D₂, HT, DT, T₂) in the source gas.

The column density ρd can be influenced by variation of the WGTS tube temperature, the gas influx and the gas density at the first pumping port. On the other hand, variations in the magnetic field strength of the WGTS lead to a change of the maximal opening angle and thereby the average track length of the β -electrons is changed as well as the amount of accepted electrons [Hoe09].

In addition, secondary source-related systematic effects arise. The precise knowledge of ρd and/or ε_T is needed for the handling of these effects.

• Nuclear recoil of molecular β -decay

The finite recoil energy of the daughter molecule can be approximated by ([KAT05]):

$$E_{\rm rec} \approx E \cdot \frac{m_e}{M_{^3{\rm HeT/H}^+}}$$
 (2.14)

In case of the decay $T_2 \rightarrow {}^{3}\text{HeT}^+$ (HT $\rightarrow {}^{3}\text{HeH}^+$) the recoil energy is $E_{\text{rec}}^{T_2} = 1.72 \text{ eV}$ ($E_{\text{rec}}^{\text{HT}} = 2.58 \text{ eV}$) [Sae00].

• Final state distribution

The first electronic excited state of ${}^{3}\text{HeT}^{+}$ has an excitation energy of 27 eV [Sae00]. Therefore electronic excitations play almost no role in the analysis interval near the endpoint. However, the just described nuclear recoil can induce a large number of rotational-vibrational states with a mean energy of 1.89 eV. The shifts for ${}^{3}\text{HeH}^{+}$ are a only 1.14 eV in average. A contamination of T₂ with HT or DT has only a little effect since the corresponding shift is compensated by the change in recoil energy [KAT05].

However, the final state distribution ultimately limits the resolution which can be obtained in molecular tritium β decay.

• Doppler broadening

Spectral lines are broadened by the stochastic movement of the β electron emitting molecules in the WGTS. The non-relativistic approximation for a 18.6 keV electron emitted by a molecule flying exactly in the direction of the spectrometer is given by ([KAT05])

$$\Delta E = m_e \cdot |\vec{v}_e| \cdot |\vec{v}_{\rm mol}| \tag{2.15}$$

where the velocity of the electron is $|\vec{v}_e| \approx 8 \cdot 10^7 \,\mathrm{m/s}$ and the mean speed of the molecule at 30 K is $|\vec{v}_{\rm mol}|$. The broadening for T₂ (HT) is $\Delta E \approx 148 \,\mathrm{meV}$ ($\Delta E \approx 181 \,\mathrm{meV}$).

• Electron scattering with molecules

The β electrons undergo elastic and inelastic scattering with the source molecules. The energy loss of the electron due to elastic scattering is ([KAT05])

$$\Delta E = 2 \frac{m_e}{m_{\rm mol}} E(1 - \cos \theta) \tag{2.16}$$

where the dependency on the molecular species is given by the mass $m_{\rm mol}$. The scattering is mostly forward peaked and therefore the effect of elastic scattering is very low. The lowest possible energy loss in an inelastic scattering process (electronic excitations) is $\epsilon_1 = 12.6 \, \text{eV}$ [Ase00]. That means that electrons with energies between the endpoint E_0 and $E_0 - \epsilon_1$ haven't suffered from inelastic scattering. Electrons detected with lower energies may have scattered. The scattering probability is dependent of the column density ρd .

The β -activity = $\rho d \cdot \varepsilon_T$ is measured by monitor detectors in rear ([Mau09]) and forward direction ([Sch08],[Bab10]). In addition the activity can be measured by the focal plane detector at lowered (e.g. $U_0 - 500 \text{ V}$) retarding voltage between the T_2 scanning periods. The column density ρd can be measured by the energy loss of a mono energetic electron beam which is shot through the WGTS, transport section and spectrometers on the focal plane detector.

Other systematic uncertainties are related to the spectrometer like trapping of particle or variations in the high voltage. The total systematic uncertainty of KATRIN is anticipated as

$$\sigma_{\rm syst.tot} \le 0.017 \, (eV)^2$$
 (2.17)

With a statistical uncertainty of the same size for 3 years of measurement, the total uncertainty is $\sigma_{\text{tot}} \approx 0.025 \,(\text{eV})^2$. This translates into an upper limit $L(90\% \,\text{C.L}) = \sqrt{1.64 \cdot \sigma_{\text{tot}}}$:

$$m_{\nu_{\rm e}} < 0.2 \,\mathrm{eV} \quad (90\% \,\mathrm{C.L})$$
 (2.18)

These facts highlight the necessity of a high precision measurement of the isotopic purity ε_T and the determination of the composition of the hydrogen isotopologues. The required design precision is 0.2 % and the 'gold-standard' is 0.1 % ([KAT05]).

These challenging requirements for monitoring the isotopic purity can be met by Laser Raman spectroscopy. The system is operated inline at the Inner Loop before the gas is injected by the WGTS buffer vessel (see figure 2.7 on page 18).

In the following chapters the theory of the Raman effect, the setup of the Laser Raman system and systematic investigations are described in detail. Within these measurements the performance of simultaneous monitoring of all six hydrogen isotopologues and the precision have been successfully demonstrated.

Chapter 3

The (Laser) Raman effect

In this chapter the parts of the theory of the Raman effect are described which are relevant for the understanding of the thesis. In section 3.2 the possible excited states of diatomic molecules are described fundamentally to understand the effects and spectra explained in section 3.3 about the Raman effect. Section 3.4 deals with the application of Raman spectroscopy on hydrogen isotopologues in the present case. Finally, in section 3.5 former Raman experiments on tritium containing gases are reported.

3.1 Introduction to Laser Raman spectroscopy

In short, the Raman effect describes inelastic scattering of light at molecules. The wavelength of the scattered light is shifted due to energy transfer into rotational-vibrational excitations of the molecule. The effect was predicted theoretically by A. Smekal in 1923 [Sme23] and finally discovered by C. Raman in 1928. With the development of lasers in the early 1960's as excitation sources, Laser Raman Spectroscopy was established in quantitative spectroscopy [Hen70].

The typical experimental setup for Raman spectroscopy is shown in 3.1. The relative low efficiency of the Raman scattering may be seen as drawback of the technique. Only one of about incident 10^7 photons does Raman scattering [Atk96]. But for rapid multispecies analysis it becomes very attractive since a wide spectral range can be covered with



Figure 3.1: Principle of measurement setup for observation of the Raman effect. The sketch shows constituent parts of a standard Raman experiment. The observation direction is preferably perpendicular to the excitation beam to reduce the intensity of the primary light in the detection system. (according to [Hak03])

only one excitation wavelength. In contrast, techniques like LIF¹ need tunable lasers or a combination of many lasers which make a system very complex [Tel07].

Molecules without a permanent electric dipole momentum like gases as H_2 , T_2 or O_2 cannot be detected by infra-red absorption spectroscopy which is a well established standard technique. However, these molecules are visible in a Raman spectrum.

For KATRIN it is an excellent instrument for the determination of the isotopic purity of the tritium gas. The measurement procedure is non-destructive, non-contact and can be performed in-line a chemical engineering process.

This thesis deals with applications of the Raman effect, so the illustration of this effect is treated semi-classically. This means that the motion of the nuclei in the molecule is treated classically subjected to empirical quantization rules. The quantum mechanical approach describes nature more precise and consistent, but to understand the content in the scope of this thesis, it is not necessary to introduce the full quantum mechanical models.

The presented theory is based on the textbooks of [Hak03], [Lon02], [Atk96].

3.2 Excited states of diatomic molecules

In this section the focus will only be set on the diatomic molecules which is sufficient to explain the Raman spectra of the hydrogen isopotologues. Excited states possible in a molecule are electronic, vibrational and rotational excitations. Only rotational and vibrational excited states play an important role for non-resonant Raman scattering, thus only these two are described below.

One thing that has to be kept in mind for the following is, that the energy states in a molecule are quantized. This means that the molecule enters a different energy state only by absorption or emission of energy quantums (e.g. photons).

Besides frequencies ν [Hz] and wavelengths λ [nm] spectroscopists usually use the notation of wavenumbers $\tilde{\nu}$ [cm⁻¹] to describe energies states or transitions. The conversion is as follows:

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{E}{hc} \quad [\text{cm}^{-1}]$$
(3.1)

3.2.1 Rotational states

The easiest model for the circular motion of a diatomic molecule is to assume a rigid rotator. The two atoms of the molecule are connected by a straight line which then form a dumbbell (figure 3.2 (a)) Classically, the rotational energy of a rigid rotator with angular momentum L and moment of inertia I is

$$E_{\rm rot} = \frac{L^2}{2I}.\tag{3.2}$$

Similar to the angular momentum eigenfunction for the electron in the H-atom [Hak00], the quantization conditions for the rigid rotator can be introduced (for rotation J is the

¹LIF=Laser Induced Fluorescence



Figure 3.2: Rotation of diatomic molecules (a) shows the rigid rotator with fixed distance between both atoms. For the case of the the non-rigid rotator (b) the atoms can oscillate with the spring constant k. In (c) the effect on the corresponding energy scheme is shown. The energy states of the non-rigid rotator are shifted to lower values since the energy level are suppressed by centrifugal stretching compared to the rigid case. (according to [Hak03])

usually used quantum number)

$$|\vec{L}| = \hbar \sqrt{J(J+1)}.$$
(3.3)

Hence the rotational eigenenergies (figure 3.2 (c)) of a rigid rotator are

$$E_{\rm rot} = \frac{\hbar^2}{2I} J(J+1) \quad (J=0,1,2,\dots).$$
(3.4)

The term common in spectroscopy is $\tilde{F}(J)$ in units of cm⁻¹ with $B = \frac{h}{8\pi^2 c^2 I}$ as the rotational constant characteristic for the concerned molecule.

$$\tilde{F}(J) = \frac{E_{\text{rot}}}{hc} = BJ(J+1)$$
(3.6)

The selection rule for optical transitions (electric dipole radiation) is $\Delta J = \pm 1^2$. That leads to the energy of the quants involved in transitions between a state with quantum number J and J + 1.

$$h\nu = E_{J+1} - E_J \tag{3.7}$$

The wavenumbers of the rotational lines are

$$\tilde{\nu}_{J \to J+1} = 2B(J+1)$$
 (3.8)

I is proportional to the reduced mass μ , so the gap between two energy levels depending on B shrinks for higher masses. That's why the rotational lines of T₂ (μ _{T₂} = 1.5 u) are

²For Raman scattering the selection rule will be $\Delta J = \pm 2$



Figure 3.3: Potential curves of oscillators. Displayed are two different models to describe vibrational energy states. R_e is the equilibrium position and v the vibrational quantum number. Left: The potential curve for the harmonic oscillator is a parabola which provides equidistant energy levels, which is a fair approximation for small v. Right: The Morse potential leads to the anharmonic oscillator. For higher values of v the equidistance of the energy levels is not valid. The dissociation energy from the minimum of the potential curve is D_e , above of it the continuum begins. (according to [Hak03])

closer to each other than those of H_2 ($\mu_{H_2} = 0.5 \, u$)

Only the rotation perpendicular to the longitudinal axis of the molecule has to be taken into account. For rotations around this axis the moment of inertia is so small that the transition energies would become very large accordingly.

The spectral analysis of diatomic molecules with high resolution show that the rigid rotator approximation is not valid for wide ranges of the quantum number J. For higher J the transition energies become smaller than expected in the hitherto model. From that it follows that the moment of inertia I increases with higher rotation quantum numbers which can be related to centrifugal stretching of the molecule.

Therefore the non-rigid rotator model has to be introduced at which both nuclei are coupled by a elastic spring constant k (figure 3.2 (b)). The modified term scheme is

$$\tilde{F}(J) = BJ(J+1) - DJ^2(J+1)^2;$$
(3.9)

here D is a stretching constant with $D/B \approx 10^{-3} - 10^{-4}$. This correction has only an impact for higher values of J. Higher order correction terms can be added to the energy scheme to obtain even better accuracies. The wavenumbers of transitions of the non-rigid rotator are

$$\tilde{\nu}_{J \to J+1} = \tilde{F}(J+1) - \tilde{F}(J) = 2B(J+1) - 4D(J+1)^3$$
(3.10)

Note that the selection rules stay invariant, since symmetries of rotational states don't change because of the spring force.

3.2.2 Vibrational-rotational states

The harmonic oscillator Normally, vibrational spectra always come along with rotational structures, but for reasons of didactics the pure oscillating diatomic molecule will be introduced first.

The simplest approximation in this case is to assume the model of the dumbbell (figure 3.2 (b)) forming a harmonic oscillator with a spring constant k in the following parabolic potential

$$V = \frac{k}{2}(R - R_e)^2$$
(3.11)

R is the internuclear separation and R_e the equilibrium position. The energy levels result from quantum mechanical calculations including the quantum number v (e.g. [Nol09])

$$E_{\rm vib} = h\omega(v + \frac{1}{2}) \quad v = 0, 1, 2, \dots$$
 (3.12)

The usual notation in molecule spectroscopy is again using wavenumbers $[cm^{-1}]$

$$\tilde{G}_{\nu} = \frac{E_{\text{vib}}}{hc} = \tilde{\nu}_e (v + \frac{1}{2}) \tag{3.13}$$

The eigenfrequency of the harmonic oscillator is ν_e and the corresponding wavenumber $\tilde{\nu}_e$. The dependence on the reduced mass μ of the molecule is

$$\tilde{\nu}_e = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \tag{3.14}$$

The eigenfrequencies are anti-proportional to the square root of the reduced mass. Like for the (non)-rigid rotator, T₂ has lower vibrational energy levels than H₂ because of the three times higher mass. The selection rule for optical transitions is $\Delta v = \pm 1$ from which monoenergetic transitions follow with a quantum energy of $E_{v+1} - E_v = h\nu_e$.

The anharmonic oscillator In reality the potential curve differs from the parabolic shape. Since a reduction of intermolecular distance R_e induces an increasing repulsion, the curve becomes steeper for $R < R_e$. On the other hand an increase of the atomic distance leads to a loosening of the bound and finally to a dissociation, which should result in a less steep potential curve

The Morse potential is often used as an empirical ansatz (see right of figure 3.3)

$$V = D_e \left[1 - e^{-a(R - R_e)} \right]^2.$$
 (3.15)

Here D_e is the dissociation energy and $a = \sqrt{\frac{\mu}{2D_e}} \cdot \tilde{\nu}$.

For $R > R_e$ Schrödinger's equation can be solved with the Morse potential. A good approximation for the energy terms of the anharmonic oscillator is

$$\tilde{G}_v = \tilde{\nu}_e(v + \frac{1}{2}) - x_e \tilde{\nu}_e(v + \frac{1}{2})^2$$
(3.16)

$$=\underbrace{\tilde{\nu}_e\left(1-x_e(v+\frac{1}{2})\right)}_{\tilde{\nu}_e}(v+\frac{1}{2}) \tag{3.17}$$

In this term x_e is the anharmonic constant, typically of the size 0.01. For higher quantum numbers the effective frequency ν_v decreases. This small anharmonicity modifies the selection rule and introduces the possibility that also transitions with $\Delta v = \pm 2, \pm 3, \ldots$ can occur, albeit with in general reduced probability with respect to transitions with $\Delta v = \pm 1$.

Rotational-vibrational excitations Until now rotational and vibrational states have been treated separately. However, if both are considered together the picture become complex than just the simple approximation

$$E(v, J) = E_{vib}(v) + E_{rot}(J).$$
 (3.18)

Besides the centrifugal stretching of the bond length for higher J an additional factor by vibrational stretching has to be taken into account. Because of the anharmonicity of the Morse potential (see right of figure 3.3) the average $\langle R \rangle$ of the internuclear separation increases with growing quantum number v. Therefore there has to be a coupling between rotational and vibrational states. According to this the rotational constant B is dependent on the quantum number v and has to be written as B_v , the same holds for the stretching constant D.

The behaviour of both constants can be described by the following *ansatz* with α, β as molecular specific numbers:

$$B_v = B_e - \frac{\alpha}{2}(v + \frac{1}{2}) \tag{3.19}$$

$$D_v = D - \beta(v + \frac{1}{2})$$
(3.20)

Finally, the terms measured in units of cm^{-1} are

$$\tilde{T}_{v,J} = \tilde{G}_v + \tilde{F}_{v,J} \tag{3.21}$$

$$=\tilde{\nu}_e(v+\frac{1}{2}) - x_e\tilde{\nu}_e(v+\frac{1}{2})^2 + B_vJ(J+1) - D_v[J(J+1)]^2$$
(3.22)

The rotational-vibrational spectrum corresponds to transitions between the $\tilde{T}_{v,J}$ terms from $(v' \leftarrow v'', J' \leftarrow J'')$. Transitions have to be observable according to the selection rules.

$$\tilde{\nu} = \tilde{\nu}_e(v' - v'') - x_e \tilde{\nu}_e \left[(v' + \frac{1}{2})^2 - (v'' + \frac{1}{2})^2 \right] + B_{v'} J' (J' + 1) - B_{v''} J'' (J'' + 1) + \dots$$
(3.23)

Note that equations (3.22) and (3.23) only give an approximate description of the true energy levels and spectra which, however, is sufficient for application with ordinary spectral resolutions. For higher precision further effects and related corrections have to be taken into account. Further reading e.g. [Her64] (citation by [Hak03]).

3.3 Basic principle of Raman scattering

Light can be absorbed or emitted by molecules if the resonance condition $\Delta E = h\nu$ is met. Aside, light of every wavelength can be scattered at the molecule.

Classically, this can be explained by the fact that the $\vec{\mathcal{E}}$ -vector of the light field couples to the electrons in the shell of the molecule and induces an electric dipole moment

$$p_{\text{ind}} = \vec{\alpha} \cdot \vec{\mathcal{E}} \tag{3.24}$$

where $\vec{\alpha}$ is the polarisability tensor. This induced electric dipole oscillates with the frequency ν_p of the incident light and irradiates light of the same frequency. This case is called Rayleigh scattering.

$$\vec{p}(\nu_p) = \vec{\alpha}^{Ray} \vec{\mathcal{E}}(\nu_p) \tag{3.25}$$

The quantum mechanic picture of the Rayleigh scattering is shown in figure 3.4 (a). Besides this elastic scattering process the molecule can end up in a higher excited state after scattering than its initial state. The scattered photon is red-shifted due to the energy transfer to the molecule. This process is called Stokes Raman scattering (see figure 3.4 (b)).

Also the vice-versa process is possible, as the molecule can remain in a lower energy state than its initial state. The corresponding photon will than be blue-shifted. The process is named anti-Stokes Raman scattering (see figure 3.4 (c)). All three processes involve two photons which lead to the selection rule of the $\Delta J = \pm 2$.

The selection rules of these processes are summarized in table 3.1. Figure 3.5 provides an overview of a typical Raman spectrum including all terms and definitions treated so far. Theoretical Raman spectra of hydrogen isopotologues are found in section 3.4 with a description of the various branches and quantum numbers (see figure 3.6 further below)

Intensity It has been shown that the knowledge of the spectroscopic constants like B_e, D, \ldots allows a description of the line positions within a Raman spectrum. The accuracy is depending on the quality of available data and the number of involved correction terms. Nevertheless, these calculation only provide the line positions but not the corresponding intensities. The calculation of Raman line intensities will now be briefly discussed.

The intensity $I(\Theta, p^s, p^i)$ of the scattered radiation from a population of diatomic molecules exposed to an irradiance \mathcal{I} is given by following expression [Lon02]

$$I(\Theta, p^s, p^i) = k_{\tilde{\nu}} \cdot \tilde{\nu}_s^4 \cdot N_i \cdot \Phi(a^2, \gamma^2, \Theta) \cdot \mathcal{I}.$$
(3.26)



Figure 3.4: Energy level diagram for non-resonant photon excitation. The incoming photon excites the molecule to a virtual (dressed) state. This is followed up by a transition to the final state of the molecule by irradiation of a scattered photon. The mutual positions of final and initial state define the type of scattering. (a) If $|i\rangle = |f\rangle$ it is called Rayleighscattering $(h\nu_{\rm in} = h\nu_{\rm out})$, (b) if $|i\rangle < |f\rangle$ it is called Stokes Raman-scattering $(h\nu_{\rm in} > h\nu_{\rm out})$, scattered photon is red-shifted) and (c) if $|i\rangle > |f\rangle$ it is called anti-Stokes Raman-scattering $(h\nu_{\rm in} < h\nu_{\rm out})$, scattered photon is blue-shifted). (according to [Lew07], [Lon02])

Table 3.1: Selection rules of scattering spectra. In this thesis the notation convention for the branches of the Raman spectra introduced by R.Lewis [Lew07] is used. The anti-Stokes Raman branch is only stated for completeness of the notation, but it doesn't play any role in the scope of this thesis.

| Type of scattering | Selecti Δv | on rules ΔJ | Branch name | Raman shift |
|---|--------------------|---------------------|--|--|
| anti-Stokes Ra- man (pure rota- tion) | 0 | -2 | <i>O</i> ₀ | $\tilde{\nu}_p + \tilde{\nu}_{\rm rot}$ |
| Rayleigh Stokes Raman (pure rotation) | 0 0 | 0 + 2 | $egin{array}{c} Q_0 \ S_0 \end{array}$ | $\tilde{ u}_p - \tilde{ u}_{ m rot}$ |
| Stokes Raman (rotation- vibration) | 1 1 1 | $-2 \\ 0 \\ +2$ | $egin{array}{c} O_1 \ Q_1 \ S_1 \end{array}$ | $\begin{split} \tilde{\nu}_p &- \tilde{\nu}_{\rm vib} + \tilde{\nu}_{\rm rot} \\ \tilde{\nu}_p &- \tilde{\nu}_{\rm vib} \\ \tilde{\nu}_p &- \tilde{\nu}_{\rm vib} - \tilde{\nu}_{\rm rot} \end{split}$ |



Figure 3.5: Schematic view of a typical Raman-spectrum of a diatomic molecule. The Rayleigh line at the frequency of the primary line $\tilde{\nu}_p$ is surrounded by pure rotational Raman lines (S_0, O_0) . S-branches are always associated with $\Delta J = +2$, Q-branches with $\Delta J = 0$ and O-branches with $\Delta J = -2$. The index of the branches indicates the Δv . At multiples of $-\tilde{\nu}_{\rm vib}$ from the Rayleigh line the Q,S and O-branches can be found in the Stokes region with weaker intensities for higher orders. The corresponding anti-Stokes lines at multiples $+\tilde{\nu}_{\rm vib}$ are normally much more faint at room temperature, because the excited states are less populated according to the Boltzmann distribution. (Note that the axis is labeled with wavelength λ . For the representation in wavenumbers $\tilde{\nu}$ the diagram has to be read in reversed order.)(according to [Hak03])

- Θ Definition of the collection geometry.
- $\mathbf{p^s}, \mathbf{p^i}$ Polarizations of the scattered and incident light.
- $\mathbf{k}_{\tilde{\nu}}$ The prefactor $k_{\tilde{\nu}}$ is only a constant containing the permittivity of vacuum (ϵ_0)

$$k_{\tilde{\nu}} = \frac{\pi^2}{\epsilon_0^2} \approx 1.259 \cdot 10^{23} F^{-2} m^2.$$
(3.27)

- $\tilde{\nu}_{\rm s}^4$ The term contains the fourth power of the absolute wavenumber of the scattered radiation. This is familiar from the derivation of the Rayleigh scattering which goes with λ^{-4} . The strong wavelength dependence of the scattering means that blue light is scattered much more readily than red light.
- N_i The population factor N_i expresses the number of molecules in the initial state N_i

$$N_{i} = \frac{N \cdot g_{i} \exp\left(-\frac{E_{i}}{kT}\right)}{\sum_{j} g_{j} \exp\left(-\frac{E_{j}}{kT}\right)}$$
(3.28)

N is the total number of irradiated molecules proportional to the partial pressure, kT is the thermal energy, g_i is the statistical weight and E_i the energy of the initial state consisting of vibrational and rotational parts. The denominator of expression (3.28) is the molecular partition function. The statistical weights of vibrational energy states are non-degenerated ($g_{v_j} = 1$) however this is not true for the g_J of the rotational states. The reason lies in the symmetry of the total wave function. For hetero-nuclear molecules (eg. HD, DT, HT) no parity can be defined resulting in $g_J = 1$, but in the case of homo-nuclear molecules the nuclear spin statistic has to be taken into account.

$$\Psi_{\text{tot}} = \Psi_{\text{spin,nuc}} \cdot \Psi_{\text{elec}} \cdot \Psi_{\text{space}} \tag{3.29}$$

The wave function of molecules with two fermionic nuclei (H_2, T_2) has to be antisymmetric under inversion since it has to follow Pauli's principle. According to this the wave function of bosonic nuclei (D_2) has to be symmetric. Since a rotation of 180° is equivalent to an exchange of both atoms the rotational excited state J of the molecule has to be taken into account [Atk96]. The influence of nuclear spin statistics on hydrogen isotopologues is demonstrated in table 3.2. A visualization of this effect is found in subsection 3.4, the discussion of theoretical spectra of hydrogen (see figure 3.6).

 $\Phi(\mathbf{a}^2, \gamma^2, \Theta)$ The line strength function Φ is given by the isotropic averages of squares of the transition polarisability tensor components. These components are depending on the experiment's geometry and light polarization, during the course of this work only a $\Theta = 90^{\circ}$ collection geometry was used with p-polarization in excitation and observation direction (a detailed derivation can be found in [Lon02]):

$$I(\pi/2, \perp^s, \perp^i): \ \Phi(a^2, \gamma^2, \Theta) = \left\langle (\alpha_{yy})_{fi}^2 \right\rangle$$
(3.30)

Table 3.2: Nuclear spin statistics and influence on relative intensities. The rotational line intensities of the homo-nuclear hydrogen isotopologues H_2 , D_2 and T_2 are effected by the nuclear spin. This leads to an 3:1 (H_2 , T_2) or 1:2 (D_2) alternation for the odd:even values of J [Lew07]

| Isotopologue | $\mathrm{H}_2,\mathrm{T}_2$ | D_2 |
|---------------------------------------|-----------------------------|--------------|
| Total nuclear spin I | $\frac{1}{2}$ | 1 |
| Nuclear spin degeneracy $2I + 1$ | $\overline{2}$ | 3 |
| Statistics | Fermi | Dirac |
| Ground electronic state | Σ_{q}^{+} | Σ_q^+ |
| Nuclear spin statistical weight g_N | 5 | 5 |
| J odd / J even | $3 \ / \ 1$ | 3 / 6 |
| Relative intensities of Raman lines | | |
| $J { m odd} / J { m even}$ | 3 / 1 | $1 \ / \ 2$ |

A more detailed description of this line strength function would go beyond the scope of this thesis and is not necessary for the understanding of the following contents. Nevertheless, it has to be noted that the tensor invariants of the line strength function for each isotopologue are specific. From the knowledge of the relative strength for all isotologues, conclusions could be drawn for a quantitative determination of the gas composition.

 \mathcal{I} The irradiance is the value for the incident excitation light. For a correct calculation an integration over the scattering volume has to be performed. Of course this term has no impact on the calculation of relative intensities.

3.4 Laser Raman spectroscopy on hydrogen isotopologues

In some respect Raman spectroscopy on hydrogen isotopologues is the most simple application imaginable. Only two nuclei and two electrons form the considered molecules. No complicated orbital structures have to be taken into account. A theoretical Raman spectrum of T_2 is shown in figure 3.6 with a resolution comparable to the spectrometer described in section 4.2.8. All S_0, S_1 and O_1 branches shown are well separated and do not tend to overlap.

The isotopic effects for the three hydrogen species (H, D, T) are most distinct compared to other isotopes (e.g. ${}^{12}C : {}^{13}C$). The mass ratio of H : D : T is 1 : 2 : 3, and as shown in section 3.2, the Raman shifts are smaller for higher reduced masses μ and vice-versa. In figure 3.7 the theoretical spectra of all hydrogen isotopologues are plotted. It can be seen that all the Q_1 -branches are distinctively separated from each other which is due to the pronounced mass ratios. Some minor overlaps of Q_1 -branches with S_1 and O_1 lines of other hydrogen isotopologue are to be found in the inset of figure 3.7. The impact on the analysis is discussed in chapter 5.3.3. In principle, all branches within the recording range of the spectrometer used in this work (see 4.2.8) - the pure rotation and as well as the rotational-vibrational ones - can be used for analysis, since all start at the same levels in the lowest vibrational state v'' = 0. Equation (3.28) shows that no other vibrational level needs being considered because of their extremely low relative population, N_v , at room temperature:

$$N_v = \frac{N \cdot \exp\left(-\frac{\tilde{G}_v \cdot hc}{kT}\right)}{\sum_i \exp\left(-\frac{\tilde{G}_i \cdot hc}{kT}\right)}$$
(3.31)

For example, for the heaviest hydrogen isotopologue, T_2 , $\tilde{G}_v \approx 2400 \text{ cm}^{-1}$ and with $kT \approx 200 \text{ cm}^{-1}$ at 300 K, one finds $N_{v=1} \approx 6 \cdot 10^{-6} N$. Within the dynamic range of the detection system this is well below threshold.

The population of the rotational levels, which follow the distribution function, is

$$N_J = \frac{N \cdot g_J \cdot (2J+1) \exp\left(-\frac{\tilde{F}_{v,j} \cdot hc}{kT}\right)}{\sum_j g_j \cdot (2j+1) \exp\left(-\frac{\tilde{F}_{v,j} \cdot hc}{kT}\right)}$$
(3.32)

For room temperature (300 K) one finds that only very few rotational levels are populated significantly above the noise level. A relative population > 10^{-4} is found for the rotational levels with about $J'' \leq 10$ in the case of T₂, and a mere $J'' \leq 5$ in the case of the lightest isotopologue, H₂.

For the 'shape' of the various bands (see figure 3.5) one expects - in first approximation - a nearly equal appearance, i.e. for example the S_0 - and S_1 -branches, with the main difference being the intensity. The Raman probability for the S_0 -transitions ($v' = 0 \leftarrow v'' = 0$) is significantly larger than that for the S_1 -transition ($v' = 1 \leftarrow v'' = 0$). The O_1 -branch is rather similar to the S_1 -branch, only that it commences at J'' = 2 rather than J'' = 0.

The Q_1 -branch lines 'pile up' and appear nearly as a single line under the spectral resolution encountered in the KATRIN Raman spectrometer as seen in figure 3.6. This is due to the fact that because of J'' = J' very little line spacing is present (safe for a small anharmonicity contribution), so that a 'line'-like feature is observed rather than a branch-type feature. While this is unfavorable for high-precision rotational spectroscopy, it is beneficial for Q_1 -branches in composition analysis.

There are three main reasons why in quantitative analysis the use of the Q_1 -branches has advantages over the (normally more intense) S_0 -branches:

- 1. Rather than having to evaluate individual lines in the S- or O-branches whose intensity will alter with temperature, in the Q-branch by and large one integrates over all rotational levels, and hence has (i) higher peak intensity, and (ii) the signal is temperature-independent. Thus measurable changes in the peak amplitude reflect total number density variations, and thus relative concentration values (provided all other experimental parameters are kept unchanged) - the determination of which indeed has been the goal of this investigation.
- 2. Another effect confining the quantitative use of the S_0 -branches is being discussed in the following chapters. Briefly, the razor edge filter cutting the excitation line of the laser (see section 4.2.8) is also suppressing the first rotation line of T₂ and DT, reducing their usefulness for analysis with it.



Figure 3.6: Theoretical spectrum of T_2 . The shown Raman spectrum of T_2 has been simulated with SpecGen [SPE09] from R.Lewis. The settings are excitation wavelength 532 nm, gas temperature 300 K and width of the peaks $\sigma = 8.5$ (matched to the resolution of the HTS spectrometer). The J" indicates the initial rotational quantum number of the associated transition. The relative intensities of the $S_0 : S_1 : O_1 : Q_1$ branches are not correct because of the lack of data for the line strength function of T_2 (note that this has been set to equal 1 for all rotational and ro-vibrational transitions). The relative intensities within one of the branches is valid since it is independent of the line strength function. The S_0, S_1 and O_1 branches show very distinctively the 3 : 1 alternation for the odd:even values of J explained by the Fermi statistics in table 3.2

3. A severe problem is a parasitic peak in the spectral region of the S_0 -branches coming from Raman scattering with the SiO₂ windows of the sample cell. The detailed description is found in chapter 5.3.4.

For these reasons the focus of quantitative analysis for KATRIN will be set on the Q_1 -branches.

3.5 Former Raman experiments on tritium containing gases

Raman spectroscopy of hydrogen isotopologues is of cause not only a niche for neutrino mass experiments as KATRIN. Since T_2 , DT and D_2 are used as fuel for nuclear fusion reactors much research has been done on this sector. Still the full potential of this technology hasn't been tapped yet.

In 1978 Edwards, Long and Mansour measured the rotational and rotation-vibrational Raman spectra of T_2 to obtain rotational constants, vibration-rotational constants and bond



Figure 3.7: Overview of the Raman spectra of all hydrogen isotopologues. The figure shows simulated spectra for all six isotoplogues. The simulation was done by SpecGen [SPE09] with the same setting as in figure 3.6. The same applies here: the ratio between S_0 and Q_1 branches are as yet not correctly represented in the simulation. The reason why all single spectra were plotted atop of each other instead of chosing one sum spectrum, is to demonstrate the multiple overlappings in the S_0 -branch region $(120 - 1250 \text{ cm}^{-1})$. In contrast, the Q_1 branches are well separated. The inset reveals a minor problem, that is a possible overlap of the Q_1 -branch of T₂ with $O_1(J'' = 3)$ peak of DT and an overlap of the Q_1 -branch of DT with $S_1(J'' = 2)$ of T₂.

lengths [Edw78]. Then, in 1987 Veirs and Rosenblatt remeasured again the line positions of all six isotopologues up to an accuracy of $\pm 0.1 \,\mathrm{cm}^{-1}$ [Vei87]. The first Laser Raman measurements with tritium performed at FZK³ where done by Engelmann, who focussed on high resolution spectroscopy on S_0 , Q_1 branches and the time dependence of tritium exchange reaction with methane [Eng92]. In the same year S.O'hira et al. designed a remote fibre-coupled Laser Raman System for real-time analysis of isopologue compositions in TSTA⁴ [Ohi92]. They showed then, as well as later in the TPL⁵ that online monitoring of all six hydrogen isotopologues is possible with respectably low detection limits of 3 mbar partial-pressure in 100 s [Ohi96]. The previous Raman system used in TLK including the ASER⁶ developed by Taylor et al. [Tay01] has never been used with tritium. The active external resonator was capable to enhance the signal by factor > 40 by multi-passing of the laser beam, but was shown that it is unable provide the stability for long term runs.

Conclusion for KATRIN Laser Raman spectroscopy has been identified to be the most practicable method for the continuous monitoring of the hydrogen gas composition before being injected into the WGTS. Its advantages are that the procedure is non-contactive, non-destructive and features a quite excellent separation between the constituents (due to ratios of the reduced mass of the isotopologues). Additionally, the method allows the Raman system to be located outside of the second containment of the Inner Loop which prevents contamination of the box.

No commercial Raman system available meets these special requirements, therefore a custom-made system is set up. In the following chapter the realization of this system is presented and followed up by first results of successful tritium measurements.

³at this time KfK (Kernforschungszentrum Karlsruhe)

⁴TSTA=Tritium Systems Test Assembly at the Los Alamos National Laboratory

 $^{^5\}mathrm{TPL}{=}\mathrm{Tritium}$ Process Laboratory in the Japan Atomic Energy Research Institute

 $^{^{6}\}mathrm{ASER} = \mathrm{actively \ stabilized \ external \ resonator}$

Chapter 4

Experimental setup

In this chapter the experimental setup of the system used in TLK is described. It starts with a brief summary of the KATRIN requirements. After that an overview of the analysis procedure and the system is given, followed by the description of the main components with their particular features. The chapter is finished by the depiction of the acquisition software.

4.1 KATRIN requirements

Raman spectroscopy is a standard technique, but the imposed conditions of the KATRIN experiments are challenging. The requirements for the Laser Raman system can be divided in two sub-items: physical requirements already mentioned in section 2.7 and technical requirements.

• Physical requirements

- It is necessary to reach low detection limits, in order to detect even tiny quantities of constituents in the gas. For 100 mbar the detection limit has to be at least 0.1 mbar.
- One of the major requirement is the high reproducibility of the signals. The desired precision for KATRIN is < 0.1% in less than 250 s and 100 mbar.

• Technical requirements

- The optical path has to be stable for a KATRIN measurement period of 60 days. Therefore every part needs to have a high mechanic stability.
- The enclosure has to be light tight to avoid background and to provide laser safety.
- The active elements like excitation source and detector have to provide a good signal stability over long terms. In the optimal case fluctuations of the signal are below the desired precision.
- The measurement duration has to be as close to real-time as possible to allow the detection of fluctuations on minute or even second time scales.

- In particular the requirements for tritium safety are:
 - * Activities higher than $10^{10}\,{\rm Bq}$ have to be confined in second containments, normally glove boxes.
 - * The system should provide the opportunity that only the sample gas cell is placed in the second enclosure. The rest of the laser system remains uncontaminated in case of a tritium contamination. The cell itself has to fulfill UHV¹ compatibility.
 - * The mounting and adjusting procedure of sample gas cells and auxiliary parts has to be as easy and flexible as possible, since the inner part of the second containment can only be reached by gloves.

Within the scope of this thesis the Laser Raman system developed by R.Lewis in 2005-2007 was been used, improved and modified for tritium measurements.

4.2 Hardware

4.2.1 Raman measurement of gaseous samples – a general scheme

The path from an unknown hydrogen gas sample to the final quantitative result includes several steps. However, the processes can be divided in two mayor parts. The first part contains everything connected to spectroscopy shown in figure 4.1 and the second part is the software post-processing of the data discussed in the dedicated section 4.3.



Figure 4.1: Steps of spectrum acquisition. Explanation in plain text.

- 1. The laser is the excitation source of the setup providing monochromatic light.
- 2. In the Laser Raman cell light scatters at the sample molecules within a defined volume.
- 3. The scattered light is collected by a combination of lenses.
- 4. The collected light is transported from the optics via a fibre into the filter unit.
- 5. The edge filter is used for suppression of the Rayleigh and excitation source light by 8 to 9 orders of magnitude.
- 6. The spectrometer splits the light and diffracts it wavelength dependently by a grating.

 $^{^{1}\}mathrm{UHV}{=}\mathrm{Ultra}$ high vacuum

4.2. HARDWARE

7. The spectrum is finally detected by a CCD camera producing a raw, two-dimensional spectrum.

In this section the implementation of the just presented scheme meeting the KATRIN requirements is explained.

4.2.2 Overview of LARA setup at TLK

Before the relevant parts of the setup are presented in detail, an overview of the whole setup is given in figure 4.2. At the time of this work the LARA-system hasn't been connected at its final destination to the Inner Loop, since the latter was still in the assembly and commissioning phase. Instead it was placed in room 174 inside the TLK. Here, only measurements with 'static' cells are possible, i.e. the cell is not incorporated into a loop but filled at an extern place (e.g. CAPER-facility). Without the second containment of a glove box, the maximum activity allowed in the Raman cell is 10¹⁰ Bq.

4.2.3 The excitation laser (Coherent VERDI V5)

The inevitable core of every Raman setup is the excitation source. Stringent requirements have to be met for the laser to be used for KATRIN LARA setup. On the one hand it has to be very powerful to compensate the rarefied density of molecules within the scattering volume, but on the other hand the power stability should be at least 0.1% over a period of up to 60 days, if the absolute signal is of interest.

From former experiments with the ASER² by Taylor et al. [Tay01] the TLK was still in possession of the excellent single-mode Verdi^M 5W Laser. In figure 4.3 a schematic drawing of the resonator can be found including a short description of the functionality. The specifications can be found in table 4.1. It has to be noted that every tuning and control of components (Vanadate, etalon, LBO,...) within the laser cavity is done via temperature regulation. This highly complex temperature stabilized feedback loop makes the laser output susceptible for power fluctuations, power drift and possibly mode hops.

| Parameter | Specification |
|--------------------|--|
| Power | 5 W |
| Wavelength | $532\mathrm{nm}$ |
| Beam diameter | $2.25\mathrm{mm}$ (nominal) at exit port |
| Beam divergence | $< 0.5\mathrm{mrad}$ |
| Power stability | $\pm 1\%$ over 2 h after $15{\rm min}$ warm up |
| Pointing Stability | $< 5\mu rad/^{\circ}C$ |
| Noise | < 0.03% rms from 10 Hz to 1 GHz |
| Polarization | > 100: 1, vertical, linear |

Table 4.1: Specification of the Verdi[™] V5 laser. According to data sheet [Ver99].

 $^{2}ASER$ =actively stabilized external resonator



Figure 4.2: Top view on LARA Setup. The pictures shows the core components as laser, LARA cell, fibre, spectrometer and CCD which are described in the text below. Not included in the detailed explanations are the beam dump which completely absorbs the power of the laser beam and the focusing lens necessary to decrease the beam diameter from about 2.25 mm down to 56 μ m in the LARA cell. The recess at the place of the LARA cell can either be connected to the Inner Loop appendix or to a cover including a hood connection to the TLK exhaust ventilation system. The picture doesn't include the top covers necessary for laser safety and light tightness.



Figure 4.3: Schematic illustration of the Verdi V5 cavity. Two diode arrays pump the vanadate (Nd: YVO₄) crystal. Inside this gain medium the fundamental laser line at 1064 nm is stimulated. The LBO (LiB₃O₅) is used as the second harmonic generator enabling 532 nm light. This visible wavelength is advantageous for Raman intensity because of the $\frac{1}{\lambda^4}$ suppression compared to near infrared. The etalon is finally used to suppress unwanted modes and to establish single frequency operation.

4.2.4 Laser power monitoring

During the course of the thesis a laser power monitoring system has been installed. The purpose of the system is to measure the laser power during the acquisition and to check for the beam integrity. The fluctuation in the recorded laser power of many acquisitions could be used as correction for the Raman intensity signal. If the power signal abruptly drops, the laser beam has to be blocked immediately to avoid hazards (e.g. fire) by the possible beam displacement. The optical setup is described in figure 4.4. The digitalized signals of the photo diode are then recorded by LabVIEW.

4.2.5 Safety equipment

Several safety precautions are installed into the system to avoid risks for man and machine. The laser itself is a class 4 device³, that means it can burn skin, and in some cases, even scattered light can cause eye and/or skin damage. Normally, this type of laser can only be operated in a laboratory with restricted access. Any kind of permanent entry restriction is not possible in the TLK and the KATRIN experiment. Thus, the laser is fully covered by a light tight enclosure and is legally regarded as a class 1 laser. Additionally, a magnetic switch system is installed in the top cover which closes a shutter in the beam path if the top cover is accidentally opened. This has been set up in the scope of this work. The system is also ready for unattended operation whereas the signal of the photo diode is used for the continuous monitoring of the laser beam. The detailed principle of operation of the whole systems is shown in appendix F.

 $^{^{3}}$ classified by EN_60825-1



Figure 4.4: Laser power monitoring. The laser beam passes through the concave lens and is blocked in the beam dump. About 0.25% percent of the light is reflected at the lens surface and collected by a photo diode. The signal current is converted by a custom built transimpedance amplifier into a voltage signal with is afterwards digitalized by a NI:DAQ.

4.2.6 The Laser-Raman cell

Standard commercial Raman cells cannot be used for Raman spectroscopy with tritium containing gas. In KATRIN the cell will be part of the primary system as integrated into the Inner Loop. The following conditions have to be fulfilled to ensure tritium compatibility. [Eng92].

- Ultra-high vacuum tightness (maximum leak rate $L \leq 1 \cdot 10^{-9} \frac{\text{mbar} \cdot 1}{\text{s}}$).
- Fully metal construction.
- Volume as small as possible to minimize to radioactive inventory.

The cell design used for KATRIN has been developed at the TLK [Tay01] for the Raman spectroscopy including the ASER⁴. They benefited from the experience of Engelmann et al. who published a procedure to connect fused silica windows of high quality to stainless steel without deformation of the window [Eng92]. The description of the cell is found in figure 4.5.

Fused silica is a advantageous material for the long term measurements with permanent laser irradiation. Because of the production process it is the glass type with minimal impurities. Therefore, the internal absorption is less than 0.01 % and thermal effects are very low [MEL09]. In addition, the fluorescence yield of fused silica which may produce background underlying on the Raman spectra is as well lower than compared with others [SCH04].

⁴ASER=actively stabilized external resonator



Figure 4.5: Cross sectional view and photo of Raman cell. Left: All windows are made of fused silica and diffusion bonded into CF16-flanges. The laser windows are coated with an anti-reflection coating optimized for 532 nm. The Raman windows are recessed into the cell to enhance the acceptance angle and to reduce the dead volume. They are coated with a broad band AR-coating to provide a good transmission of the scattered light [Tay01]. Right: Shown is a completely assembled Raman cell consisting of cell body, laser windows, Raman windows and manual valves.

During the course of this work the cells have been checked for tritium compatibility to get the concession for the use with tritium. All parts used in primary system in the TLK have to fulfill the technical terms of delivery and acceptance [TLA09]. Therefore every existing cell had to be tested by a three-fold procedure: (1) pressure test with a test gauge pressure of 3 bar, (2) leak test (leak-rate $L \leq 10^{-9} \frac{\text{mbar} \cdot l}{\text{s}}$) and (3) spectral analysis of the stainless steel (1.4301). Because of the successful tests the cells have been finally permitted for the use for tritium measurements. Furthermore, additional cells and windows have been remanufactured. Thereby the nearly 10 year old contacts with the producing companies have been revived, which turned out to be very smoothly since still the same responsible persons were available at the companies (windows bonding in CF16⁵ by UKAEA⁶ - Culham; window coating by Laseroptik Garbsen; cell body by main workshop of FZK; valves by B.E.S.T).

In spite of all efforts to provide a very high performance tritium compatible Raman cell, it does have an unfavourable effect on the Raman spectra with will be reported in 5.3.4.

4.2.7 The light collection system

The dimension of the scattering region within the LARA cell is about 9 mm length and 56.4 μ m diameter (detailed calculation is found in appendix E). The region has to be imaged as complete as possible to maximize the intensity in the detector. Photos of collection

 $^{^5\}mathrm{CF16}{=}\mathrm{Conflat}^{\textcircled{R}}$ with 16 mm inner diameter

 $^{^{6}\}mathrm{UKAEA}{=}\mathrm{United}$ Kingdom Atomic Energy Authority



Figure 4.6: Light collection and transportation system The plano convex lenses image the scattering region onto the fibre slit as visualized in the picture. Note that the sequence of the single fibres is scrambled in the bundle. (Fibre drawing adapted from [Lew07].)

and light transportation system can be found in figure 4.6.

The Raman cell windows have a half opening angle of about 21.25° . To cover the full light cone outside the recess in the cell area a 2" plano convex lens with the focal point in the scattering region is used to parallelize the beam. Another plano convex lens is placed subsequently to focus the beam down on the fibre.

The fibre consists of 48 single adjoining fibres with a core / cladding diameter of $100 \,\mu\text{m}/125 \,\mu\text{m}$. The fibre is mounted at a $XYZ\Theta$ mount to align the slit of 6 mm length at the fibre until it catches the scattering volume. On the other side of the fibre can be adjusted by a $XY\Theta$ mount to align for matching the entrance slit of the spectrometer. The easy adjustment is one advantage of fibre coupling over mirror imaging, because the collection side and spectrometer side can be aligned separately. Once adjusted the setup remains very stable and rigid. The fibre even allows a coupling with another spectrometer outside the enclosure. The disadvantages is of course that about 32% of the light is lost due to geometrical, reflection, attenuation and diffration losses. A detailed description is found in [Lew07]. Note that the polarization of the light is not conserved by the fibre, which is important to know because of the polarization dependent efficiency of the diffration grating.

4.2.8 The high throughput spectrograph (PI-Acton HTS)

The High Throughput Spectrograph (HTS) from Princeton Instruments⁷ consists of two elements. The first is a filter unit which is attached to the second part, virtually the spectrometer. The plan view can be found in figure 4.7.

The filter unit houses a Semrock RazorEdge filter which suppresses the excitation line of the laser at 532 nm by a factor of $10^8 - 10^9$. This is required because the contributions at this wavelength by Rayleigh scattering and inner cell reflection are at least three orders of magnitude higher than the Raman intensity. Without the filter unit the high intensity at the excitation line would produce a lot of stray light within the spectrometer unit, which than would induce background over the whole CCD chip.

The spectrometer itself is a transmitting optics-type spectrometer. In this type, lenses are used to pass light through the system in contrast to Czerny-Turner spectrometers which

 $^{^7\}mathrm{Princeton}$ Instruments - Trenton, New Jersey 08619 USA

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Figure 4.7: Plan view of the High Throughput Spectrograph (HTS). The footprint of the system is unit very compact even with the filter attached. The light is passed through the system by lenses set to a focal length of 85 mm. The width of the entrance slit can be adjusted by a micrometer screw determining the light coming in the HTS. (According to [Lew07])

use spherical mirrors instead⁸. The grating used by the HTS has $600 \frac{\text{grooves}}{\text{mm}}$ allowing the detection of all hydrogen isotopologues at one time. The true strength of the HTS is its high light throughput specified by the so-called f-number. The f-number f/# defines the ratio of focal length f and entrance pupil (or slit) D of the instrument and is a measure for the solid acceptance angle Ω

$$f/\# = N = \frac{f}{D} \tag{4.1}$$

$$\Omega = \left(\frac{1}{f/\#}\right)^2 \tag{4.2}$$

The smaller the f-number the more light is accepted by the instrument. The f-number of the HTS is f/1.8. Standard mirror-based spectrometers have f/4.0 [ACT09] or even more. That means an at least four times lower light collection power compared to the HTS. Thus this spectrometer is exactly the instrument needed for the KATRIN application hence high light throughput is important to get intense Raman lines. The little disadvantage is that image abberations are induced by the short focal length due to astigmatism. Further details about astigmatism and possible corrections are given in section 4.3.1.

The slit width b is generally determining the width of fibre image on the CCD chip and with it the amount of light coming in the spectrometer, as well. The smallest possible slit width is limited by the diffraction [Dem07]:

$$b_{\min} \approx 2\lambda f/\#$$
 (4.3)

$$\approx 2 \cdot 0.532 \,\mu\mathrm{m} \cdot 1.8 \tag{4.4}$$

$$\approx 2\,\mu\mathrm{m}$$
 (4.5)

 $^{^{8}\}mathrm{A}$ comparison between transmitting optics type and Czerny-Turner type spectrometer is given in [Lew07]

The slit width used at the HTS is $100 \,\mu\text{m}$ for Raman acquisitions and $25 \,\mu\text{m}$ for calibration measurements with spectral lamps. Both configurations are not diffraction-limited. The correlation between slit width and resolution is discussed in the following section.

4.2.9 The CCD array detector (PI PIXIS:2K)

The last element completing the Laser Raman setup is the detector chosen to enable an appropriate interplay with the other components. The PIXIS:2KB CCD array detector from Princeton Instruments comprises many beneficial features of which some are mentioned here.

- A back-illuminated chip offering a quantum efficiency of $\approx 95\%$ allowing to catch nearly every incident photon (see figure 4.10)
- A thermo-electrically Peltier element cooling down the chip to -75 °C and a permanent insulation vacuum to reduce the temperature-dependent dark noise by many orders of magnitude.
- A 2048×512 pixel array on a 27×7 mm chip generating a raw 2D-spectrum as shown in figure 4.9 (*Left*). Each pixel has a width and height of $13.5 \,\mu$ m.
- A selectable read-out speed of the ADC. The slow read-out is used for low noise acquisition and the fast but more noisy read-out is adequate for alignment purposes.

Several remarks on the resolution and the noise sources occurring during CCD acquisitions are given in the following two paragraphs.

Resolution The narrower the slit the finer the resolution, but the light coming into spectrometer is reduced at the same time. The best trade-off between light amount (peak intensity) and resolution has been found at a slit width of $100 \,\mu$ m.

Of mayor importance for the selection of a dedicated CCD detector is the geometry to fit the experimental conditions. The imaging of the slit onto the CCD is described in figure 4.8.

The spectral range given by the grating is from about 500 nm - 775 nm capable to cover all six hydrogen isotopologues. Every of the 2048 pixels covers about 275 nm/2048 = 0.13 nm. The narrower the slit the finer the resolution, but the light coming into spectrometer is reduced at the same time. The best trade-off between light amount (peak intensity) and resolution has been found at a slit width of $100 \mu \text{m}$. At a this slit width the image on the CCD has about the same FWHM⁹ as the slit. Thus 7.5 pixels each $13.5 \mu \text{m}$ wide are used to image one peak. The FWHM is in this case $7.5 \cdot 0.13 \text{ nm} \approx 1 \text{ nm}$.

The criterion for an effectual peak detection is that the pixel resolution is at least double the optical resolution [Hen07], an example is given in figure 4.9 (*Right*). The pixel coverage of the FWHM is about 7 pixels whereas 2-3 pixel are sufficient.

 $^{^9\}mathrm{FWHM}{=}\mathrm{full}$ width half maximum



Figure 4.8: Imaging of the entrance slit onto the CCD. The sketch clarifies how the slit with a height of $h \approx 6$ mm and a width of $b \approx 100 \,\mu$ m is imaged onto the CCD chip. The imaging of the two dimensional object is indicated by the top view and the side view at the same time. In the horizontal layer the grating diffracts the light coming from the slit and splits it into the different wavelengths along the x-axis. The width of the image on the CCD is determined by the slit width b. In the vertical layer the grating acts like a mirror because the light plane is parallel to the grooves of the grating. The slit image of the CCD in y-direction has a height of about 6 mm and contains the structure of the 48 single fibres.



Figure 4.9: Raw spectrum of the CCD and criterion for effectual peak detection. Left: The raw CCD-image shows the 2D spectrum of all 48 fibres arranged vertically. The sample is a H_2 : HD : D_2 mixture with a composition of $29 : 47 : 24(\pm 1)$. Right: The spectral line has a Gaussian shape marked by its spectral resolution (FWHM). The pixel resolution is the number of pixels related to a length unit along the x-axis. An effectual peak detection is permitted if the pixel resolution is that least the double of the spectral resolution. The graph shows that the FWHM of the exemplary peak is covered by more than two pixels (dots between straight lines), thus the criterion is fulfilled. [Hen07]

In the vertical direction the about 6mm broad slit coming from the fibre has to be imaged completely onto the chip. Since the chip height is 6.9 mm the fibre fits vertically without magnification.

Noise For any electronic measuring system, the signal-to-noise ratio (SNR) characterizes the quality of a measurement and determines the ultimate performance of the system. [HAM09]. The SNR value is given by the quotient of a signal (S) above a noise floor (N) consisting of several contributions (shot noise, dark noise and read-out noise) which will be discussed below.

$$SNR = \frac{S}{N}$$
 with $S = P \cdot Q_e \cdot t$ (4.6)

The signal S in equation (4.6) is given by the product of the incident photon flux P, the detector quantum efficiency at the given wavelength Q_e and the integration time t. One possibility to obtain a high SNR is to enhance the signal as much as possible. A high photon flux P is provided by the VERDI laser as a strong excitation source and the HTS spectrometer offering a high light throughput. A quantum efficiency of about 95% can be reached by back-illumination of the CCD chip (see figure 4.10).

The undesired noise components which occur on every measurement are the following [HAM09], [Dem07]:

Shot noise The so-called shot noise originates from the inherent statistical variation in the arrival rate of photons. The randomly incident photons generate electron - hole

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Figure 4.10: Quantum efficiency curve for PIXIS:2KB The back-illumination allows a quantum efficiency in the region of interest (530 - 700 nm) of $Q_E > 90\%$ [PIX07]

pairs within the semiconductor which leads to the fluctuation in the signal at each pixel on the CCD. Since the photon arrival is Poisson distributed, the shot noise is equivalent to the square-root of the signal.

$$N_S = \sqrt{P \cdot Q_e \cdot t} \tag{4.7}$$

The shot noise is inherent for every CCD and cannot be avoided. It normally constitutes a natural fundamental limit on noise performance of a CCD camera (or any light detection system)

Dark noise Independent from an incident photon flux, a thermal generation of electrons in the silicon structure is always present. The rate of the statistical electron generation is called dark current. The noise is equivalent to the square-root of the number of thermal electrons generated per pixel and second (I_D) within the image exposure time (t).

$$N_D = \sqrt{I_D \cdot t} \tag{4.8}$$

The noise rate is highly sensitive to the CCD temperature. A reduction of the temperature by about 5-9 °C halves the value of the dark current. Because of this strong dependence which can be seen in figure 4.11 (a) the PIXIS can be cooled down to -75 °C. The specified dark current at -70 °C is $0.001 - 0.006 \frac{\text{electrons}}{\text{pixel-second}}$ [PIX07].

Read-out noise The last contribution to the noise level is given by the read-out system consisting of the conversion of charge to voltage signal and the subsequent analog to digital conversion. The read-out noise is independent of integration time and less sensitive to the chip cooling, but it is dependent on the read-out rate. Two read-out modes are available for the PIXIS:2KB. At the slow 100 kHz read-out between 3.5(typical) and 6(maximum) electrons (RMS) are generated per pixel. For the fast 2 MHz mode the noise is between 14 and 20 electrons (RMS) [PIX07]. The slow read-out is the adequate choice for the long exposure times (≈ 250 s) aimed for the KATRIN application, because then the readout time of the order 10 s is negligible. The fast read-out rate is only useful for alignment purposes (see appendix A).



Figure 4.11: (a) Temperature dependence of the dark current and (b) comparison between dark noise and read-out noise. In (a) the specified dark current of $0.001 \frac{e^-}{\text{px}\cdot\text{s}}$ [PIX07] and temperature increase factor of 10 per $\approx 17 \,^{\circ}\text{C}[\text{Lew07}]$ are used in the representative graph. (b) shows that the dark noise exceeds the read-out noise for $-75 \,^{\circ}\text{C} (-70 \,^{\circ}\text{C})$ after an exposure time of about $t = 6800 \,\text{s} (t = 3500 \,\text{s})$

This finally leads to detailed expression for the signal-to-noise ratio

$$SNR = \frac{P \cdot Q_e \cdot t}{\sqrt{\frac{P \cdot Q_e \cdot t}{N_S^2} + \frac{I_D \cdot t}{N_D^2} + N_R^2}}$$
(4.9)

The impact of these noise sources on measurements is considered with some remarks:

- Figure 4.11 (b) shows that the dark current exceeds the read-out noise only after thousands of seconds for the present cooling configuration (-75 °C). This means that the noise of the measured background spectra¹⁰ is mainly dominated by the read-out within acquisition times of 100 to 1000 seconds. Binning of vertical pixels normally reduces the noise level by averaging out the fluctuations.
- The noise in a binned background spectrum is measured as the sum of dark noise and read-out noise $N = \sqrt{N_D^2 + N_R^2}$. This single fractions of dark/read-out noise are unknown. This combined noise N can be measured at each spectrum at wavelength < 532 nm where the razor edge filter completely suppressed all incident light. The noise can be measured by standard statistical procedures as being two times the standard deviation.
- The SNR is additionally affected by the shot noise when spectral lines occur in the spectrum. Then, the determination of the noise level for shot noise is more complex. The *gold standard* for KATRIN is to measure the contribution of the isotopologues in the sample with a precision 0.1%. An example is given here to clarify what this

 $^{^{10}}$ background spectrum = acquisition without excitation source
4.2. HARDWARE

means for the spectral line intensities

$$0.1\% \text{ precision} \equiv SNR = 1000 \tag{4.10}$$

$$SNR = 1000 = \frac{1,000,000}{\sqrt{1,000,000}} \tag{4.11}$$

A single pixel would need 1,000,000 counts to reach this SNR. Hence, about 450 pixels are binned per column, which then reduces the necessary counts to an average of 2,222 counts per pixel in one vertical column. Additionally, every peak is spread over several columns, for very distinct peaks it is more than 10 - 15 columns. The sum of all intensity lines has than be greater than 2,222 counts. In figure 4.12 a possible peak is shown fulfilling SNR of 1000 only taking shot noise into account. It shows that even if dark current and readout noise are suppressed noticeable the binned and averaged peak height has to be at least 355 counts.

This shows that for a suppression of shot noise binning is unavoidable. In that case the high resolution (2048x512 pixels) of the PIXIS:2KB is beneficial.

The noise sources described above are statistical uncertainties because it is possible to minimize the noise they generate by longer acquisition time or multiple binning of several spectra.

A further discussion about noise is placed in section 6.4.8.4 of chapter 6 where all noise sources are included and compared with the results of long term stability measurements. The investigations show that additional systematic errors are resident on the spectrum. These uncertainties are noise and drift of the excitation laser, its pointing stability and unaccounted cosmic rays.



Figure 4.12: Shot noise on an example peak with SNR=1000. The graph shows a Gaussian distributed spectral line with $\sigma = 2.5$ px spread over several pixel. The discrete sum over all intensities at each pixel under the curve is 2222. This is multiplied by the number of rows binned vertically, which is about 450. The overall counts contained in this peak is than approximately 1 million corresponding to a signal-to-noise ratio of 1000 only including shot noise. The peak height of this spectral line is about 355 counts.



Figure 4.13: Post-acquisition procedures of the raw data. Explanation in plain text.

4.3 Acquisition and processing software

Several treatments of the raw data are necessary before a prediction a the quantitative composition is possible after the acquisition by the CCD detector (see figure 4.9 (*Left*)). Figure 4.13 contains an overview of the various software post-processing routines.

- 1. The spectrum is stretched along the x-axis of the CCD detector. The wavelength calibration is done once by spectral lines from spectral lamps (like mercury or neon). From that a table is created which assigns a wavelength value to every pixel of the x-axis.
- 2. Then aberrations due to astigmatism of the spectrometer are occurring on the raw two dimensional data. The correction of this effect is found in subsection 4.3.1.
- 3. The detector is hit continuously by cosmic rays during the acquisition, the peaks arisen from these events have to be removed. The corresponding procedure is explained in subsection 4.3.2.
- 4. The efficiencies of the grating, the CCD and the coatings are wavelength dependent. This is accounted by the measurement of the integral spectral efficiency of the system. The correction function is created from the difference of a theoretically calculated and experimentally measured black body radiator spectrum. At the time of the work the black body light source was not yet ready to use.
- 5. The preprocessed 2D-spectrum is binned, which means that all intensity values within one column are averaged to obtain a mean intensity value for each pixel on the x-axis (wavelength).
- 6. The processed spectrum is the input for a quantitative analysis finally outputting the isotopic composition. The analysis method selected for the LARA system is the indirect hard modeling approach. The functional principle and first result are reported in chapter 7.

4.3.1 Astigmatism correction

The mayor advantage of the HTS spectrometer is its high light collection capability using short focal length and lenses for imaging. But it comes with an unwanted side-effect, as

well. Being a well known problem with spectrometers in general, astigmatism always occurs if imaging with imperfect lenses on short focal lengths. The result is that the image of the entrance slit on the CCD is bent parabolic. The impact of distortion of the slit image on the binned peak is shown in figure 4.14. Its shape gets very deformed even if the area under the peak is preserved, but it is not conform to a theoretical predicted spectral line needed for quantitative analysis.

Therefore a software correction routine written by Richard Lewis [Lew07] is used to restraighten the lines. The tool AstCalc calculates once the bending of one reference slit image acquired for example by an 633 nm laser pointer. The program determines the shift of the highest intensity of each row relative to the middle row (y=255) as seen in figure 4.14 (d)

When a recorded Raman spectrum is processed the individual shifts are applied to each row to straighten the slit image. However, this algorithm only works properly for one wavelength at which the reference measurement (e.g. with the laser pointer) has been performed. The characteristic of the astigmatism is wavelength dependent and gets more severe for higher wavelength. In the optimum case, the astigmatism determination by Ast-Calc has to be done for each individual wavelength to reach the best achievable correction.



Figure 4.14: Influence of astigmatism on binned peak shape. The top three graphs show the image of the entrance slit on a two-dimensional intensity plot, e.g. a Raman line on the CCD chip. From left to right increasing astigmatism is added intentionally. The one-dimensional graphs below show the line shape after binning over all rows. The astigmatism-less scenario (a) preserves the ideal Gaussian shape. If light astigmatism (b) occurs the line shape resembles to be Gaussian, but the the mild broadening causes a reduction of the peak height (shown by the red, dashed line). If the astigmatism gets severe (c), the resulting peak becomes distorted unambiguously. (d) The astigmatism correction shifts are calculated from the deviation in x-direction relative to the middle row.



Figure 4.15: Cosmic Ray event. The graph shows the Q-branches of the isotopologues T_2 , DT, HT, HD and H_2 in one row of the CCD. At pixel number 1088 a very sharp and thin peak appears which is caused by an incident cosmic ray. Note that the intensity (height) of a cosmic ray event is averaged out when binning over about 450 CCD rows.

4.3.2 Cosmic ray removal

Our earth is hit permanently by cosmic rays. If their energy is high enough they are able to produce secondary particles in the atmosphere, mainly electrons, positrons and muons. These particles then form showers approaching the earth surface. They are able to interact with single pixels of the CCD and generate electrical charge depending on the type, the charge and the kinetic energy of the particle. One exemplary cosmic ray event is shown in figure 4.15. The event is irrelevant, if the x-position is out of the region of interest. But the situation gets unfavorable if the cosmic ray coincides spatially at the wavelength of a spectral line, leading to a miscalculated intensity or a faked peak. Even if the particle hits pixels in the vicinity of a peak, it could have great influence on the baseline fit which is essential for appropriate peak determination.

Especially for long exposure times (> 1000 s) cosmic rays can become a serious issue. The artifacts introduced by cosmic ray events are removed by the software routine *DCRR* from Richard Lewis, therefore there is no need for active or passive shielding of the cosmic rays. The routine uses the double differentiation to create a pattern distinct for the spiked cosmic ray events. This pattern is used for tagging and subsequent removal of the tagged pixels. A detailed description is found in figure 4.16.

4.3.3 Automated acquisition

During a KATRIN measurement period of about 60 days the Laser Raman system has to run completely unattended for 24 hours a day. Therefore acquisition, software postprocessing and analysis have to be performed fully automatically. In the course of this



Figure 4.16: Principle of 'Double-differential Cosmic Ray Removal' (DCRR). A double-differentiation is performed along the y-axis. A singular cosmic ray event would generate the distinct picture shown in the figure. If this pattern appears above a certain threshold the cosmic ray is tagged. A normal Raman peak has naturally a smoother slope and is spread over several pixels, thus it hasn't the distinct pattern. Finally the pixel is replaced by the harmonic mean value along the chosen column. For further reading, the PhD-Thesis of Richard Lewis is recommended [Lew07].

thesis a custom LabVIEW VI^{11} was written which provides automated acquisition and processing of measurements.

The VI allows direct access to PIXIS functions, like temperature setting or acquisition, without the software WinSpec from Roper Scientific. In parallel, the voltage signal of the photo diode is recorded. The tools AstCalc and DCRR described above as well as binning are used for the post-processing during the acquisition of one frame (spectrum). The acquisition time of the actual frame is used for the post-processing routine of the previous frame whereby no acquisition time is wasted.

The user only has to chose the measurement settings and to define the resource files for wavelength calibration and astigmatism correction. The software finally creates up to three time-stamped files for each measurements: (1) the raw spectrum in WinSpec .spe format, (2) the processed spectrum as a two column text file and (3) the trend of the photo diode signal.

A detailed description of the VI is found in appendix D.

 $^{^{11}\}mathrm{VI}{=}\mathrm{Virtual}$ Instrument, the typical denotation for a LabVIEW programme

CHAPTER 4. EXPERIMENTAL SETUP

Chapter 5

First Laser Raman measurements with tritium at TLK

The Laser Raman System described in the previous chapter has already been in the field at the TILO¹ test setup in 2008 and showed the feasibility of monitoring the dynamic changes in the isotopologic composition [Lew08]. The precision reached for short exposures of 100 s was reported at the $\pm 1\%$ level and for 1000 s the $\pm 0.1\%$ has been reached.

All TILO measurements only have been performed with H_2 , HD, D_2 . As subsequent step, measurements at the Inner Loop should follow including all six hydrogen isotopologues. But since the auxiliary tritium loop LOOPINO was still under construction, all measurements within the scope of this thesis were performed with static (non-flowing) mixtures.

In this chapter the first Laser Raman measurements with tritium at the TLK are reported. Additionally, the capability of simultaneous monitoring of all six hydrogen isotopologues is proven, background effects of the cell are analyzed and a first detection limit for these isotopologues is stated.

5.1 Preparation of the measurements

After the Raman system has been transferred from its former location at the TILO setup to room 174 of the TLK, the setup has been modified to provide laser-safety (described in section 4.2.5) and tritium-safety. The latter is ensured by a connection to the hood of the TLK ventilation system. Figure 5.1 shows a picture of the system at its actual position.

The tritium containing samples are mixed and filled into the Laser Raman cells by the CAPER team. The CAPER facility [Bor05] is not especially designed for high accuracy sample preparation, but for the first qualitative measurements it is sufficient. Mixtures or pure gases without tritium are produced at a simple gas filling system. Both procedures and the corresponding mixing hardware are presented in the appendix B in more detail.

The laser system has been optically aligned, spectral-calibrated and the astigmatism correction files were generated, when it was re-commissioned after the transfer. From time to time the system needs to be re-aligned, especially if cells are replaced or additional

 $^{^{1}}$ TILO = Test of Inner Loop; performed outside the TLK

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components are included into the optical path. The description about all steps necessary for the system preparation is found in the appendix A.



Figure 5.1: LARA-setup at actual measurement location. The picture shows the ready-to-measure LARA setup at room 174 (TLK)

5.2 Measurements of all hydrogen isotopologues

All spectra presented in this and the following chapters are in wavelength representation. The usual representation is the Raman shift, because it is independent of the excitation wavelength. This notation is beneficial to compare high resolution spectroscopic measurements with data reported in literature. However, the goals of this study were to demonstrate the capability and performance of the actual setup, thus the wavelength representation is adequate. The determination of the excitation wavelength of the laser by a wavemeter or a high-resolution spectrograph will be performed for future measurements when accurate line positions are studied.

The overview on the various hydrogen samples presented in this chapter is given in table 5.1. All mixtures were in thermodynamical equilibrium when the correspondent measurements were performed. The samples are chosen in a way that each of the six hydrogen isotopologues is a prominent constituent in one of the mixtures. The mixtures without tritium could be filled up to 1 bar, but the tritium containing samples are limited to an activity of less than 10^{10} Bq. This sets an upper pressure limit for the sample containing almost pure T₂ to about 13 mbar. If other hydrogen isotopologues as H₂,D₂ are added to the pure tritium, the amount of T₂ shrinks under formation of HT and/or DT in thermodynamical equilibrium, like in sample 5 and 6.

5.3. DISCUSSION OF SPECTRA

Table 5.1: Overview on samples discussed in chapter 5. The accuracies of composition of the stated sources are: (1) purity 6.0 (99.9999%); (2) purity 2.7 (99.7%); (3) values from CAPER-gas chromatograph with an accuracy of $\approx 10\%$, the stated values are averages of two independent analyses (may not add up to 100%); (4) accuracy as quoted. The labeling and the order of the samples are not chronological, but chosen for purposes of clarity.

Key: ^{gbc}: pressure measured under CAPER glove box conditions ($T = 25-28 \circ C$); ^{sc}: pressure measured under standard conditions; nr: not recorded. Sources: (1) Messer-Griesheim, (2) Air Liquide, (3) CAPER, (4) Linde Gas.

| Sample | Pressure [mbar] | $\mathrm{H}_2[\%]$ | HD[%] | $D_2[\%]$ | $\mathrm{HT}[\%]$ | $\mathrm{DT}[\%]$ | $T_2[\%]$ | Source |
|-------------------------|-------------------------|---------------------|---------------------|------------------------|-------------------|-------------------|-----------|--------|
| S1 (pure H_2) | 941 ± 1 | 100 | - | - | - | - | - | (1) |
| S2 (pure D_2) | 905 ± 1 | - | - | 100 | - | - | - | (2) |
| S3 (pure T_2) | $13.0 \pm 0.2^{ m gbc}$ | \mathbf{nr} | nr | $\mathbf{n}\mathbf{r}$ | 2.2 | 5.0 | 96.0 | (3) |
| $S4 (mix D_2/H_2)$ | 985 ± 1 | 29 ± 1 | 47 ± 1 | 24 ± 1 | - | - | - | (4) |
| S5 (mix T_2/H_2) | $95.6\pm0.2^{\rm sc}$ | 66.0 | 3.5 | $\mathbf{n}\mathbf{r}$ | 24.0 | 0.77 | 2.9 | (3) |
| S6 (mix T_2/D_2) | $93.4\pm0.2^{\rm sc}$ | nr | 1.9 | 69.0 | 0.30 | 23.0 | 2.2 | (3) |
| S7 (mix $T_2/D_2/H_2$) | $154.8\pm0.2^{\rm gbc}$ | 82.0 | 8.3 | nr | 8.5 | 0.49 | 0.27 | (3) |

The Raman measurements described in this section were performed with the following parameters, if not stated otherwise: Laser power 5 W, acquisition time 1000 s and a slit width of 100 μ m. The spectra were subsequently treated by astigmatism correction and cosmic ray removal. The spectra of the pure and binary mixtures are found in figure 5.2. On the left side of this figure the spectra of the pure isotopologues (H₂, D₂ and T₂) are shown and on the right side the spectra with significant amounts of HD, HT and DT. The spectrum containing all six isotopologues is found in figure 5.3.

5.3 Discussion of spectra

In this section the spectra of the samples S1-S6 (see figure 5.2) and S7 (see figure 5.3) are discussed.

5.3.1 General comments

• In the pure spectra of H_2 (sample S1) and D_2 (sample S2) contaminations by other isotopologues are visible. The spectrum of pure H_2 contains a notable D_2 line. The amount of D_2 in this mixture can be approximated by the intensity ratio of the Q-branches:

$$c(D_2)_{\text{rel.}} = \frac{Q_1(D_2)}{Q_1(H_2)}$$
(5.1)

$$=\frac{7}{13800}=0.05\,\%\tag{5.2}$$

This value is higher than the claimed hydrogen purity of 6.0 (\geq 99.9999) because of residual gas in the filling device from the previous filling of D₂. In the pure D₂ sample HD was detected in a concentration of about 0.2 %, which is within the claimed purity



 $T_2(Q_1)$ $\mathbf{D}_{2}(\mathbf{Q}_{1})$ S6 (93.4 mbar) 600 S3 (13.0 mbar) $\mathbf{T}_{\mathbf{A}}(\mathbf{Q}_{\mathbf{A}})$ 3000 (S 400 2000 DT(Q Intensity (arb.) 1000 - $DT(O_1)$ $DT(S_1) HD(Q_1)$ $DT(Q_1)$ 300 150 HT(Q₁) (**C** 100 200 50 100 $N_2(Q_1)$ 0 0 620 640 660 680 700 720 740 640 680 700 720 740 540 560 580 600 620 660 600 Wavelength (nm) Wavelength (nm)

Figure 5.2: Raman spectra of all hydrogen isotopologues. Explanation and discussion are found in the text. The rotational lines of the prominent constituents are labeled with the rotational number of the initial state J''. Note the break in the intensity scale is to visualize intense and weak lines at the same time.



Figure 5.3: Raman spectrum containing all hydrogen isotopologues. The spectrum contains Q-branches from an intensity of about 3000 a.u. of the main component H_2 down to 2 a.u. of the N₂ contamination. Further explanation and discussion are found in the text.

of 2.7 (\geq 99.7). Further, a line at the Raman position of oxygen is visible. But, from the absence of nitrogen it can be excluded that residual air was in the cell.

The detection of these extremely rare impurities is only possible by the use of the Q_1 branches. The just described impurities would be invisible within the line congestion and the noise of the S_0 -branches and valuable information for the KATRIN measurements would be lost.

• The rotational lines of the S_0 -branch in the spectrum of sample S3 with almost pure T_2 are labeled with the rotational quantum number of the initial state (J''). The rotational line for J'' = 0 is not visible, because the line is suppressed by the razor edge filter as already discussed in chapter 4.

5.3.2 Actual mixing performance and capability of TLK facilities

The measured spectra indicate the performance of sample preparation of the facilities within the TLK. The various methods of mixing are described in appendix B.

• Pure tritium. Sample S3 is a gas which is provided by the TLK infrastructure as pure tritium. The according spectrum and the values from the CAPER gas chromatograph clearly show that the T₂ is coming along with impurities of DT and HT of about 5%. The highest possible tritium purity provided by the isotope separation system (ISS) is about 98% [Doe02]. To some extent these species also form during the gas cleaning by exchange reactions with H₂ and D₂ in the stainless steel surface and subsequent equilibration at the permeator.

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• Mixture samples. Sample S5 is a mixture of 'pure' tritium with pure protium (H₂) from a bottle. Sample S6 is about the same but instead of protium the mixing was performed with deuterium. The spectra reveal that in the T/H mixture traces of D₂, DT and HD are contained even if not recorded at CAPER gas chromatography (see table 5.1). The T/D mixture is impurified by the H-containing isotopologues on the other hand. Mixing vessels with stainless steel surfaces and catalysts have a kind of memory effect. Molecules from previous mixtures diffused and stored in the surface are released by exchange reactions when the mixture sample is changed(e.g. [Abr05], [Mar05]). These effect always introduce a deviation between the desired and the actual isotopic composition of the mixed gas. Therefore, it is hard to prepare exact, calibration-suitable mixtures, in particular for the CAPER facility, but as well in general when mixing hydrogen gases.

These facts again stress the necessity of the quantitative measurements of the isotopic purity. Especially in the early stages of the KATRIN operation, the isotopic composition is anticipated to change because of exchange reactions at the stainless steel components. The surface of Inner Loop and WGTS is approximately 8 m^2 . Laser Raman spectroscopy will monitor these changes and will be useful to make assumptions of the tritium contamination of the source surface.

Later it will be important to measure the repurged tritium batches coming from the ISS. It is assumed that the provided purity from the separation system slightly alters from batch to batch.

5.3.3 Simultaneous measurement of all hydrogen isotopologues

Figure 5.2 shows that the Q_1 branches surrounded by the O_1 and S_1 lines can be detected from the lightest (H₂) to the heaviest (T₂) hydrogen isotopologue. Within the spectra of samples S1-S5 hardly no overlap of the lines occurs. In the spectrum of sample S6 (mixture of T₂ with D₂) some overlap of S/O lines from T₂, DT or D₂ with the Q-branch of another species is visible. The interference of the Q_1 branch of DT and the $S_1(J''=2)$ line of T₂ is already mentioned in the section 3.4 of the Raman effect chapter. The main constituent in the gas for KATRIN measurements will be T₂ ($\approx 90 - 96\%$) with a little amount of DT ($\leq 9\%$) and even less amounts of the other isotopologues. For this reason the said interference has to be taken into account if the quantitative analysis is performed. Another interference is found at the Q_1 branch of D₂ and the $S_1(J''=1)$ line of DT. DT will not be a major constituent of the gas mixture for KATRIN. The D₂ amount would rise by about 0.1% by an assumed concentration of 5% for DT and about 50 times weaker S-branches than Q-branches.

The final test for the capability to record all hydrogen isotopologues simultaneously is the measurement of sample S7, being a mixture of $T_2 + D_2 + H_2$ in thermodynamical equilibrium containing every possible hydrogen isotopologue at a measurable concentration. The spectrum is shown in figure 5.3. The sample pressure is about 150 mbar, however, a bit higher than the assumed operation pressure at the Inner Loop. The detection of the components ranges from 80% downto 0.3% and less. The weakest line is T_2 with an intensity of about 20 a.u. and the strongest is H_2 with about 3000 a.u. covering a range of a factor of 150.

5.3.4 Background effect in cell

The spectrum of nearly pure tritium (sample S3 in figure 5.2) exhibits that the peaks are not settled on a flat baseline. In every Raman spectrum a background is existent on which the real Raman peaks are resident, best visible at low cell pressures. This observation initially appeared to be puzzling, but an acquisition of an evacuated Raman cell answered that question. Without any molecules inside the volume, all peaks appearing in the spectrum have to be originated to the cell itself. The spectrum of this evacuated cell is shown in figure 5.4. At the least three effects explain the structures appearing

- The reason for the peak-like structure around 550 nm is that the excitation light induces Raman scattering in the fused silica of the cell windows. Measurements of Raman spectra in glass where done in the early 1930th resembling clearly to the spectrum in figure 5.4 [Kuj38]. The Raman light is reflected specular and diffuse at the cell walls into the collection optic as sketched in figure 5.5. Raman light from SiO₂ seizes the same wavelength region as the S_0 -branches of the hydrogen isotopologues. This demonstrates another shortcoming of the pure rotational S_0 -branch use for quantitative analysis: there is an unknown contribution of the underlying SiO₂ Raman lines. The rotational-vibrational O_1, Q_1 and S_1 branches, however, are unaffected.
- Independently, fluorescence is mainly generated by point defects in the glass material, originated by impurities (like rare earth elements), ions or previous radiation



Figure 5.4: Spectrum of evacuated cell. Acquisition parameters: laser power 5 W; exposure time 1000 s; slit width 127 µm. The spectrum shows two independent features resident on any other spectrum, too. The peak like structure around 550 nm is due to Raman scattering within the fused silica of the cell windows. The marked peaks (cm^{-1}) agree with the assignment published in [Wal81] within the limit of $\pm 25 \text{ cm}^{-1}$. In [McM86] the peak at 3690 cm⁻¹ is suggested to arise from vibrational excitation of free hydroxyl-sites in the glass. The slow declining feature is due to fluorescence effects in the windows and contributions from the excitation line of the laser to its Lorentz-wing [Dem07].

[SCH04]. In the last-mentioned publication by SCHOTT various fluorescence emission spectra of different glass-types for excitation at 550 nm are shown. The shape and the width of these fluorescence peaks are very similar to the feature observed in figure 5.4 for $\lambda > 570$ nm. The material fused silica used for the Raman cell windows is naturally very pure due to the production process therefore the fluorescence yield is lower compared to other glass types.

• Additionally, the whole spectrum is subjected to the far-ranging Lorentz-wing of the excitation line profile [Dem07]. Even though the filter cuts incoming light with a wavelength < 532 nm, the light with longer wavelength of the Lorentz-wing can pass. Rayleigh scattered light alone has an intensity about 1000 times higher than Raman scattered light. Figure 5.5 shows how reflections from windows and walls can reach the collection optics piling up at the same wavelength as the Rayleigh-light. In figure 5.4 the excitation line is visible with an intensity of about 10 a.u. in spite of the suppression by the filter by $10^8 - 10^9$. If the filter wouldn't be used the intensity at 532 nm would be about 1 billion. Thus, the Lorentz-wing contribution to the spectrum is not negligible, even if not implicitly visible.

The prediction or modeling of the background is very difficult since all occurring effect have their very own dependence on the cell geometry or position as it is for the orientation of the laser beam. Measurements not reported in this thesis have shown that the features due to Raman scattering in SiO_2 and to fluorescence don't scale proportional. In addition, the



Figure 5.5: Raman scattering, fluorescence and reflexions from the cell interior. The sketch shows two possible effects occurring in the cell and their arrival at the collection optics. (a) In the first window Raman scattering or fluorescence generation is sketched. (b) On the second window a back-reflexion is adumbrated increasing the Lorentz-wing of the excitation wavelength. The collection optics is reached by the light in both cases by diffuse or specular reflections.



Figure 5.6: Investigation of the background features. The spectra of the evacuated cell and the cell filled with air are subsequently acquired after venting of the cell. Laser power: 3 W, exposure time: 1000 s and slit width: 127 µm. *Left:* The coincidence of both graphs shows the regions where the spectrum is dominated by the cell background. *Right:* The difference spectrum is totally free from background features.

convolution of quantum efficiency of the detector and grating efficiency of the spectrometer distorts the background spectrum.

The successful removal of the cell background is shown in figure 5.6. In this case an evacuated cell has been installed at the cell holder and a spectrum was acquired. Afterwards the cell was ventilated by ambient air and the same measurement was repeated with the same acquisition parameters. Finally, the spectrum of the evacuated cell was subtracted from the spectrum with air inside. The resulting difference spectrum looks as clean as if only air is in the beam path.

The result is not reproducible if one spectrum of a sample in cell A is intended to be corrected by an evacuated cell B because of small differences in the windows and the cell geometry.

5.3.5 Detection limit for hydrogen isotopologues

The detection limit is a measure of the sensitivity of detector systems. The inherent noise of the spectrum (dark and readout noise) can be measured according to figure 5.7. A peak can be detected if its height is at least three times the noise level 3σ [Lon83]. The minimal detectable partial pressure is corresponding to this minimal peak intensity (signal-to-noise ratio SNR_{min} = 3). The total cell pressure corresponds to the sum of the intensity of all available peaks, assuming equal scattering intensities for each isotopologue.

Table 5.2: Calculation of the detection limit. The values for the intensities and the total pressure are derived from sample S3. The calculation is performed according to equation (5.4).

| I_{T_2} | $I_{\rm DT}$ | $I_{\rm HT}$ | $\sum I$ | $I_{\rm min} = 3 \cdot \sigma$ | $p_{ m tot}$ | p_{\min} |
|--------------------|--------------|--------------|----------|--------------------------------|---------------------|----------------------|
| 503 | 34 | 14 | 551 | 0.19 | $13.0\mathrm{mbar}$ | $0.015\mathrm{mbar}$ |

An approximation for the detection limit is:

$$\frac{p_{\min}}{p_{\text{tot}}} = \frac{I_{\min}}{\sum_{i} I_i}$$
(5.3)

$$p_{\min} = \frac{\frac{i}{3 \cdot \sigma}}{\sum_{i}^{\text{peaks}} I_i} \cdot p_{\text{tot}}$$
(5.4)

The calculation of the detection limit from the spectrum of sample S3 (pure T_2) can be found in table 5.2. The resulting minimal detectable partial pressure (3σ) is about 0.015 mbar at 5 W and 1000 s acquisition time. A reduction of the acquisition time down to 250 s increases this level by about a factor 4 being about 0.06 mbar meeting KATRIN requirements.



Figure 5.7: Noise determination. The figure shows the part of the spectrum around the excitation line at 532 nm, here all light is suppressed by a the razor edge filter. The noise is measured in the marked region. The frequency counts show a nearly Gaussian intensity distribution. The level of detection is defined as $I_{\text{LOD}} = 3 \cdot \sigma$ according to [Lon83].

5.3.6 Conclusions

The first Laser Raman measurements with tritium at the TLK have been performed successfully. The followings conclusions can be drawn from the first results reported above.

- The simultaneous monitoring of all six hydrogen isotopologues is possible with the present setup. Only two overlaps of spectral lines exist, but these are manageable.
- The Raman measurements are possible within a wide dynamic range. Main constituents of about 100 mbar down to traces near the detection limit < 0.1 mbar can be detected at the same time. This feature is necessary for the KATRIN scenario.
- All acquired spectra are subjected to background features induced by the cell. The subtraction of the background features is possible by a spectrum of the same evacuated cell at the same cell position. This method may not be convenient in longer measurement terms, because the in-line evacuation disturbs the measurement procedure. In section 6.4.4 of the following chapter it is shown, that the background intensity rises during continuous laser emission. It can not be anticipated that the background spectrum from the evacuated is able to be used as a correction for a time span of 60 days. An accurate fitting routine taking into account the background of the actual spectrum is a more elegant way to allow precise quantitative analysis.
- The Raman scattering in the SiO₂ of the windows adds a peak like structure to spectral regions where the S_0 branches are found. This background effect and the congestion of the Raman lines at given resolution, impede the use of the S_0 branch and stress the advantages of the Q_1 branches.
- The detection limit for an acquisition of 1000 s at 5 W is about 0.015 mbar exceeding the KATRIN requirements. Therefore shorter measurement intervals are proposed. A duration of about 250 s means a lower sensitivity of a factor of about 4, but this value is closer to the foreseen β -spectrum scanning duration of 5 min [KAT05].
- In this chapter the precision and detection limit were derived from a single acquisition regarding noise level and signal strength of the spectrum (SNR). This value represents the theoretical optimum value for the precision of the measurement. In long term measurements the reproducibility of the spectral line intensity has to be proved regarding statistical fluctuations from a multitude of spectra.
- The influence of the cell position on the signal performance and background effect has to be investigated in more detail.
- The feasibility of the mixing of gaseous samples containing hydrogen isotopologues is limited in accuracy and precision. This constrains the generation of definite calibration samples for quantitative analysis.

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Chapter 6

Investigation of systematic effects with present setup

This chapter deals with the characterization of the performance and systematic effects within Laser Raman measurements. In section 6.1 a short introduction is given, followed the explanation of the analysis routine used for all investigations in section 6.2. Section 6.3 sums up the results of several systematic investigations which have been shifted to the appendix for the sake of clarity. The major section 6.4 is about the long term measurements and related effects. Finally, a summary and a conclusion on the impact for KATRIN are given in section 6.5.

6.1 Motivation and intentions

The capability of the system to monitor all six hydrogen isotopologues at the same time was shown in the previous chapter. All reported results are based on single measurements. For KATRIN it is inevitable to investigate the behavior of the system in long term experiments. In particular, the reproducibility of absolute and relative intensities is a main objective of the studies. This chapter reports on systematic investigation of the cell position, the light exposure and the long term performance. The basis for all performed measurements is that always the same composition in a static cell is used which should be well equilibrated. Thus, it can be excluded that intensity variations should be related to a change in composition.

6.1.1 Terms and Definitions

In the sections below terms like 'absolute, relative intensity or precision' are frequently used. These terms are defined as following:

Peak intensity is a value for one peak of a specified isotopologue in a single measurement. It can be determined in two different ways. One possibility is to use the peak height, the other possibility is to use the area under the peak. The differences and advantages of both options are described in detail in section C.1 of the appendix.

- **Relative intensity** or normalized intensity, is the value for a peak which is normalized to the sum of all other peaks forming the composition. It is normally stated as a percentage in this report. These values shall not be taken as being directly proportional to the partial pressure of the constituents since the spectral efficiency and the scattering tensors are not yet implemented in this thesis.
- **Precision** is the significant quantity which defines the reproducibility of the measurements. A measure for the precision is $\Delta I = \frac{2 \cdot \sigma}{I_{\text{aver.}}}$ where σ is the standard deviation divided by the average intensity in repeated measurements.

6.2 Analysis procedure

The series of measurements are analyzed by an appropriate procedure which provides equal treatment of every spectrum and minimum bias from the user. The analysis method constitutes a two-step procedure. The first part is the so-called post-processing by routines (DCRR, Astigmatism correction,...) described in chapter 4.3 about the experimental setup. These are executed during the automated acquisition. The second part of the analysis is done after all spectra are acquired (off-line).

A LabVIEW program has been written to automatically analyze a multitude of subsequent spectra. The first step of this procedure is the subtraction of the baseline which is needed before the execution of the ORIGIN Peak-Analyzer. Its return values for each Q-branch in the spectrum are 'peak area', 'peak height', 'FWHM' and 'peak center'. In addition, the 'intensity' of the fluorescence background is determined by the difference of the spectral intensity at two points ($x_1 = 596.037 \text{ nm}$ and $x_2 = 762.164 \text{ nm}$). The background determination is visualized in figure 6.1.

The average values of the photo diode signals acquired every second during the exposure time of one measurement are used as an estimate of the laser power. Thus, peak information from ORIGIN Peak-Analyzer for each isotopologue, the background intensity and the mean photo diode signal are stored for each measurement, complemented with a time stamp.

For a precise determination of peak areas or peak heights it is vital to subtract the baseline very efficiently. In the actual case the major contributions to the baseline are fluorescence and the Lorentz-wing, incorporating dark and read-out noise as well. In this analysis the baseline is not determined by a single-function fit. Instead, the baseline is described by a combination of linear functions with about 30 base points snapping to the actual spectrum. The deviation from an 'optimum' baseline is within the noise level, which is sufficient.

6.3 Investigation of systematic effects

Besides the analysis of long term measurements a number of systematic effects in Raman measurement and analysis have been investigated in detail. The measurements and discussion can be found in appendix C. The results are summarized here:

• The intensity of the spectral lines is determined by the peak area. The investigation reported in appendix C.1 shows that this method is inherently more accurate



Figure 6.1: Determination of the background intensity. The amount of fluorescence background is measured as the difference of the counts at pixel 580 (596.037 nm) and pixel 1900 (762.164 nm). At both points the average of the surrounding five pixels is used to minimize the noise.

and twice as precise as the determination by peak height. The described analysis procedure is useful for the systematic investigations. However, for KATRIN a multi-variate analysis program is intended to be used. The goal is a quantitative analysis which is expected to provide accurate results and reduces noise by hard modeling of the all constituents and baseline. First results from this approach are presented and discussed in the following chapter 7 further below.

- Between measurements cells are removed and subsequently the same or another cell is re-inserted. The influence of this re-insertion process has been measured for an extensive number of spectra. The results and discussion is found in appendix C.2.1. The new cell holder produced during the course of this thesis provides a very precise reproduction of the cell position. It features a very tight dovetail for the cell and has a stop at its end, which permits a precision of less than 0.5% for the absolute values. If only relative intensities are taken into account, a precision of < 0.17% is reached, which ensures that the exchange of cell doesn't introduce great systematic uncertainties.
- In addition, measurements with lateral cell shift have been performed to investigate the reproducibility (appendix C.2.2). It showed that the 10 year old laser windows exhibit a non-isotropic absorption at the surface which doesn't appear for a new window. The reason for the region of higher absorption is possibly the degraded anti-reflection coating. The precision of the relative intensity is about 0.2%.
- The investigation with different laser powers showed that the determination of relative peak intensity is connected to the light exposure on the CCD (appendix C.3). The resulting dependence is plotted in 6.2. At a light exposure of less than 50 % of

the maximal reference value, the intensities of major mixture constituents are relatively more suppressed than smaller ones. Therefore the relative intensities change. It is important to remember that this behaviour is not directly connected to the laser power but in general to the amount of total light exposure. A misalignment of the collection optics and fibre or a beam walk which lowers the collected light by 50 % should have the same effect as a tune-down of the laser from 5 to 2.5 W. For a quantitative analysis, in particular for KATRIN runs, it will be of major importance to monitor the laser power very precisely and guarantee that the alignment is extremely stable.

The origin for the light exposure dependence on the relative intensities is related to the performance of the analysis at low signal-to-noise ratios. The detailed explanation is found in appendix C.3.



Figure 6.2: Relative intensity dependency on nominal laser power. The variation in the relative intensity determined at each laser power setting vanishes for power higher than 2 W. The D_2 peak representing the major component of the mixture is suppressed for the low powers (< 2 W). The minor constituents DT and HD are elevated.

6.4 Long term measurements

6.4.1 Outline of the measurement philosophy

In section 5.3.5 of the previous chapter the detection limit has been introduced as a measure of the sensitivity of the system. With long term experiments the reproducibility of the Raman spectra can be investigated in order to make a statement on the precision of the measurements.

The measurements with a non-flowing (static) sample in thermodynamical equilibrium are useful for stability investigation of the system. All noise or variations occurring in the spectra and data then originate in the measurement and analysis procedure. The long term measurements have been performed with three different samples (see table 6.1 with

Table 6.1: Overview on the samples discussed in chapter 6. The composition of the gas is either determined by the certificate of (1) Linde Gas or by the gas chromatography of (2) CAPER. Composition accuracy from (1) Linde Gas as quoted. The accuracy of the (2) CAPER composition is $\approx 10\%$ (gas chromatograph), the stated values are averages of two independent analyses (may not add up to 100%). The spectrum of sample S4 was already shown in figure 5.2 on page 60, the spectra of sample S8 and S9 are shown in figure 6.3. Key: nr: not recorded.

| Sample | Pressure [mbar] | $\mathrm{H}_2[\%]$ | HD[%] | $D_2[\%]$ | $\mathrm{HT}[\%]$ | $\mathrm{DT}[\%]$ | $T_2[\%]$ | Source |
|--|------------------------------------|---------------------|---------------------|---------------------|-------------------|-------------------|-----------|---------|
| S4 (mix D_2/H_2) S8 (mix $T_2/D_2/H_2$) | 985 ± 1 103 4 ± 0 2 | 29 ± 1 22.36 | 47 ± 1 27.45 | 24 ± 1 12.85 | - | - 0.74 | - 9 22 | (1) (2) |
| S9 (mix $T_2/D_2/T_2$) S9 (mix T_2/D_2) | 103.4 ± 0.2 431.5 ± 0.2 | 22.50 nr | 27.45 nr | 87.37 | 0.09 | 5.86 | 0.08 | (2) (2) |



Figure 6.3: Spectra of samples S8 and S9. The spectrum of sample S8 (*left*) and sample S9 (*right*) are acquired in 250 s with a laser power of 5 W.

| Run | Sample | Cell | Exposure time | Number of acquisitions | Date |
|-----|---------------|------|------------------|------------------------|---------------------|
| 1 | S4 | 2 | $1000\mathrm{s}$ | 577 | 14.04.09 - 21.04.09 |
| 2 | S4 | 2 | $250\mathrm{s}$ | 2400 | 21.04.09 - 28.04.09 |
| 3 | S8 | 1 | $250\mathrm{s}$ | 1329 | 30.04.09 - 04.05.09 |
| 4 | S9 | 2 | $250\mathrm{s}$ | 918 | 04.06.09 - 08.06.09 |
| 5 | S9 | 2 | $250\mathrm{s}$ | 751 | 08.06.09 - 10.06.09 |
| 6 | $\mathbf{S9}$ | 2 | $250\mathrm{s}$ | 1547 | 10.06.09 - 15.06.09 |

Table 6.2: Measurement overview of long term acquisitions. The table below contains all long term runs discussed in chapter 6. The laser power was set to 5 W for each run.

the corresponding spectra in figure 6.3) in six different runs (see table 6.2). The measurements were performed with the following parameters, if not stated otherwise: Laser power 5 W and a slit width of $100 \,\mu$ m.

Long term measurements offer the possibility for the investigation of the performance of the Laser Raman system and a great number of systematic effects, as well. The following sections are dedicated for the discussion of various effects with different impact for KATRIN:

(A) Laser drift and noise

In section 6.4.2 fluctuation and noise of the laser power is investigated. The stability of the excitation source directly affects the absolute intensity of the spectral lines. The actual results are compared with the specifications of the laser manufacturer.

(B) Discussion of one-time events: disruption in laser power

In one of the runs a singular event occurred which finds its expression by a sudden drop of the measured laser intensity. The possible reasons are discussed in section 6.4.3.

(C) Investigations of laser induced color center formation in the cell windows The trend of all long term measurements shows that the intensity of the fluorescence background is not stable over time. It even shows a correlation with the laser power measured by the photo diode signal. The reason is found in the formation of optical defect sites in the SiO_2 of the cell windows. The corresponding graphs and discussion are found in section 6.4.4.

(D) Pointing stability of the laser

Measurements discussed in section 6.4.5 show that the laser beam walks off the observed scattering volume. The result is a signal drop by up to about 22 %. The signal drop can be correlated to an unstable beam pointing due to temperature changes of the laser head base plate.

(E) Investigations of thermal effects

An additional measurement series has been performed to investigate influences of thermal effects on the system. The measurements and discussions are described in 6.4.6.

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(F) Changes within the mixture sample

The premise of all long term measurements is that the cells contain static samples in thermodynamical equilibrium, which means that the composition is in a steady-state. In 6.4.7 it is shown that the composition changes on long time scales due to exchange reactions with the cell walls.

(G) Quantification of measurement precision

The reproducibility of the Raman measurements is the most important question for the KATRIN experiment.

- (1) Section 6.4.8.1 deals with the precision of the absolute peak intensities determined by the statistics of the long term measurements.
- (2) The same is done for the relative intensities in section 6.4.8.2. It shows that the relative intensities are more precise due to the robustness with respect to laser power fluctuations.
- (3) The analysis can be enhanced in precision if intensity values of more than one measurement are added up. This affects the sensitivity for short term fluctuations. A proposal for a strategy for KATRIN is given in section 6.4.8.3.
- (4) Section 6.4.8.4 deals with the question whether the precision determined by the experiment is in agreement with the theoretical prediction from the known noise sources. It shows that the expected fluctuations of the relative intensities can be calculated very accurately.

In section 6.5 all effects are summarized.

6.4.2 Laser drift and noise

In section 4.2.3 the specifications of the VERDI laser are summarized. The power stability (drift) is claimed to be $\pm 1\%$ over 2 hours in the VERDI datasheet [Ver99]. The maximum noise claimed in the data sheet [Ver99] is < 0.03% (rms)¹. If these values are worse than specified, they can emerge as drawbacks for long term measurements.

The drift and the noise of the laser for run#2 are presented in the diagrams of figure 6.4. The first diagram shows the trend of the photo diode signal U in a single 250 s recording. The noise of this single measurement is $\sigma/U = 0.056\%$ which is about two times above the specified value. The main fluctuation is especially due to regulation processes within the laser head.

The noise of the long term trend in the second diagram of figure 6.4 is measured in the flat period from 70.2 h - 85.15 h. The noise is about 0.024 %. Fluctuations are averaged out within one acquisiton and therefore the long term trend is less noisy.

The drift of the absolute voltage signal is about -0.5% in 140 h. A KATRIN measurement period lasts 60 days, which is about 10 times longer than the duration of this long term run. The total voltage drift is in the order of 4 - 6% if the drift is assumed to persist over 60 days.

¹rms=root mean square. Noise value stated as single standard deviation

Conclusion In summary, it can be said that the noise of the laser is higher than stated in the product specifications. But within one acquisition these short term fluctuation are averaged out to a level lower than the desired precision of 0.1% in the KATRIN requirements.

The estimated drift in a 60 day neutrino mass measurement period of KATRIN is only 4-6%. However, since it is monitored continuously, corrections can be applied off-line. Overall, the stability of the relative intensities is not affected.

6.4.3 Discussion of one-time events: disruption in laser power

In run #2 (see table 6.2) a one-time event occurred. This event is now described and possible explanations are given.

Figure 6.5 shows the trend of the laser power of the measurement started at 27^{th} April 2009, 08:43 and the complete trend of corresponding run#2. In the latter the background intensity is plotted, as well. As can be seen, a sudden event occurs which instantaneous leads to a drop in photo diode signal and a rise in background intensity. Afterwards both trends tend back diametrically. Two explanations for this behavior are possible:

1. A mode-hop in the laser head occurred turning up jointly with a slight beam dislocation. Therefore the beam may be pointed at a little different location of the window with a higher absorption. Spots of higher absorption have shown up during the investigations of the lateral shift of the cell (see appendix C.2.2). In this case, the peak intensity has to be affected by the beam displacement vertical to the collection plane, as well. This is, however, not found in the trend of the absolute peak intensities (not shown here).



Figure 6.4: Laser drift and noise. Left: Trend of laser power during acquisition 1048 of run#2. The spike-like variations are probably related to regulation processes of the optical components in the laser. Nevertheless, the standard deviation is $\sigma = 0.007$ V at a mean value of $\overline{U} = 13.040$ V corresponding to a noise of $\sigma/U = 0.056$ %. Right: Trend of laser power of the first 140 h of run#2. Each data point represents a mean value of the laser power in a single 250 s acquisition. The noise was measured in the highlighted period from 70.2 h - 85.15 h. The standard deviation is 0.0032 V corresponding to a noise of $\sigma/U = 0.024$ %. The measured photo diode signal drifted from 13.056 V down to 12.989 V. This is a relative drift of 0.5% in the time of the first 140 hours.



Figure 6.5: Disruption in laser power. Left: The chart shows the trend of the photo diode signal of acquisition #1986 of run#2. At the 27^{th} April 2009 the signal drops abruptly from 12.993 V down to 12.120 V. The relative descent is about -7%. Right: The trend of the long term runs shows that the background intensity rises abruptly at the same time of the photo diode signal drop. The photo diode signal re-rises after this event while the background intensity recedes diametrically.

2. A dust particle clinged at the entrance window, produced more diffuse reflections or scattering and then was slowly disintegrating, being burned off by the laser radiation. But in this case the caveat is that the dust particle disintegration may heat up the coating surface. As a consequence, the temperature rises above the threshold that might cause irreversible damage to the coating. In the case of this damage the recession of the background intensity would not occur.

Conclusion Dust around the cell windows will be kept out in the final Laser Raman setup at the Inner Loop glove box. Light trapping tubes will avoid particles clinging on the window surface.

It was evident that only photo diode signal and the background intensity were influenced by this one-time event. As outlined in section 6.4.8, no changes in the relative isotopologue intensities are found associated with this event. Therefore, such an event is not of concern for the KATRIN measurements.

Nevertheless, a recurrence of this event might give a greater insight into this effect and an identification of the basic cause may be possible.

6.4.4 Investigations of laser induced color center formation in the cell windows

The correlation of background intensity and photo diode signal is also present in other runs aside the event just discussed in the previous section. In figure 6.6 the trends of monitored laser power, background intensity and peak area of several long term measurement runs are shown. For each of these runs the diametric behavior of monitored laser power (photo diode signal) and background intensity is obvious. This stresses the observation that both quantities are directly connected to each other. The overall trend of the laser power is by and large downwards while the background intensity is rising.

The trend of the peak intensity follows the laser power value. This can be seen generally in all runs.

Laser-induced color center formation The most likely reason for the anti-correlation of measured laser power and fluorescence background intensity can be found in the formation of color centers in the laser windows of the cell. The cell windows are made of fused silica which is mainly pure SiO_2 , as described in chapter 4.2.6.

Color centers are defects in the SiO_2 crystal at which light can be absorbed or scattered. If an unpaired electron is at a vacancy of the crystal it is called an 'electron' color center. A 'hole' color center is formed if an electron is missing from a location where there is usually an electron pair. These electrons or holes are able to absorb incident light since the defects have possible excited energy states. The de-excitation can be followed by fluorescence light emission [Nas78].

Lonzaga et al. investigated the color center formation in soda-lime glass by laser pulses. The laser radiation induces crystal defects and simultaneous absorption was observed. The absorption peak near 620 nm associated with trapped H_3^+ hole centers and a peak near 460 nm related to trapped electron centers. The color center can recombine by diffusion processes. Partial recovery of the coloration is on the scales of $\mu s - s$, but a part of the defects is nearly stable at room temperature. The observed coloration on the sample was stable on the time scale of months [Lon03]. At a temperature of about 400 °C the displaced electrons can be released and return to the hole centers [Nas78]. Natura et al. presented an advanced model of defect generation. The Si – O – Si bonds absorb photons and in the presents of the impurities OH and H it can then form SiOH and SiH, which generate electron and hole centers [Nat03].

Fused silica is due to its production a very pure material with only a few dopants like OH or other impurities (10-1000 ppm). Thus, fused silica is much more insensitive to the laser induced color center formation compared to the optical standard material BK7 [Esc98]. BK7 contains additional components like B_2O_3 (7-13%) which facilitate the formation of electron and hole centers.



Figure 6.6: Trends of monitored laser power, background intensity and peak area of run #1,#3,#4 and #6. In runs #1,#3 and #6 the diametrical behavior of the trends of photo diode signal and background intensity is obvious. On the other hand, the peak area of D_2 is more or less following the photo diode signal trend. In run #4 the time of the exponential drop of the peak area is $t_1 \approx 9$ h, the descent of the photo diode signal is rather linear and ends after $t_2 \approx 26$ h.

Conclusion The laser induced generation of color centers may explain the diametrical behavior of the background intensity and photo diode signal. The increasing number of color centers yields more absorption of the incoming light, thus the signal at the photo diode is declining. At the same time the fluorescence emission is rising.

The absolute rise is in average 5 a.u. within a run of up to 7 days. The most extreme increment was noticed in $\operatorname{run} \# 1^2$ with 50 a.u.. The average background rise of 5 a.u. in 7 days can be extrapolated for a 60 day run to approximately 40 a.u. This should be not regarded as critical at the moment for a single neutrino mass measurement period.

In the worst case scenario the linear rise of 5 a.u./week stays constant. Therefore, this would mean a rise in 3 years of the order of 600 a.u. which would excessively deform the Raman spectrum. However, this extrapolation is only a speculation. But it points out the necessity of further investigations. It has to be checked if the coloration saturates at a certain level and if the coloration recovers during the maintenance time between the KATRIN runs.

The monitoring of the background level can be definitely used as an indicator for the status of the windows. Spare windows for the cells are available and can be replaced if required.

6.4.5 Pointing stability

The next investigation was about the pointing stability of the laser beam. The intensity in the Raman spectrum is lowered when a beam is walking off the region from where the scattered light is collected. Therefore, investigations on the pointing stability of the laser were required.

A hint to this effect is given in the trend of run#4 (see figure 6.6). This does not exhibit the diametrical behavior of the background intensity and photo diode signal as established in section 6.4.4. After the measurement started the peak area value dropped from more than 1800 down to less than 1400 (-22%) within $t_1 \approx 9$ h. During that time the photo diode signal and the background intensity sank as well. After that exponential decrement of the peak intensity, the photo diode signal continued to fall linearly until $t_2 \approx 26$ h.

The proportionality of photo diode signal and peak intensity is shown in appendix C.3. But in the case of run#4 the declining of the peak intensity of D_2 is not proportional to the photo diode signal. It can be assumed that the absolute laser power remains mostly stable. The decrease of the peak and background intensity can then be explained by a change in the beam pointing. A beam displacement in the collection plane wouldn't have a large impact since the scattering region would just walk slightly out of focus. However, the change of the pointing up- or downwards reduces the amount of light falling on the fibre. The impact on the photo diode signal is much lower since the beam is widened to a size slightly greater than the active region of the photo diode. Therefore, it doesn't follow the trend of peak intensity and background intensities which both are determined at the light from the scattering region.

The amplitude of the dislocation can be calculated in the following way: The intensity

 $^{^2\}mathrm{each}$ acquisition has $1000\,\mathrm{s}$



Figure 6.7: Beam displacement due to instable pointing of the laser. Left: The curve shows the correlation of beam displacement and the integral light intensity which is falling onto the 100 μ m wide fibre core. Right: The graph shows a beam profile image centered on the fibre and a profile shifted from the center by 38 μ m. The white area of the curve represents the light missing the fibre core. The laser beam profile was calculated with a beam radius of $\omega_0 = 30 \ \mu$ m at which the intensity drops to $1/e^2$ of the maximum value.

profile of the beam in the scattering region according to Paschotta [Pas09] is:

$$I(r) = \frac{P}{\pi \omega_0^2 / 2} \exp\left(-2\frac{(r-d)^2}{\omega_0^2}\right).$$
(6.1)

P is the laser power, $\omega_0 = 30 \,\mu\text{m}$ is the waist of beam calculated in appendix E and *d* is the beam displacement. The integral intensity imaged onto the fibre core with a radius of $100 \,\mu\text{m}$ for a centered beam is

$$I(d) = \int_{0}^{100\,\mu\rm{m}} \frac{P}{\pi\omega_{0}^{2}/2} \exp\left(-2\frac{(r-50\,\mu\rm{m}-d)^{2}}{\omega_{0}^{2}}\right) \mathrm{d}r$$
(6.2)

The reduction of the relative integral intensity due to beam displacements is shown in figure 6.7. For an intensity drop of -22 % a displacement of about 38 μ m at the scattering region is necessary. This value corresponds to an angle of 0°0'9.2". The claimed pointing stability of the VERDI is < 5 μ rad for each °C change of the baseplate temperature [Ver99]. This would mean that the baseplate temperature has risen by 9 °C during the first $t_1 = 9$ hours. The temperature has not been monitored during the run, so the 9 °C can not be verified. However, it showed in successive measurements that the baseplate needs hours to reach the target temperature after the laser has been switched on.

Conclusion It has been shown that the beam pointing can reduce the peak intensities significantly. The strength of this effect is most likely related to the baseplate temperature of the laser head. The remedy may be found in a stabilization of the laser head's baseplate. A lead-time of about a day after the power-on of the laser may be sufficient for the temperature stabilization.

Slight beam walks $(0 - 15 \,\mu\text{m})$ wouldn't concern the KATRIN measurements as indicated by figure 6.7 (left). Any further walk reduces the peak intensity significantly which would worsen the signal-to-noise ratio and the aimed precision cannot be reached anymore.

6.4.6 Investigation of thermal effects

One possibility for time dependent changes of the signals are thermal effects occurring in the optical components. The laser dissipates thermal energy into the glass substrate by absorption at the coating surface and the bulk of a lens, or window. The temperature influx changes the refractive index, and thus the propagation of the light waves is changed [Win91]. Since such effects can disturb the Laser Raman measurements investigations have been performed. The aim was to get an idea of the magnitude of this effect.

Measurement setup The investigation of possible thermal effects has been performed using the following principle of measurement

- The laser was running continuously at 5 W for the whole measurement period. The exposure interval was 250 s.
- At some points in this long term measurement the external shutter has been shut intentionally to interrupt the laser beam. The absence of laser emission allows cooling for all optical components. The time interval of interruption varied from 17 to 208 minutes.
- After each blocking interval the shutter was opened to re-establish laser emission. The subsequent measurements should exhibit possible effects induced by heating up of the optical components.

The changing of the shutter status (shut/open) was performed during the readout of the CCD chip to provide the full $250 \,\mathrm{s}$ of acquisition.

Results The trends of the measurements for the thermal effect investigation can be found in figure 6.8. Besides the overview of the complete period, details of short time spans are shown. The short time trend of the laser power measured by the photo diode signal makes apparent that the laser power is notably higher after the re-establishment of laser emission than before. The relative increase is less than 0.1%. The background intensity is unaffected by the cooling time and remains near the level it has been before the shutter was closed. The diametrical behaviour of laser power and background intensity described in the section 6.4.4 is visible on the hour time scale.

However, the peak intensity (area) shows almost no dependence on the photo diode signal and is unaffected by the cooling times like the background intensity.

Discussion The trend of the photo diode signal before and after the beam shutting is a hint for thermal effects. Thermal lensing is induced if temperature gradients occur in a medium heated by the laser. The substrate of the window or lens is normally hotter on the beam axis, compared with the outer regions, typically causing some transverse gradient



Figure 6.8: Influence of thermal effects on the photo diode signal. All three charts show trends of the photo diode signal, background intensity and peak intensity. The laser beam has been intermediately shut 9 times. The shutting time can be seen when all values are 0. The upper figure represents the full experimental time span of about 77 h. The middle figure shows the details of the time between 1000 min and 2200 min. The increase of the photo diode signal after the shutter is reopened is obvious. Peak area and background intensity remain unaffected. This is highlighted in the three bottom charts which show the trend around the last shutting time of 208 min between 1630 min and 1990 min. Note the break in the time axis.

of the refractive index [Pas09]. An approximation for the dioptric power (inverse focal length) of a thermal lens can be found in [Pas09]

$$f^{-1} = \frac{\partial n/\partial T}{2\kappa \cdot A} P_{\text{heat}}$$
(6.3)

The temperature coefficient of the refractive index for fused silica is about $\frac{\partial n}{\partial T} \approx 13 \cdot 10^{-6} \,\mathrm{K}^{-1}$ [Toy83], the thermal conductivity is $1.38 \frac{\mathrm{W}}{\mathrm{mK}}$ and the irradiated area $A = \pi \cdot r_{\mathrm{beam}}^2$. The beam radius at the entrance window of the cell can be approximated by the intercept theorem to be $r_{\mathrm{beam}} \approx 150 \,\mu\mathrm{m}$. The internal transmission for fused silica is much better than 99.99% [MEL09], thus the absorption is $a \leq 0.01\%$ which equates to a heat influx of $P_{\mathrm{heat}} = 0.0005 \,\mathrm{W}$ at 5 W laser output. The dioptric power of the entrance cell window, with the parameters above, would be

$$f^{-1} = \frac{13 \cdot 10^{-6}}{2 \cdot 1.38 \cdot \pi \cdot 150^2} 0.0005 \frac{1}{\mathrm{m}}$$
(6.4)

$$= 3.2 \cdot 10^{-2} \frac{1}{\mathrm{m}}.\tag{6.5}$$

The corresponding focal length is $f \approx 31 \,\mathrm{m}$ which is about one order of magnitude higher than the length of the optical laser path.

The spot at the position of the photo diode (about 0.5m away from the cell) is shifted by a small margin, if this thermal lens is formed after heating of the fused silica. The spot of the beam is slightly larger than the active area of the photo diode and therefore the voltage signal is changed. The intensities of peak and background are largely unaffected by the small beam walk because the distance from cell window to interaction region is only about one centimeter ($\ll f \approx 31 \text{ m}$).

Lensing is possible as well by the Kerr effect. It describes the non-linear interaction of light in a medium introducing a nonlinear refractive index with is intensity-dependent [Pas09]. In the given case the Kerr lensing is negligible. The focal length of the Kerr lens is of the order $5 \cdot 10^5$ m.

Conclusion The investigations with the shutter interrupted measurement showed that thermal effects like lensing seem to occur. However, only a low effect is apparent at the photo diode signal. The peak intensity is not influenced. Therefore, this effect is not expected to play an important role for the monitoring measurement at KATRIN.

6.4.7 Changes within the mixture sample

The use of mixtures in static cells is the underlying principle for the long term measurements, because it may be assumed that no changes of the sample composition occur. This assumption is verified in the following section.

The plots in figures 6.9 and 6.10 show the relative intensities of $\operatorname{run}\#1$ and $\operatorname{run}\#4-6$ (see overview in table 6.2 on page 74). However, from the trends it can be seen, that the equilibrated mixture of H₂, HD and D₂ in $\operatorname{run}\#1$ slowly exchanges isotopologues with the walls of the cell which was filled with pure H₂ (sample S1, see table 5.1 on page 59) prior to this measurement. The trend of the run#4 (figure 6.10) illustrates these exchange reactions in the cell even more explicit. One may argue that the change of relative intensities is conditional upon the drop in laser power of -22% as discussed in section 6.4.5 (pointing stability). The drop occurred over about $t_1 = 9$ h as shown in figure 6.6. These 9 h are also marked in the first chart in figure 6.10. It is obvious that this time constant is not compatible to the time constants of the changes in the relative peak area intensity. The sample S9 used in this run was filled just two days before the beginning of run#4 (see table 6.1 on page 73). The CAPER gas chromatograph analysis before filling recorded no HD. HD-gas was released from the walls during the two days before run#4 and appeared in the sample gas. The continued exchange reactions are visible at the slope of the relative intensities of the following two runs(#5,#6).



Figure 6.9: Trend of the relative composition of run #1. Shown is the relative intensity of H₂, HD and D₂ as a function of time. In the trend of the relative amount of HD a slight upward slope is visible, the slope of D₂ tends downwards. The reason is probably found in the exchange reactions from residual gas in the stainless steel wall from prior cell fillings.

The next observation can be found at the relative intensities of run#4 compared with run#5. The compositions measured at the end of run#4 and at the beginning of run#5 change significantly:.

$$\overline{c(\text{DT})}: 6.25\% \to 6.33\%$$
 (6.6)

$$c(D_2): 91.05\% \to 89.55\%$$
 (6.7)

$$c(\text{HD}): 2.70\% \to 4.12\%$$
 (6.8)

The time between both runs was only about one hour. But the relative intensity changed more than could be expected from the slopes in run#4. The rise of HD of about a factor

of 2 within just a few hours can not be explained by exchange reactions.

Note that the absolute intensity of the spectral lines in the spectra was reduced by a factor 4 due to a misalignment between run#4 and run#5 $(I(D_2)_{run#4} \approx 1380 \text{ a.u.} \rightarrow I(D_2)_{run#5} \approx 410 \text{ a.u.})$; hence the increase in apparent noise of the relative intensity.

In appendix C.3 power variation measurements are discussed. It is shown that, the relative intensity has a small dependence on the overall light exposure. According to these measurements, a reduction of the laser power by a factor of 4 influences the relative peak intensity by less than 0.1 percent. However, the change of HD as written in equation (6.8) is 1.4 percent. A satisfactory explanation for these intensity changes still has to be found.



Figure 6.10: Trend of the relative composition of run#4-6. The three charts show consecutive measurements with sample S9. Displayed is the relative intensity of DT, D₂ and HD as a function of time for each run (4,5,6). The first chart shows the measurement which started two days after the cell filling at CAPER. The relative intensity of HD has a small upwards slope, while the D₂ intensity tends downwards. Both tendencies are visible in the middle and right chart (run #5 and #6), as well. This trend is probably due to exchange reactions with hydrogen isotopologues in the wall from the prior H₂, HD, D₂ sample S4.

Conclusion The results of these investigation are only partly relevant for KATRIN. On the one hand the changes of the composition by exchange reactions with the cell wall should not play a major role for measurements under gas flow conditions.

But on the other hand, the observed composition changes imply that the generation of reliable calibration samples is hardly feasible.

The sudden change of the relative intensity is still puzzling. It needs to be investigated, if this is only an artifact from the analysis or a even weakness of the whole system.
Table 6.3: Precision of absolute intensities. The table shows the precisions of the absolute intensities in the long term runs 1-6. Only the peaks with the highest and lowest precision have been selected for tabulation in order to provide better clarity. In addition, the corresponding isotopologue is noted together with the absolute intensity. *The exposure time at each run was 250 s for each acquisition except 1000 s at run#1.

| Run | Sample | Precision (lowest) (peak, abs. int.) | Precision (highest) (peak, abs. int.) |
|-----|-----------------|--------------------------------------|---------------------------------------|
| 1 | $\mathrm{S4}^*$ | 0.34% (H ₂ , 14980) | 0.20% (HD, 24149) |
| 2 | S4 | $0.18~\%~({ m ~H}_2,~3679~)$ | $0.16~\%~({ m HD},~5965~)$ |
| 3 | S8 | 2.21~% (T ₂ , 29.01) | 0.72% (HT, 196.8) |
| 4 | $\mathbf{S9}$ | $4.36~\%~({ m HD},~39.16~)$ | 1.04% (D ₂ , 1357.35) |
| 5 | $\mathbf{S9}$ | 6.28% (DT, 24.61) | 4.81% (D ₂ , 379.24) |
| 6 | $\mathbf{S9}$ | 11.06% (HD, 17.70) | 0.85% (D ₂ , 380.73) |

6.4.8 Quantification of measurement precision

The reproducibility of the Raman measurements is of major importance for KATRIN. In this subsection the long term measurements of the absolute and relative intensity value are analyzed with regard to their precision. For that reason, the analysis has been performed in a specific way as it will be explained in the following subsections.

6.4.8.1 Precision of the absolute intensity

The first question to be dealt with is about reproducibility of the absolute peak intensities. The procedure is as following: A statistics of the peak intensity for each peak in the spectrum is generated from the long term measurements. The standard deviation σ of the statistical distribution characterizes the precision $\Delta I = 2\sigma/I_{\text{aver.}}$. Table 6.3 provides an overview of the precision of the absolute peaks intensity in each run.

The data ranges for the statistics was specified in flat regions of the intensity trend. This should ensure that only the noise is measured.

A high (< 0.2%) absolute precision is only reachable for high pressures and/or long acquisitions. Runs #4-6 provide very imprecise values, which is probably due to a strong fluctuation of the laser power during those runs.

Sample S8 used in run#3 provides the mixture of highest interest for the requirements of KATRIN, since the pressure ($\approx 100 \text{ mbar}$) is quite similar to the operation pressure of the Inner Loop.

Conclusion It can be seen that the absolute intensities are not appropriate for the precise determination of the sample composition for KATRIN. This is evident from the low precisions in table 6.3. This observation agrees with the investigations described in the previous sections where the influences of various effects of the intensity like beam pointing have been pointed out.

Table 6.4: Precision of relative intensities. The table shows the precisions of the relative intensities in the long term runs 1-6. Only the peaks with the highest and lowest precision have been selected for tabulation in order to provide better clarity. In addition, the corresponding isotopologue is noted together with the relative intensity. ^{*}The exposure time at each run was 250 s for each acquisition except 1000 s at run#1.

| Run | Sample | Precision (worst) (peak, rel. int.) | Precision (highest) (peak, rel. int.) |
|-----|-----------------|-------------------------------------|---------------------------------------|
| 1 | $\mathrm{S4}^*$ | 0.13% (H ₂ , 29.48 %) | 0.09% (HD, 47.50%) |
| 2 | S4 | $0.14~\%~({ m ~H}_2,~29.38~\%~)$ | 0.09% (HD, $47.61%$) |
| 3 | S8 | 1.98% (T ₂ , $2.28%$) | 0.31% (HD, $33.84%$) |
| 4 | S9 | 2.10% (HD, $2.60%$) | 0.10% ($\mathrm{D}_2,\ 91.50\%$) |
| 5 | S9 | 3.69% (DT, $5.76%$) | $0.30\%~({ m D}_2,~90.23\%~)$ |
| 6 | $\mathbf{S9}$ | 6.19% (HD, $4.36%$) | 0.35% (D ₂ , 89.90%) |

6.4.8.2 Precision of the relative intensity

The reproducibility of the relative peak intensities is investigated next. The precision is determined in the same way as described in the previous subsection 6.4.8.1, but here the statistic is generated from the relative intensities.

Since a slope is apparent in most of the runs (e.g. run#4-6 in figure 6.10) the trend of the runs has been fitted by a linear function. A statistical analysis is then performed on the residuals which represent the noise component. The overview of the precision of relative intensities is shown in table 6.4.

In the determination of relative intensities, all fluctuations should be minimized since a variation in light exposure is affecting each individual branch simultaneously. Generally, the relative precisions surpass the absolute ones by roughly more than a factor of 2.

Run#1 (1000 s), run#2 (250 s) and run#4 (250 s) are providing satisfactory results with regard to relative precision ($\leq 0.1\%$). However, the cell pressures of the corresponding samples S4,S9 are a factor 4–10 higher than the Inner Loop operation pressure. Therefore it is more meaningful to look at run#3 which is closer to the KATRIN operating conditions. It is astonishing, that the T₂ amount which is roughly 2% (partial pressure ≈ 2 mbar) can detected precisely at a level of 2%. The HD amount is approximately 33% at a precision of 0.31%.

Conclusion The KATRIN conditions demand about 95 % tritium content at ~ 100 mbar–150 mbar, thus a three times higher peak than HD in run#3 is expected for T₂. An extrapolation of the precision lets it seem feasible to advance into the 0.1 % gold standard region.

6.4.8.3 Enhancement of the precision by accumulation of intensity values

In the following it is investigated how the precision of the intensities behaves under accumulation of multiple measurement points. The precision is higher if more than one measurement is drawn together, since the signal to noise is higher for longer exposures

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(e.g. $2 \times 250 \, s = 500 \, s, \, 3 \times 250 \, s = 750 \, s \dots$).

In figure 6.11 the precision $(\frac{2 \cdot \sigma}{I_{\text{aver.}}})$ is plotted against the number of accumulated measurements, here shown for two runs. The curves have of an square root decay shape due to the Poisson distribution of the shot noise. The precision has nearly converged to a lower limit for greater than 30 accumulations.

The smaller the absolute peak intensity, the greater influence has an accumulation of single values. This can be seen in the plot of run#3 in figure 6.11. The T₂ peak precision improves by a factor of about 2, if 4 measurements are accumulated respectively. The enhancement of the HD-peak precision is negligible in comparison to that.



Figure 6.11: Precision dependence on number of accumulated measurements. *Left:* $\operatorname{Run} \# 2 (2400 \times 250 \text{ s})$ with 985 mbar *Right:* $\operatorname{Run} \# 3 (1329 \times 250 \text{ s})$ with 103.4 mbar. Note the logarithmic scale providing better clarity.

Conclusion Short measurement periods are advantageous for the detection of short time fluctuations, but the precision is lower compared to longer acquisition times. The accumulated measurement results described here identify a new chance for the KATRIN measurements. It can be considered that the measurement time is reduced to be more sensitive to short time fluctuations with a precision at the percent level. During the final neutrino mass data analysis it can be decided how many measurement points are integrated to obtain a higher precision.

6.4.8.4 Discussion of the link between noise sources and measurement precision

In section 4.2.9 shot noise, dark noise and read-out noise have been introduced as noise sources. The following subsection compares the precision which is quantified by the long term experiments with a theoretical prediction for the expected noise.

Before the noise contribution is calculated, some comments about the way ORIGIN calculates peak areas are necessary. Peak D_2 from run#2 is used as an example, as sketched in

figure 6.12 (a). A single peak consists of many slices $\frac{\Delta I}{\Delta \lambda}$ which contain intensity counts per bin. In the given case the bin size $\Delta \lambda$ is of the unit nm. The total area (peak intensity) is calculated as following:

$$I_{\text{peak}} = \sum_{x=815}^{840} \frac{\Delta I}{\Delta \lambda}(x) \cdot \Delta \lambda(x)$$
(6.9)

where pixel 815 and 840 are the lower and upper peak limit in the case of example D_2 peak, corresponding to 630.5319 nm and 634.0750 nm.

The noise sources are:

1. Dark noise and read-out noise

The dark current and CCD read-out generate isotropic distributed noise all over the CCD chip. The noise is measured in a single spectrum as $\sigma_{\text{dark,readout}} \approx 0.5 \text{ a.u./pixel}$. The dark and read-out noise contribute to the peak area, as shown in figure 6.12 (b). This noise in the peak area could be simulated by equation (6.9), where $\frac{\Delta I}{\Delta \lambda}$ is Gaussian noise with a standard deviation of $\sigma_{\text{dark,readout}} = 0.5 \text{ a.u.}$ Under the assumption that $\Delta \lambda(x)$ is independent of x within one peak, the modified equation (6.9) for the simulation of dark and read-out noise is

$$I_{\text{dark,readout}} = \Delta \lambda \cdot \sum_{x=815}^{840} (\text{Gaussian random noise}, \sigma = 0.5).$$
 (6.10)

where the bin size is $\Delta \lambda = \frac{634.0750 \text{ nm} - 630.5319 \text{ nm}}{840 - 815}$. This term was simulated 1 million times to generate 1 million area contributions by dark and read-out noise. Finally, the standard deviation of the statistics of all calculated noise areas is determined as σ_a .

2. Noise by baseline mis-detection

Additional noise arises by mis-detection of the baseline before peak analysis. The baseline subtraction is dependent on the intensities values of defined pixels between the peaks, the baseline points. These points are influenced by noise, as well. The additional area contributed to the peak area can be estimated as a trapezoid $(A = \frac{1}{2}(a+b) \cdot w)$ (see figure 6.12 (c)). *a* and *b* are the noise on the nodes of the baseline at the peak limits, *w* is the width of the peak. Again, these trapezoids have been simulated 1 million times with Gaussian distributed random numbers for *a* and *b* with $\sigma_{\text{dark,readout}} = 0.5$ a.u.. The standard deviation for the series of trapezoid values is σ_b .

3. Shot noise

The shot noise is described by a Poisson distribution and therefore $\sigma_{\text{shot}} = \sqrt{\text{counts}}$. But it has to be noted that the area is not equal to the number of counts on the CCD. Equation (6.9) can be solved for the number of counts (using $\Delta\lambda(x) = \Delta\lambda$):

$$\underbrace{I_{\text{peak}}}_{\text{intensity}} = \underbrace{\sum \frac{\Delta I}{\Delta \lambda}(x)}_{N=\text{counts}} \cdot \Delta \lambda \tag{6.11}$$

$$N = \sum \frac{\Delta I}{\Delta \lambda}(x) = \frac{I_{\text{peak}}}{\Delta \lambda}$$
(6.12)

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In section 4.2.9 it was demonstrated that N has to be multiplied by 450 which is the number of rows over which the intensity is averaged (binned). (Compare figure 4.12 on page 51). Finally, the total number N_{tot} of counts and σ_{shot} can be calculated:

$$N_{tot} = N \cdot 450 = \frac{450 \cdot I_{\text{peak}}}{\Delta \lambda} \tag{6.13}$$

$$\sigma_{\rm shot} = \sqrt{N_{\rm tot}} = \sqrt{\frac{450 \cdot I_{\rm peak}}{\Delta \lambda}} \tag{6.14}$$

This value can finally be transformed back into the dimension of the peak intensity $I_{\rm peak}$

$$\sigma_c = \sigma_{\rm shot} \cdot \frac{\Delta\lambda}{450} = \sqrt{\frac{I_{\rm peak} \cdot \Delta\lambda}{450}} \tag{6.15}$$

The calculated theoretical contributions stemming from the three error sources are listed in table 6.5 together with the values from experiments.

The calculated precision is of the same order as the precision of the absolute intensities from the experiment. But the precision of the experiment is still slightly lower than theory predicts. The missing contribution is possibly due to the instability of the laser power, which was not included in the simulation.

Nevertheless, the calculated precisions are matching very closely the experimental precisions of relative intensity. The relative intensities are affected less by variations in laser power and therefore the agreement between the model of noise and the actual measured uncertainty is good.

It should be noted that, the noise by imperfect cosmic ray removal is not included in the assumptions above.



Figure 6.12: Area determination and noise contributions. (a) Illustration how ORI-GIN calculates the peak area. The partial intensity contributions $\Delta I/\Delta\lambda$ are multiplied by $\Delta\lambda$ and added up to I_{peak} . (b) Dark and read-out noise produce random contribution to the peak area. (b) A trapezoidal area is contributed to the peak area by a random mis-detection of the baseline due to noise or cosmic rays at the baseline nodes. (c) The incoming light intensity follows a Poisson distribution and thus shot noise should be dominant over the peak area.

| Peak | D_2 | HD | H_2 |
|--|-------|-------|-------|
| I_{peak} : Peak area | 2902 | 5988 | 3681 |
| σ_a : calc. noise by dark/read-out noise | 0.35 | 0.38 | 0.27 |
| σ_b : calc. noise by baseline mis-detection | 1.77 | 2.15 | 2.10 |
| σ_c : calc. shot noise | 0.96 | 1.33 | 1.02 |
| $\sigma = \sqrt{\sigma_a^2 + \sigma_b^2 + \sigma_c^2}$ | 2.04 | 2.56 | 2.35 |
| calc. precision $2 \cdot \frac{\sigma}{I_{\text{peak}}}$ | 0.14% | 0.09% | 0.13% |
| exp. precision (abs. int.) | 0.18% | 0.16% | 0.18% |
| exp. precision (rel. int.) | 0.13% | 0.09% | 0.14% |

Table 6.5: Calculated noise contribution and precision for run #2. The experimental precisions from the longterm run analysis are found in table 6.3 (absolute) and 6.4 (relative).

Conclusion The very good agreement between the precision of the relative intensity and the theoretical prediction suggests that the uncertainties of the Laser Raman system are well understood. Table 6.5 also reveals that the greatest contribution is the noise by baseline mis-detection. Therefore, proper baseline detection has to be included in future analysis procedures.

6.5 Summary and implications for KATRIN

The Laser Raman system for KATRIN was subject of extensive systematic investigations within the scope of this thesis. The results presented in this chapter can be summarized as following:

(A) Laser drift and noise

The laser exhibits short time fluctuations which are two times higher than claimed in the specification. Within an acquisition time of 250 s these fluctuations are averaged out and so they are significantly lower than 0.1%. The maximum extrapolated laser drift is about 4 - 6% within a neutrino mass measurement period of 60 days.

(B) Discussion of one-time events: disruption in laser power

An one-time event occurred which is probably related to a dust particle hitting the laser windows in the beam path. The dust scattered or absorbed a part of the incident light and thus a higher fluorescence background was generated while the photo diode signal monitoring the laser power dropped.

(C) Investigations of laser-induced color center formation in the cell windows It was shown that the continuous laser irradiation induces absorption centers into the fused silica of the cell laser windows. The absorption is followed by an increase in fluorescence underlying the Raman spectra. This effect of color center formation is a well known phenomenon in the literature. The reverse process can be lasting up to months. Thus, the monitoring of the background intensity is an indicator of the status of the windows. During the measurement breaks between two neutrino mass measurement periods the windows can be replaced if required.

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(D) Pointing stability of the laser

If the beam pointing is not under control, beam walks are possible. The light collection from the scattering region is very sensitive to beam shifts. Beam walks need to be avoided as much as possible to provide the highest peak intensities and thereby high signal-to-noise ratios. It has to be investigated if the pointing stability improves when the base plate temperature of the laser head is stabilized.

(E) Investigations of thermal effects

The investigations with the shutter interrupted measurements showed that thermal effects like lensing occur. However, the effect on the peak intensity is negligible.

(F) Changes within the mixture sample

The mixture samples in supposed thermodynamical equilibrium showed changes in their composition most likely due to exchange effects at the cell walls. The Laser Raman system is meant to monitor the composition of the gas during KATRIN runs. Therefore, the impact of these investigation is not relevant for KATRIN, but constitutes an interesting tool to follow possible wall contamination.

However, in addition to these effects a sudden change in the relative intensity has been noticed once. The change is thought to be related to a misalignment of the optical fibre which reduced the total light exposure; but a comprehensive explanation of the phenomenon cannot be given at the moment.

(G) Quantification of measurement precision

The reproducibility of the Raman measurements has been investigated under several aspects:

- (1) It has been shown that the precision gold standard 0.1% of KATRIN cannot be reached based on absolute intensities in a measurement time of less than 1000 s.
- (2) However, relative intensities offer a precision which is better than a factor of 2 compared to absolute values. Influences from fluctuations in light exposure affect all peaks at the same time which minimize the impact on the relative values. The required KATRIN precision 0.1% seems to be feasible.
- (3) It has been shown that an averaging over several measurement points can increase the precision. This, however, is at the expense of the sensitivity to short time fluctuations.
- (4) The calculation of theoretically expected uncertainties from dark/read-out noise, baseline mis-detection and shot noise showed agreement with the precision values for the relative intensities. The baseline mis-detection has been identified as the major contribution to the error in the Raman measurement.

6.5.1 Final conclusion

• The most important result of the long term investigation is, that the Laser Raman system is about to meet the KATRIN requirements within 250s of signal acquisition. The final validation of the gold standard has to be done in the next experiment phase. The operation of the Inner Loop will be tested using the LOOPINO loop, which enables flowing-sample measurements at higher tritium concentrations. Here

additional windows and vibrations from the glove box may lower the measurement precision. If it turns out that the requirements cannot be reached anymore, it should be considered how to optimize the light exposure. The investigations in this chapter reveal important hints how to establish the optimal configuration. An optimal alignment of the optical components is the most trivial, but nevertheless still demanding, thing to do. Furthermore the pointing stability has to be investigated, to avoid intensity-costing beam-walking. If these actions are insufficient, then several single measurements can still be added up afterwards to reach the 0.1 % precision. In addition, it can be considered to install extra hardware like a spherical mirror which retro-reflects the Raman light at the opposite side of the collection optics. Qualitative experiments which have been performed (but are not reported here) show that these mirrors can increase the light exposure by a factor of at least 1.7. However, the installation and alignment of this retro-mirror in the small glove box appendix is very complicated, although feasible.

- The correct quantification of the noise is a great success. It turned out that the greatest uncertainty in the analysis is the correct baseline detection. From this it follows, that future analysis programs need a more sophisticated baseline detection. A fit with an appropriate function as a polynomial may be a solution which is less sensitive to noise than the combination of linear function used here.
- The investigations of color center effects helped to understand the permanent rise of the background. Yet, the durability of the cell windows in the measurement time of the KATRIN cannot be predicted at present. Therefore the monitoring of the fluorescence background trend is an important measure of the status of the windows. The LOOPINO measurement period which is intended to be 2-3 weeks will provide more information about the long term performance of the windows.

The peak area determination by ORIGIN Peak-Analyzer turned out to be a powerful method for the investigation of stability, dependencies of relative intensity and background intensity. However, this analysis provides only relative intensities of the spectral lines which is a first order approximation for the chemical composition. The quantitative composition can only be determined if the line strength functions are known and implemented properly.

The first approach to the quantitative analysis is reported and discussed in the following chapter 7.

Chapter 7

Quantitative analysis

The reproducibility of spectral lines on the 0.1% level is a challenge itself. But an analysis which is accurate and precise on the same level is another story. The general requirements for an appropriate quantitative analysis are:

- The peaks have to be identified properly and the full intensity of the peaks has to be taken into account.
- The baseline has to be determined unambiguously.
- The composition has to be derived very accurately, preferentially with minimal calibration effort.

7.1 Challenges in standard calibration techniques

A wide range of basic and advanced chemo-metric methods for the quantitative analysis exists for quantitative analysis. Here, two established concepts are summarized here:

- Classical least squares (CLS). Pure component spectra are fitted to the (unknown) mixture spectrum. The composition is predicted from the weighted sum of the pure components. However, CLS cannot take into account non-linear effects like peak shifts or shape changes [Kri08].
- Principle component regression (PCR) and partial least squares (PLS). These methods are so-called soft modeling methods, because no physical structure is underlying. The spectral data and the constituent concentrations are treated as vectors which are linked by a correlation matrix. This matrix is formed during an extensive calibration process in which it has to be ensured that each region of interest is covered with input data. These methods are inherently linear and do not always accommodate nonlinear response well. Also, the extrapolation capabilities of the method are restricted because of the absence of a underlying physical (hard) model. Further reading about multivariate calibration (MLR, PCR, PLS,...) can be found e.g. in [Bre00].

The general problem with all techniques is the accurate calibration. In the case of pure spectra, the absolute pressure has to be known very precisely (< 0.1%) and it has to be assured that the laser power and the optical alignment don't change at the same level within all calibration measurements. For hydrogen isotopologues this cannot be ensured at all. Furthermore, the heteronuclear isotologues cannot be produced in isolation because they will undergo exchange reactions (via collisions) to form the homonuclear components (e.g. $2DT \rightleftharpoons D_2 + T_2$).

Multivariate methods using soft-models like PLS need many calibration samples, and the content of these mixture samples has to be known very accurately (< 0.1%). In the previous chapters it was highlighted that at the moment the TLK has no analysis or mixing possiblilities to provide this accuracy. In addition, it has been reported that the composition slightly changes due to exchange reactions with hydrogen isotopologues gettered in the stainless steel walls. (See e.g. [Abr05])

7.2 Roadmap to quantitative analysis: Indirect hard modeling

The Laser Raman system at KATRIN measures the composition of the gas which is injected into the source. Issues of precision have been successfully investigated, as outlined in chapter 6. Regardless of this, quantitative analysis is still needed which provides accurate sample compositions (0.1%) with ideally requires only minimal calibration efforts. The so-called indirect hard modelling (IHM) offers a promising alternative to the techniques mentioned in the previous section.

Below a brief outline of the indirect hard modeling approach is given, along the lines provided by E.Kriesten et al. about 'Fully automated indirect hard modeling of mixture spectra' [Kri08].

7.2.1 Principle ideas

An unknown mixture spectrum is modeled as a weighted sum of pure component spectral models. Each component model is a sum of parameterized peak functions. The parameterized peak functions are approximated by a pseudo-Voigt function which constitutes a simplification for the full convolution of a Gaussian with a Lorentzian line profile [Bru99]:

$$V(\nu) = \beta \alpha \underbrace{\exp\left[-\frac{4\ln 2(\nu-\omega)^2}{\gamma^2}\right]}_{\text{Gaussian part}} + (1-\beta) \alpha \underbrace{\frac{\gamma^2}{(\nu-\omega)^2 + \gamma^2}}_{\text{Lorentzian part}}$$
(7.1)

where α (height), β (Gauss-Lorentz weight), γ (width) and ω (position) are the parameters used in the subsequent fitting of the hard-model.

A model of the Q_1 branch of D_2 is plotted in figure 7.1. It can be seen that it consists of single parameterized peaks representing the individual Q_1 -lines. The width parameter is fixed within the component model, because each line should have the same width due to the image from the spectrometer entrance slit.

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Figure 7.1: Building a model of a Q_1 -branch. The figure shows the modeling of the Q_1 branch of D_2 , which is a convolution of individual Q_1 -lines. The relative intensities between the single lines are fixed and can only scale proportional. The same is true for their positions. A common shift is applied to all single lines of the model peak, if it is shifted during the fitting routine. The width of the peak is also a common parameter which is physically determined by the slit width.

A model like this can be generated by the manual input of rigorous physical models like theoretical spectra. In this case the substructure of the component is known exactly, unlike the pure components spectra in the CLS method.

The two-step structure of the indirect hard modeling is sketched in figure 7.2.

1. A non-linear spectral model is generated first. The model is composed of the individual components like the Q_1 branch in 7.1. The use of hard models allows to compensate for nonlinear effects like peak shift or peak shape change. A peak shift can occur if the excitation frequency changes or if the excitation laser is exchanged (even lasers of the same make may exhibit slightly different center wavelength). The shape of the single peaks is mostly determined by the width of the entrance slit. Thus IHM is able to compensate for the influence of slit width or spectrometer resolution.

In this first step the non-linear spectral model is fitted to the mixture spectrum. The number of open fitting parameters can rise up to several hundred in case of a many component system. Therefore the optimization problem is broken up in smaller problems. A detailed description is found in [Kri08].

2. A linear calibration model predicts the concentrations from the pure component weights. The weights are either generated during a calibration or they are already included in the physical model. Soft-model routines like PLS normally need numerous calibration spectra [Dav06].



Figure 7.2: Two-step structure of indirect hard modeling. Explanation in plain text. (According to [Kri08])

7.2.2 First results

Indirect hard modeling is implemented in the software PEAXACT. This spectral analysis tool is being developed by a group of the AVT¹ at the Aachen University (RWTH²). The IHM research is still in progress and a development version of the program was kindly licensed to KATRIN for evaluation. In this section the first experiences with this software are reported.

Model generation A full quantum mechanical model of the Raman spectra of hydrogen wasn't available during the time period of this thesis. The spectrum simulation SpecGen from R.Lewis contains the intensity calculation presented in section 3.3 of chapter 3 (in which the Raman theory is covered). The correct values for the transition probability are not implemented in the simulation. However, it can be used to model Q_1 -branches even if the pure component weights aren't provided. The relative compositions determined in the standard ORIGIN analysis (see chapter 6) were used as pure component weights which proved to be sufficient for the first tests.

Fitting performance First, it was investigated how well the modeled peaks do fit the data in real, measured spectra. In figure 7.3 the Q_1 -branch of H₂ is shown as an example. It can be seen that the agreement between model and data is poor for parts of the peak structure. The positions and relative intensities of the model look adequate if the shape is neglected. The problem of the mis-match in shape could be traced to the use of the pseudo-Voigt function which doesn't describe the physical situation appropriately. The data shows a flattened top and steep edges which is due to the geometry of the spectrometer entrance slit (convolution of the Raman line profile with a 'window'-function).

One further line shape problem needs to be considered. In figure 7.4 a sketch of the wavelength dependence on aberrations by astigmatism can be found. It shows that the bending of the slit images is not equal at all wavelengths. For this reason the correction described in section 4.3.1 is only working exact for a specific wavelength (e.g. 633 nm). Especially, peaks at higher wavelength are more distorted. Thus, agreement between data and theory cannot be fully accomplished, but an additional 'broadening' is observed.

¹AVT=Aachener Verfahrenstechnik

 $^{^2 \}rm Rheinisch-Westfälische Technische Hochschule Aachen$



Figure 7.3: Shortcomings of the peak modeling of IHM. The figure shows the measured peak of the Q_1 -branch of H_2 and the hard modeling fit. It can be seen that the fitting of the peak performs insufficient at several spots. The top of the model peaks overhangs the data peaks. On the other hand the edges are less steep compared to the data peak. The same is true for the foot of the spectral line. The decline of model curve is at these points much too soft.



Figure 7.4: Aberrations by astigmatism on CCD chip. The sketch shows the influence of astigmatism in an exaggerated way. The aberration is more severe for longer wavelengths. Therefore, spectral lines at the high wavelength regime are more distorted than at lower wavelength.

Table 7.1: Precision enhancement by indirect hard modeling. The table shows the precision for each constituent of sample S5. The set of 332 measurements of run#3 was analyzed once by the standard method described in section 6.2 and once by PEAXACT (IHM). The enhancement is precision is about a factor of 1.5.

| Method | T_2 | DT | D_2 | ΗT | HD | H_2 |
|---------------------------|---|---|---|---|---|----------------|
| Peak areas [%] IHM [%] | $\begin{array}{c} 1.31 \\ 1.02 \end{array}$ | $\begin{array}{c} 0.87\\ 0.37\end{array}$ | $\begin{array}{c} 0.52 \\ 0.35 \end{array}$ | $\begin{array}{c} 0.61 \\ 0.31 \end{array}$ | $\begin{array}{c} 0.28\\ 0.18\end{array}$ | $0.40 \\ 0.22$ |

Reproducibility of the fitting The analysis of the 332 first spectra of long term run#3 has been redone with PEAXACT to compare the precision of the IHM method and the 'standard way' including the **Origin Peak-Analyzer** as described in 6.2. The standard deviation is determined from the statistics of the measurement series. The precision of the standard method is compared in table 7.1 with the precision of the IHM approach. IHM has improved the precision by a factor of about 1.5. The best precision is found for the HD-peak, it is enhanced from 0.28% to 0.18%. The improvement is mainly due to less uncertainties at the baseline since the whole spectrum is taken into account and not only two pixels near the peaks.

7.2.3 Next steps

The following steps have to be accomplished for before the analysis system is finally suitable for KATRIN.

• IHM

The test revealed that the pseudo-Voigt function is not appropriate to produce a good agreement of theory and data. Therefore, the fit function has to be extended by window functions which take the geometry of the spectrometer entrance slit into account.

Furthermore, the fluorescence-dominated background in the spectral region of the hydrogen isotopologues cannot be fitted by a single quadratic function. A polynomial of higher order is needed to fit the background shape.

• Software post-processing of experimental raw data

The astigmatism correction in one dimension as described in 4.3.1 performs only well in the vicinity of the reference laser line (e.g. 633 nm).

The problem can be solved by an algorithm which includes a wavelength dependence of the astigmatism correction. Those algorithms exist in open source image manipulation programs [Lew09]. The challenge is to characterize the correction function while taking misalignments (e.g. rotation of the CDD) into account.

• Hard modeling

The spectrum simulation SpecGen contains only an approximation for the vibrational transition probability. A more precise quantum mechanical calculation is necessary to compute all individual matrix elements of the line strength of each isotopologue. This model will include the relative intensity between all branches which is more or less already a calibration. Schwartz and LeRoy published 'nonadiabatic eigenvalues

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and adiabatic matrix elements for all isotopes of diatomic hydrogen' [Sch87]. They obtained expectation values of average polarizability and polarizability anisotropy and developed a scaling procedure to report result for HT, DT and T_2 . These published data look very promising for the intended hard modeling and will be tested in the near future.

• Hardware

Indirect hard modeling with quantum mechanical input will generate inaccurate results as long as the knowledge of the integral spectral efficiency of the Raman system is unknown. The measurement of this wavelength dependent transmission will be done by a blackbody radiation source. The spectrum of a black body radiator can be calculated by Planck's law. The ratio between measured and theoretical black body spectrum will then be used to adapt the theoretical spectrum to the experiment response.

• Validation measurements

After all items above are done, the hard model has to be verified. The line position can be verified accurately by high-resolution spectroscopy. Some of these measurement have been already performed, but they aren't reported here since it is beyond the scope of this thesis. In addition, a hydrogen - deuterium equilibration loop is built at TLK, this facility should provide accurate mixture samples of H_2 , HD and D_2 . These measurements can be used to verify the performance of the model.

Finally, indirect hard modeling is expected to be possibly the best answer to the quantitative analysis problem for the KATRIN Laser Raman system. Its advantages are enhanced precision, accountancy for non-linear effects and calibration from full quantum mechanical models.

CHAPTER 7. QUANTITATIVE ANALYSIS

Chapter 8

Summary and Outlook

8.1 Summary

The aimed sensitivity of $0.2 \,\mathrm{eV/c^2}$ of the neutrino mass measurement by KATRIN can only be reached if both, statistical and systematical uncertainties, are below $0.017 \,\mathrm{eV^2/c^4}$. The systematic errors are minimized by stabilization of the various subsystems on the 0.1 %level and by the monitoring of the relevant experimental parameters like column density, high voltage, etc.

The parameter ε_T describes the isotopic purity of the tritium gas which is being injected into the WGTS. A change in gas composition primarily causes a change in the count rate at the main detector. In addition, systematic effects occur within the source as scattering or the distribution of final-states which depend on the gas type.

Constant isotopic purity shall be obtained by the removal of impurities from the closed circle of the Inner Loop as well as the feeding of pure tritium into it. The composition of this gas mixture is monitored by in-line Laser Raman Spectroscopy with a precision of 0.1%.

The performance of the Laser Raman System developed by R. Lewis in 2005-2007 [Lew07] has been investigated within the scope of this thesis. Laser Raman measurements on tritiated gas samples have been performed for the first time at TLK and KATRIN. The first important achievement is the successful demonstration of the simultaneous monitoring of all six hydrogen isotopologues. Within these measurements a detection limit (3σ) of about $p_{\min} = 0.015$ mbar in an acquisition time of 1000 s is determined.

Moreover, systematic effects within the Laser Raman measurements have been investigated. These investigations in long term runs show that the system is stable except for few identified factors like laser induced color center formation or beam pointing instability. A precision of about 0.1% is reachable in 250 s for gas samples similiar to those used for KATRIN. The quantification of the experimental precision is consistent with the theoretical prediction by the known noise sources.

Indirect hard modeling (IHM) turns out be an appropriate tool which allows the quantitative analysis on the basis of quantum mechanical calculations and transition probabilities. The program is tested and the first results show an increase of the measurement precision compared to the method deployed before (e.g. $0.28\% \rightarrow 0.18\%$). However, the peak fitting of theoretical models to the measured spectrum has to be improved on the software and hardware side. From these first experiences a feedback was given to the development group of the IHM software.

In addition to these measurements and investigations within the scope of this thesis, new Raman cells and windows have been manufactured. In the field of laser power monitoring and laser safety, electronic systems are designed and installed. Furthermore, parts of the optical setup like fibre mounts have been replaced to enhance mechanical stability and more comfortable alignment. On the software side, the spectra acquisition software has been implemented in LabVIEW which allows an automated spectrum acquisition without external programs. This software includes already the spectrum post-processing and with some modifications it can be finally used for KATRIN runs.

8.2 Outlook

Several questions concerning the Laser Raman system have been answered within this thesis. However, new questions have arisen:

8.2.1 Investigation for signal and laser stability

- A calibrated laser power meter can be used independently in addition to the photo diode for the measurement of laser power stability during the long term runs. The pointing stability of the laser head can be investigated by beam tracing with a standard webcam. With these measurement the time and temperature dependence on power and pointing of the laser can be obtained [Fis10].
- The next logical steps are tritium measurements at Loopino to simulate the Laser Raman operation in KATRIN gas flow conditions. The interface between tritium circulation loop and the LARA system is realized by the ISS glove-box appendix as sketched in 8.1. In this situation, additional windows in the optical path have to be considered. The windows will pick-up vibrations from the glove box which may influence the measurements. The Loopino measurements are primarily planned as long term runs of several weeks. Results will be found in [Stu10].

8.2.2 Possible enhancements

• Back reflecting mirror

The signal can be enhanced by a factor of about two by the use of a spherical mirror. At the moment the mirror is not implemented to reduce the number of parts in the appendix which need optical alignment. The installation of such a mirror can be considered if the long term measurements at Loopino reveal that the precision of the measurement is worse than 0.1%.

• Cell surface coating, cell material

It can be assumed that another enhancement is achieved by using different materials



Figure 8.1: Sketch of ISS glove box appendix. (a) Situation as present within this thesis. (b) Situation for future measurements at Loopino and Inner Loop. The construction enables the interface between tritium circulation loop and LARA system. The second containment includes three view ports for laser beam and scattered light. The laser beam is surrounded by tubes and bellows to ensure light tightness of the LARA system. Note that all parts within the appendix can only be reached by gloves once the loop is commissioned with tritium.

for the Raman cell or by the application of coatings. Matted surfaces like Al_2O_3 can reduce the scattering and reflection contributions from the cell. An application of gold or copper coatings with lower permeabilities than stainless steel can reduce the diffusion of hydrogen into the cell walls. This cell may be useful for calibration issues because possible exchange reactions are minimized.

8.2.3 Quantitative analysis

The steps which have to be accomplished before the analysis system is finally suitable for KATRIN have been explained in detail in chapter 7. Thus it is summarized briefly. The fit functions have to be adapted to be compatible to the measured branches, the astigmatism has to be corrected wavelength dependent, the spectral efficiency has to be measured and finally the quantum mechanical calculations have to be implemented.

8.2.4 Suggestions for a second LARA System

In case of a system failure, a downtime of the whole KATRIN experiment cannot be tolerated. Therefore, a second LARA system is being assembled to act as backup system. Each single component is each cheaper and offers a slightly lower total light exposure: the maximum laser power is 2 W, the spectrometer's f-number is f/4 and a CCD with lower pixel number is used (1340 × 400). This system will also be used for further systematic investigation as long as the first system is connected to the Inner Loop.

8.2.5 Remarks on Resonant Laser Raman Spectroscopy (SRS and CARS)

Besides the linear Raman spectroscopy many modern spectroscopic techniques have been evolved which offer much higher sensitivities. These techniques allow a lower level of detection (a higher precision) in the same acquisition time or the other way around, shorter exposures at the same level of precision. However, the implementation of those techniques is sophisticated due to the great number of active parts working together.

The range of possible techniques is wide, examples are Stimulated Raman scattering (SRS) or Coherent anti-Stokes Raman scattering (CARS). An example for the capability of SRS, is given by Kyrlov et. al who reached an amplification factor of 10^9 for Raman scattering at H₂ [Kry96].

The question of composition determination of hydrogen mixtures at high sensitivity is also interesting in fusion technology. In some parts of the fusion reactor processing system the pressures are 1 bar and more [Bor09]. These conditions allow monitoring within 10 - 30 s on a 1% level precision with the present system. But in some parts of ITER, as the breeder blankets, minor traces of tritium have to be detected in the processed gases. The partial pressure is in the order of 0.01 mbar [Ric08]. For short term monitoring (< 250 s) at this high sensitivity one of the enhanced spectroscopy techniques is required.

A thorough investigation will reveal the method best suitable for the needs of the KATRIN experiment.

Appendix A

Alignment and calibration of the measurement setup

A.1 Alignment procedure of the optical path

Three different parts of the setup haved to be aligned in order to maximize the Raman signal before a measurement can be performed. The parts involved can be found in figure A.1. Pictures of the fibre mount can be found in the experimental chapter in figure 4.6.



Figure A.1: Sketch of the Raman setup Legend: M1, M2: laser beam steering mirrors. L1: f = 250 mm plano convex focusing lens. L2: laser monitoring lens. L3,L4: f = 75 mm plano convex collection lenses. CSM: collection side (fibre) mount. SSM: spectrometer side (fibre) mount. P: photo diode.

1. Alignment of the laser beam

The laser beam adjustment is necessary if modifications within this beam have been applied. Examples are the installation of additional optical components like lenses, polarizers or $\frac{\lambda}{2}$ -plates or the replacement of the Raman cell post.

The intention of the alignment is to confine the beam to the middle of the Raman cell to minimize inclined reflections and to maximize the solid angle of the scattering light cone.

The steering of the beam is performed by the HR coating mirror M1 mounted into an ultra stable kinematic mount. For the exact beam positioning iris diaphragms and target discs are used as auxiliary tools. If the beam passed two almost shut iris diaphragms at the same height in a certain range the beam is finally parallelized to the bread board.

The mirror M2 is used to steer the beam into the beam dump. The tilt of the lens L2 is determining the reflection angle to hit the photo diode P.

2. Collection side fibre adjustment

For a first order adjustment of the fibre the use of a cell filled with ethanol is utile. The liquid provides a higher particle density than gases and thus a very high Raman scattering. Even at low excitation powers (< 250 mW) ethanol provides distinct intensities within one second.

The alignment will be performed by using the collection side mount (CSM). It provides a travel in X,Y,Z direction and a rotation of the fibre as well. The steps of alignment are the following

- (a) The scattered light from the ethanol cell is clearly visible at the fibre as a tiny green line. With the gauge for forward and backward coarse positioning the point of focus has to be found. This is found if the image is the most sharp at the fibre surface. Then the fibre has to be moved by the gauges for up/down and left/right until the green light line fits approximately the 48 single fibres.
- (b) The subsequent fine tuning cannot be done by eye. The programme WinSpec[™] allows a full binning of all columns in the setting of the region of interest. The acquisition time is set to one second or below, the ACD read-out rate has to be set to 2 MHz and the acquisition is performed in 'focus'-mode¹. Now the three gauges (up/down, left/right, forward/backward) have to be fine-adjusted alternately to maximize the Raman signal of the ethanol peaks.
- (c) The rotation of the fibre can be checked with the non-binned 2D-spectrum in WinSpec[™] focus mode. If the fibre is twisted compared to the scattering image, parts of the 48 fibres appearing in the 2D-spectrum are only weakly illuminated. Note that the order of the fibres appearing at the CCD is scramble with the fibre cable bundle. If all fibres are illuminated more or less equally the rotation is optimized and can be locked by a screw.
- (d) Finally the ethanol cell has to be replaced by the cell intended to be used for the foreseen measurement. With the full binning focus mode the intensity of the peaks have to be maximized in the same way as in (2b).

¹focus-mode is continuous acquisition for alignment purposes

3. Spectrometer side fibre adjustment

The fibre mount at the spectrometer has to be aligned independently. The focus has to fit perfectly to the entrance slit of the spectrometer. Here no visible rough adjustment is possible because the slit is unaccessible hidden between filter unit and spectrometer enclosure, thus the focus-mode of $WinSpec^{TM}$ has to be used again. But in this case the full 2D-spectrum view is preferable. The steps of adjustment are the following:

(a) The first adjustment is to find the correct distance where the fibre exit is in the focus of the spectrometer imaging system. If the fibre is off-focus the spectrum is blurred, the mount plate has to be moved back and forth until the spectrum is sharp. At this point the mounting plate has to be locked.

- (b) The left/right adjustment has to be performed. If the fibre is mounted to far left or right, the light hits partly or completely on the jaws of the slit. Before adjusting, the slit width has to be set to a wide opening. The left/right adjustment will then be performed to maximize the intensity on the spectrum while closing the slit bit by bit.
- (c) The up/down adjustment entails the movement of the complete 48 single fibre on the 2D spectrum up and downwards. If all fibres are visible an the CCD image (ideally vertically centered) the alignment in this direction is fine.
- (d) If the fibre is twisted at the spectrometer side, the upper and lower part of the 48 fibres are faded out. The rotation has to be corrected until all 48 single fibres are visible with almost equal intensity.

It is clear, that an alignment at the collection side end of the fibre requires an optimal alignment at the spectrometer side and vice versa. This necessitates an alternating alignment at both sides until the optimum is reached. Before measurements are performed the ADC read-out rate has to be set back to 100 kHz for low noise acquisitions.

Usually only the collection side has to be aligned, since it is most sensitive to the actual scattering region. If a new cell is installed it is recommended to redo the collection side alignment because of little shifts in the optical path due to manufacturing tolerances.

A.2 Wavelength calibration of the CCD array detector

After every alignment of the spectrometer side fibre mount (SSM) the wavelength calibration of the CCD needs to be redone because of potential pixel shifts.

The spectral range of the hydrogen isotopologues is covered by the spectral lines of mercury and neon. Mercury emits generally in the blue and violet regime and neon has many spectral lines with higher wavelength (appearing red). The spectral lamp is placed at the position shown in figure A.2. For the acquisition of the spectral lines very short exposure times (< 1 s) are sufficient. The entrance slit of the spectrometer is closed to 25 µm to get very narrow lines. All spectral lines of mercury and neon are tabled. The pixel number (x)



Figure A.2: Place of the spectral lamp for wavelength calibration. The lamp is placed directly in front of the fibre input. If the CCD chip is saturated by the high luminosity a piece of paper can be placed between lamp and fibre to attenuate the light.



Figure A.3: Place of the laser pointer. At this position the laser pointer can point into the spectrometer to get a clean spectrum of a monochromatic line. This spectrum is used for astigmatism correction.

and the corresponding wavelength (λ) from about 10 lines are used to calculate a pixelto-wavelength conversion function. A second order polynomial turned out to be the most meaningful function. This computation can be done 'by hand' or by *Calibration-Utility* which is a LabVIEW VI by R.Lewis.

The generated calibration file is used in the automated acquisition software.

A.3 Generation of spectra for astigmatism correction

Before the correction of the image aberrations by astigmatism can be applied, the impact of this effect has to be characterized first. The bending of the lines is calculated by *AstCalc* from R.Lewis [Lew07] needing the spectrum of a monochromatic line as an input.

A laser pointer is a cheap tool providing monochromatic light and sufficient luminosity. Depending on the desired wavelength region a 633 nm or a 670 nm laser pointer can be chosen. The entrance slit width is set to $25 \,\mu$ m. To avoid the fibre structure on the 2D spectrum the laser has to point next to fibre into the spectrometer as shown in figure A.3. The laser pointer has to be adjusted until the whole spectrum is vertically covered by the laser line. This spectrum is than used as the input file for *AstCalc*. A detailed description of the *AstCalc* LabVIEW VI is found in its documentation [AST08]. The resulting astigmatism correction file is used in the automated acquisition software, as well.

Appendix B

Filling of cells

B.1 Filling of tritium containing mixtures

The filling of the cell for the Laser Raman measurements was performed by the team of the CAPER experiment. The CAPER facility is used for final clean-up of all tritium-containing waste gases at TLK [Bor05].

For purposes of clarity only the parts which are important for the mixing and filling process are shown in figure B.1. One of two loops can be activated; loop 1 incorporates



Figure B.1: Flow-chart diagram of filling facility. The relevant parts of the CAPER facility are shown, in which the tritium gas mixtures are prepared. (a) Different gas compositions are produced by mixing the desired amounts of the homo-nuclear gases T2, D2 and/or H2; for details of the loop 1 and loop 2 functionality, see text. (b) The sample cylinder (SC) is transferred from the mixing site for filling of the Laser Raman cell; monitoring of the gas filling is by gas chromatographic analysis and through a total pressure measurement (sensor P). (According to [Le09])

a permeator while loop 2 is built around an exchange reactor. The latter was used when hydrogen had to be added to a mixture, in order to prevent rarefying of the nearly-pure T_2 gas in the storage vessel. The exchange reactor runs at a temperature of about 290 °C; this provides thermodynamical equilibrium of the gas mixture within > 4 hours. Note that the exchange reactor could be by-passed if equilibration was not desired. Note also, that the operating principle of the permeator automatically generates equilibria. After mixing, a sample cylinder (SC) can then be connected at appropriate locations in the loops, and be filled with the prepared mixture, either behind the permeator output in loop 1, or after the exchange reactor in loop 2. The sample cylinder is then transferred to a cross to which a pressure sensor (P), a gas chromatograph and the Laser Raman cell are connected as well. After the gas mixture has been analyzed for purposes of recording the overall tritium content, using gas chromatography, the Raman cell is filled up to the desired pressure. Note that in the preparation of our tritium-containing samples we were limited to an equivalent of about 13 mbar of T₂ within the overall static-cell volume of 7.1 ± 0.7 cm³. This was dictated by the need that the Laser Raman cell had to be at an activity level of less than 10^{10} Bq when being handled under the extractor hood (i.e., outside a glove box).

B.1.1 Preparation of an almost pure tritium gas sample

Nearly-pure T2 gas produced in TLK's Isotope Separation System (ISS) [Doe02] is transferred from the tritium storage via the TLK-infrastructure to the CAPER storage vessel. Afterwards, the gas is circulated through the permeator back into the storage vessel, to clean the gas from impurities (loop 1 in B.1); note that because of the use of the permeator the isotopologues will be at thermodynamical equilibrium.

B.1.2 Preparation of tritium gas mixtures with deuterium D₂

Deuterium was expanded from a gas bottle into the loop until the desired pressure for the mixture was reached. Then circulation through loop 1 in figure B.1 was performed to obtain a thermodynamically equilibrated mixture.

B.1.3 Preparation of tritium gas mixtures with protium H_2

To prepare these mixtures, circulation through the permeator was avoided, in order to prevent rarefying of the nearly-pure T_2 gas in the storage vessel. Therefore, H_2 was added into the system only for circulation through loop 2 in figure B.1.



Figure B.2: Flow-chart diagram of filling equipment for inactive mixtures The procedure of filling is the following: the Raman cell is connected and evacuated by the vacuum pump. The tubing between gas bottle and connection cross is evacuated and flushed several times to avoid impurities. Finally, the valve in the gas supply pipe is closed and the volume to the cell is evacuated. Subsequently, the vacuum pump valve is closed and the gas supply valve is opened until the pressure sensor P reads the desired value.

B.2 Filling of mixtures without tritium

The mixtures without the tritiated constituents (T_2, DT, HT) are filled at a simple facility in room 219 (B.451) outside the monitored area of the Tritium Laboratory. It consists of three main components: a gas bottle, a vacuum pump connected to the TLK ventilation system and a pressure sensor. Unlike at the CAPER facility no possibilities for gas mixing or equilibration are provided, thus only pure or premixed gases are available. The procedure of filling is described in the caption of figure B.2.

APPENDIX B. FILLING OF CELLS

Appendix C

Supplements to the investigation of systematic effects with present setup

C.1 Investigation of the difference between peak height and peak area analysis

The ORIGIN Peak-Analyzer provides peak height as well as peak area as output. The following section reports on the investigation about which of both measures is advantageous for the analysis. The peak height and area determination of the Q_1 -branch are presented in figure C.1. Both methods are compared with regard to the accuracy and precision. The visualization of precision and accuracy is found in figure C.2 which shows the distribution of the relative intensities.



Figure C.1: Determination of peak area and peak height and the influence of noise. The D_2 peak is shown as an example. For the determination of the height only the highest point is used. For area determination in the present case 17 points are used, whereat the noise averages out.



Figure C.2: Distribution of relative intensities. Each of the three graphs is showing the distribution of the relative intensity of D_2 , HD or H_2 over a period of 173 h. The FWHM of the Gaussian indicates the precision of the relative intensity. All three graphs show that the determination of intensity by peak area (*blue*, *dashed*) has a higher precision than the determination by peak height (*red*, *solid*). The shift of the Gaussian center of each peak shows the discrepancy in accuracy between the 'area' and the 'height' method.

Table C.1: Discrepancy of peak intensity determination. The relative peak height is determined by the single Q_1 -branch height normalized by the sum of the height of the Q_1 -branches of all three species. The second method uses the area under the peaks normalized to the total area under all three peaks. The discrepancy $\frac{I-A}{A}$ is the relative deviation between the value of I= rel. peak height (%) and A= rel. area (%).

| Isotopologue | Rel. peak height $[\%]$ | Rel. peak area $[\%]$ | Discrepancy $[\%]$ |
|---|-------------------------|-----------------------|--------------------|
| $\begin{array}{c} \mathrm{D}_2\\ \mathrm{HD}\\ \mathrm{H2} \end{array}$ | 23.913 | 23.006 | 3.9 |
| | 47.545 | 47.613 | -0.1 |
| | 28.544 | 29.381 | -2.8 |

• Accuracy

In table C.1 the relative intensities of the Q_1 -branch of each isotopologue in sample S4 are listed in two ways. Once the intensity is determined by height and once by area. Normally, one would expect the same results. But an discrepancy $\frac{\text{rel. height-rel. area}}{\text{rel. area}}$ exists, which is nearly 4% for the D₂ line. The explanation for this effect is shown in figure C.3 where the Q_1 -branches for each of the three isotopologues are shown. The higher the mass of the molecule the smaller are the gaps between two single Q-lines. For D₂ all Q-lines appear to form a single nearly Lorentzian-shaped peak because of the resolution of the spectrometer. At HD the left wing of the peak is a bit more augmented. Finally, the shape of the H₂ peak doesn't remind to be a Lorentzian or Gaussian peak. In this case the single Q-lines are nearly so far apart as to be resolved by the spectrometer.

The peak height is proportional to the area under the peak, if the resolution of the



Figure C.3: Distortion of Q-branches. The figure shows the Q_1 -branches of D_2 , HT and H_2 (from left to right). The shape of the peaks is defined by the underlying lines of the Q_1 -branch. The lighter the isotopologues, the wider the energy-shift between the different Q-lines convoluted under a 'single' peak. Therefore, the distortion of the peak shape is maximal for H_2 .

spectrometer is coarse enough to convolute all single lines to one common line (or branch). This case is more or less given for D_2 . If the resolution is good enough to resolve single lines, the total branch height misses the contribution by the outer lines and hence it is not proportional to the peak area. For the very distorted lines like H_2 the height would be under-emphasized in comparison to its area. This trend can be found in table C.1.

• Precision

Table C.2 and figure C.2 show the precision of all peaks for each isotopologue determined by the peak height and the peak area method. The precision of the peak area determination is widely twice as high as for peak height determination. The peak height is only represented by one value, therefore it is directly affected by the noise. The area is a sum of contributions from many points, thus the randomly distributed noise should be averaged out for the determination of the intensity by area. This is visualized in figure C.1 on page 115.

C.2 Investigation of the influence of cell positioning

From time to time it is necessary to exchange the cells between two measurements. The reproducibility of the cell position and the influence of the Raman cell position on the absolute intensity, relative composition and the background intensity has to be investigated.

Two series of measurements are performed to investigate these possible influences. The first series are measurements with repetitive cell re-insertion reported in section C.2.1.

Table C.2: Precision of intensity determination. The precision of the intensity is determined by the double of the standard deviation of the Q_1 -branch intensity in 2400 spectra $(2 \cdot \sigma)$. The values below show, that the peak area intensity determination is nearly as double as precise as by peak height. In figure C.2 this difference is visualized by the smaller FWHM of the distributions shown there.

| Isotopologue | rel. int. (peak) $[\%]$ | rel. int. (area) $[\%]$ | $2\cdot\sigma$ (peak) [%] | $2\cdot\sigma$ (area) [%] |
|--------------|-------------------------|-------------------------|---------------------------|---------------------------|
| D_2 | 23.913 | 23.006 | 0.0777 | 0.0321 |
| HD | 47.545 | 47.613 | 0.1104 | 0.0503 |
| H_2 | 28.544 | 29.381 | 0.0985 | 0.0434 |

The second sequence of measurements are performed with a lateral shift of the cell. These results are found in section C.2.2.

C.2.1 Repetitive cell re-insertion

The measurements are performed with sample S4 at 985 mbar and 5 W laser power. The cell is mounted on the corresponding pillar post and two acquisitions are taken $(2 \cdot 250 \text{ s})$. Afterwards, the cell is removed and re-inserted to perform the next two measurements. This sequence is repeated 18 times.

C.2.1.1 Correlation between background, laser power and intensities

In figure C.4 (top) the peak area of D_2 is plotted together with the background intensity and the photo diode signal representing the laser power. For the trend of the D_2 -peak, it's immediately obvious that every first of the points of each reinsertion pair is always quite a bit lower than the second. This is due to some effect in the CCD, that the measurement after a short rest pause shows lower intensities. If this would be reduced the curve would be much less noisy. Further reading is found in the appendix D. With a rough view no correlations or anti-correlations are visible.

At the background curve, it can be seen that always the two measurement points belonging to one insertion have a quite similar intensity value. The absolute variation of the fluorescence background is nearly of the same order as the intensity of the peak, as it can be found in table C.3.

C.2.1.2 Stability of absolute intensities and relative intensities

Table C.3 contains all statistical data about absolute and relative intensities of the three isotopologues included in the measurement series. For the determination of mean and standard deviation, the first and the 18th measurement are excluded, since these measurement points are severe outliers. The exclusion of these points improves the statistic very much. The precision of the absolute intensities $(2 \cdot \sigma/I)$ is of the order 0.28 - 0.45%, which is surprisingly good for measurements with multiple reinsertions in between. From this it follows, that the cell position can be reproduced very precisely.



Figure C.4: Measurements of repetitive cell re-insertion. *Top:* Correlation between background, photo diode signal and intensity of the D_2 peak. After every second spectra the cell was reinserted. *Bottom:* Relative intensity of the three isotopologues.

The relative peak areas are plotted in figure C.4 (bottom). Here, the precision is 0.10% for HD, 0.11% for D₂ and 0.17% for H₂. This shows that the relative uncertainty of the reinsertion measurements is in the same order as in the longterm measurements with the same cell. These are discussed in section 6.4.

Influence of cell positioning - Conclusion The new cell holder produced during the scope of this thesis provides a very precise reproduction of the cell position. It features a very tight rail for the cell and has a stop at its end, which permits a precision of less than 0.5% for the absolute values. The relatively highest influence is on the background intensity. If only relative intensities are taken into account, a precision of < 0.17% is reached, which is very promising.

| Value | Isotopologue | Mean |
|-------------------|--------------|-----------------------|
| Peak area | D_2 | 2886.8 ± 4.2 |
| | HD | 5985.9 ± 10.8 |
| | H_2 | 3677.0 ± 8.2 |
| Rel. intensity | D_2 | $23.003\pm 0.013\%$ |
| | HD | $47.698 \pm 0.023\%$ |
| | H_2 | $29.299 \pm 0.025\%$ |
| Photo diode sign. | - | $13.3446 \pm 0.0045V$ |
| Bkg. intensity | - | 7.7 ± 1.6 |

Table C.3: Statistics of repetitive cell re-insertion measurements. The outlier at the 18th measurement is excluded from statistics.

C.2.2 Lateral shift of the cell

In this section the focus is set on the cell position and its influence on absolute and relative peak intensities. On the one hand these experiments are an extension to the reported re-insertion measurements, on the other hand it offers additional information on spatial reflection contributions.

C.2.2.1 Experimental setup

A movable cell post is used to test the influence of a slight beam offset within the cell. A sketch of the setup can be found in figure C.5. The maximum displacement of the cell is ± 3.5 mm since the laser entrance windows have only a diameter of 7 mm. The zero point is linked to the micrometer screw setting of 5 mm and all position data in the following plots are related to this arbitrarily defined central position.

The measurements are performed with sample S4 at 985 mbar and 5 W laser power. At each cell position a measurement is done with a acquisition time of 120 s.

C.2.2.2 Results

Absolute intensities, background and laser power In figure C.6 (top) the peak area of the D_2 , the background intensity as well as the photo diode signal are plotted against the cell positions.

The first observation is that the laser power signal at the photo diode decreases rapidly if the cell position reaches extreme values. There, the laser beam touches the borders of the entrance windows. At the final position (+3.25 mm) the background intensity rises from value < 10 up to 426, which is induced by reflections of the laser beam onto the stainless steel surface. The curves are mostly free of slope between the outer positions. In the photo diode signal four drops have to be noticed which seem to be symmetrically distributed at +2.25 mm/-2 mm and +0.75 mm/-0.5 mm. That points to a ring-like distribution in two dimensions. The peak area also descends partially at each photo diode drop, but the background intensity rises diametrically.



Figure C.5: Sketch of experimental setup. A cell post has been mounted on a travel stage able to translate via a micrometer screw towards or away from the collection optics.

Table C.4: Statistics of lateral shift measurements. The numbers are corresponding to the relative intensities of the three isotopologues in the lateral shift measurements.

| Isotopologue | Mean $(\%)$ | Standard deviation $(\%)$ |
|--------------|-------------|---------------------------|
| D_2 | 23.153 | 0.023 |
| HD | 47.451 | 0.039 |
| H_2 | 29.392 | 0.039 |

Probably, the cell geometry offers some special angles at which more light is reflected into the collection side than at the other angles. But the normal operation with the beam in a region of ± 0.5 mm around the central point is undistrubed.

These symmetrical distributed effects are almost gone in a repeated measurement series including a cell equipped with new laser windows. The overview about these measurements is plotted in figure C.7. The new windows appear to be free of the ring-like structure which is assumed for the old cell windows. These rings with higher absorption may be due to manufacturing or aging effects of the coating. The new windows are equipped with a more endurable coating [Hae09].

Relative intensities In figure C.6 (bottom) the relative intensities of all three isotopologues (D_2, HD, H_2) are plotted against the cell displacement. Only at +0.75 mm an outlier is found. The standard deviation of relative intensities (excluding the +0.75 mm-measurement) can be found in table C.4. The value for the precision $2 \cdot \sigma/I$ of the values is about 0.2% in 120 s. This proves that the relative intensity is mostly unaffected by wide cell displacements as expected.



Figure C.6: Measurements of lateral cell shifts. *Top:* Correlation between background, photo diode signal, intensity of the D_2 peak and cell displacement. The center cell position at 0 mm is chosen arbitrarily. *Bottom:* Relative intensity of the three isotopologues.


Figure C.7: Repeated measurement series with new laser windows. The correlation between background, photo diode signal, intensity of the D_2 peak and cell displacement is shown. The anti-correlation of photo diode signal & peak intensity towards background intensity observed in the former measurement (figure C.6 (top)) is not visible.

C.2.3 Conclusions

The measurement of repetitive cell re-insertion and lateral shift have been performed to investigate the reproducibility. The precision of absolute value is 0.5% and better. This result is beneficial for future calibration samples which need to be filled outside the Raman system and to be inserted afterwards for the measurement. The precision of the relative intensity is about 0.2%. The 10 year old windows used with the ASER [Tay01] are compared with new windows. It showed that the old windows exhibit a spatial distribution of regions with higher absorption. The absorption effects are investigated during the long term measurement (see section 6.4.4).

C.3 Variation in laser power

The laser power can fluctuate or drift just as well as the adjustment of the light collection can degrade mechanically during a long term acquisition. Therefore, the dependence of the amount of light exposure on the peak intensities is investigated.

C.3.1 Experimental setup

The cell is filled with sample S9 at about 431.5 mbar. The laser power is ramped from 0.5 W to 5 W in 0.5 W steps. At each power setting $4 \cdot 250 \text{ s}$ acquisitions are performed. The peak intensity, photo diode signal and background values reported in the following are the means of the four measurements of each power setting.

C.3.2 Results

- The first check is whether peak intensity, photo diode signal and background intensity are proportional to the nominal laser power (value on display of laser controller). Figure C.8 shows the corresponding graph. This graph proves that all quantities scale linear with the laser power. The linear fits are found in figure C.8, plotted with 95% confidence bands. On the one hand it affirms that the photo diode is an adequate measurement instrument for the laser power passed through the cell and on the other hand it shows that no non-linearities occur within the peak or background intensities.
- The last point to check is whether the relative intensities of the three isotopologues remain the same for different laser powers. In figure C.9 the dependence of relative composition on the laser power is shown. The lower the power the greater the error bar, because the signal-to-noise ratio gets worse. Despite of these uncertainties, a clear trend of the relative intensities is visible. The relative intensities are nearly constant for power settings between 2 5 W. For power settings the below 2 W the differences in intensity rises up to about 0.2 0.4 percent points. The relative intensities of the minor components DT and HD are enlarged relative compared to the main constituent D₂.

The reason for this phenomenon is found in the peak area determination. The peak analyzing program routine cannot detect the limits of the peak unambiguously at low the signal-to-noise ratios. Therefore, the routine includes the surrounding background or noise beyond the borders of the actual peak. In this case the peak area of the small peak is overvalued artificially in comparison to high peaks with very distinctive peak borders [Tel09].

C.3.3 Conclusion

The investigation with different laser powers showed that the determination of relative peak intensity is connected to the light exposure on the CCD. At a light exposure of less than 50 % of the maximal reference value, the relative intensities change in disfavour for major components. It is important to remember that this behaviour is not only connected to the laser power but in general to the amount of total light exposure. A misalignment of the collection optics and fibre or a beam walk which lowers the collected light by 50 % should have the same effect as a tune down of the laser from 5 to $2.5 \,\mathrm{W}$.

For a quantitative analysis especially for KATRIN runs it will be of major importance to monitor the laser power very precisely and to guarantee that the alignment is extremely stable.



Figure C.8: Signal proportionality on nominal laser power. The linear fits and the 95% confidence bands are plotted in each of the five charts. Note that the error bars given by the standard deviation as well as the confidence bands are only visible for the background intensity plot. It is shown that peak intensity, photo diode signal and background intensity show a very high linearity.



Figure C.9: Relative intensity dependency on nominal laser power. The constance of the relative intensity determined at each laser power setting vanishes for power lower than 2 W. The D_2 peak representing the major component of the mixture is suppressed for the low powers (< 2 W). The minor constituents DT and HD are elevated.

Appendix D

Software for data acquisition and automated processing

In this appendix a brief description on the custom-made data acquisition software for the LARA system is given. Details are available in the program documentation [Sch09].

The program PIXIS-Camera Control is written for the automated acquisition and processing of Raman spectra. A sketch of the program flow is shown in figure D.1. It consists of three basic parts: (1) the initialization of the acquisition hardware, (2) the parameter setup by the user and (3) the main program loop. This loop contains the acquisition of the raw data from the CCD, the processing of these data and the recording of the photo diode signal for laser power monitoring. Finally, the raw data, the processed spectra and the photo diode trend are stored in individual files. For convenience, an ini-file can be used to store the acquisition parameters and filename of resources data (astigmatism file, calibration file and WinSpec header-file).

The program is implemented in the graphical programming language LabVIEW. It offers fast building of graphical user interfaces and easy access to external measurement and control units. Programs written in LabVIEW are called Virtual Instruments (VIs), because their appearance and operation imitating physical instruments. Every VI uses functions that manipulate input from the user or external measurement sources and displays the information or moves it into files or other computers [LAB05]. The so-called block diagram of the PIXIS-Camera Control is shown in figure D.3 whereby the three basic parts of the program are visualized. For the sake of clarity and structure most of the routines are contained in sub-programs, called 'sub-VIs', which appear as icons in the block diagram. Short descriptions of the written sub-VIs are found in table D.1 for the 'initialization' part, in table D.2 for the 'setup' part and in table D.3 for the 'main loop'.

One group of VIs are created for the direct control of CCD cameras from Roper Scientific without additional software. This access to the camera hardware is offered by the so-called PVCAM¹ library [PVC04] (contained in a DLL).

The PVCAM interface and the camera are initialized by the according sub-VI whereat a handle is generated which is needed as identification input for all following PVCAM operations (see tables D.1, D.2 and D.3).

 $^{^1\}mathrm{PVCAM}{=}\mathrm{Programmable}$ Virtual Camera Access Method



Figure D.1: Schematic structure of the program flow



Figure D.2: Two tabs of the front panel of PIXIS-Camera Control. Settings for the acquisition(s) (*left panel*) and for the CCD temperature and pre-amplifier (*right panel*).

In each iteration of the main loop the spectrum acquisition is performed via the PVCAM routines. These output raw data is processed by (a) cosmic ray removal (DCRR) [Lew07], (b) Astigmatism Correction (AstCor) [Lew07], (c) spectral binning and (d) wavelength calibration file during the subsequent iteration parallel to next spectrum acquisition to avoid downtime. During the duration of the acquisition the photo diode signal is recorded each second.

The trend of photo diode and the processed spectra are saved as ordinary ASCII files. The raw data is saved in the file format (*.SPE) of the custom software WinSpec by Roper Scientific/Princeton Instruments. Therefore the raw spectra are accessible on computers with WinSpec but without LabVIEW license. Writing and reading to and from *.SPE files is permitted by the access through a sub-VI to a custom-written DLL².

The modular program design by using sub-VIs offers flexibility for changes or upgrades of the software. For example, the future sub-VIs for quantitative analysis can be easily integrated into the program. Therefore, this program is the fundament for the final laser Raman acquisition software for KATRIN.

²DLL=dynamic link library



Setup

Figure D.3: Block diagram of main LabVIEW VI. The graphs shows the 'program code' of the main program, the three basic parts are marked. Sub-VIs are indicated by square-like icons. A brief description of each sub-VI is found in tables D.1 to D.3.

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Table D.1: Sub-VIs in the part 'Initialization' of PIXIS-Camera Control. The connections to the sub-VI's icon on the left represent inputs. The right stands for the outputs.

| Name & Icon | Short description |
|---|--|
| Get camera name PVCAR Namee Cam-Names Error | Initializes the PVCAM interface and returns an array of the names of all connected CCD-cameras. |
| Camera selection Camera Names error in (no error) Camera Selection OK error out | Opens a dialog for the user to select a CCD-camera to operate. |
| Open camera Standard open first Cam? (T) Open Cam Number OPEN Error | Initializes the selected CCD-camera and returns the handle which is needed for all PVCAM accesses. |
| Load from Ini-File .spe Header-file Calibration file Astigmatism file ROI SetTemperature Gain ReadoutMode PreClear CCD Binning | Loads the stored settings from the ini-file 'config.ini'. |

| Name & Icon | Short description |
|--|--|
| Get CCD size Handle Parallel CCD Size Error | Reads the width and height of the CCD chip (pixel). |
| RS config_Path RSConfig_Path error out | Executes the external program RSConfig.exe from Roper Scientific to configurate the CCD cameras. |
| Get pre-amp settings Handle Fixel Time Readout Mode ADC Offset | Reads out the actual settings from the CCD pre-amplifier: Gain, readout speed (reciprocal to pixel time), readout mode and ADC offset. |
| Set pre-amp settings Handle Gain Readout Speed | Writes settings for the CCD pre-amplifier: Gain and readout mode. Readout mode and ADC offset are determined by the readout speed automatically. |
| Get temperature settings Handle | Reads out the actual temperature and temperature set-point of the thermal control element (Peltier) on the CCD. |
| Set temperature settings Handle Temperature Setpoint Error | Writes the temperature set-point for the thermal control element (Peltier) on the CCD. Afterwards the temperature will be regulated until the set-point is reached. |
| Auto path/filename (1) Description Laser Power Slit Width CCD Temperature Acquisition Time CCD Temperature | Generates the first part of the auto-named filename in the following format: (descr.)_powerW_slitu_tempdeg_acq.times |
| Save to Ini-File ReadoutMode Gain SetTemperature ROI Astigmatism file Calibration file Spe Header-file Binning PreClear CCD | Save the present settings to the ini-file 'config.ini'. |

Table D.2: Sub-VIs in the part 'Setup' of PIXIS-Camera Control. The connections to the sub-VI's icon on the left represent inputs. The right stands for the outputs.

Table D.3: Sub-VIs in the part 'Main loop' of PIXIS-Camera Control. The connections to the sub-VI's icon on the left represent inputs. The right stands for the outputs.

| Name & Icon | Short description |
|--|---|
| Acquire spectrum Handle Exposures Acquisition Time ROI | Starts the spectrum acquisition and reads out the data from the region-of-interest (ROI) after the acquisition time. The output is an unsigned 16 bit one dimensional array. |
| Post-processing Info-Stream Astigmatism Data Raw Data Rol Calibration Data Time Stamp Bin-Dimensions | Applies all post-processing routines which are (a) cosmic ray removal (DCRR) [Lew07], (b) Astigmatism Correction (AstCor) [Lew07], (c) spectral binning and (d) wavelength calibration. Afterwards the processed spectrum is saved. |
| Auto path/filename (2) Path (Folder) Time Stamp Concated Path (String) Extension | Second part of the filename generation. This VI adds the destination folder, a time stamp (YYMMDD-HHMM), the acquisition number and an extension (.spe, .proc, .stab). |
| Write to *.SPE ADC_offset Gain CCD Temp Exposure Time Header-File Filename Data Stream Width (X) Height (Y) Time Stamp Readout_Mode | Saves the raw data in the native WinSpec format *.spe. It requires many inputs for the file header. |

Appendix E

Calculation of the interaction region's geometry

The calculation of the dimensions of the scattering region is carried out according to [Lew07]. The focal region of a focused Gaussian beam is shown in figure E.1. The spot size of the focused beam at the beam waist ω_0 can be calculated by

$$\omega_0 = \frac{\lambda}{\pi \tan \Theta} = \frac{\lambda \cdot f}{\pi \cdot R} \tag{E.1}$$

where f is the focal length and R the radius of the laser beam at the lens [Lew07]. For the optical configuration of the LARA system (f = 250 mm, $\lambda = 532 \text{ nm}$, R = 1.5 mm) the beam waist is at

$$\omega_0 = \frac{532\,\mathrm{nm} \cdot 250\,\mathrm{mm}}{\pi 1.5\,\mathrm{mm}} \approx 28.2\,\mu\mathrm{m} \tag{E.2}$$

This corresponds to a minimal beam diameter of $56.4 \,\mu\text{m}$. The confocal parameter b is dependent on the depth of the focus (the length of scattering region) and can be calculated based on [Lew07].

$$b = \frac{2\pi\omega_0^2}{\lambda} = \frac{2\pi(28.2\,\mu\text{m})^2}{532\,\text{nm}} \approx 9\,\text{mm}$$
 (E.3)



Figure E.1: The geometry of a focused Gaussian beam. The red bend line represents the beam radius $\omega(z)$ with in scattering region with the beam waist ω_0 . Θ is the beam divergence and b is the focal parameter.(According to [Lew07])

Appendix F

LARA Safety Interlock system

F.1 Introduction

The purpose of an interlock system is to protect the operating people from the potential risk of injuries, as well as the LARA system itself in case of malfunction. The safety principle of the LARA system (XTA4¹) installed at TLK is based on the use of a certified laser shutter, which is connected to an interlock chain. If the chain is broken at any position, the shutter (positioned directly in contact with the laser output aperture) will immediately interrupt laser emission.

The potential causes for breaking the interlock chain are:

- 1. unauthorized opening of the top cover, which encloses the laser beam
- 2. the accidental dislocation of the laser beam away from its safe beam energy dump; or
- 3. power failure to the system.

F.2 Normal operation of the LARA-setup

If the top cover is closed (see figure F.1), the magnetically encoded switches in the interlock chain are closed.

At the end of the laser beam path the beam dump absorbs the laser power. By using a beam sampler glass plate, a small fraction of the light is reflected out of the laser beam onto a photo diode detector. Its photo current is amplified by a current-to-voltage converter circuit. If its output voltage is higher than a set threshold, the comparator activates a relay, which closes the full interlock chain. As long as the laser beam reflection is recorded by the photo diode, the relay switch remains in its active position, and the laser shutter is open.

 $^{^{1}\}mathrm{TLK}\text{-code}$



Interlock chain

Figure F.1: Normal operation of the interlock system

F.3 Safe state



Figure F.2: Safe state. Laser is blocked by shutter

If the shutter has been closed by an interruption in the interlock chain, or by manually closing, the laser emission is completely blocked. The laser continues to operate, however, until it is switched off manually (a manual switch-off procedure needs to be followed to avoid potential damage to the laser itself). The shutter is capable to absorb a maximum optical power of 20 W [Las07].

Note that even if any electronics would fail, or the overall power to the system be removed, the shutter will continue to operate since it defaults to its gravity-driven "fail-safe shut" position.

The shutter never opens automatically; it is always necessary to re-activate the interlock system and the shutter manually.

F.4 Interlock activation after to opening of the top cover



Figure F.3: Top cover lifted, which causes a break in the interlocking chain

If the cover lid is lifted accidentally, or intentionally, one or both magnetic switches will open and break the interlock chain. As a consequence, the activation voltage to the shutter is removed, it defaults to its safe-position, and the laser beam is prevented from entering the LARA system. This prevents the laser beam from posing a potential risk to personnel in the room.

F.5 Interlock activation after laser beam dislocation



Figure F.4: Dislocated laser beam, which causes a break in the interlock chain

During long-term laser operation with high power the very unlikely case may occur that an optical part fails. As a consequence, the laser beam might become dislocated and be directed to an area of the system enclosure, which might not withstand prolonged exposure to high-power laser radiation.

After a laser beam dislocation the photo diode would not be illuminated any longer. Thus, the output voltage at the amplifier will fall below the set threshold voltage, and the comparator will de-activate the relay. This breaks the interlock chain, and the laser shutter will revert to its fail-safe shut position.



F.6 Re-activation of the interlock system after failure

Figure F.5: Procedure of activation / re-activation of the interlock system.

As long as the laser shutter is in its closed position, the relay switch remains open as well, because the monitoring photo diode is not illuminated by the laser. Since the relay switch is also a fail-to-safe device, the shutter cannot be opened again until the fault has been rectified and the interlock system has been re-activated.

To re-activate the system, first one has to manually bridge the relay switch by operating a momentary-action bypass toggle-switch. This closes the interlock chain, and the shutter can be opened again to admit laser radiation to the LARA system.

If the laser power is high enough so that the received photo current signal surpasses the comparator threshold, the relay bypass-switch can be switched back to "normal" operational mode.

Full safe-operation conditions are then re-established.

F.7 Alignment mode

The interlock can be bypassed if the optical system has to be aligned with the laser activated. The by-pass supplies the shutter with power ignoring the status of the magnetic switches and the comparator circuit. During the alignment mode the access to the room in which the setup is located has to be restricted.

Normal measurements mustn't be performed in alignment mode because laser safety is only provided without the bypass.

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