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„Quantum Diffraction of Biomolecules:  
From Source to Interference“

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## 0.1 Abstract

In quantum physics the investigation of wave-like behaviour of complex particles and testing the principle of quantum superposition for these particles has become a field of interest over the last decades. Additionally, the application of this phenomenon in metrology becomes relevant. Quantum interference allows the study of molecular properties by imprinting a nanoscale density pattern onto molecular beams. By utilizing this technique in the Kapitza-Dirac-Talbot-Lau interferometer (KDTLI) – a matter-wave interferometer in the near-field regime – we investigated optical and electronic properties of vitamins with spatial resolutions orders of magnitude higher than achieved with classical experiments.

Furthermore, we demonstrated the first quantum interference of tripeptides, the building blocks of life. This motivates further investigation of even more complex biomolecules.

All these experiments foremost require a stable molecular beam. Although nowadays a variety of different beam sources exist, not all of them are suitable for our purposes. For interference experiments we need stable beams of neutral particles with high intensity. An effusive source fits our purposes as well as the detection scheme in the KDTLI. However, the Knudsen cell used in the KDTLI has its limits when it comes to fragile and thermolabile molecules. Thus we developed a new furnace with improvements in terms of beam intensity and heating rate allowing the launch of more fragile particles like biomolecules. A working interferometer, though, is more than just its components – it needs an alignment of high accuracy to obtain interference in the first place.

In summary, this thesis considers the molecules' travel as matter waves: starting with the transition from the solid state into the gas phase in an improved furnace, passing a well aligned interferometer up to the point of detection and thus, obtaining an interference pattern, which in turn allows the investigation of the molecular properties.

## 0.2 Zusammenfassung

In der Quantenphysik hat die Untersuchung der Welleneigenschaften komplexer Teilchen im Laufe der vergangenen Jahrzehnte an Interesse gewonnen. Nicht nur der Nachweis des Superpositionsprinzip spielt dabei eine Rolle, sondern auch die Anwendung dieses Phänomens in der Metrologie. Quanteninterferenz erlaubt es, Moleküleigenschaften zu studieren, indem einem Molekülstrahl ein Muster im Nanometerbereich eingeprägt wird, welches anschließend detektiert werden kann. Am KDTLI – einem Materiewelleninterferometer im Nahfeldbereich – haben wir diese Technik angewendet, um sowohl optische als auch elektronische Eigenschaften von Vitaminen zu bestimmen. Die räumliche Auflösung übersteigt dabei jene klassischer Experimente um mehrere Größenordnungen.

Weiters gelang es uns, erstmalig Quanteninterferenz für Tripeptide – die Grundbausteine des Lebens – zu demonstrieren. Dies motiviert zu weiterführenden Experimenten in diese Richtung mit noch komplexeren Biomolekülen.

Um derartige Experimente überhaupt durchführen zu können, benötigt man zuerst einen stabilen Molekülstrahl. Obwohl mittlerweile zahlreiche verschiedene Quellen für Molekülstrahlen existieren, eignen sich nicht alle für Quanteninterferenz-Experimente. Eine wichtige Anforderung an die Quelle ist es, einen Strahl neutraler Teilchen mit hoher Intensität zu produzieren. In unserem Fall eignet sich dafür eine Effusivquelle, da sie sowohl einen stabilen Strahl neutraler Teilchen liefert, als auch mit unserer Detektionsmethode kompatibel ist. Allerdings stoßen Effusivquellen – so auch jene, die wir am KDTLI verwenden – bei der Verdampfung leicht fragmentierender und hitzeunbeständiger Moleküle an ihre Grenze. Daher haben wir eine modifizierte und verbesserte Version entwickelt, deren höhere Strahlintensität und Heizrate die Verdampfung eben jener leicht fragmentierender Teilchen – zu denen auch Biomoleküle zählen – ermöglicht. Ein funktionierendes Interferometer ist jedoch noch mehr als nur die Summe seiner einzelnen Bestandteile – es muss sehr akkurat justiert sein, um überhaupt einen Interferenzkontrast zu liefern.

Zusammenfassend behandelt diese Masterarbeit daher die "Reise" von Molekülen in der Form von Materiewellen – beginnend bei deren Übergang vom festen in den gasförmigen Zustand durch Verdampfung in einer verbesserten Effusivquelle über die Erzeugung des Interferenzmusters in einem präzise justierten Interferometer bis hin zur Detektion dieses Musters, welches dann wiederum die Untersuchung der Moleküleigenschaften erlaubt.

# 1 Introduction

In 1923, Louis de Broglie developed the theoretical concept of the wave nature of matter. However, in our everyday life we do not experience this wave nature, but need tools to proof this theoretical concept. One possibility to do so is matter-wave interferometry, which nowadays has a broad field of applications. It allows for probing fundamental physics [5] [47] [65] [80] [86] and serves as an important tool for atom optics [18] [61], advanced quantum sensors [8] [39] [38] [73] [81] and in quantum technology in general [16] [85]. Furthermore, the wave nature has been shown for large molecules like fullerenes [4], molecular clusters [48] and tailor-made macromolecules [35] as well.

This thesis considers such a matter-wave interferometer for large particles operating in the near-field regime using the Talbot-Lau configuration as well as the Kapitza-Dirac effect. In chapter 2 I will introduce the theory of a Kapitza-Dirac-Talbot-Lau interferometer (KDTLI). It consists of three gratings positioned at equal distances to each other. The first grating creates the transverse coherence of the molecular beam. The molecules then are diffracted at a standing light wave, which is the second grating. The third grating scans over the molecular beam to obtain the interference pattern. After the theoretical concept follows a description of the experimental setup of the KDTLI including the molecular source as well as the detection scheme and the peripheral devices.

Chapter 3 contains the alignment protocol for such an interferometer. Here, I will discuss the required accuracy of the gratings' alignment with respect to each other as well as to gravity and to the molecular beam.

Besides the interferometer itself, another crucial part of such an experiment is its molecular source, which I will discuss in chapter 4. The KDTLI operates with an effusive source. A thermal source is easy to handle, provides a high flux of the molecular beam as well as a good signal-to-noise ratio. However, for thermolabile massive molecules the heating process can lead to fragmentation before they evaporate, such that they don't form a molecular beam at all. This is

especially true for biomolecules like vitamins and peptides. Thus, we decided to develop a fast heating effusive source. In chapter 4 I introduce the new design of our source as well as the theoretical considerations of a Knudsen cell.

After describing the experiment itself including the source, I will finally show some results of measurements with the KDTLI in chapter 5. Quantum interference provides a tool to investigate molecular properties in the gas phase. Especially biomolecules are particles of interest, since their electrical and optical properties influence their behaviour in living organisms. However, in living organisms the molecules are not isolated at all, while the characteristic feature of the gas phase is the absence of bulk matter such that the molecules cannot exchange energy with their environment. This allows for studies of their intrinsic properties like structure and reactivity with high precision in a well-defined system and provides an understanding of their intermolecular interactions. Furthermore, computational modelling of the intermolecular interactions is easier for isolated particles in the gas phase. For the verification of these models experimental investigations in the gas phase are necessary. [37, p. 13] [57] [84]

We determined the optical polarizability of neutral vitamins via their interaction with the standing light wave. Furthermore, we measured the shift of the interference fringes induced by applying an external electric field. This allows for the extraction of the molecules' electric properties. While the vitamins have masses between around 430 amu and 540 amu, we also demonstrated quantum interference with a tailor-made tripeptide with a mass of more than 1000 amu. This is the first demonstration ever of quantum interference with peptides, which are building blocks of life.

# 2 A Kapitza-Dirac-Talbot-Lau Interferometer

## 2.1 Theory of a matter-wave interferometer

The Kapitza-Dirac-Talbot-Lau interferometer (KDTLI) is a near-field matter-wave interferometer. In this chapter I will first describe the basic concepts of interference, matter waves and their diffraction in the near- and the far-field. Subsequently, I will introduce the phenomena used in the KDTLI for preparation, diffraction and detection of the molecules - namely the Talbot-Lau effect as well as the Kapitza-Dirac effect which are the determining factors not only for the name of the experiment, but also for the observation of matter-wave interference in this setup.

### 2.1.1 Matter waves

In 1938 Einstein noted on the duality of particles and waves:

It seems as though we must use sometimes the one theory and sometimes the other, while at times we may use either. We are faced with a new kind of difficulty. We have two contradictory pictures of reality; separately neither of them fully explains the phenomena of light, but together they do. [31]

However, Einstein's proposition is not only true for light, i.e. photons which are particles without rest mass, but it is equally valid for particles with rest mass, i.e. elementary particles such as electrons as well as compound particles like atoms or molecules. A full description of their behaviour is not possible by characterizing them as localized and distinguishable, in addition the wave-particle dualism has to be taken into account as well.

In analogy to the concept of wavelength for electromagnetic waves, Louis de Broglie combined Einstein's theory of relativity and the relation between energy and frequency of light quanta and

introduced the de Broglie wavelength for particles with rest mass  $m$  as [11, p. 6]

$$\lambda_{dB} = \frac{h}{mv} = \frac{h}{p} \quad (2.1)$$

where  $h$  is the Planck constant,  $v$  the particle's velocity and  $p$  its momentum. This concept describes the center-of-mass motion of a free particle in terms of a wave-like behaviour where the different position states of one particle can be in superposition. The state of a quantum system can be described by its wave function  $\psi$ , which is a vector in Hilbert space. Throughout the last century scientists proved this concept experimentally for a variety of particles. The first demonstration for the wave nature of electrons was given in two independent experiments. In 1927, G. P. Thomson fired electrons through a thin metal foil [97] and C. Davisson and L. Germer diffracted an electron beam at the lattice of a crystal [19]. In both experiments electron diffraction was observed. Later on, experiments also showed the wave nature of neutrons [77], atoms [32] and even molecules [4].

The observation of the wave nature of matter in quantum physics is not possible directly, but rather on the basis of counting localized particles after diffraction by a grating. Thus, the interference after the interaction appears in terms of a density pattern. A more detailed description of interference and visibility follows in chapter 2.1.3.

In order to reveal diffraction, a coherent particle beam has to interact with structures, i.e. slits/apertures/gratings, delocalized over at least two slits of that structure. Since the de Broglie wavelength of massive particles is often very small compared to the wavelength of light due to their high momenta even at low velocities, the wave nature is usually not observable in the macroscopic world, but it plays an important role in the description of the microscopic world which is well described by quantum mechanics.

## 2.1.2 Coherence

To observe interference of a particle beam, the beam has to be sufficiently coherent, i.e. the correlation between two separate space-time points of the matter wave has to be stable spatially (transversely) and temporally (longitudinally). [53]

Transverse or spatial coherence over at least two slits of the diffraction grating is necessary. For incoherent sources, the transverse coherence depends on the size of the beam source, which may



be an aperture or slit of size  $s$  illuminated by an initially incoherent particle beam. According to the Van Cittert-Zernike theorem, the coherence width  $W_c$  of the beam after a distance  $L$  behind the aperture can be estimated by [53]

$$W_c \propto 2 \cdot \frac{L\lambda_{dB}}{s} \quad (2.2)$$

Thus, small particle wavelengths  $\lambda_{dB}$  require either a small aperture  $s$  or a long distance  $L$  to obtain a sufficient coherence width  $W_c$ .

For the temporal or longitudinal coherence the distribution of de Broglie wavelengths within the beam is the determining factor. A measure for the longitudinal coherence is the coherence length  $L_c$  according to the Wiener-Khinchin theorem, which is proportional to the beam's velocity distribution [53]:

$$L_c \propto \frac{\lambda_{dB}^2}{\Delta\lambda_{dB}} \sim \frac{\Delta p}{p^2} \sim \frac{\Delta v}{v^2} \quad (2.3)$$

In the experiment, the preparation of longitudinal coherence is realized by velocity selection.

### 2.1.3 Interference and visibility

Interference describes the phenomenon of at least two coherent waves interacting with each other. At each point in space the resulting amplitude is the sum of the individual amplitudes of the waves at this location. The resulting interference pattern depends on the relative phase of the waves. This leads to constructive interference, if the waves are in phase, and to a decrease of the interference contrast, otherwise.

The normalized mutual coherence function describes the correlation between two points of the field by

$$\gamma_{12}(\tau) = \frac{\langle (\psi_1(t+\tau)\psi_2^*(t)) \rangle}{\langle \|\psi_1\|^2 \rangle \langle \|\psi_2\|^2 \rangle} \quad (2.4)$$

where  $\psi_1$  and  $\psi_2$  are the amplitudes of two waves [49, p. 570]. The intensity pattern of the interference contrast resulting from the superposition of two partially coherent waves depends on

the real part of the coherence function and is given by

$$I = I_1 + I_2 + 2\sqrt{I_1 I_2} \operatorname{Re}(\gamma_{12}(\tau)) \quad (2.5)$$

If the intensities  $I_1$  and  $I_2$  are equal, the fringe visibility of the interference pattern  $V = \|\gamma_{12}\|$  can be expressed in terms of the modulus of the coherence function [49, p. 571]. Experimentally the visibility  $V$  for a sinusoidal density distribution is given by

$$V = \frac{I_{max} - I_{min}}{I_{max} + I_{min}} \quad (2.6)$$

which is the amplitude of the intensity over its mean value.  $I_{min}$  and  $I_{max}$  are the numbers of particles detected at the minima and the maxima of the interference pattern respectively. In the KDTLI the detected signal is nearly sinusoidal. Hence, equation 2.6 offers a good approximation for the obtained interference contrast. The exact expression for the visibility used in the KDTLI is discussed in chapter 2.1.6.

It is noteworthy that in the KDTLI the molecules are distinguishable in terms of their internal states such that each molecule's delocalized center-of-mass wave function interacts with itself. Thus, the interference pattern would be the same even if the beam density were reduced to only one molecule passing the interferometer at a time.

#### 2.1.4 Coherent diffraction in the near- and far-field

According to Richard Feynman, "No one has ever been able to define the difference between interference and diffraction satisfactorily. It is just a question of usage, and there is no specific, important physical difference between them." The difference is one of convenience and convention. If the waves to be superposed originate from a few coherent sources, say, two, the effect is called interference. On the other hand, if the waves to be superposed originate by subdividing a wavefront into infinitesimal coherent wavelets (sources), the effect is called diffraction. [98, p. 380]

The Kirchhoff-Fresnel integral describes the propagation of a wave behind an aperture  $s$  using the Huygens-Fresnel principle, which assumes that every point of the wavefront is a source of secondary spherical wavelets.

The superposition of these secondary waves leads to interference [49, p. 444f]. Each secondary wave  $\psi_{sec}$  in the aperture contributes to the emanating field amplitude  $\psi_P$  in point  $P$  with

$$d\psi_P = C \cdot \frac{\psi_{sec} \cdot ds}{r} e^{-ikr} \quad (2.7)$$

where  $C$  is a proportionality factor containing the wavelength as well as the direction of the emanating wave,  $k = 2\pi/\lambda$  is the wavenumber and  $r$  is the distance between the source point and the image point [21, p. 340].

The Kirchhoff-Fresnel integral then gives the total field amplitude of the emanating field at point  $P(x, y, z)$  over the transmission function of the aperture  $f(s)$  [21, p. 571]:

$$E_P(x, y, z) = C \cdot \int_{s(x)} \int_{s(y)} E_s \cdot \frac{e^{-ikr}}{r} dx dy \quad (2.8)$$

Instead of the Kirchhoff-Fresnel integral for calculating the diffraction, one can use either the Fraunhofer approximation for far-field diffraction or the Fresnel approximation for near-field diffraction, depending on the distance  $r$  between the source point  $P_s(x_s, y_s, 0)$  and the image point  $P_i(x_i - x_s, y_i - y_s, z_0)$ . Figure 2.1 shows the geometrical relation of the two points. The distance  $r$  is given by [21, p. 341]

$$r = \sqrt{(x_i - x_s)^2 + (y_i - y_s)^2 + z_0^2} \quad (2.9)$$

where  $z_0$  is the plane of the screen. For the approximations,  $r$  is expressed in terms of a Taylor expansion in the coordinates of the aperture:

$$r = z_0 \left( 1 + \frac{(x_i - x_s)^2}{2z_0^2} + \frac{(y_i - y_s)^2}{2z_0^2} + \dots \right) \quad (2.10)$$

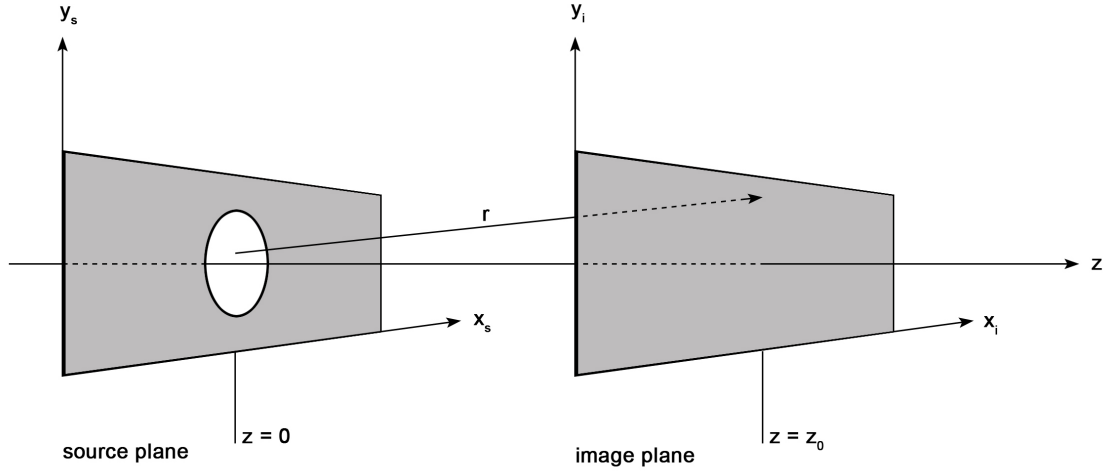


Figure 2.1: Diffraction geometry with the source plane at  $z = 0$  and the image plane at  $z = z_0$ . The distance between a source point  $P_s(x_s, y_s, 0)$  in the aperture and an image point  $P_i(x_i - x_s, y_i - y_s, z_0)$  on the screen is then given by  $r$ .

The characteristic distance  $L$  for the transition from the near- to the far-field regime for the diffraction at a grating not only depends on the wavelength  $\lambda$  of the beam and the period  $d$  of the grating, but also on the number  $N$  of illuminated slits:

$$L = \frac{d^2 N}{\lambda} \quad (2.11)$$

If the distance between the source and the image plane is  $z_0 \gg 1/\lambda \cdot (x_s^2 + y_s^2)$ , the quadratic and all higher order terms of the Taylor expansion for  $r$  are neglectable, since the incident wavefront on the screen can be supposed to be plane. This is the far-field regime, where the Kirchhoff-Fresnel integral for the field amplitude can be replaced by the Fraunhofer approximation. [21, p. 341]

Diffraction experiments of matter waves in the Fraunhofer regime were first realized with electrons [58]. Later on, such experiments were also made with neutrons [102], atoms [62] [14] [91] and even beams of cold helium clusters [87] [13] as well as with more complex molecules, e.g. hot fullerenes [4] [71] and molecules with masses beyond 1000 amu [59]. Although the setups for such far-field diffraction experiments are easy in principle since they only consist of one grating, they require a well collimated particle beam which is significantly narrower than the diffraction angle. This requirement decreases the particle flux and thus increases the measurement time. Furthermore, experiments with higher masses demand either lower particle velocities or longer

interferometers in order to obtain sufficient coherence according to equations 2.2 and 2.3, since their de Broglie wavelength grows linearly with the particle's mass.

In contrast, the requirements for near-field diffraction in a Talbot-Lau setup are not as strict. In the near-field regime the Fresnel approximation of the Kirchhoff-Fresnel integral is valid. The distance  $r$  between the source point and the image point is large compared to the values  $x_s, y_s$  of the aperture. This allows for the approximation of  $r$  by  $r \approx z_0$ . But since in the near-field the curvature of the wavefront is not negligible, the phase of the wavefront still depends on  $r$ . Thus, the quadratic terms of the Taylor expansion must be taken into account as well, leading to the Fresnel approximation which is given by [21, p. 341]

$$\psi_i(x_i, y_i, z_0) = i \cdot \frac{e^{-ikz_0}}{\lambda z_0} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \psi_s \cdot e^{\frac{-ik}{2z_0}[(x_s-x_i)^2+(y_s-y_i)^2]} dx dy \quad (2.12)$$

In general, this integral cannot be analytically solved. A near-field interferometer in a Talbot-Lau configuration – which i will describe in more detail in chapter 2.1.5 – relaxes the requirements compared to a far-field setup. A given grating period  $d$  depends only weakly on the de Broglie wavelength of the particles by  $\sqrt{\lambda_{dB}}$  according to the Talbot length  $L_T = d^2/\lambda_{dB}$ . Since material gratings have a fixed period, this allows for diffraction experiments with a broader range of particles. Furthermore, the collimation of the source is not as strict, since a grating instead of only one slit provides an array of point-like sources. Here, all diffraction orders interfere and produce the observed interference fringes. [53] Along these lines near-field diffraction experiments based on the Talbot-Lau effect offer advantages especially for experiments with more complex and larger particles.

### 2.1.5 Talbot-Lau effect

William H. F. Talbot discovered the self-imaging of a diffraction grating at a distance  $L_T$  when a spatially coherent plane wave illuminates the grating [96]. The self-image of the grating with period  $d$  appears at integer multiples  $n$  of the so-called Talbot length  $L_T$ , which is also the characteristic distance for the transition from the near- to the far-field for a grating with two slits:

$$L_T = \frac{d^2}{\lambda_{dB}} \quad (2.13)$$

For a grating with  $N$  slits  $n = N/2$  Talbot-orders exist. If  $n$  is odd, the grating image is shifted by  $d/2$  such that the maxima appear in the shadows of the grating bars. This corresponds to odd multiples of the Talbot length  $L_T$ . For even  $n$  the maxima reappear exactly at the positions of the slits. Sometimes the Talbot length  $L_T$  therefore is defined as  $L_T = 2d^2/\lambda$ . At regular fractions of the Talbot length self-images with smaller periods arise. The Talbot carpet is the pattern of the appearing self-images with different sizes and periods shown in figure 2.2. The intensity pattern of the Talbot carpet is calculated by solving the Fresnel-integral for a given grating and wavelength [15].

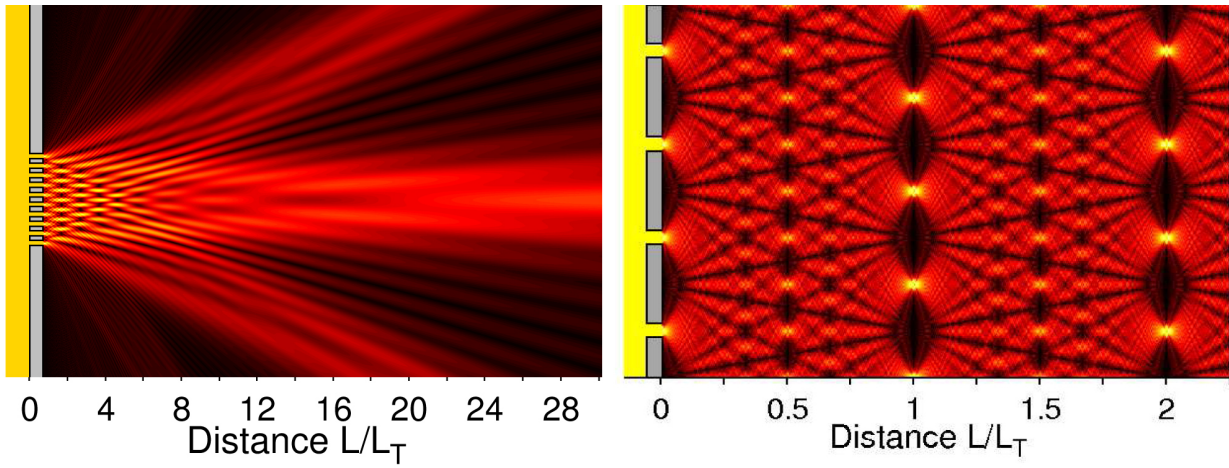


Figure 2.2: Both pictures show the evolution of a wave diffracted at a grating. The left pictures shows a plane wave illuminating a grating with ten slits. The transition from the near- to the far-field is clearly visible. For small distances, the density pattern reproduces the grating structure at multiples of the Talbot length  $L/L_T$ , while for larger distances the diffraction pattern of far-field diffraction appears where the extension of the diffraction pattern is larger than the extension of the aperture. The right picture shows a close-up of the Talbot carpet in the near-field. At the Talbot-order  $n = 1$  the maxima of the density pattern appear in the shadows of the grating bars. For  $n = 2$  the maxima reproduce an exact image of the grating without a shift. For  $n = 0.5$  the period is doubled and the pattern is halved in size due to the fractional Talbot effect. Both pictures from [53].

From the Talbot length  $L_T$  one can deviate the Talbot time  $t_T$ . The Talbot time is the time after which all molecules reproduce the grating pattern independent of their distance to the grating. It is obtained by dividing the Talbot length by the particle's velocity and reads  $t_T = md^2/h$

with  $m$  the particle's mass. An interferometer can be operated in either one, the space- or the time-domain. [53, p. 163f] The former one is the case for the KDTLI, since the gratings are positioned in fixed distances corresponding to the Talbot length.

For a spatially incoherent source, the Talbot pattern washes out. This is due to the incoherent superposition of the matter waves that result from the diffraction of molecules which incident on the grating under different angles. However, if we position a second grating in front of the diffraction grating with a distance close to a multiple of the Talbot length it serves as an array of point-like sources and refocuses the waves. This is the so-called Talbot-Lau effect. Each wavelet emanating from a slit of the first grating coherently illuminates several slits of the diffraction grating. [66]

In terms of wave mechanics, the first grating prepares a momentum uncertainty  $\Delta p$  of the transmitted molecule, since its position  $x$  is confined to the slit width  $s$  of the grating according to Heisenberg's uncertainty relation:

$$\Delta p = \frac{h}{\Delta x} = \frac{h}{s} \quad (2.14)$$

Due to the momentum uncertainty in the grating slits, a position uncertainty arises, i.e. the molecule's center of mass is delocalized. This delocalization grows linearly with the distance between the gratings and leads to a coherent illumination of several slits of the diffraction grating by the molecule's center-of-mass wave function.

The distances between the gratings and the plane of the interference pattern can be symmetrical or asymmetrical due to the fractional Talbot effect at regular fractions of the Talbot length. For the asymmetric version, the distances  $L_i$  as well as the periods  $d_i$  have to fulfill the following two conditions in order to obtain an interference pattern, with  $r_i$  being rational numbers [10]:

$$\frac{L_1 + L_2}{L_2} \frac{d_2}{d_1} = r_1 \quad (2.15)$$

and

$$\frac{L_1 + L_2}{L_1} \frac{d_2}{d_3} = r_2 \quad (2.16)$$

Additionally the periods  $d_i$  have to fulfill

$$\frac{1}{r_1} \frac{d_2}{d_1} + \frac{1}{r_2} \frac{d_2}{d_3} = 1 \quad (2.17)$$

The gratings in our symmetric KDTLI have equal distances  $L_1 = L_2$  and equal periods  $d_1 = d_2 = d_3$ . Since in the KDTLI the diffraction grating is a phase grating, the visibility is proportional to  $\sin(\pi L/L_T)$  according to equation 2.22, which I will discuss in more detail in chapter 2.1.6. As follows, the interference contrast would vanish for a setup with  $L$  being multiples of the Talbot length  $L_T$ , while it has its maximum for  $L/L_T = 1/2$ . Thus, the chosen configuration in the KDTLI is a fractional one in the second order. Due to a geometrical magnification  $(L_1 + L_2)/L_1 = 2$  of the symmetrical setup, the reduction of the period cancels though.

Since we need two gratings for a Talbot-Lau interferometer, the observed intensity pattern could be mimicked by the classical Moiré effect. However, a distinction between quantum diffraction and the classical Moiré effect is possible by studying the fringe visibility as a function of the particle velocity, since the visibilities differ in their functional dependence as well as in their values. [53] [54]

### 2.1.6 Kapitza-Dirac effect

The Van der Waals-interaction between the molecular beam and the bars of material gratings narrows the effective slit width. In a near-field interferometer this effect only allows a narrow velocity spread within the beam as well as specific velocity ranges in order to obtain high visibility [72]. Hence, instead of a material diffraction grating we use an optical phase grating in the KDTLI. Figure 2.3 shows the grating setup of our Kapitza-Dirac-Talbot-Lau configuration.

In 1933, Kapitza and Dirac already predicted the reflection of electrons by a standing light wave due to stimulated Compton scattering [60]. The deflection of the electrons due to momentum kicks of multiples of  $\pm 2\hbar k$  follows Bragg's law given by  $2d \sin(\theta) = n\lambda$  [9]. The standing light wave acts as a beam splitter where the amount of deflected electrons is proportional to the square of the field amplitude of the standing light wave  $E^2$ . However, at high intensities of the standing



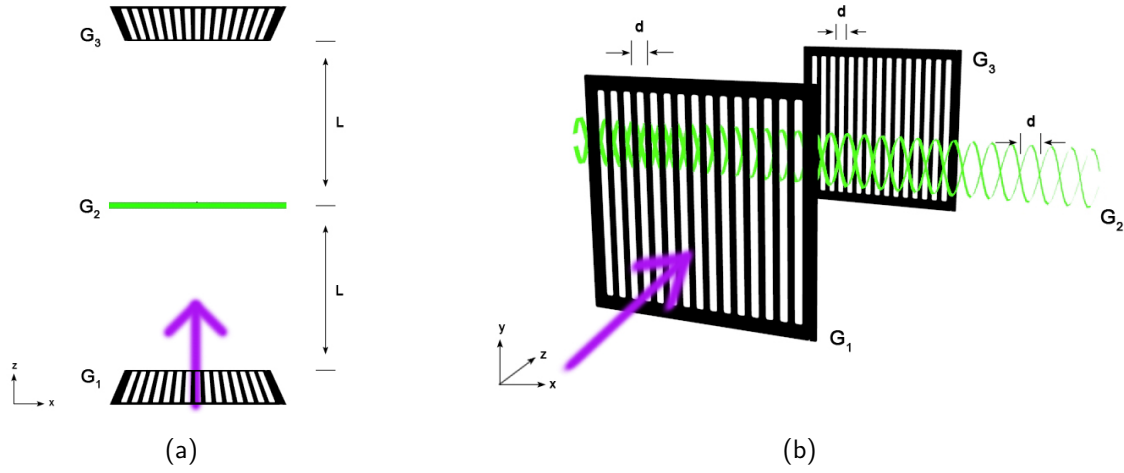


Figure 2.3: The KDTLI consists of three gratings of the same period  $d$  positioned at equal distances  $L$ .

$G_1$  and  $G_3$  are material gratings, whereas  $G_2$  is a standing light wave realized with a laser of wavelength 532 nm. The purple arrow indicates the molecule's flight direction  $z$ . (a) shows a sketch of the setup from above, while (b) shows a more realistic view of the setup with the period  $d$  of the gratings.

light wave channeling effects occur. The standing light wave consists of two counter-propagating beams with equal wavelengths such that the lattice spacing is half the wavelength. In 1985 and 1988, Pritchard and his group first experimentally demonstrated the diffraction of neutral atoms by a standing light wave due to absorption and stimulated emission of photons [44] as well as the dipole interaction between the atoms and the standing light wave, which leads to a momentum exchange of multiples of  $\pm 2\hbar k$  between the photons and the atoms [69].

In general, different types of light gratings are possible depending on the type of interaction between the particles and the standing light wave and thus, the properties of the particles and the light source. Depending on optical polarizability  $\alpha_{opt}$ , absorption cross section  $\sigma_{abs}$  and ionization energy  $E_{ion}$  of the particles, the interaction potential involves phase shifts [44] [69] [71], coherent photon recoil [54] [17] or depletion [22] [48].

The diffraction grating in the KDTLI operates in the off-resonant regime below the ionization threshold using a light grating wavelength of 532 nm yielding a grating period of 266 nm. Thus, the optical polarizability  $\alpha_{opt}$  is the main particle property determining the interaction, leading to a pure phase grating effect for the most molecules used in the KDTLI [60] [42]. The standing light wave induces an oscillating dipole moment in the molecule, shifting the molecule's phase

depending on the local intensity of the spatially varying light field. The electric field vector  $\mathbf{E}$  in the standing light wave oscillates at  $\omega_L$ , which is much faster than the interaction time. Thus, the optical dipole potential  $W$  of the standing light wave depends only on the time averaged squared electric field and accordingly the laser's intensity profile  $I$  and is given by

$$W(x, z) = -\frac{1}{4}\alpha_{opt} \cdot E(x, z)^2 = -\frac{1}{2c\epsilon_0}\alpha_{opt} \cdot I(x, z) \quad (2.18)$$

where  $\alpha_{opt}$  is the real part of the molecule's polarizability at a given laser frequency  $\omega = 2\pi c/\lambda_L$ , while the imaginary part of the polarizability includes the molecule's absorption cross section at this frequency given by  $\sigma_{abs} = 4\pi\omega \cdot \text{Im}(\alpha(\omega))/c$ . Assuming that the molecules pass the grating in its center allows neglecting the vertical position within the grating, since the molecular beam's height is small compared to the one of the light grating.

The laser used in the KDTLI provides an almost Gaussian beam profile forming a standing light wave perpendicular to the flight direction  $z$  of the molecules with an intensity profile  $I(x, y, z)$  of [54]:

$$I(x, y, z) = \frac{8P}{\pi w_y w_z} \exp\left(-\frac{2y^2}{w_y^2} - \frac{2z^2}{w_z^2}\right) \sin^2\left(\frac{\pi x}{d}\right) \quad (2.19)$$

where  $P$  is the laser power,  $w_y$  and  $w_z$  are the laser beam waists in vertical and longitudinal directions respectively and  $d$  the light grating period given by  $d = \lambda/2$ .

In the eikonal approximation the position-dependent phase shift  $\phi(x)$  of the matter wave is calculated by integrating the grating potential  $W(x, z)$  along a straight line in longitudinal direction of the molecular beam:

$$\phi(x) = -\frac{1}{\hbar} \int_{-\infty}^{+\infty} W(x, v_z t) dt = \phi_0 \sin^2\left(\frac{\pi x}{d}\right) \quad (2.20)$$

Here,  $v_z$  is the longitudinal velocity component of the molecules and  $\phi_0$  the maximum phase shift in a vertical node of the grating given by

$$\phi_0 = \sqrt{\frac{8}{\pi}} \cdot \frac{\alpha_{opt}}{\hbar c \epsilon_0} \cdot \frac{P}{w_y v_z} \quad (2.21)$$

The maximum phase shift – and thus, the phase shift in general according to equation 2.20 – increases linearly with the applied laser power  $P$  and the optical polarizability  $\alpha_{opt}$  of the molecule, while it decreases with higher velocities  $v_z$  in forward direction. [54]

The dipole potential  $W(x, z)$  from equation 2.18 defines the transmission function of the light grating. A Fourier decomposition of the transmission function yields the self-image of the diffraction grating with the Fourier coefficients given by Bessel functions  $J$  for the sinusoidal potential. The transmission functions of the first and third grating – which are material ones – are rectangular yielding sinc functions after the Fourier transformation. This gives a visibility in our KDTLI of

$$V = 2 \operatorname{sinc}(\pi f_1) \operatorname{sinc}(\pi f_3) J_2(\phi_0 \sin(\pi L/L_T)) \quad (2.22)$$

as a function of the maximum phase shift  $\phi_0$ . Here,  $f_1$  and  $f_3$  are the opening fractions of the first and third grating given by the ratio  $d/s$  of the grating's period  $d$  and the slit width  $s$ ,  $J_2$  is the Bessel function describing the transmission function of the phase grating and  $L/L_T$  the distance between the gratings in multiples of the Talbot length. The phase grating transfers the particle's initial momentum state  $|p\rangle$  into a superposition of  $|p + 2\pi\hbar n/d\rangle$  with an integer  $n$ . For a detailed mathematical description of the momentum transformation after the KDTLI setup refer to [72].

Since the interference pattern in the KDTLI is detected in terms of a particle density distribution after the third grating, experimentally the visibility is given by the mean signal over its amplitude:

$$V = \frac{S_{max} - S_{min}}{S_{max} + S_{min}} \quad (2.23)$$

In the KDTLI the signal's shape is nearly sinusoidal and thus, higher order Fourier components can be neglected. This leads to the following expression for the interference pattern  $V$  obtained by a pure phase grating in terms of truncated Fourier series with the Talbot coefficient  $B_2$  [54]:

$$V = 2 \frac{|S_1|}{S_0} = 2 \operatorname{sinc}(\pi f) \left| B_2 \frac{L}{L_T} \right| \quad (2.24)$$

Additionally to the phase shifts the molecules also absorb photons when passing the light grating yielding an amplitude modulation in the matter wave as well as a beam splitting in the transverse momentum state. These are coherent processes too, since it is indistinguishable whether the photon comes from the right or the left side. Actually, already the mere possibility of absorption changes the wave function. The absorption rate depends on the time averaged intensity profile of the standing light wave and is given by  $\Gamma_{abs} = \sigma_{abs} \cdot \langle I(x, z) \rangle / h\nu$ . The mean number of absorbed photons  $n_0$  in the light grating's antinodes depends on the molecule's absorption cross section  $\sigma_{abs}$  at a specific laser wavelength  $\lambda_L$  and is given by [54]

$$n_0 = \frac{8}{\sqrt{2\pi}} \cdot \frac{\sigma_{abs} \lambda_L}{hc} \cdot \frac{P}{w_y v_z} \quad (2.25)$$

Absorption almost always reduces the interference contrast, therefore we usually choose a laser power  $P$  in the range of 4 W and 17 W giving the highest contrast and thus, the lowest absorption rate according to equation 2.25. However, for a full quantum model description of the obtained interference contrast, absorption has to be taken into account as well. Thus, the expression for the visibility from equation 2.24 changes to [17]

$$V = 2 \operatorname{sinc}^2(\pi f) e^{-\epsilon_{abs}} \left( \frac{\epsilon_{coh} + \epsilon_{abs}}{\epsilon_{coh} - \epsilon_{abs}} \right) J_2 \left( \sqrt{\epsilon_{coh}^2 - \epsilon_{abs}^2} \right) \quad (2.26)$$

with  $J_2$  the second order Bessel function,  $\epsilon_{coh} = \phi_0 \sin(\pi L/L_T)$  accounting for the phase modulation and  $\epsilon_{abs} = n_0/2 \cdot [1 - \cos(\pi L/L_t)]$  describing the momentum state splitting by photon absorption.

## 2.2 From source to interference - the experimental setup

The KDTLI consists of three main parts: the source to produce a molecular beam, the interferometer and the detector. Figure 2.4 shows the experimental setup of this interferometer. Every part is located in its own vacuum chamber. These vacuum chambers are connected, but can be separated with valves. Additionally, we need peripheral devices, i.e. vacuum pumps, optics, a

laser or translation stages. Some of these devices are mounted in one of the chambers, some are located outside. In this section I will discuss the required elements and their arrangement for a matter-wave interferometer based on the Talbot-Lau configuration with a standing light wave as diffraction grating.

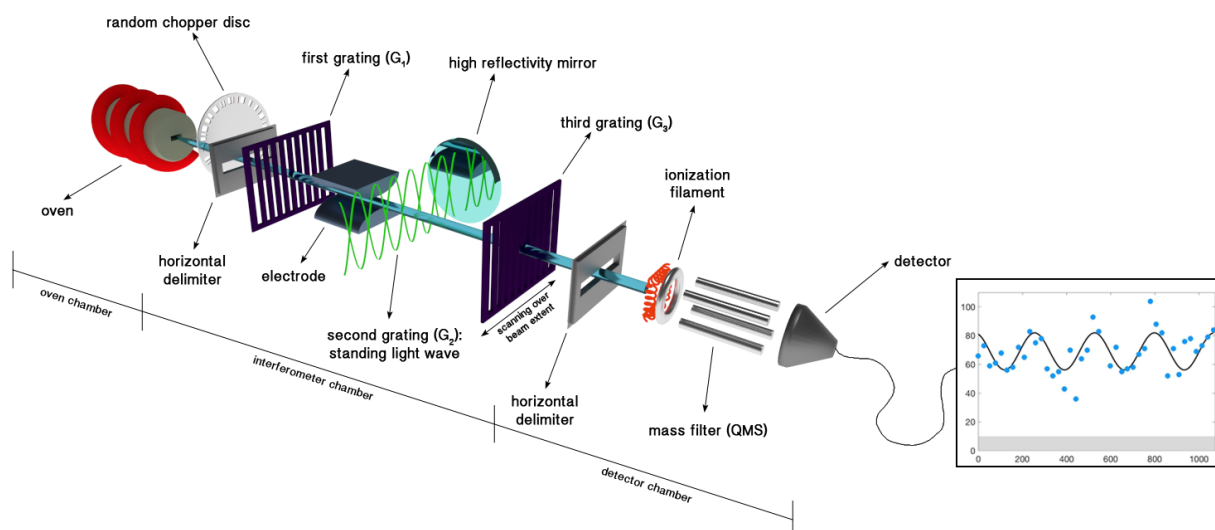


Figure 2.4: Sketch of the experimental setup of the KDTLI. We evaporate the molecules from an effusive source. For velocity selection we define the beam's path with horizontal delimiters. With the random chopper disc right after the oven we can measure the velocity distribution of the molecular beam. After passing the interferometer consisting of the three gratings the ionization filament ionizes the molecules in order to allow the mass-selection and detection in the QMS. The plot on the right side shows the result of an interference scan with a tripeptide. In the plot, on the x-axis there is the position of the third grating, which scans over the horizontal beam extent. The y-axis shows the number of detected molecules at each position of the third grating. For deflectometry measurements, we can insert an electrode between the first and the second grating.

## 2.2.1 The source

In the KDTLI we use a Knudsen cell to emit a molecular beam. Figure 2.5 shows a picture of our oven. There are other options of molecular sources as well which I will review in chapter 4.1. The oven consists of a cylinder sealed by a cap. Both are made of Shapal which is a ceramic with high thermal conductivity and a low thermal expansion coefficient. The cylinder is surrounded by a heating wire (ISOMIL 73.4V2A10), which is connected to a power supply via electronic

feedthroughs in the flange. The cap has a small slit of the dimension  $1\text{ mm} \times 200\text{ }\mu\text{m}$  and can be removed to refill the oven.

The source is surrounded by a tantalum shield for thermal isolation. This is to prevent the vacuum chamber from heating up due to blackbody radiation. The furnace is screwed together tightly to provide a good sealing between the cylinder and the cap. A baffle in the source chamber cooled with liquid nitrogen improves the vacuum conditions by adsorbing scattered molecules from the chamber.

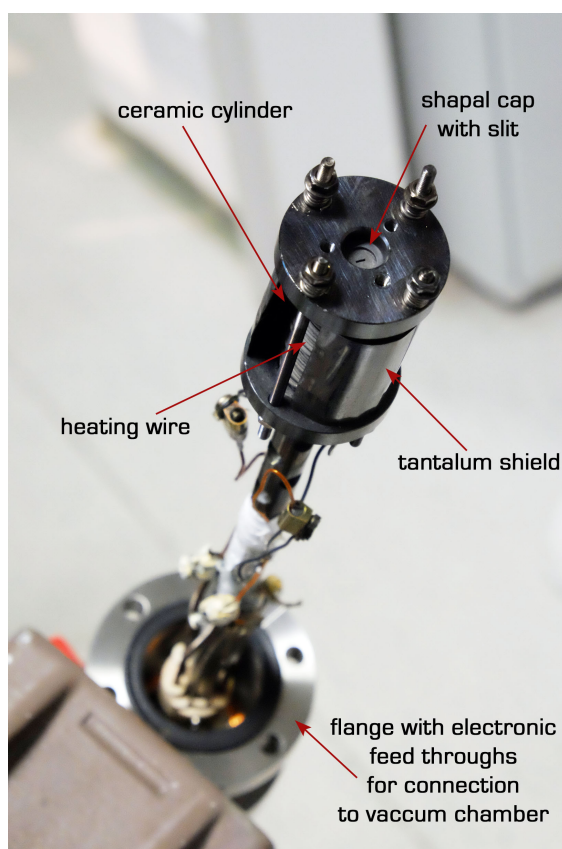


Figure 2.5: Photo of the thermal source used in the KDTLI to transfer the molecules into the gas phase.

The cylinder containing the molecules as well as the cap with the slit are made of Shapal. The heating wire is wound around the ceramic cylinder. To prevent heating up the chamber by heat radiation, the whole oven is surrounded by a tantalum shield. A metal plate and four rods hold the cylinder and the cap together. We use springs to compensate for the different thermal expansion coefficients of the different materials to ensure that the cap is fixed tightly to the cylinder during heating and cooling processes of the oven. Additionally, we use a silver ring between the cylinder and the cap to avoid leaking when molecules melt before they evaporate. Picture courtesy of Lukas Mairhofer.

We can operate the oven at different temperatures. For each type of molecule we need a different working temperature for evaporation at maximal vapor pressure and without fragmentation. The typical temperatures for the molecules used in the KDTLI are in the range of 500 K to 1100 K. A k-type thermocouple mounted within the oven monitors the temperature continuously.

The molecules leave the oven through the small slit in the Shapal cap. The velocity distribution of the emitted molecules follows the Maxwell-Boltzmann distribution  $F(v)$ . However, the experiment usually shows a slight velocity offset due to collisions within the exit slit. A perfect Maxwell-Boltzmann curve would be expected, if the mean free path of the molecules were longer than the characteristic size of the aperture. More details about the characteristics of an effusive source follow in chapter 4.2.1.

As discussed in 2.1.2, we need a molecular beam with sufficient longitudinal coherence to obtain interference. In our case that means a narrow velocity distribution of the molecules. The typical velocity spread in our KDTLI is between 10 % and 25 %, obtained by selecting only a small velocity range of the beam.

### 2.2.1.1 Velocity selection

For the velocity selection we use three slits defining a parabolic flight path for the molecules. In the gravitational field of the earth the path of the flying molecules only depends on their velocity. Hence, all molecules being too slow or too fast to pass through all three slits are extracted from the beam.

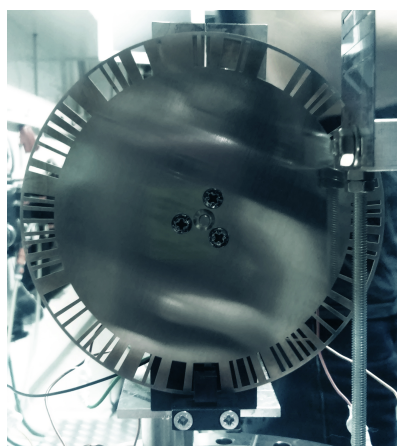
The aperture in the cap of the furnace defines the first of the three slits. Since the oven is mounted on an X-Y-translation stage, we can adjust its position.

The second slit is located in front of the first grating  $G_1$ . A piezo regulates the width of this slit with a maximum aperture of 1500  $\mu\text{m}$ . This slit is mounted on a translation stage as well to adjust the height of the slit relative to the molecular beam.

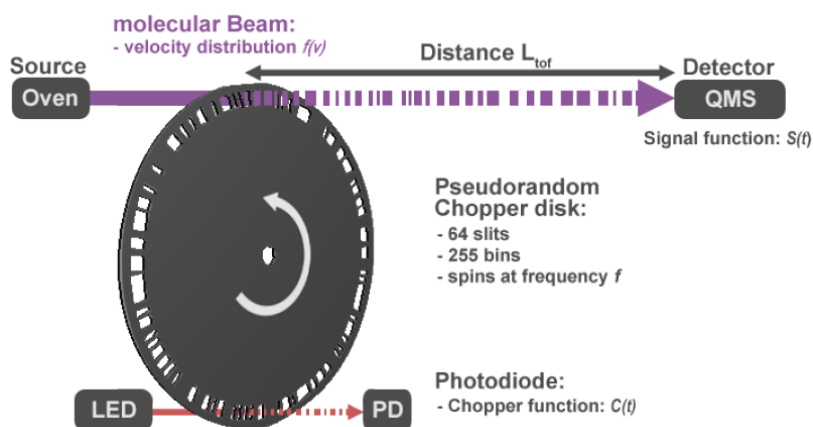
The third and last slit is an aluminum plate with three different slit widths of 100  $\mu\text{m}$ , 200  $\mu\text{m}$  and 500  $\mu\text{m}$ . This mask is mounted in front of the detector. Depending on the kind of molecule and the signal intensity we use different slit widths, which we can select by moving the mask with a translation stage.

### 2.2.1.2 Random chopper

To measure the velocity classes of the molecules within the beam we use a random chopper mounted perpendicular to the beam in the oven chamber. The random chopper is a disc with a pseudo-random pattern of slits with different weights and intervals. Figure 2.6 shows a photo of our chopper disc. Overall the chopper contains 64 slits, while the pattern is divided into 255 bins, which are either open or closed. It is driven by a DC motor (Maxon) and spins with a frequency up to 30 Hz. The rotation of the disc chops the molecular beam into small packages with their size depending on the width of the slit. They are detected in the QMS which is sensitive to the beam density.



(a) Photo of the random chopper disc used in the KDTLI



(b) Sketch of the chopper setup for a TOF measurement. Picture courtesy of Johannes Bischoff, from [7].

Figure 2.6: Chopper disc for the measurement of the velocity classes within the molecular beam. The disc consists of a pseudo-random pattern of 64 slits. A trigger slit acts as starting point for the correlation between the molecular packages and the photodiode-signal. A DC motor spins the disc up to 30 Hz to chop the molecular beam into small packages. The disc is mounted on a flange with power connections for the DC motor.

A photodiode simultaneously detects the starting point on the chopper disc so that the beam density can be correlated with the slit pattern and hence allows calculating the time of flight of the molecules. The photodiode signal is converted into TTL-pulses.

Mathematically, the chopper function  $C(t)$  describes the distribution of these TTL-pulses. The time-dependent signal  $S(t)$  at the detector obtained by chopping the molecular beam is a con-



volution of the chopper function  $C(t)$  and the molecules' time-of-flight distribution  $F(t)$ . It is given by [51]

$$S(t) = \int C(t - \tau)F(\tau)d\tau \quad (2.27)$$

If the chopper function's autocorrelation function resembles a delta function, it is possible to apply another convolution  $C(t)$

$$\int S(t - \tau)C(\tau)d\tau = \int C(t - \tau)C(\tau)F(\tau)d\tau \quad (2.28)$$

yielding the expression for the time-of-flight distribution

$$F(t) = \int S(\tau)C(t - \tau)d\tau \quad (2.29)$$

since the convolution of  $C(t)$  with itself again is a delta function. Finally, the time-of-flight distribution  $F(t)$  is converted into a velocity distribution when knowing the length  $L$  of the molecule's path:

$$I(v) = I\left(\frac{L}{t}\right) = I(t) \quad (2.30)$$

## 2.2.2 The interferometer

The interferometer itself consists of three gratings, with the first ( $G_1$ ) and the third ( $G_3$ ) being material masks whereas the second grating ( $G_2$ ) is a standing light wave created by a retroreflected laser. Figure 2.7 shows a photo of the interferometer chamber with the mounts for the gratings and the focus lens for the light wave.

The first grating acts as an array of point-like sources for transversely coherent waves. These waves get diffracted at the second grating, which is a non-absorptive phase grating formed by a laser retroreflected from a mirror. To detect the interference pattern, the third grating scans over the beam so that the QMS can measure the beam density at each transverse position.

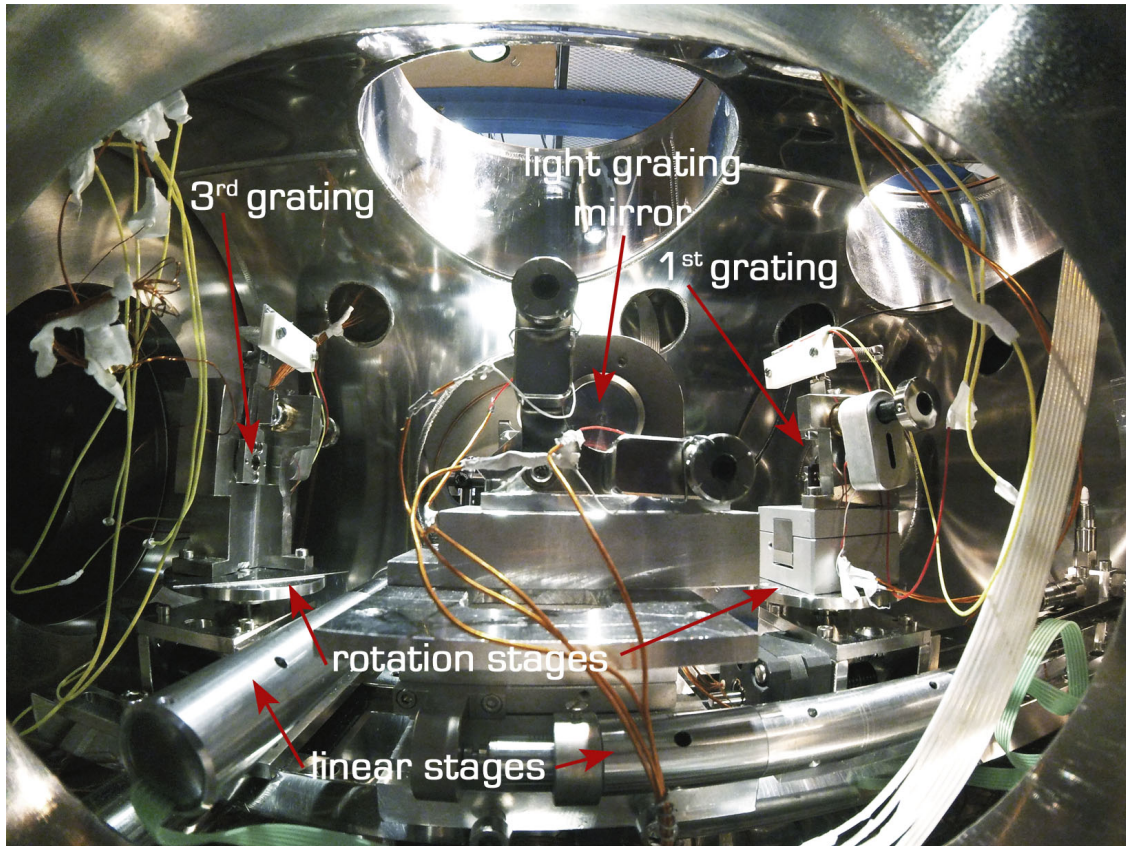


Figure 2.7: Picture of the interferometer inside the vacuum chamber taken with a fisheye camera. The molecules enter the interferometer from the right passing the first grating, continuing their path to the diffraction grating made up by a standing light wave at the position of the mirror onward to the third grating on the left side of the picture. The material gratings are mounted on rotational stages to adjust their yaw angle in-situ. Linear stages allow the adjustment of the axial and the longitudinal positions of the light grating. The motorized light grating mirror permits the alignment of the light grating's yaw angle as well as its adjustment orthogonal to gravity. Picture courtesy of Maxime Debiossac.

The distance between each of the gratings is 105 mm. Since the KDTLI is a symmetric interferometer, the distance between first and second grating equals the distance between second and third one. The typical de Broglie wavelengths  $\lambda_{dB}$  for our experiments are in the range of 0.5 pm to 5 pm. According to that we chose the distances between the gratings. The de Broglie wavelengths of the particles lead to Talbot orders from 1 to 10. For  $C_{60}$ , one of our most important molecules used for aligning and calibrating the machine, the mean velocity is about 200 m/s. Hence, the wavelength of the molecules is 2.76 pm and they are diffracted in the 4<sup>th</sup> Talbot order.

### 2.2.2.1 Mechanical gratings

The material gratings are etched into a silicon nitride substrate  $SiN_x$  with a thickness of 190 nm and a size of 3 mm  $\times$  3 mm. The grating period is 266.38 nm with an opening fraction of 42 % [42]. Since the period of the mechanical gratings is slightly larger than the one of the light grating, the former ones can be adapted by yawing. The gratings have a horizontal support structure with a height of 1.5  $\mu$ m for stabilization. Figure 2.8 shows such a grating observed under an electron microscope with different magnifications.

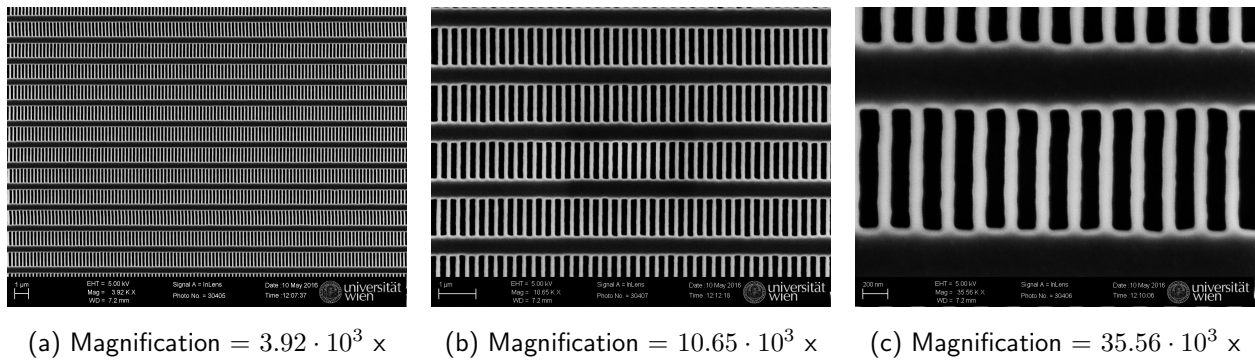


Figure 2.8: Image of a mechanical grating such as used in the KDTLI observed under a scanning electron microscope with different magnifications. The vertical structure of the grating has a period of 266.38 nm while the period of the horizontal support structure is 1.5  $\mu$ m. The whole grating is etched into a silicone nitride substrate.

The grating mounts have roll motors and are fixed on motorized rotation stages. That allows us to move the gratings in two angles (yaw and roll) without venting the vacuum chamber. Only the pitching has to be done manually inside the chamber with sufficient accuracy, since this angle can't be adjusted within an evacuated chamber. On each grating mount there is an electrolytic tilt sensor (Spectron SH50054-A-003) to monitor the grating positions relative to gravity over time with a resolution of 10  $\mu$ rad over a range of  $\pm 3^\circ$ .

Since the grating slits are quite small, the molecules slowly start to block the slits such that the signal decreases continuously over time. After seeing this effect in the measurements on our machine we decided to exchange the gratings. This was a decision which led to a complete realignment of the interferometer itself after the exchange. The details of such a realignment process will be discussed in chapter 3.

Figure 2.9 shows a test grating with the slits blocked by molecules. The grating is in general identical to the ones we use in the KDTLI, but with less uniform period and small defects such that it is unfeasible for interference experiments. However, with this grating we tested the effect of a high intensity molecular beam on the blocking of our gratings. For the test, we used tetraphenylporphyrin (TPP) evaporated from the newly designed oven described in chapter 4. We positioned the oven a lot closer to the grating than it is the case in the KDTLI. We thereby simulated the blocking process of a longer time period in only one run, since the beam intensity is much higher due to the shorter distance between source and grating. Furthermore, we know from past experiments that TPP tends to stick better to surfaces than  $C_{60}$  does. The observation of the grating under a scanning electron microscope showed that already one oven load led to a massive blocking of the grating slits.

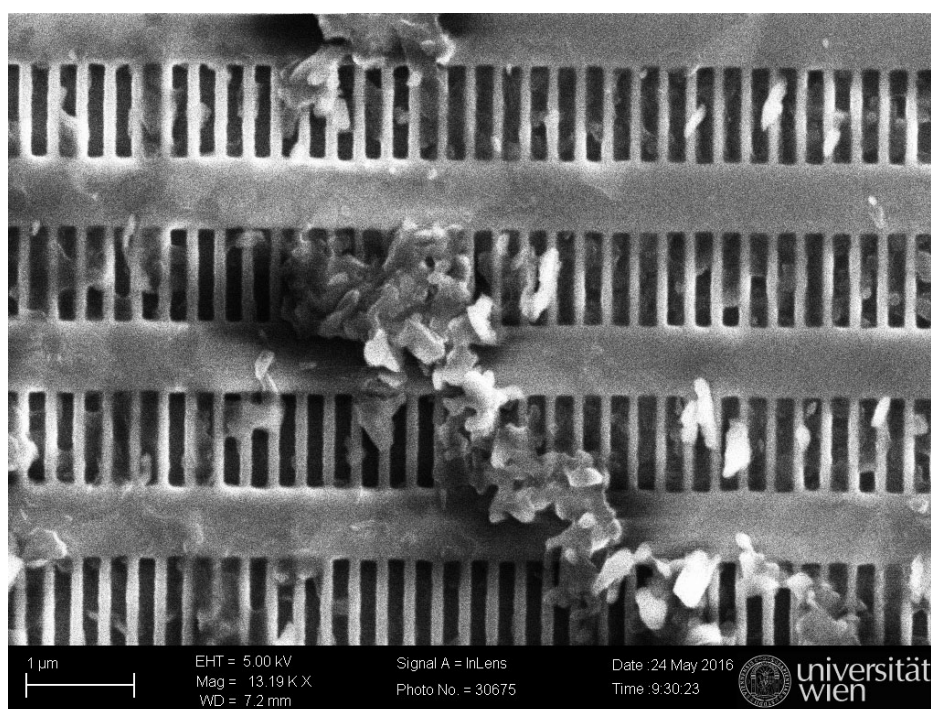


Figure 2.9: Tetraphenylporphyrin molecules stuck to the mechanical grating and thereby blocking the slits. We took the picture with a scanning electron microscope with a magnification of  $13.19 \cdot 10^3$ . This was not a grating used in the KDTLI, but only a test-grating to see the effect of blocking by a high intensity molecular beam of TPP.

### 2.2.2.2 Light grating

A green laser (Coherent Verdi V18 and V20) with a wavelength  $\lambda$  of 532.26 nm provides the diffraction grating as the laser is retroreflected from a high-reflectivity mirror. The laser produces

a Gaussian beam with a waist of about 1 mm. It forms a standing light wave with a period of  $d = \lambda/2 = 266.13\text{nm}$  and an intensity profile according to equation 2.19.

However, we saw slight differences in the output wavelength depending on the laser model and the emitted output power. Since a stable wavelength and pointing of the laser beam is crucial for our experiments, we adjust the laser power entering the vacuum chamber – and thus, the intensity of the light grating – by guiding the laser through a  $\lambda/2$ -plate followed by a polarizing beam splitter. By rotating the  $\lambda/2$ -plate we can control the light grating intensity without changing the laser's output power directly. This setup provides a stable wavelength and pointing of the laser beam.

After the polarizing beam splitter the laser passes a  $\lambda/4$ -plate which prevents the laser beam from shining back into the laser head after getting retroreflected by the mirror. To guide the light into the interferometer chamber, we use a periscope. The upper mirror of the periscope setup can be adjusted in height such that we can vary the light grating height (LGH) to overlap the molecular beam with the diffraction grating. Inside the vacuum chamber a cylindrical lens with a focal length of 100 mm focuses the laser to a horizontal waist of  $w_z = 20\mu\text{m}$  at the position of the mirror while maintaining a vertical waist of  $w_y = 900\mu\text{m}$ .

The mirror and the lens are mounted on motorized translation stages such that we can adjust the axial and the radial position of the light grating relative to the molecular beam in-situ. The mirror is held by a motorized mount, which allows the alignment of pitch and yaw to overlap the incoming and outgoing laser beam.

Compared to mechanical gratings an optical grating has a few advantages: Van der Waals-interactions between the molecules and the grating are avoided. These interactions would narrow the effective slit width of the diffraction grating. Furthermore, the whole molecular beam is transmitted through the grating which leads to a higher signal compared to mechanical diffraction gratings. Under the assumption of an otherwise perfect alignment the grating period depends only on the wavelength of the laser. Thus, it is very precise and the interaction strength of the grating can be tuned by varying the laser power.

Indeed, the realization of a light grating requires the laser to be very stable over time in terms of its pointing, profile and output power. Thermal drifts of the retroreflecting mirror can also lead to a perturbation of the light grating, and hence to a decrease of the interference contrast. To ensure stability during the measurements, we monitor profile and pointing of the laser beam leaving the chamber after being retroreflected by the mirror with a Coherent knife edge beammaster (Coherent BM-3 UV PCI).

### 2.2.3 The detector

For the detection of the molecules we use a quadrupole mass spectrometer (QMS Extrel 150-QC) located in the detection chamber. Figure 2.10 shows a schematic drawing of our QMS.

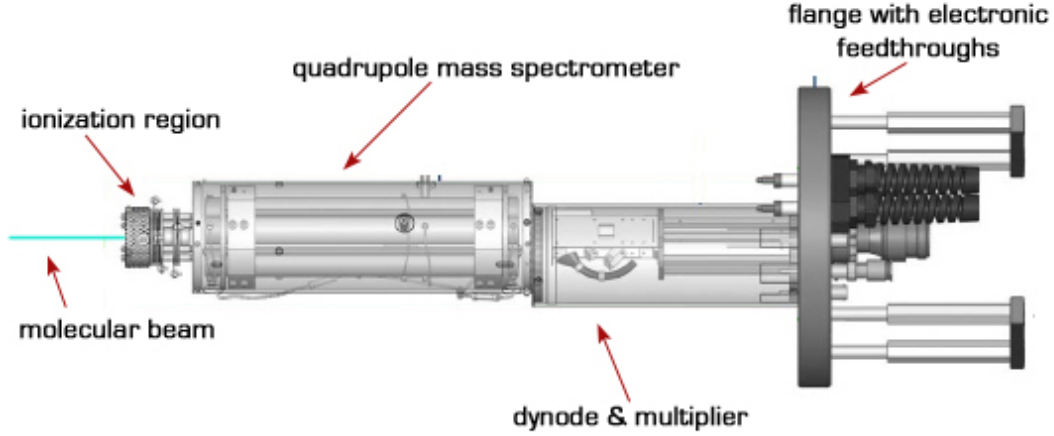


Figure 2.10: Schematic drawing of the QMS. The molecules get ionized by electron impact before entering the quadrupole mass filter. According to their mass-to-charge ratio they are selected in the quadrupole mass spectrometer. The selected molecules hit the high voltage dynode and lead to a secondary emission of electrons, which are detected in the channeltron multiplier. The current pulse is converted into TTL voltage pulses such that we can count the molecules. Picture from [93] with additional labels from the author.

First, the molecules are ionized by electron impact, with four tungsten wires in front of the mass selector emitting the required electrons. The efficiency of this process is quite low with a rate  $\Gamma$  of only about  $10^{-4}$  [92] given by

$$\Gamma = nv\sigma \quad (2.31)$$

where  $n$  is the electron density,  $v$  the velocity of the molecules and  $\sigma$  their electron impact cross section. In our case the electron impact cross section is in the order of  $10^{-15} \text{ cm}^2$  for  $\text{C}_{60}$  with an electron energy of 70 eV to 100 eV [76]. Since there is a limit to the space charge density due to Coulomb repulsion of the electrons, the efficiency of the process cannot be increased arbitrarily. After the ionization, electrostatic lenses guide the positive ions into the quadrupole mass spectrometer which filters the ions according to their mass-to-charge ratio  $m/z$ . The filter consists of

four metal rods arranged parallel to each other. The opposing rod pairs have the same potential, while between the neighbouring ones a voltage  $U_{total}$  is applied consisting of a DC offset voltage and a radiofrequency AC voltage of frequency  $f = \omega/2\pi$  yielding a total electrical field given by

$$U_{total}(t) = U + V \cos(\omega t) \quad (2.32)$$

The motion of the ions traveling through this external electric field can be described by the Mathieu differential equations which give stable and unstable regions for the ions' trajectories. Only ions within the stable region can pass the filter, whereas the other ions collide with the rods. Figure 2.11 shows the stability diagram of our QMS. For a setup with four rods the load line is given by the fraction  $A/Q$  of the two parameters:

$$A = \frac{4zeU}{m\omega^2 r^2} \quad (2.33)$$

$$Q = \frac{2zeV}{m\omega^2 r^2} \quad (2.34)$$

Here,  $r$  is the diameter of the metal rods,  $m$  is the ion's mass and  $z$  its elementary charge,  $U$  is the applied DC voltage and  $V$  the applied AC voltage. Thus, only the ions with a specific mass-to-charge ratio according to equations 2.33 and 2.34 arrive at the detector depending on the applied DC and AC voltages. In the current QMS setup we use rods with a diameter of 9.5 mm and a resonator 880 kHz for the AC voltage.

A high-voltage dynode accelerates the molecules that pass the filter. Usually we operate the dynode with 9 kV, but it is conditioned to 10 kV. The impact of the ionized molecules on the dynode leads to the emission of electrons, which are multiplied in a channeltron. The resulting signal is converted into TTL pulses such that we can read out a digital signal giving the number of molecules arriving at each position of the scanning grating yielding a position-dependent density pattern.

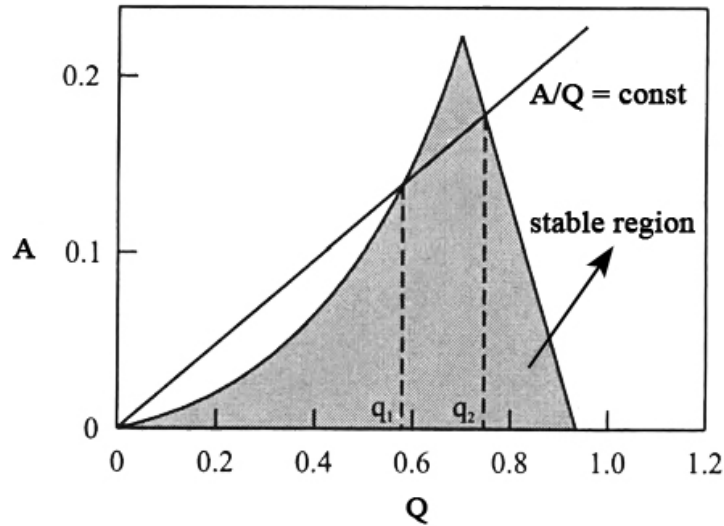


Figure 2.11: Stability diagram of the QMS with parameter  $A$  on the y-axis and parameter  $Q$  on the x-axis. The shaded area indicates the pass band of the QMS dependent on the parameters  $A$  and  $Q$  and thus, the particles mass-to-charge ratio  $m/z$ . The ratio  $A/Q$  of the parameters gives the load line of the QMS and defines the possible mass range. For a flat slope, though the resolution of the QMS is low, the transmission is high. For steeper slopes, the resolution increases though with decreasing transmission, and therefore a lower signal. Picture from [74, p. 244] modified by the author.

## 2.2.4 Experimental conditions

Since the interference pattern is very sensitive to perturbations caused by vibrations and collisions with the background gas, we need to prepare the necessary conditions for such experiments.

The whole setup is mounted on an optical table (Melles Griot) lifted by inflatable piston feet. Compressed gas pumps these feet with a pressure of around 5 bar. Thereby the experiment is isolated from vibrations of its environment. We monitor the position of the optical table relative to gravity with another electrolytic tilt sensor (Spectron SH50054-A-003) as used on the gratings already, but directly mounted on the optical table. A housing made of plexiglass protects the setup from dust. This is especially important for the optical elements to avoid disturbance of the laser beam profile and change of its pointing. Two flow boxes pressurize the housing with filtered air. Figure 2.12 shows the experiment from outside.

Quantum interference experiments with molecules are only possible in high vacuum, otherwise there would be collisions between the molecules and particles in the background gas. This would cause random shifts of the molecules and therefore destroy the interference pattern. The colli-



sions can be interpreted as yielding which-path-information, destroying the quantum interference pattern as well. [52] The whole experiment is situated in three vacuum chambers which we can vent separately by closing the respective valves. Especially for refilling the oven this is crucial, since we only vent the source chamber to do so. Aside from that, the differential pumping stages allow for obtaining good vacuum conditions.

The source chamber is connected to two turbomolecular pumps (Pfeiffer HiPace700 and Pfeiffer TC600). They provide a pressure in the range of  $1\text{e-}7$  mbar to  $1\text{e-}8$  mbar. Another turbomolecular pump (Pfeiffer HiPace700) on the interferometer chamber together with an ion getter and titanium sublimation combination pump (Varian VacIon Plus 300) yields a pressure of  $5\text{e-}8$  mbar to  $1\text{e-}9$  mbar. The detection chamber is pumped by a turbomolecular pump (Pfeiffer HiPace700) yielding the same pressure range as the interferometer chamber. As roughing pumps we use a Pfeiffer XtraDry-150 and an Adixen ACP-15.

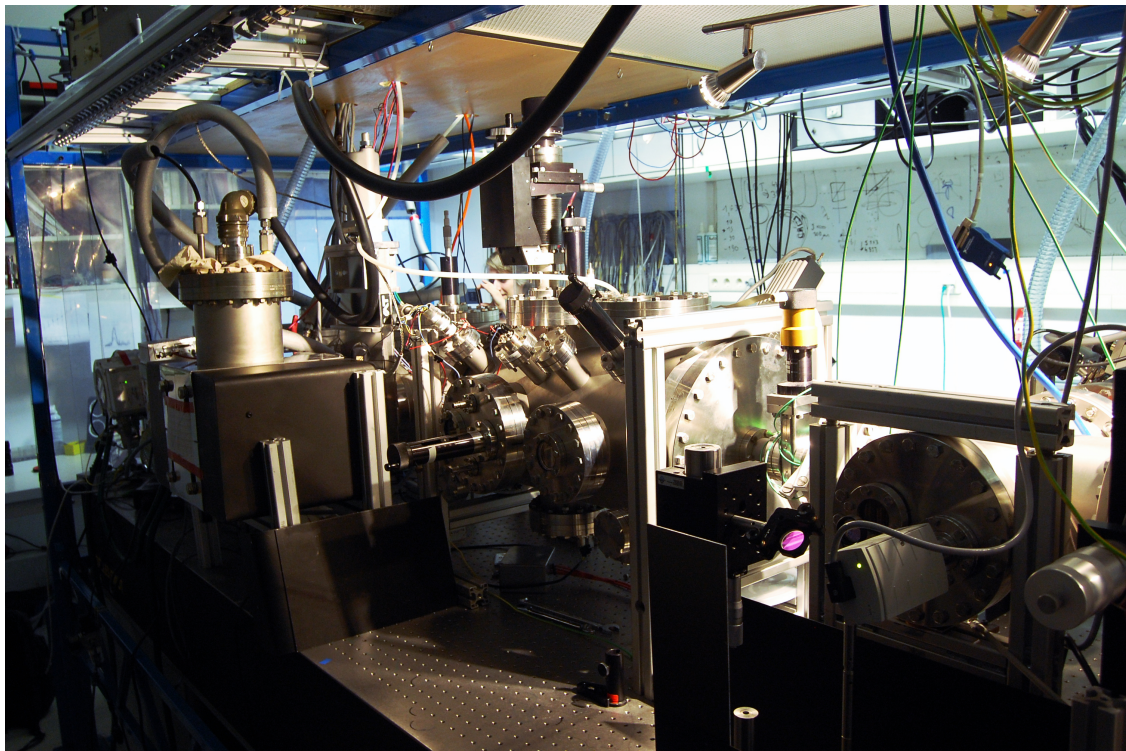


Figure 2.12: Photo of the KDTLI mounted on the optical table with some of the peripheral devices.

This is where the magic happens. Picture courtesy of Lukas Mairhofer.



## 3 Alignment

The alignment of the machine is a crucial point, since there are strict requirements and only small ranges for the parameters within which the formation of an interference contrast is possible at all. In this section I will discuss the required accuracy as well as the procedures to obtain it.

The alignment can be separated into two main procedures: First, we pre-align the interferometer while the whole experiment is vented. Second, we optimize the interference pattern by further adjustment with a molecular beam in the evacuated chamber. The latter step consists of iteratively changing all parameters while performing interference measurements until we get the best interference contrast. Since the experiment is very sensitive to misalignment, we collimate the molecular beam to a vertical spread of  $100\text{ }\mu\text{m}$  for the alignment process. This leads to the illumination of less than 400 slits, while for regular measurement runs the molecular beam width is about 1 mm such that it illuminates about 3800 grating slits.

### 3.1 Grating distances

The KDTLI is based on the Talbot effect as mentioned in chapter 2.1.5. Since we work with a symmetric interferometer setup the distance  $L_1$  between  $G_1$  and  $G_2$  is the same as  $L_2$  between  $G_2$  and  $G_3$ . The ideal distance  $L = L_1 = L_2$  in our setup is 10.56 cm. That corresponds to the 4<sup>th</sup> Talbot order for  $C_{60}$  with a mean velocity of 200 m/s.

Since only the light grating is adjustable relative to the the other gratings in the axial direction of the molecular beam, it has to be positioned exactly between  $G_1$  and  $G_3$ . To achieve that, we hold a thin wooden rod against the grating chip of  $G_1$  and burn a mark onto the rod using the light grating laser. We repeat this procedure for the grating chip of  $G_3$ . Then we measure the distance between the two marks. Subsequently we minimize the distance between the marks as much as possible. After a few iterations we obtain an accuracy of  $200\text{ }\mu\text{m}$  for this alignment.

A misalignment  $\Delta L$  of the distances leads to a blur  $D$  of the interference pattern dependent on the grating period  $d$  and the number of illuminated slits  $N$  [54]:

$$D = N \cdot \frac{d}{2} \cdot \frac{\Delta L}{L} \quad (3.1)$$

The blur  $D$  has an upper limit in order to still maintain interference, which is  $D < d/2$  and hence,  $1/N < \Delta L/L$ . This allows a maximal misalignment of the grating distances by  $27 \mu\text{m}$  for a molecular beam of 1 mm width illuminating 3800 slits. However, with the restriction of the beam to 0.1 mm yielding about 400 illuminated slits for the alignment procedure, the tolerable misalignment increases in one order of magnitude to  $270 \mu\text{m}$ , which we obtained in our pre-alignment.

## 3.2 Material gratings

The material gratings have three degrees of freedom, i.e. the three angles yaw, pitch and roll. Figure 3.1 shows an illustration of these angles and their influence on the effective grating period and position.

For the pre-alignment of the three angles we use a blue laser. To level the laser beam orthogonal to gravity we reflect it from an optical level mirror (Davidson Optotronics) back into itself. The gravitationally leveled laser beam is then pointed onto the gratings  $G_1$  and  $G_3$ . We place neutral density filters in front of the blue laser to prevent damage of the gratings.

For all three angles the estimation of the accuracy  $\Delta\theta$  is given by the ratio of the distance of the light path  $L$  between the optical level mirror and the respective grating and the deviation  $\Delta x$  of incoming and outgoing laser beam at the position of the optical level mirror:

$$\Delta\theta = \frac{\Delta x}{L} \quad (3.2)$$

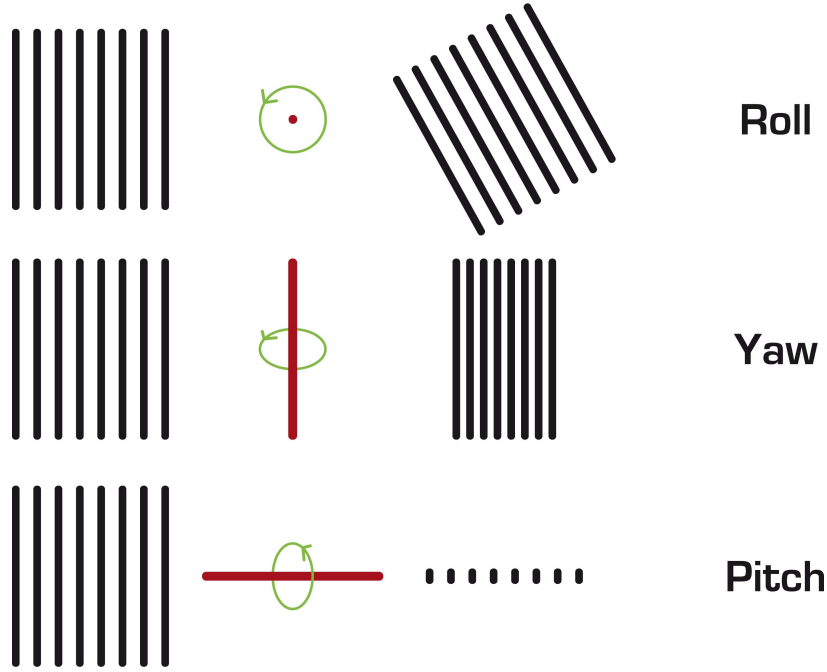


Figure 3.1: Illustration of the effect of roll, yaw and pitch on the material gratings' period and position.

The roll angle is a rotation around the z-axis and changes the relative angle to gravity such that the molecules interact with different grating positions depending on their vertical position within the beam. Furthermore, due to different velocity classes each molecule interacts with another relative position of the grating and lastly the effective period of the grating changes. A rotation around the y-axis leads to a change of the grating's yaw angle and thus, a change in the effective period as well as different distances  $L$  between the gratings depending on the horizontal position. The pitch angle correlates with a rotation around the x-axis leading to a change in distance between the gratings depending on the vertical position.

### 3.2.1 Pitch

We can align the pitch angle  $\alpha$  only in-situ within the vented chamber. For the alignment we shine the leveled laser onto the gratings, where it is backreflected into itself. We change the pitch until incoming and outgoing beam overlap within about 0.5 mm. With this procedure we obtain an accuracy of 0.3 mrad for  $G_1$  and 0.75 mrad for  $G_3$ . Figure 3.2 shows the alignment setup of the laser beam.

A misalignment of the gratings relative to each other leads to a height-dependent change of the distance between the gratings and therefore loss of interference contrast. Additionally, different velocity classes in the molecular beam have different path lengths between the gratings.

The deviation of the distance  $L$  in dependence of a misalignment of the pitch angle  $\alpha$  is given by

$$\Delta L(\Delta\alpha) = \frac{h\Delta\alpha}{2} \quad (3.3)$$

where  $h = 3\text{mm}$  is the height of the material gratings. Since  $\Delta L/L \stackrel{!}{<} 1/N$ ,  $\Delta L$  has to be smaller than  $L/N$  where  $N$  is the number of illuminated slits. Thus,  $\Delta\alpha$  has to be smaller than  $20\text{ mrad}$ , which is more than one order of magnitude more than what we achieved in our pre-alignment.

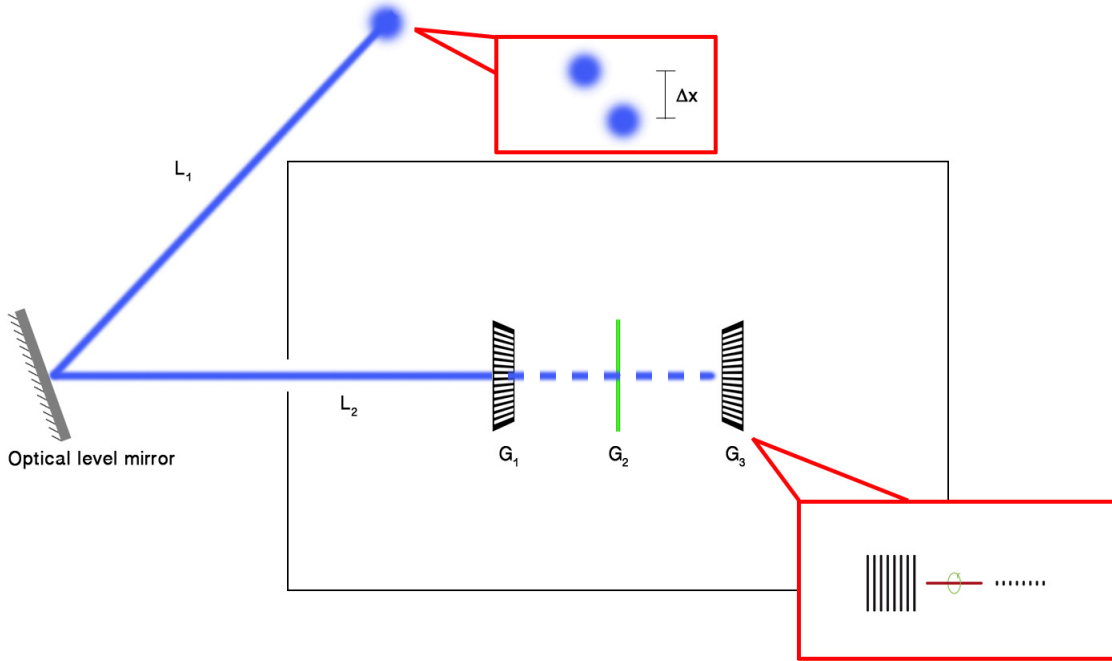


Figure 3.2: Illustration of the alignment setup for the adjustment of the gratings' pitch angle within the vacuum chamber. The blue line indicates the blue alignment laser, which we backreflect from the grating chip of  $G_1$  and  $G_2$ . To ensure that the alignment laser runs orthogonal to gravity we use an optical level mirror. First, we align the pitch angle for  $G_3$  while  $G_1$  is removed from the setup. After we have obtained a sufficient accuracy for  $G_3$  we insert  $G_1$  and repeat the procedure. The estimated accuracy is given by the vertical distance between the outgoing and incoming laser beam  $\Delta x$  over its total light path  $L = 2(L_1 + L_2)$ , where  $L_2$  is about 20 cm longer for the alignment of  $G_3$ .

### 3.2.2 Yaw

The alignment process of the yaw angle  $\beta$  is the same as for the pitch angle – we overlap the outgoing laser beam with the backreflected one from the grating. Figure 3.3 shows the alignment setup. To ensure that the molecules hit the gratings perpendicularly, we define the molecules' path by inserting two horizontal delimiters at the positions of the molecular beam such that the alignment laser for the pre-alignment follows the same path. With this procedure we obtain an accuracy of 0.5 mrad for both gratings  $G_1$  and  $G_3$  in the pre-alignment.

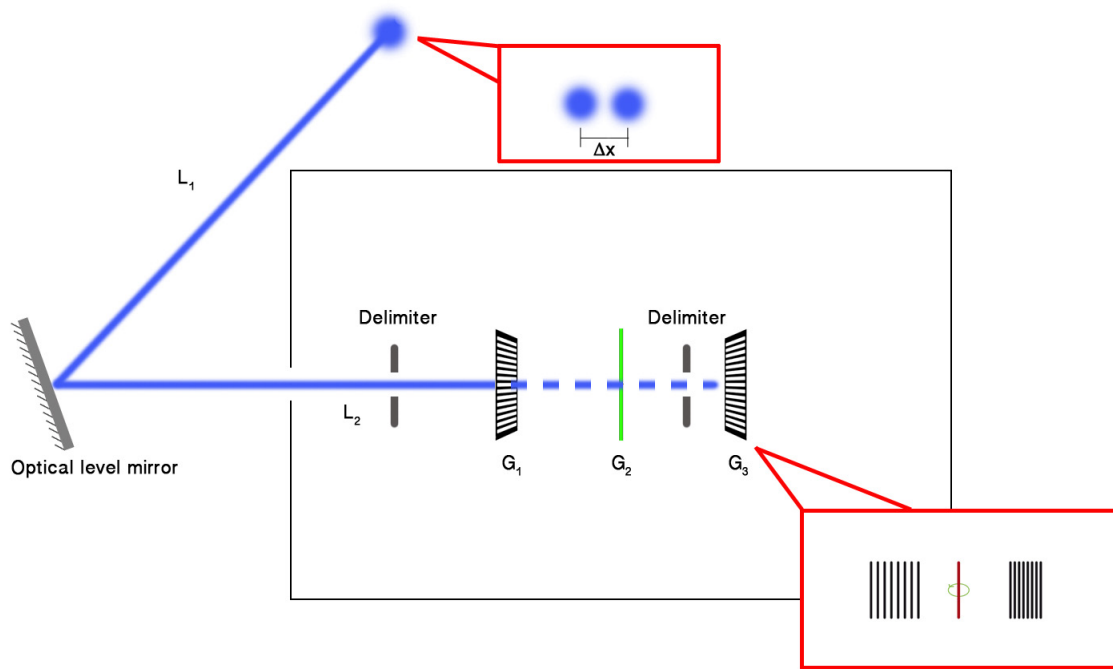


Figure 3.3: Illustration of the alignment setup for the adjustment of the gratings' yaw angle within the vacuum chamber. The setup is in principle the same as for the alignment of the gratings' pitch angle, where the blue line indicates the blue alignment laser. In addition to the optical level mirror for the laser's alignment orthogonal to gravity, we defined the laser's path with two horizontal delimiters (i.e. vertical slits). The delimiters are at the same positions as for interference measurements with a molecular beam, such that we ensure that the molecules hit the gratings perpendicularly after the alignment process. Here,  $\Delta x$  is given by the horizontal distance between the outgoing and incoming laser beam. Again, we estimated the accuracy of our pre-alignment by  $\Delta\theta = \Delta x/L$ .

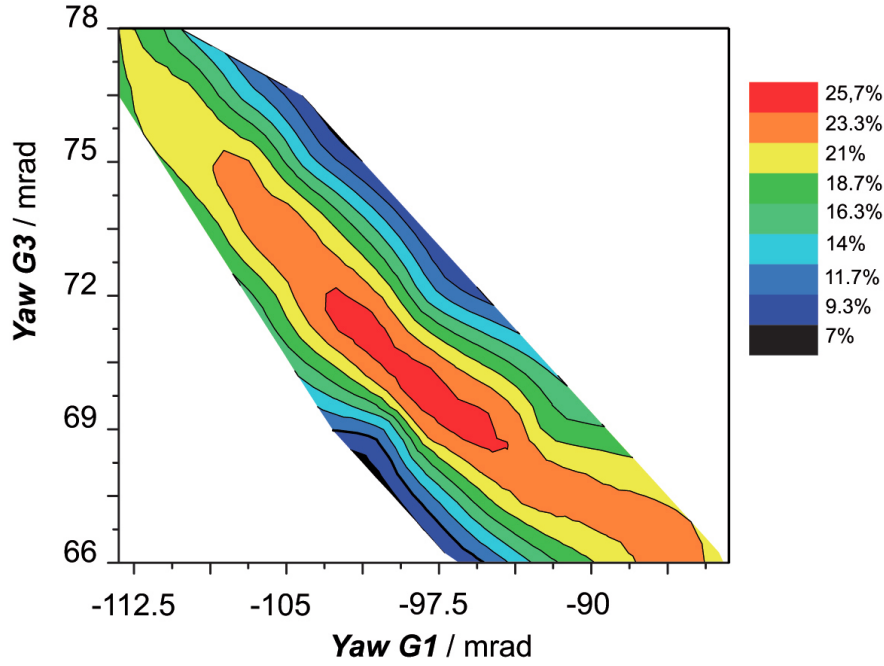


Figure 3.4: Visibility as a function of the yaw angles of the gratings  $G_1$  and  $G_3$  with the colors indicating the achieved visibility for different yaw angles of the two material gratings. The data was recorded by Sandra Eibenberger and Lukas Mairhofer with  $C_{60}$ . Picture from [67].

A misalignment of the yaw angle leads to the deviation of two parameters: the distance between the gratings and their effective period change. Both lead to a decrease of the interference contrast. Figure 3.4 shows experimental results for the visibility in dependence on the mismatch between the gratings  $G_1$  and  $G_3$ .

The change in the grating distance dependent on the yaw angle  $\beta$  is given by

$$\Delta L(\Delta\beta) = \frac{h\Delta\beta}{4} \quad (3.4)$$

where  $h$  again is the height of the gratings. Here, we assume the pivot point to be in the grating's center. For a beam width of 1 mm we thus need  $\Delta\beta$  to be smaller than 50 mrad. This accuracy we already achieved in our pre-alignment.

The change in the grating's period  $d$  is much more crucial. The effective period  $d_{\text{eff}}$  of the gratings dependent on the yaw angle  $\beta$  is given by

$$d_{\text{eff}} = d \cos(\beta) \approx d - \frac{d\beta^2}{2} \quad (3.5)$$



A phase shift of  $d/2$  between first and last slit of the grating leads to a complete loss of the interference contrast. This corresponds to a misalignment of the grating period by  $\Delta d = d/2N$ . Thus,  $\Delta d$  in our case has to be smaller than 0.35 nm which in turn correlates with a mismatch of the gratings of  $\Delta\beta < 14$  mrad.

Since the periods of the material gratings are slightly larger than the one of the light grating, we yaw the material gratings after the initial pre-alignment by 43 mrad to match them to the light grating period.

### 3.2.3 Roll

Since the grating period  $d$  is too small to obtain a far-field pattern with visible light, we have to align the roll angle of the gratings using the Littrow configuration. This is because in far-field diffraction  $d$  cannot be smaller than  $\lambda$ , since  $\sin \theta = n\lambda/d \leq 1$ , where  $n$  is the diffraction order.

In the Littrow configuration we look at the back-reflection of the laser from the grating bars themselves. Here, the equation changes to  $2d \sin(\theta_{\text{Blaze}}) = n\lambda$  with  $\theta_{\text{Blaze}}$  being the Blaze angle. This angle depends on the wavelength  $\lambda$  of the incident light. [21, p. 335] We choose the angle such that it fits the wavelength of our alignment laser and change the roll of the gratings until incident and backreflected beam overlap. Figure 3.5 shows the setup of the alignment laser. To monitor the roll of the gratings relative to gravity, we use the tilt sensors mentioned in chapter 2.2.2.1. With this procedure we obtain an accuracy for the alignment of the grating roll to gravity better than 0.1 mrad.

The roll angle is the most critical one since it influences the interference contrast in multiple ways. On the one hand, a roll of the grating relative to gravity causes the molecules to interact with different transverse positions at the gratings depending on their vertical position within the molecular beam. A collective tilt of all three gratings relative to gravity induces a phase shift dependent on the velocity of the molecules.

On the other hand, different velocity classes in the molecular beam fall over different distances due to the gravitational field. This leads to interaction at different relative positions of the gratings and thus introduces a height-dependent phase shift of the molecules. Finally, the effective grating period  $d_{\text{eff}}$  changes if the gratings are rolled with respect to each other.

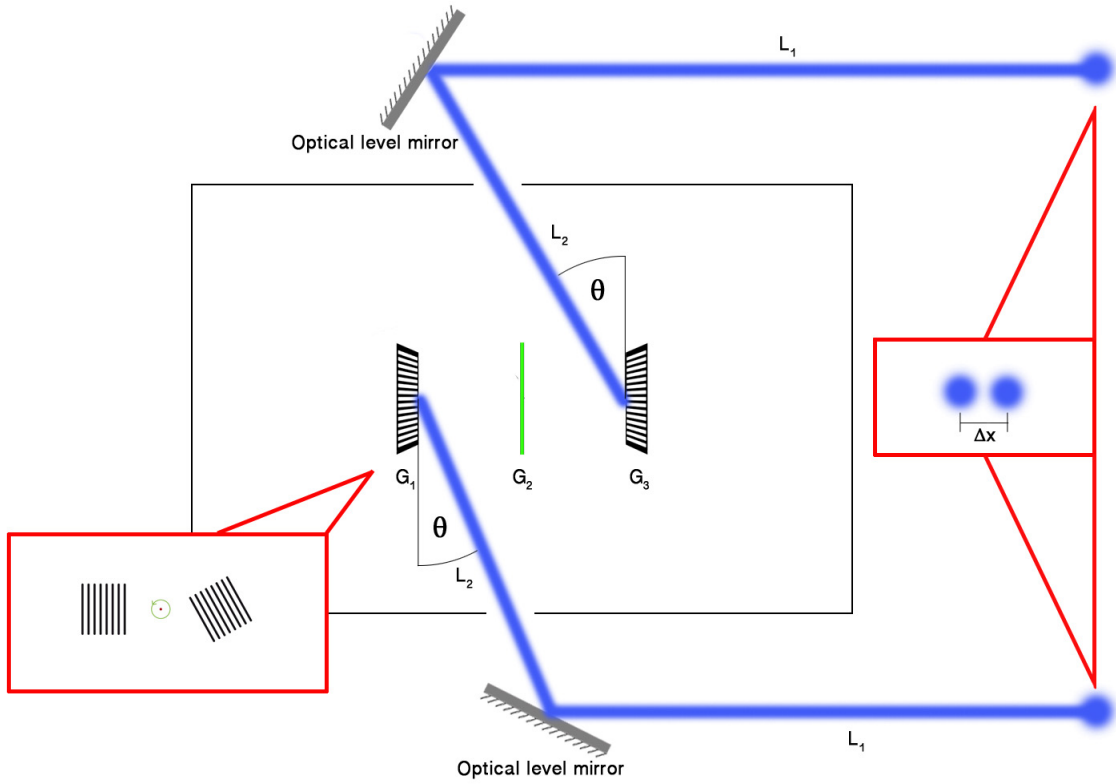


Figure 3.5: Illustration of the alignment setup for the adjustment of the gratings' roll angle. Since the grating's period is too small for a far-field diffraction pattern behind the grating using visible light, we instead use the Littrow configuration. If we shine the laser onto the grating bars under the Blaze angle  $\theta$ , the laser gets backreflected so that we can again overlap outgoing and incoming beam by rolling the grating and thus, aligning them parallel to gravity. The optical level mirror ensures that the alignment laser runs orthogonally to gravity.

For the influence of a misalignment relative to gravity we assume all three gratings to be perfectly aligned parallel to each other. A tilt of the grating bars with respect to gravity under an angle  $\gamma_{\text{grav}}$  leads to a shift of the interference fringes by

$$\Delta\phi_{\text{grav}} = \frac{L^2}{v_z^2} g \sin(\gamma_{\text{grav}}) \quad (3.6)$$

with  $g$  being the gravitational constant,  $L$  the distance between the gratings and  $v_z$  the mean velocity of the molecules in forward direction. Since the phase shift depends on the molecules' velocity, for a finite velocity distribution with a standard deviation  $\sigma_z$ , a misalignment leads to the reduction of the visibility by the factor  $R$  given by

$$V = V_0 \cdot R = V_0 \cdot \exp \left[ -2 \left( \frac{\pi g \sin(\gamma_{grav}) L^2 \sigma_z}{dv_z^3} \right)^2 \right] \quad (3.7)$$

with  $V_0$  being the visibility for a perfect alignment. [26] Figure 3.6 shows the reduction of the visibility in dependence of the misalignment of the grating bars relative to gravity for different mean velocities. This plot indicates that for the pre-alignment of the roll angle our accuracy of 0.1 mrad is enough to obtain interference.

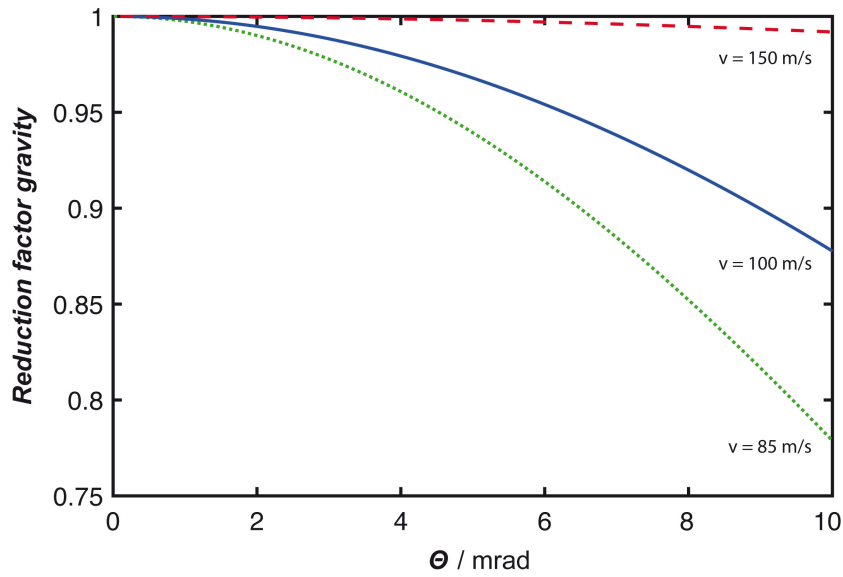


Figure 3.6: Simulation of the reduction factor  $R$  according to equation 3.7 for different velocity classes.

The influence of a misalignment of the gratings relative to gravity depends on the molecule's velocity. The dotted green line shows the effect for a most probable velocity of 85 m/s within the molecular beam, the solid blue line for 100 m/s and the dashed red line for 150 m/s. The velocity spread is 20 % (FWHM) for all three velocities. The simulation clearly shows that a misalignment of the grating's roll angle reduces the visibility more for lower velocities. Since we obtained an accuracy for the grating's roll angle better than 0.1 mrad, the reduction of the visibility is negligible, especially since the most probable velocity for our molecules is around 200 m/s.

Analogous to the misalignment of the grating's yaw, a misalignment of the roll angle influences the effective period the molecules interact with as well.

If the gratings are tilted relative to each other under an angle  $\gamma_{\text{rel}}$ , the effective period  $d_{\text{eff}}$  increases by

$$d_{\text{eff}} = \frac{d}{\cos(\gamma_{\text{rel}})} \approx d + \frac{d\gamma_{\text{rel}}}{2} \quad (3.8)$$

As discussed in chapter 3.2.2 the alignment of the roll angle has to be better than 14 mrad in order not to destroy the interference contrast due to a mismatch of the effective grating periods.

Besides the change of the effective grating period, non-parallel grating bars lead to a phase shift dependent on the vertical position of the molecules within the beam. Here, we neglect the alignment to gravity and assume a perfect match of the gratings in this respect. A molecule at the vertical position  $y$  will receive a phase shift of  $\Delta x_{\text{rel}} = y\gamma_{\text{rel}}$ . Since the detector is not sensitive to the molecules height within the beam, different phase shifts due to the vertical positions wash out the interference contrast. Thus, the total phase shift in terms of the misalignment of each grating can be expressed as

$$\phi_{\text{rel}} = \frac{2\pi}{d} (\Delta x_1 - 2\Delta x_2 + \Delta x_3) \quad (3.9)$$

If we use the light grating  $G_2$  as reference and thus set  $\gamma_2 = 0$ , we can rewrite the total phase shift as  $\phi_{\text{rel}} = 2\pi/d \cdot (y_1\gamma_1 + y_3\gamma_3)$ . This gives an expression for the detected signal  $S(x)$  at the QMS (with  $x$  being the axial position at  $G_3$ ) by integrating over the beam heights  $h_1$  and  $h_3$  for the gratings  $G_1$  and  $G_3$  respectively:

$$S(x) = \frac{1}{h_1 h_3} \int_{-h_1/2}^{h_1/2} \int_{-h_3/2}^{h_3/2} S(x + y_1\gamma_1 + y_3\gamma_3) dy_1 dy_3 \quad (3.10)$$

Computing this integral leads to the detected signal  $S(x)$  in the form of

$$S(x) = S_0 + 2|S_1| \sin\left(\frac{2\pi x}{d}\right) \text{sinc}\left(\frac{2\pi h_1 \gamma_1}{d}\right) \text{sinc}\left(\frac{2\pi h_3 \gamma_3}{d}\right) \quad (3.11)$$

where  $S_0$  and  $S_1$  are the first Fourier components.

This leads to a reduction of the visibility  $V = 2|S_1|/S_0$  dependent on a sinc function. Thus, if the relative roll angles are misaligned by only 0.5 mrad, the visibility is already reduced by 50% for a beam height of 100  $\mu\text{m}$ . But since our achieved accuracy for the roll angle is 0.1 mrad for both material gratings, we fulfill the necessary conditions to obtain interference.

### 3.3 Light grating

The light grating ( $G_2$ ) is our diffraction grating and has multiple parameters which have to be aligned. The light grating laser has to run orthogonal to gravity. We also have to align the distance between the retroreflecting mirror and the lens such that the focal point of the lens is at the position of the mirror and thus, the horizontal waist is as small as possible at the position where the molecules pass. Furthermore, we minimize the distance between the mirror and the molecular beam so that the molecules pass the standing light wave within the light grating's Rayleigh length. The horizontal position of the laser has to be in the center between the two other gratings, since the distances have to be equal to the Talbot length, like mentioned in chapter 3.1. And finally, we align the light grating's height such that the standing light wave and the molecular beam overlap.

#### 3.3.1 Pre-alignment of the light grating

First, we ensure that the diffraction laser enters the interferometer chamber orthogonally to gravity. By using an optical level mirror (Davidson Optotronics) we adjust the guiding mirrors until the incoming and the outgoing beam overlap. Once that is done, we shine the diffraction laser onto the retroreflecting mirror inside the chamber and tilt the mirror with motors to overlap incoming and outgoing beam again. This axis corresponds to the pitch angle of the mirror with an alignment accuracy of about 2 mrad.

The light grating has to be orthogonal to the molecular beam as well. This mirror axis corresponds to the yaw angle of the light grating. For the alignment, we define the beam path of the molecular beam with two horizontal delimiters between source and detector. The delimiters have widths of 0.5 mm and 0.1 mm, respectively. With this clearly defined beam path we are able to align the mirror parallel – and thus the light grating orthogonal – to the molecular beam by moving the mirror into the molecular beam. Then we tilt the mirror around its yaw axis until the count

rate is maximized. The light grating has a horizontal waist ("thickness") of about  $20\text{ }\mu\text{m}$ . Since the grating period is  $266\text{ nm}$  and thus about one order of magnitude smaller, a misalignment of the mirror's yaw would lead the molecules to pass multiple periods when crossing the diffraction grating so that the phase shifts would average out. A misalignment of  $4\text{ mrad}$  would theoretically still be alright, but the experiments showed that for a tilt of  $2\text{ mrad}$  relative to the ideal position the interference contrast already vanishes [41, p. 59].

As mentioned in chapter 2.2.2.2, we focus the diffraction laser with a cylindrical lens, where the focus has to be on the retroreflecting mirror. Therefore we monitor the outgoing laser beam profile outside the chamber after it has passed the lens and got reflected back from the mirror. We then change the distance between the mirror and the lens until we obtain a perfectly Gaussian beam. From the focused laser with a horizontal waist of  $20\text{ }\mu\text{m}$  follows a Rayleigh length of  $z_R = \pi\omega_0^2/\lambda_{\text{Laser}} \approx 2.4\text{ mm}$ . The molecular beam has to cross the light grating within this region, otherwise the wavefront is curved and the intensity varies. Hence, we move the retroreflecting mirror into the molecular beam by moving the stage where mirror and lens both are mounted. We see a decrease of the count rate as soon as the mirror cuts off a part of the molecular beam. Then we move the mirror back out of the molecular beam until we have the full count rate back again. With this procedure we ensure that the distance between the molecular beam and the mirror is about  $200\text{ }\mu\text{m}$  and thus, the molecules pass the light grating within its Rayleigh length.

Additionally to the angle alignment and the adjustment of the distance between laser and molecular beam, the period of the light grating has to match the periods of the mechanical gratings. On the one hand, we achieve that by yawing the material gratings, as described in chapter 3.2.2. On the other hand, we can also slightly tune the period of the light grating by changing the wavelength of the laser. For the laser used in the experiment this can be done by changing the temperature of its internal etalon in steps of  $0.1\text{ K}$ . This allows for a variation of the wavelength over a region of about  $0.1\text{ nm}$ . Figure 3.7 shows the dependence of the wavelength on the etalon temperature.

### 3.3.2 Fine tuning of the light grating

After the pre-alignment we adjust the light grating height such that laser beam and molecular beam overlap. A slit cut in a metal plate and positioned in front of the retroreflecting mirror in a  $45^\circ$  orientation to both, the laser and the molecular beam, acts as a reference point.

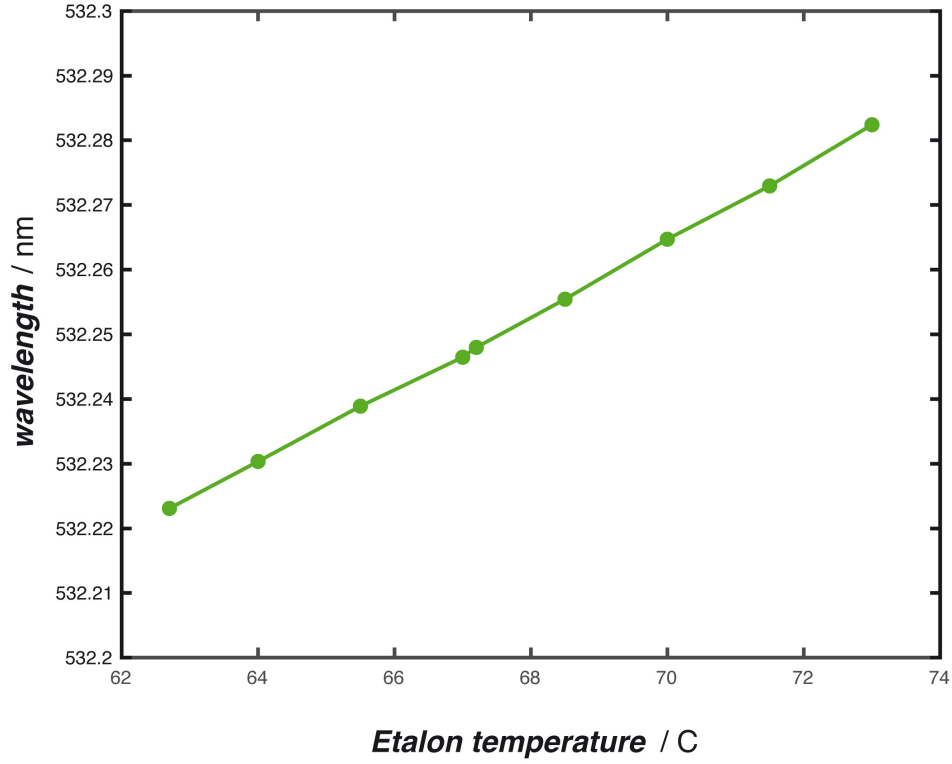


Figure 3.7: Laser wavelength as a function of its internal etalon temperature. The wavelength of the light grating laser depends linearly on the temperature of the internal etalon, such that we can slightly adjust the wavelength for alignment purposes.

For the calibration of this slit we use a beam of  $C_{70}$  molecules since this molecule has a significant absorption cross section of  $\sigma_{abs} = 1.97 \times 10^{-21} \text{m}^2$  at a wavelength of 532 nm [28]. We roughly align the molecular beam to the  $45^\circ$  slit by maximizing the detected signal. For the laser beam we basically do the same – namely optimizing the outgoing light intensity after it passes the mask. Then we detect the molecules at the QMS with laser ionization instead of electron impact ionization. For this we use an additional fiber laser (IPG GLR30) with a wavelength of 532 nm retroreflected from a mirror in front of the QMS. Since the absorption of a photon in the light grating increases the probability of ionization, we see an increase in the count rate when the molecules pass the light grating. Hence, we adjust the light grating height until we have the maximum count rate. Figure 3.8 shows the dependence of the count rate on the light grating height.

After the calibration we use  $C_{60}$  again for obtaining interference contrast and only slightly vary the light grating height together with all the other parameters.

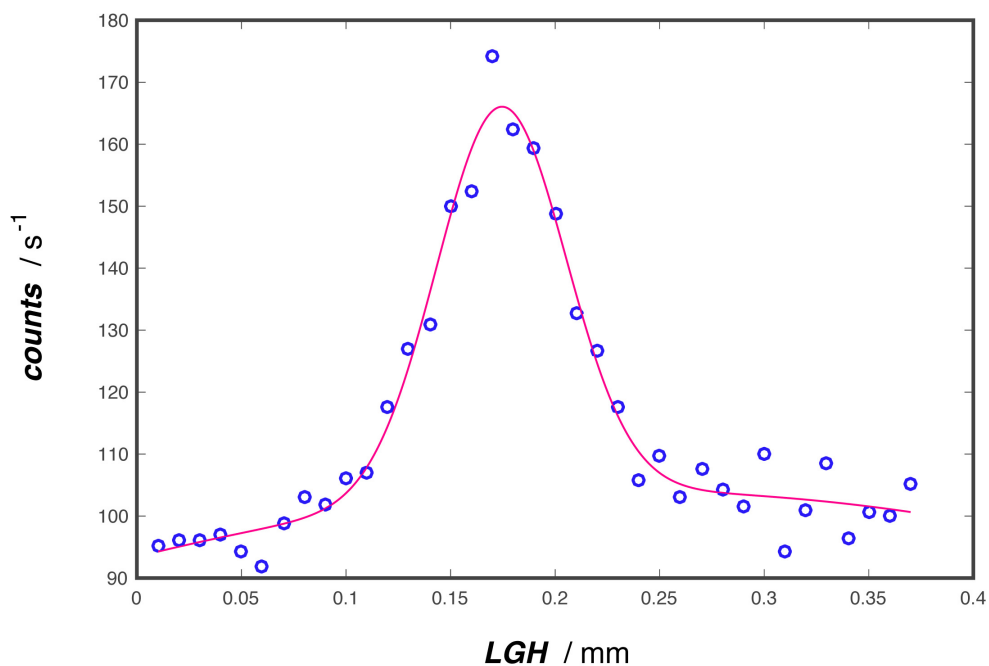


Figure 3.8: Count rate of  $C_{70}$  as a function of the light grating height (LGH). The blue circles are the recorded count rates of  $C_{70}$  averaged over 10 s at each position of the light grating height. The pink line is a Gaussian fit to the data points, since the grating laser emits a Gaussian beam profile. For the detection of the molecules we used photoionization at a wavelength of 532 nm instead of electron impact ionization. If the molecules interact with the light grating laser of the same wavelength, the probability of ionization by the detection laser increases, since  $C_{70}$  absorbs photons without re-emitting them. With this method we can determine the LGH, since we expect the highest count rate at the position of the strongest interaction with the light grating laser.



## 4 A new design for a thermal source

Molecular beams are a powerful research tool for the investigation of physical and chemical properties of atoms and molecules. This tool developed and evolved throughout the 20th century. After Louis Dunoyer produced the first molecular beam in 1911 [25], Otto Stern experimentally made the proof of the kinetic theory of gases by measuring the velocity distribution within a molecular beam [95], Stern and Gerlach demonstrated the spatial quantization of an atom's intrinsic angular momentum in a magnetic field [40] and Estermann and Stern verified the de Broglie hypothesis for heavy particles [32]. These are just a few examples for the early achievements in physics using molecular beams, followed by many other experiments and discoveries over time.

Among numerous areas in physics and chemistry, molecular beams also play an important role in quantum optics, since for many experiments – like the KDTLI – they are a basic requirement. Thus, there is a huge interest in developing new methods and further improvement of existing ones in order to obtain stable molecular beams of high intensity with minimal fragmentation of the particles. As described in chapter 2.2.1, for our interference experiments we use an effusive source, but there are other options to produce a molecular beam as well.

In this chapter I start with a short overview of different molecular beam methods, their scope of application and the relation between a specific beam method and a suitable detection scheme. Then I will focus on effusive sources, which is the evaporation method we use in the KDTLI setup. I discuss not only geometrical requirements, but also considerations in terms of the material. Finally, I introduce the design of the new oven and the results from the first test runs.

### 4.1 Sources for matter-wave interferometry

The choice of a particular method for the production of a molecular beam for matter-wave interferometry depends on several factors. Not only must the source suit the chosen detection scheme (or vice versa) and the general experimental setup with all its requirements, but the

source also has to fit the molecules of interest and their properties. Additionally, for matter-wave interferometry the production of neutral particle beams is important, since electrical stray fields would lead to decoherence. In our group, we develop and use different methods for the production of neutral particle beams depending on the specific requirements of each experiment.

**Effusive source** After the invention of molecular beams, for many years effusive sources were the only available method to produce said beams. But effusive sources have their limits, in our case the ability to evaporate massive and thermolabile particles. However, a thermal source is probably the simplest way to produce a molecular beam. An oven heats the molecules to the temperature at which they evaporate. Then the molecules exit the furnace through a small aperture into a vacuum chamber where they form a molecular beam with forward velocity according to the Maxwellian velocity distribution. A thermal source is suitable for a broad range of molecules as long as they are thermostable. Another limit is the mass of the particles, even though pretty massive particles of 10.000 amu have been launched this way already [30]. In chapter 4.2.1 I will discuss this kind of source in more detail, since that's the method we use in the KDTLI as well as the working principle of the new oven.

**Microfocus laser evaporation** As mentioned already above, an effusive source is only suitable for thermostable particles. In contrast, thermolabile particles would decompose during the heating process before reaching their evaporation temperature. Evaporation with a laser micro-source reduces the heat load to the particle by two or three orders of magnitude compared to a Knudsen cell and thus, this method allows the launch of intact molecules, even if they are thermolabile. Although locally the temperature can be high, only the particles within the focus area of the laser with a width of about  $1.5\ \mu\text{m}$  are affected. The small width of the source prepares the required transverse coherence. For the evaporation, the inner side of a window to the vacuum chamber is coated with a thin layer of molecules. A blue diode laser is focused onto the molecules and can be moved by a translation stage scanning over the sample. Our group uses this kind of source in many experiments at the far-field interferometer where the detection takes place with laser-induced fluorescence after the diffracted molecules accumulate on a plate. However, for this kind of source other detection schemes like a QMS would be possible as well, if the experiment operates in the near-field regime. [59] [64]

**Laser desorption followed by collision cooling** Pulsed laser desorption provides a source for massive particles such as large polypeptides, nucleotides or other biomolecules, which require a lot of energy to evaporate. Heating them in a Knudsen cell would lead to fragmentation

before evaporation. Hence, it is not suitable. Short laser pulses in the range of nanoseconds to femtoseconds provide enough energy to desorb the molecules from a surface coated with the sample. In our group this surface is a rotating carbon wheel which has the advantage of reloading during the rotation from a sample reservoir. The desorbed molecules are then seeded into a cold carrier gas jet to cool them and prevent fragmentation. A pulsed Even-Lavie valve emits the supersonic jets of the carrier gas [33]. Some species of molecules can also be directly evaporated in the Even-Lavie source. Thereby, the formation of molecular clusters is possible in order to study their properties. [23] Depending on the specific molecule and the experimental setup, different lengths of laser pulses and wavelengths are used for the desorption process. Since laser desorption doesn't launch a continuous molecular beam it causes a dramatic loss of signal in a continuous detection scheme. Therefore, a pulsed detection scheme such as a time-of-flight mass spectrometer (TOF-MS) is favorable over a continuous one. [35] [43] [63] [78] [90]

**Laser-induced thermomechanical stress** The launch of particles by laser-induced thermomechanical stress is a soft and minimally invasive technique for the production of neutral molecular beams with low velocities. The low velocities within the molecular beam lead to longer interaction times and longer de Broglie wavelengths compared to typical thermal beams or laser desorption into an adiabatically expanding gas jet. This type of source is suitable for thermolabile particles, even if they are massive. In contrast to other laser-assisted beam methods, here the particles never see the laser light directly. A thin metal foil is coated with the molecules on the front side. Then, an intense laser pulse irradiates the backside of the metal foil, thereby inducing heat transfer and an acoustic shock wave from the ablated metal plasma to the sample. The combination of heat transfer and acoustic shock leads to the release of the neutral particles. As for laser desorption, a TOF-MS or laser-induced fluorescence detection is preferable over a continuous detection scheme. [88]

**Electrospray ionization and charge reduction** The volatilization of complex biopolymers to produce a beam of neutral particles is still challenging. Electrospray ionization (ESI) is an efficient option for the transfer of macromolecules into the gas phase, but for interference experiments the resulting charged particles are not suitable. Thus, neutralization is necessary before they enter the interferometer. One option is the attachment of tailored covalent tags to the larger parent molecules of interest. Once the molecules are in the gas phase, a photo-induced cleavage removes the charged tags, so that only neutral and singly charged molecules remain in the beam. This procedure has been demonstrated for a few types of molecules like peptides and insulin, but is not yet implemented as a molecular source in an interferometer. [20] [83] [89]

## 4.2 A new concept for an effusive source in the KDTLI

Although there are several options to produce a molecular beam by softer and less invasive means than an effusive source, for the KDTLI an oven still is a suitable source, which has some advantages over other beam methods. On the one hand, an oven is rather simple in terms of its construction, and therefore the realization costs are in general lower compared to other sources. On the other hand, an effusive source offers a stable and high particle flux, which is important for interference experiments. The sample preparation is easy as well, since we just need to fill the molecules into the oven without any further effort. Additionally, the molecules in the KDTLI are detected with a QMS, hence a continuous source fits the detection scheme.

However, working with the oven described in chapter 2.2.1 revealed some flaws over time. The connection of the heating wire is very fragile and tends to break when removing the oven from the chamber or mounting it again after refilling. Reconnecting it was often an ordeal and pretty time consuming. Furthermore, the exit slit in the cap clogged sometimes due to the condensation of the molecules, since the cap was not heated and thus colder than the rest of the oven. A new design of the cap with a thinner wall around the slit area to avoid clogging due to a too steep and long edge indeed reduced the problem, but did not solve it for good. The clogging repeatedly led to the abortion of measurements. While this might seem tolerable when working with an abundant molecule such as  $C_{60}$ , it becomes a serious problem for experiments with tailor-made or more expensive molecules. In addition, after every changing process the oven and all the slits inside the vacuum chambers as well as the height of our diffraction grating need to be aligned again, since the exact slit position – and therefore the molecular beam path as well – always slightly changes. Although we try to always choose the same slit orientation, remounting the furnace hardly ever led to the exact same position. Realigning the molecular beam is not only a time consuming task but also a material consuming one. Again, this is a problem for expensive or tailor-made molecules where the sample sizes in general are small.

Above all, the heating process can lead to fragmentation of the molecules. As mentioned in chapter 4.1, fast heating can avoid or at least reduce fragmentation before transferring the molecules into the gas phase. Thus, a faster heating process compared to the classical version of a furnace with a heating wire is highly desirable, especially for more complex and fragile molecules as well as for molecules with higher sublimation temperatures.

On grounds of all those considerations we decided to give an improved concept of a Knudsen cell a trial using another material for the oven as well as another mounting construction and a

slightly different geometry. In the following chapter I give a brief overview of the geometrical considerations and measures of an ideal Knudsen cell. Subsequently, I introduce the new design and the results of the test runs.

### 4.2.1 Theory of a Knudsen cell

In general, a Knudsen cell or oven consists of a cylindrical volume containing the sample, surrounded by a heating wire, closed by a cap with an exit slit for the particles to leave, which in ideal circumstances can be heated separately to allow for higher temperatures than the rest of the material chamber to avoid condensation at and clogging of the aperture. The whole oven again is surrounded by a radiation shield made of highly reflective metal sheets to avoid heating up the vacuum chamber as well as reducing the power consumption by lowering heat loss to the environment. The choice of the cylinder material depends on the choice of molecules – to avoid catalytic decomposition of the molecules, ceramics are more favorable than metal surfaces.

Since the oven is connected to a vacuum chamber, the particles in the source chamber effuse into vacuum through the exit slit. A characteristic of a thermal source is the production of a beam with molecular flow instead of a gas dynamic flow. In a molecular flow no collisions of the molecules in the vicinity of the exit slit and in the resulting particle beam occur. Due to collisions in a gas dynamic flow, the velocity distribution within the beam is narrower and shifted to higher velocities. For an effusive source the mean free path in the source is large compared to the characteristic dimension of the aperture. Thus, a characteristic number for the transition from molecular flow to gas dynamic flow is the Knudsen number  $Kn$  given by [74, p. 45]

$$Kn = \frac{\bar{\Lambda}}{L} \quad (4.1)$$

with  $L$  the characteristic length of the geometrical dimension of the slit and  $\bar{\Lambda}$  the mean free path of the particles. The latter is given by an integral which can't be calculated in a closed form, but approximated by the relation [74, p. 44]

$$\bar{\Lambda} = \frac{1}{n\sigma_{scat}} = \frac{k_B T}{P\sigma_{scat}} \quad (4.2)$$

Here,  $n = N/V = P/k_B T$  is the number density of particles  $N$  per unit volume  $V$  according to the ideal gas law in terms of statistical mechanics,  $\sigma$  is the effective scattering cross section,  $k_B$  is the Boltzmann constant and  $T$  and  $P$  are the absolute temperature and the absolute pressure of the gas respectively. To ensure a molecular flow instead of a gas dynamic flow, the Knudsen number has to be greater than 1. Hence, the dimension of the aperture has to be smaller than the mean free path of the molecules. For an aperture small in size compared to the surface area of the oven, the thermal equilibrium of the gas inside the oven is not disturbed by the effusing particles. Thus, gas kinetic theory holds and the velocity distribution of the emitted molecules follows the Maxwell-Boltzmann distribution  $F(v)$  given by [74, p. 37f]

$$F(v) = \frac{4}{\sqrt{\pi}} \left( \frac{m}{2k_B T} \right)^{\frac{3}{2}} v^2 \exp \left( -\frac{mv^2}{2k_B T} \right) \quad (4.3)$$

with  $k_B$  being the Boltzmann constant and  $m$ ,  $T$  and  $v$  the molecules' mass, temperature and velocity respectively. From the Maxwell-Boltzmann distribution follows a most probable velocity of

$$v_{prob} = \sqrt{\frac{2k_B T}{m}} \quad (4.4)$$

and a mean velocity of

$$v_{mean} = \sqrt{\frac{8k_B T}{\pi m}} \quad (4.5)$$

For an effusive source with a Maxwell-Boltzmann distribution, the total molecular flux per time unit  $dN/dt$  into the solid angle element  $d\omega = \sin \vartheta \, d\vartheta \, d\varphi$  with  $\vartheta$  and  $\varphi$  the polar angles characterizing the molecules' direction can be written as [74, p. 61]

$$I = \frac{dN}{dt}(\vartheta) \, d\omega \, ds = v_0 \, ds \cos \vartheta \, \frac{d\omega}{\pi} \quad (4.6)$$

with  $v_0$  the rate at which molecules leave the source through the aperture per unit time and unit area and  $ds$  an area element of the aperture. The equation for the particle flux shows that the intensity distribution of the effusing particles is proportional to  $\cos \vartheta$ .

Replacing  $ds$  by the total aperture area  $s$  gives the expression for the flux in forward direction  $\vartheta = 0$  [74, p. 62]:

$$\frac{dN}{dt}(0) = I(0) = \frac{v_0 \cdot s}{\pi} d\omega \quad (4.7)$$

This equation can be rewritten as

$$\frac{I(0)}{\Delta\omega} = 1.118 \cdot 10^{22} \cdot \frac{P_0}{\sqrt{MT}} \cdot s \text{ [particles sr}^{-1}\text{s}^{-1}] \quad (4.8)$$

with  $P_0$  the pressure in the source,  $M$  the molecular weight,  $T$  the temperature and  $s$  the area of the exit slit. From this equation follows – in analogy to optics – the brightness  $B$  of the source defined as [74, p. 62]

$$B = \frac{I(0)}{\Delta\omega \cdot s} = 1.118 \cdot 10^{22} \cdot \frac{P_0}{\sqrt{MT}} \text{ [particles sr}^{-1}\text{s}^{-1}] \quad (4.9)$$

In order to obtain the maximum intensity of the source, the geometrical form  $s$  of the source aperture can be optimized according to the Knudsen condition. For a circular aperture, the maximum achievable intensity in forward direction with molecular flow is obtained for  $s_{circ} = \pi \bar{\Lambda}^2$ . From this condition follows that the intensity of the beam decreases with increasing pressure, since the mean free path is inversely proportional to the pressure. Thus, for increasing pressure, the aperture diameter has to be reduced quadratically. In contrast, for a slit with height  $h$ , the condition is  $s_{slit} = h \bar{\Lambda}$  and the maximum intensity is independent of the pressure, but grows with slit height. Hence, an aperture in form of a slit is preferable over a circular one.

An ideal aperture should also be thin walled, i.e. the thickness of the wall should be thin compared to the dimension of the aperture. At a steep and long edge of the exit slit, the molecules will collect and could clog the aperture. If the edge is thin, the incident molecules will spread over a larger area and the risk of clogging is reduced. Figure 4.1 illustrates the advantage of a thin walled aperture.

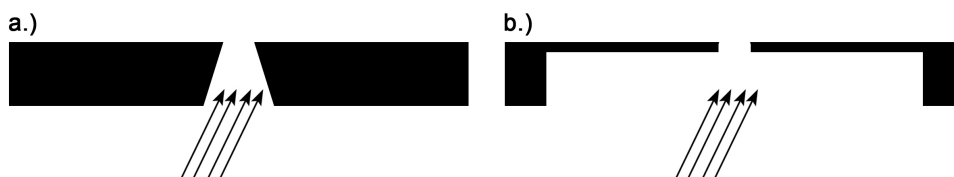


Figure 4.1: Illustration of the difference between a steep edge of the exit slit and a thin walled aperture.

a.) shows a thick walled aperture with the arrows indicating the incident molecules. The molecules will potentially clog the aperture when incoming under an angle. b.) shows the thin walled version of an aperture. Here, the condensed molecules distribute over a larger area instead of clogging the aperture itself.

## 4.2.2 A new design

### 4.2.2.1 PBN/PG heating elements

Since the potential fragmentation of the molecules during the heating process was one of the main reasons to think about a new design of our Knudsen cell, we decided to give a completely different configuration a try. Instead of a ceramic cylinder with a heating wire, we now use resistance heating elements made of pyrolytic boron nitride (PBN) in combination with pyrolytic graphite (PG) as a basis for the new furnace. PBN is a ceramic with dielectric properties, while PG is an electrical conductor. Both materials have a high thermal conductivity and anisotropy leading to thermal uniformity over the whole surface. PBN/PG heaters can reach very high temperatures compared to conventional types of Knudsen cells and work perfectly in ultra-high vacuum. Another advantage of PBN/PG heaters is that they hardly react with any kind of particles, making them suitable for a broad range of different molecules.

The operating principle is pretty simple – the heaters incorporate electrical connections with physically unclosed PG electric circuits such that the electric current runs through the PBN leading to heating due to the dielectric properties of the ceramic. Since PBN/PG heaters are thermally shock resistant, rapid heating processes and temperature changes are possible without damage to the heaters. In general, heating powers of  $35 \text{ W/cm}^2$  and more are possible [55]. The heaters can be operated with standard power supplies.

Furthermore, PBN/PG heaters can be manufactured not only as flat plates, but also as 3D-structures. In summary, all these facts sounded very promising for our purposes.



#### 4.2.2.2 Design of the oven

Even though customized 3D-structures of PBN/PG heaters can be manufactured, the possible shapes and geometrical dimensions are still limited to a certain degree by production processes. As far as possible, we took all the theoretical considerations of a Knudsen cell mentioned in the previous chapter into account and designed a PBN/PG heater consisting of two separate parts: a cylindrical volume which will contain the sample and a plate heater that closes the oven. Both parts can be heated separately. Figure 4.2 shows a sketch of the whole oven setup including the ceramic mount.

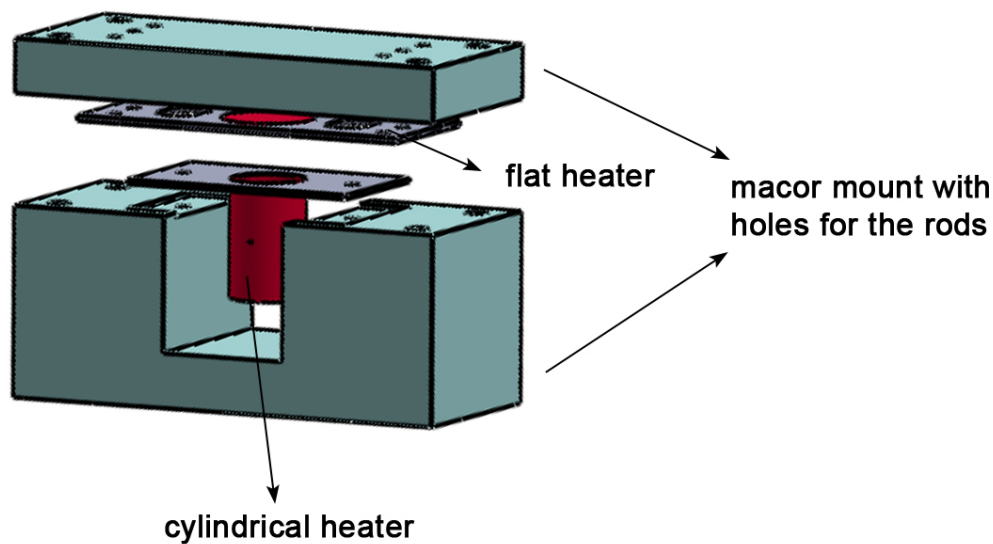


Figure 4.2: Sketch of the PBN/PG heaters within the Macor mount. The red areas on the heaters indicate the heated regions. The mount is screwed together with rods and has additional holes for the tantalum rods serving as power connections for the heaters.

The exit slit with a height of  $500\text{ }\mu\text{m}$  and a width of  $1.2\text{ mm}$  is located on the cylindrical part. The wall has a thickness of at most  $0.8\text{ mm}$ . Figure 4.3 shows a technical drawing of the heater's cylindrical part. The slit dimensions slightly differ from those of the previously installed. Technical limitations as well as material properties determine the slit height and do not allow for smaller dimensions (at least at this time). The width is chosen slightly smaller since the opening is on a curved surface instead of a flat one. Thus, the smaller width leads to approximately the same effective slit width.

To avoid potential leaking of molten molecules, the slit is positioned as high as possible on the cylinder, where the oven mount marks an upper limit due to potential reflection of the emitted molecules at the mount. A reflection and the subsequent collisions between the molecules would destroy the molecular beam. With a height of 20 mm and a diameter of 12 mm the oven offers a volume of  $2.23\text{ cm}^3$ . Here, the slit position on the cylindrical part of the heater limits the amount of molecules for one oven filling. However, the usable furnace volume is roughly the same as for the previous oven.

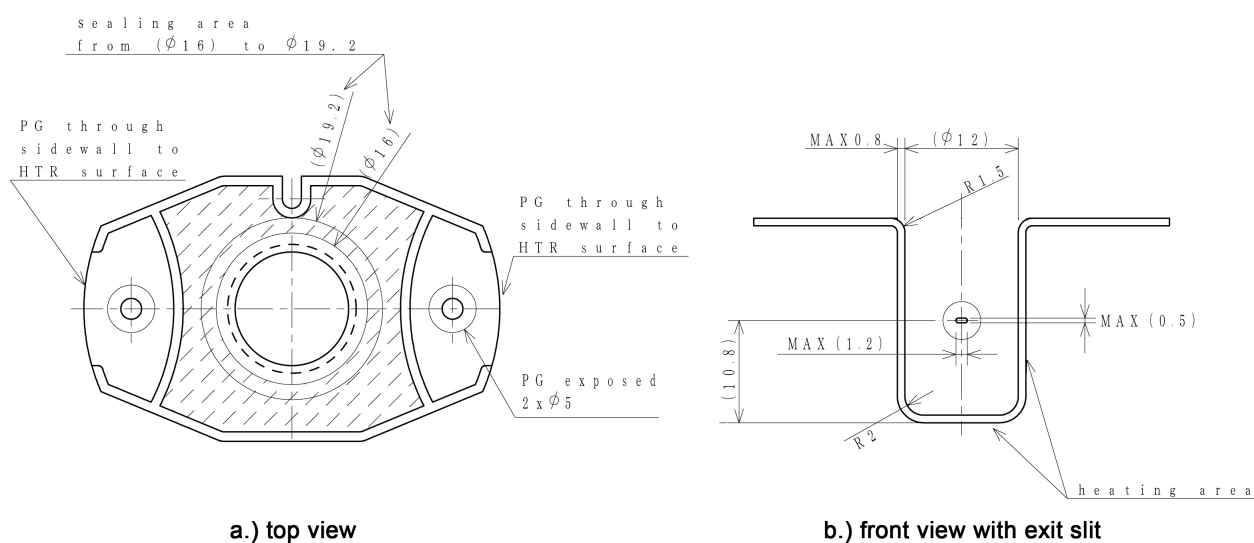


Figure 4.3: Technical drawing of the cylindrical PBN/PG heater with the most significant dimensions.

a.) shows the cylindrical heater from top with the sealing area, where the PBN sealing plate and the Grafoil sealing is positioned. The notch pictured on top of the drawing should avoid reflection of the molecules from the heater, since scattered particles would destroy the molecular beam. The electrical connection is applied on the exposed PG connectors. b.) shows the heater from the front with the exit slit, where the molecules leave the oven. The slit has a height of  $500\text{ }\mu\text{m}$  and a width of  $1.2\text{ mm}$ . With a height of  $20\text{ mm}$  and a diameter of  $12\text{ mm}$  the heater has a total volume of  $2.23\text{ cm}^3$ . The corners are slightly rounded so that the molecules do not stick within them. This makes the cleaning process easier. Picture by MOMENTIVE, modified by the author.

Figure 4.4 shows a close up of the PG circuit of the cylindrical heater. Within a Knudsen cell there are two main reasons for clogging of the exit slit: On the one hand, the molecules condensate if the material around the slit is colder than the rest of the oven. On the other hand, if the edges of the slit are too long and steep, the molecules collect there.

Technically it was not feasible to include two separate PG circuits in the cylindrical part of the oven in order to heat the area around the slit independent of the rest of the surface and thereby avoid clogging. It is noteworthy that within the previous oven we couldn't heat the cap at all. Hence, the mere fact of an exit slit with the same temperature as the rest of the oven is an advantage. Additionally, although an ideal Knudsen cell should have a thin walled slit, technical limitations of the production process lead to a minimal wall thickness of 0.8 mm. However, due to the fast response of PBN/PG heaters it is possible to heat up only for a short time period until the stuck molecules evaporate.

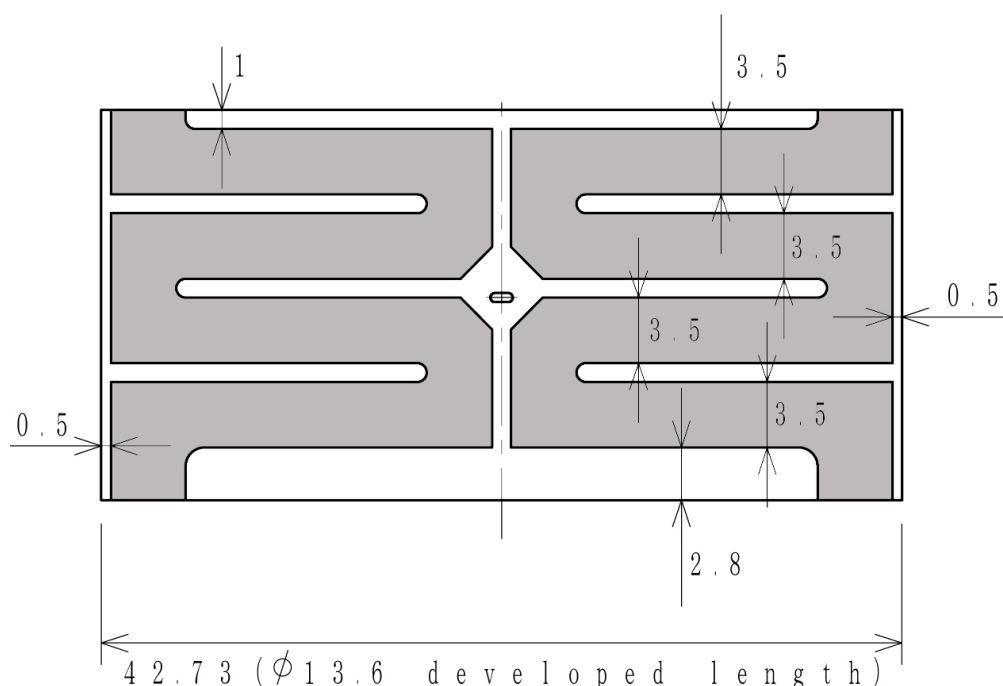


Figure 4.4: Technical drawing of the PG circuit in the surface of the cylindrical PBN/PG heater. The drawing shows the cylinder's unrolled lateral surface. The grey area is the PG circuit, while the white area is the PBN which gets heated by the current running through it. Picture by MOMENTIVE, modified by the author.

The second part of the oven is the flat PBN/PG heater as shown in Figure 4.5, which is fixed on top of the cylindrical part. The temperature of the flat heater can be adjusted separately, yet the main purpose is to close the oven volume. Usually, the two parts are heated to the same temperature. To ensure that no molecules leave the oven between the two heaters, an additional sealing plate made of PBN as well as a plate made of flexible graphite can be positioned between the heaters.

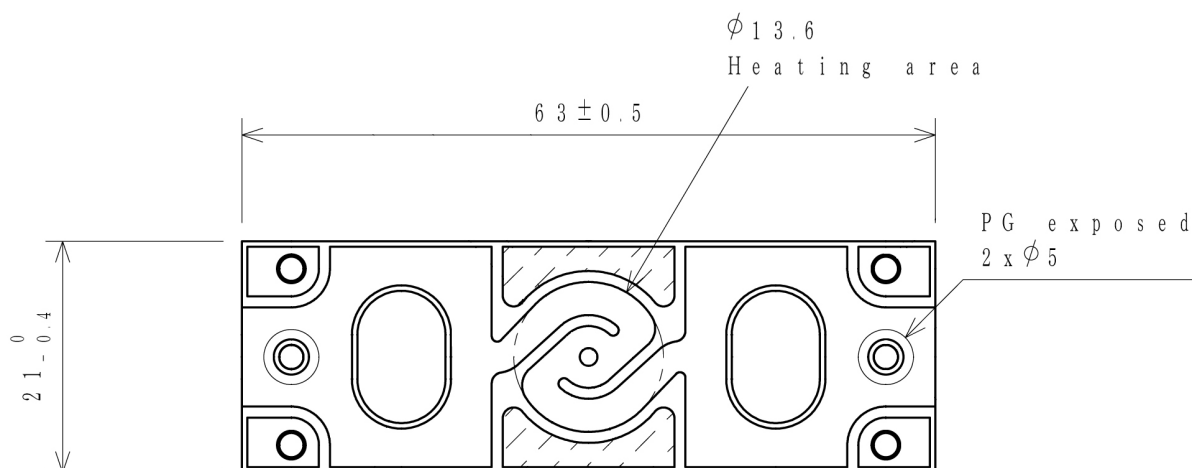


Figure 4.5: Technical drawing of the flat PBN/PG heater with the significant dimensions. The oval openings in the heater are due to construction reasons – the tantalum rods for the power connection of the cylindrical heater pass through those holes. Only the center of the heater is heated. This is the area closing the cylindrical heater, and hence it is in contact with the evaporated molecules. Picture by MOMENTIVE, modified by the author.

Tests showed that we get the best results with the flexible graphite plate made from a material called Grafoil. Compared to the rigid PBN plate it adapts much better to the slight curvature of the cylindrical heater's top and thus, provides a better sealing. Grafoil is resistant to heat, corrosion and chemicals and can easily be cut in different shapes from a sheet such that it fits perfectly – both, in terms of material properties as well as regarding the shape – to the interspace between the heaters.

A ceramic mount made of Macor holds the two heaters together. Macor is a nonporous glass ceramic with a low thermal expansion coefficient of about  $120 \times 10^{-7} \text{ K}^{-1}$  for temperatures ranging to 1000 K, a low thermal conductivity of  $1.46 \text{ W/m} \cdot \text{K}$  as well as low outgassing even at high temperatures [56]. Thus, the mount not only holds the heaters together, but also acts as shield against thermal radiation fulfilling the same purpose as the tantalum shield in the preceding setup. Due to the low coefficient of thermal expansion the risk of breaking the PBN/PG heater covered by the mount even at high temperatures is low. The mount also consists of two parts which are screwed together with steel rods.

The required periphery is fixed to the mount as well. For the power connection of the PBN/PG heaters tantalum rods are connected to the exposed heater contacts with washers made of Grafoil and PG and fixed with molybdenum nuts like shown in Figure 4.6.

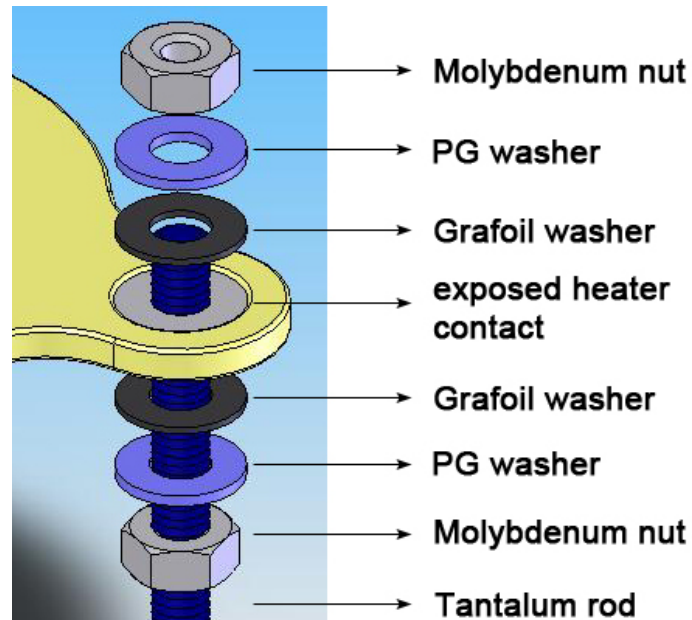


Figure 4.6: Connection assembly for PBN/PG heaters. A tantalum rod is fixed to the exposed PG contact by Molybdenum nuts with PG washers and Grafoil washers between the nuts and the contacts. At the other end of the tantalum rod the current is applied. Picture by MOMENTIVE, modified by the author.

The tantalum rods pass through the mount to electrical connectors implemented in the aluminum stage. Once the mount with the heaters is placed on the stage, the electrical connection is closed. To avoid an electric current running through the aluminum plate, we isolated the connection spots. The connectors also provide a guide such that the oven position within in the chamber stays always the same after each refilling process.

Two k-type thermocouples implemented in the mount measure the temperatures of the two heaters independently. The electrical connectors for the thermocouples are fixed on the side of the mount and on the aluminum stage such that we only have to plug them in once the oven is placed on the stage within the chamber. The aluminum stage is mounted via rods to a flange with all the necessary feedthroughs for power connections. This part of the oven always remains in the chamber and we only remove the mount holding the heaters within for the refilling process. Figure 4.7 shows a picture of the whole oven setup including the flange and the aluminum stage.

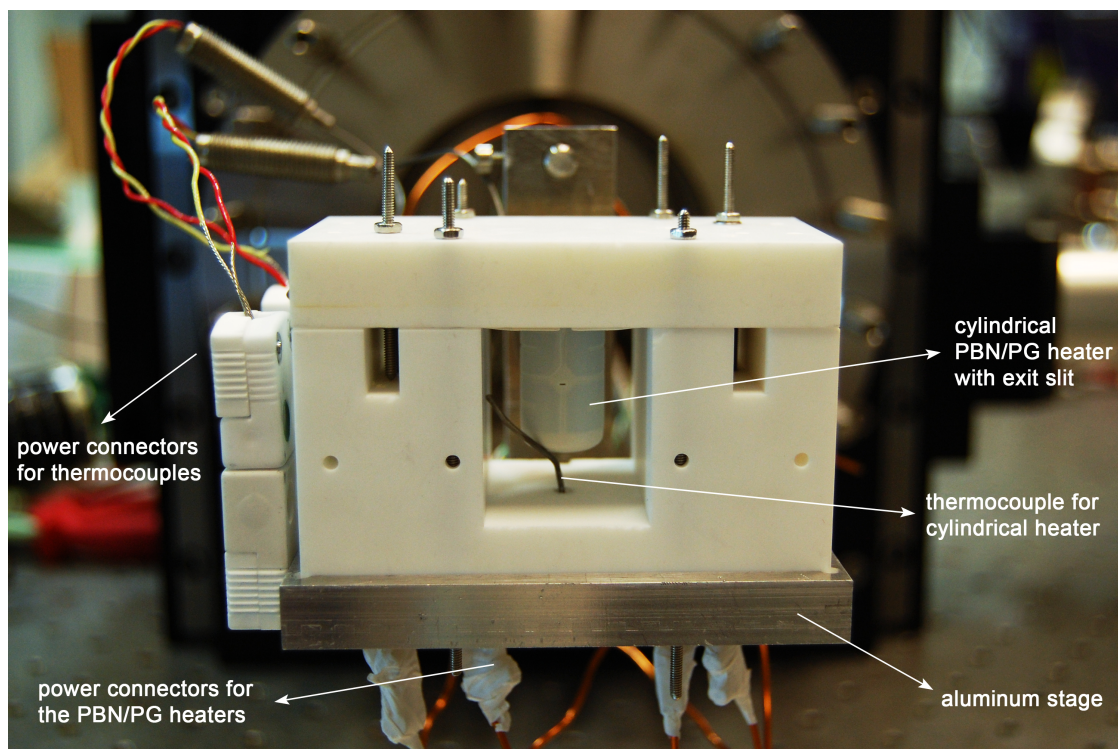


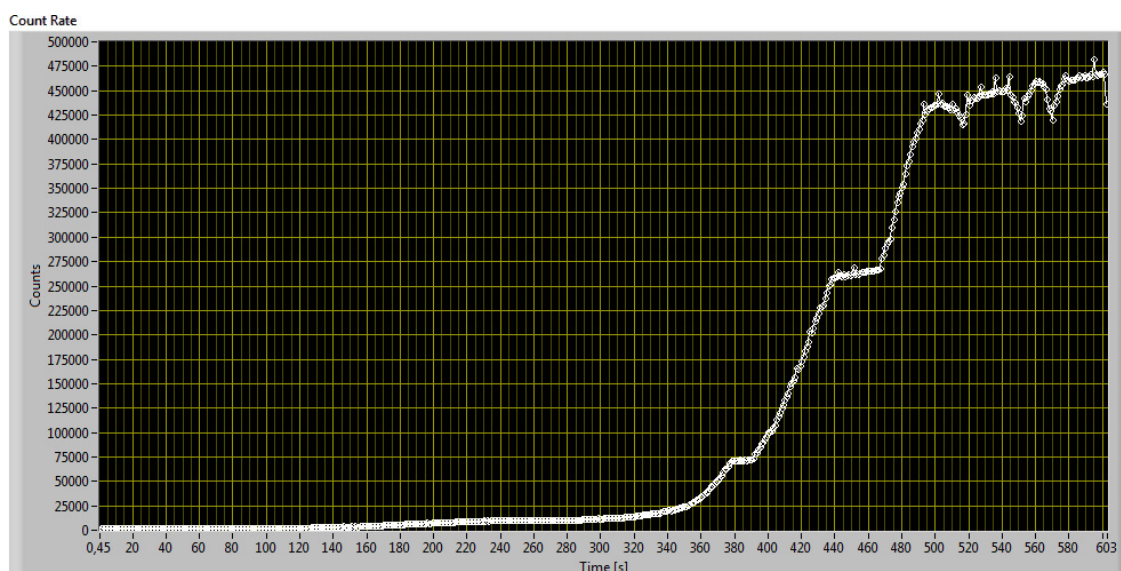
Figure 4.7: Picture of the oven setup. The PBN/PG heaters are mounted in a Macor mount which in turn is positioned on an aluminum stage including the power connectors for the heaters on the bottom. On the left side are the connectors for the k-type thermocouples, one for each heater. The aluminum stage is mounted to a flange with electrical feedthroughs attaching the setup to the vacuum chamber. Metal rods hold the mount together.

### 4.2.3 Tests and results

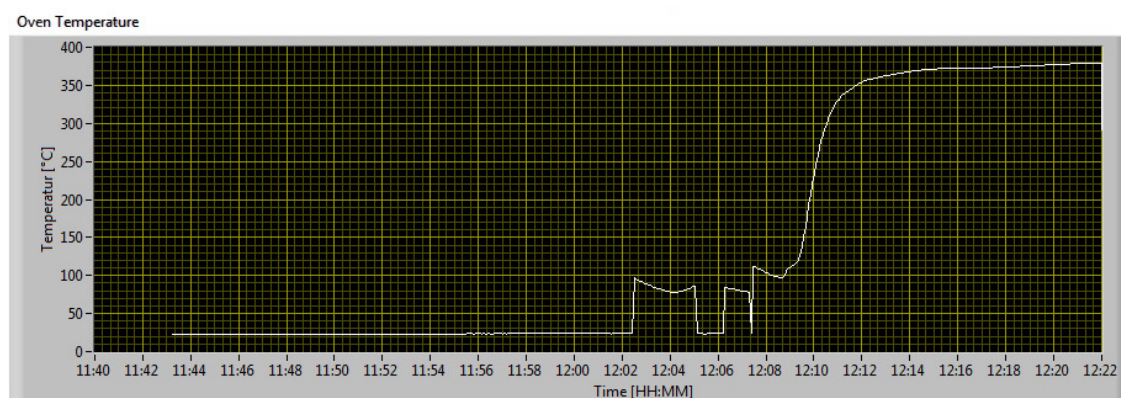
First tests with the new oven yielded convincing results in terms of count rate as well as heating rate shown in figure 4.8. We performed the tests with tetraphenylporphyrin (TPP), which is a dye with a mass of 615 amu.

For this molecule we achieved a count rate one order of magnitude larger than with the old oven. Since we did the tests in the KDTLI setup with the same detection scheme and the same path length as for interference experiments, we can expect a much higher count rate for these experiments as well. However, since we apply delimiters for velocity selection in interference experiments, we cut the molecular beam such that the count rate for these experiments will be lower than shown in the graph. Nevertheless the count rate will still be a lot higher than for the old oven design. Due to the realignment work on the KDTLI we have not been able to perform interference experiments with the new furnace yet.





(a) count rate over time



(b) temperature over time

Figure 4.8: Count rate and temperature of the new oven. The graphs were recorded with our lab software and show the count rate (a) and the temperature (b) over time. It is noteworthy that the two graphs do not show the same time interval. The temperature curve shows a time period of about half an hour while we started the record of the count rate just as the first signal appeared. The temperature is the temperature of the cylindrical part of the heater where the molecules evaporate. In less than ten minutes the oven reached a temperature of about  $360^{\circ}\text{C}$ . We could heat the oven even faster in the future by knowing the necessary voltage for a certain temperature. Here, we increased the voltage rather slowly to avoid overheating, indicated by the slow rise of the temperature curve on the left side of the graph. The mean count rate at the final temperature was about  $470.000\text{ s}^{-1}$  which is one order of magnitude larger than with the preceding oven for the same molecule.

#### 4.2.4 Improvements and outlook

Although the first tests showed good results, there is still room for improvements – mainly with respect to the sealing. We tried different combinations of the PBN sealing plate and the Grafoil sealing. From the tests with TPP we saw that the best option seems to be the Grafoil sealing without the PBN plate. TPP has an intense purple colour. If there is a leak between the heaters, the molecules dye the mount. This is an indicator for the sealing quality. Grafoil comes in sheets such that one can cut it in different shapes. For our tests we used almost circular plates in the size of the heating area on the flat heater. A different shape might improve the sealing as well as using two or even more layers of the Grafoil sealing to ensure that no molecules can exit between the heaters.

A high count rate with a low signal-to-noise ratio is desirable for interference experiments. However, another problem we might face is, that if the count rate is too high, the oven runs empty way too fast to be able to do enough interference scans. One factor that leads to an increase of the count rate compared to the old oven might be the slit height since it is about twice as large. Hence, it increases the beam intensity by a factor of 2 according to equation 4.8. Another reason is the rapid heating process where less fragmentation happens and thus, the signal of intact molecules is higher. Hence, slightly lower temperatures in comparison to the old oven might yield a sufficiently high count rate and could provide a longer-lasting signal. However, we have to determine the optimal working temperature for each type of molecule in any case.

Although we still have to figure out a few specifics with the new furnace, in general the first tests clearly showed advantages over the previous oven. Due to the increased count rate, not only the working temperature can be slightly lower which in combination with the fast response of the PBN/PG heater further reduces fragmentation of the molecules, but we can also reduce the integration time for the interference scans. This means less perturbations during the measurements due to potential drifts of the scanning grating. Especially for expensive and tailor-made molecules we can save alignment time as well as material. Furthermore, experiments with thermolabile molecules might be possible with this kind of effusive source. Thus, we don't have to implement another type of source in the KDTLI, but enlarged the range of possible molecules by integrating the new furnace concept.



## 5 Bio-Molecules

With near-field quantum interference it is not only possible to test the fundamental principles of quantum mechanics, but with an interferometer like the KDTLI we can also do metrology experiments. Our group has developed macromolecule interferometry leading to different applications – on the one hand, there is the philosophical aspect of the wave nature of matter, since it challenges our notion of reality [3]. The question arises whether there is a limit of size and complexity of particles behaving according to quantum mechanics, since in our everyday life we do not experience these phenomena. After quantum interference at the KDTLI with molecules exceeding the mass of 10.000 amu [30] the new record in quantum macroscopicity has been set at LUMI (Long baseline Universal Matter wave Interferometer) to a mass of 25.000 amu [35]. With macromolecule interferometry, fundamental quantum principles can be tested and might one day provide an answer to the question about the limits of quantum mechanics by experiments. On the other hand, matter-wave interferometry allows for the investigation of molecular properties for physical chemistry and biomolecular physics [27].

At the KDTLI the focus in recent years was on metrology with organic molecules and interference with massive organic particles such as tripeptides. In this chapter I will present the results of quantum metrology experiments with vitamins and the first quantum interference with peptides.

### 5.1 Metrology with vitamins

Vitamins are organic compounds which play essential roles in the biological functions of humans, animals, bacteria and plants. The specific functions of vitamins depend strongly on their electrical, optical, magnetic and structural properties. For example, vitamin K<sub>1</sub> serves as co-factor for mediated electron transport in the photosynthesis process of plants by accepting electrons in the photosynthetic membrane and transferring them to the reaction centers [45]. [67, p. 45]

However, the investigation of these properties in neutral isolated vitamins is rare – especially in the gas phase, where no perturbing effects due to solvents or other chemical bonds could potentially change the molecular properties. In the gas phase changes in the molecule's properties only occur due to thermal effects. While there are a few other approaches for the investigation in the gas phase [1] [24] [75] [99], the KDTLI provides a tool for studies of molecular properties using near-field quantum interference. Thus, before being able to investigate the molecular properties we have to make sure we can obtain an interference contrast with the molecule of interest at all. As mentioned in chapter 4, the production of a stable molecular beam is a crucial, but tricky task. This is valid for all particles, but even more so for isolated biomolecules. In the course of my bachelor thesis preceding this master's thesis I therefore did evaporation tests for several different vitamins in order to check whether it is possible to produce a molecular beam. Aside of the vitamins for which we measured further properties, retinal ( $C_{20}H_{28}O$ ), resveratrol ( $C_{14}H_{12}O_3$ ) and 7-dehydrocholesterol ( $C_{27}H_{44}O$ ) formed a stable beam. The beam for these three vitamins lasted between less than 30 minutes to around 120 minutes. This is generally too short for metrology based on interference measurements, although we obtained visibilities of around 5-20 %.

While the interference contrast of resveratrol and retinal is not reliable due to the low signal compared to the dark rate, for 7-dehydrocholesterol we obtained a good fringe pattern shown in figure 5.1(a). We even were able to record a power dependent visibility curve for 7-dehydrocholesterol shown in figure 5.1(b). From the influence of the light grating's intensity on the interference contrast due to phase shifts of the molecule's center-of-mass wave function we can extract the optical polarizability  $\alpha_{opt}$  of a molecule, which I will describe in more detail in chapter 5.1.1.

However, the result for the optical polarizability is not reliable for this vitamin. On the one hand, the velocity spread in the molecular beam was almost 60% (full width at half maximum). Since the signal vanished too soon, we neither were able to make more velocity measurements for comparison nor to choose a smaller velocity spread with smaller delimiters. A less time consuming aligning process would in this case crucially increase our measurement time, which is one of the goals we want to achieve with the new oven design. On the other hand, we saw the highest visibility at the laser's maximum output power and thus, might not have reached the maximum of the visibility yet. This can be due to imperfect alignment of the gratings and thermal effects leading to a reduction of the interference contrast. For a reliable fit it is necessary though to reach at least the first visibility maximum.



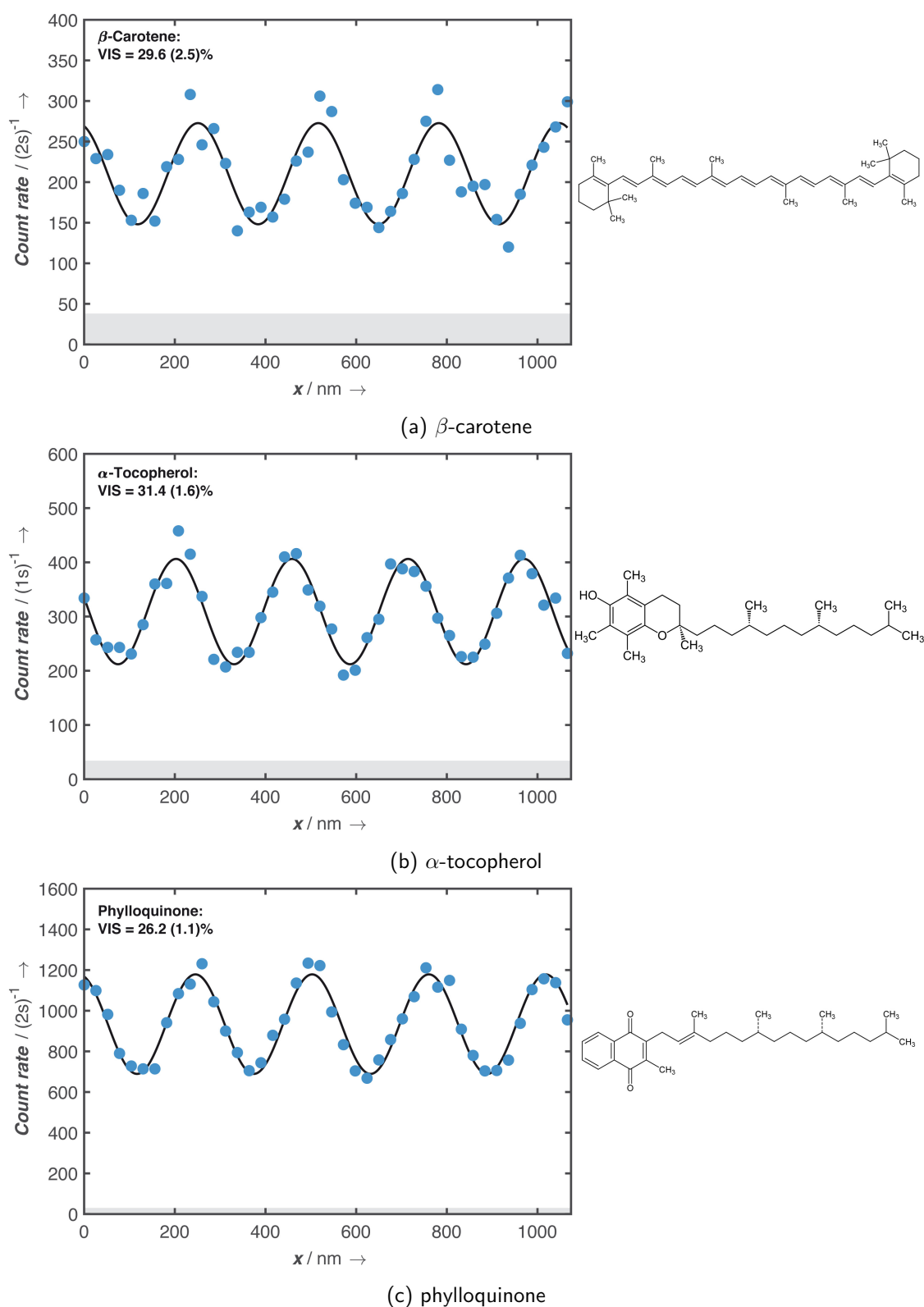


Figure 5.2: Interference pattern of vitamins and their chemical structure. For  $\beta$ -carotene (a) we achieved a visibility of  $29.6 \pm 2.5\%$ , for  $\alpha$ -tocopherol (b) the visibility is  $31.4 \pm 1.6\%$  and for phylloquinone (c) we achieved  $26.2 \pm 1.1\%$ . The grey area in the bottom of each plot indicates the dark counts. The x-axis shows the count rate, which is different for each molecule. The y-axis shows the position of the third grating, scanning over the molecular beam.

With three other vitamins we obtained a reliable interference contrast. The signal was more stable and lasted long enough for metrology measurements. These vitamins were  $\beta$ -carotene ( $C_{40}H_{56}$ ) also known as pro-vitamin A,  $\alpha$ -tocopherol ( $C_{29}H_{50}O_2$ ) known as vitamin E and phyloquinone ( $C_{31}H_{46}O_2$ ) which is commonly known as vitamin K<sub>1</sub>. Figure 5.2 shows the interference pattern and the chemical structure of these vitamins.

For the formation of a molecular beam all three vitamins were heated to temperatures between 400 K and 460 K. The working temperature is critical, since the molecules are fragile and tend to fragment rapidly when heated too much. Figure 5.3 illustrates that behaviour for  $\alpha$ -tocopherol. To ensure a stable and sufficiently intense signal, we tested the temperature dependence of the signal during the course of my bachelor thesis with a separate setup of a thermal source and a QMS as detection method. The setup was basically the same as for the KDTLI, though with a smaller distance between source and detector.

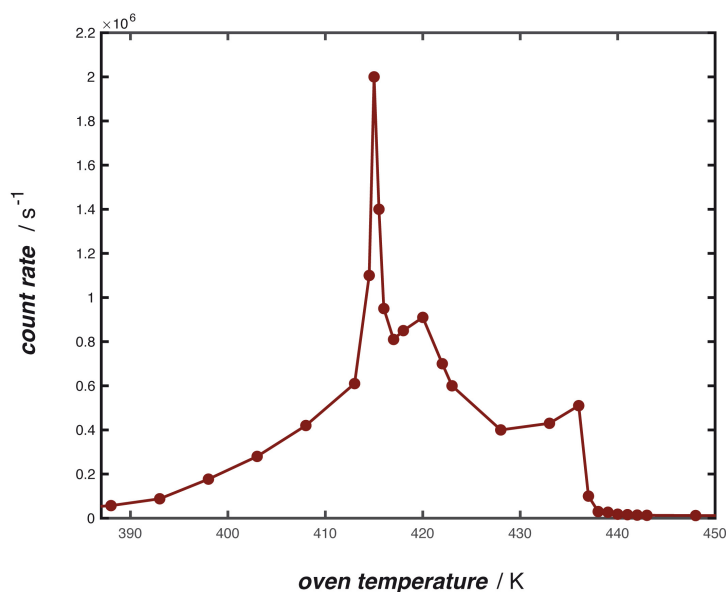


Figure 5.3: Count rate of  $\alpha$ -tocopherol as a function of the oven temperature. The curve clearly illustrates the dependence of the count rate on the source temperature which is similar for all of our biomolecules. After peaking at around 415 K the signal drops rapidly due to thermal fragmentation. The temperature window for a high count rate without fragmentation is rather small. In contrast to the count rate obtained in the KDTLI, it is four orders of magnitude higher, since the curve was recorded in a separate setup with a smaller distance between source and detector. Furthermore, for interference scans we insert delimiters for the velocity selection, which also reduces the signal. Data from [79].

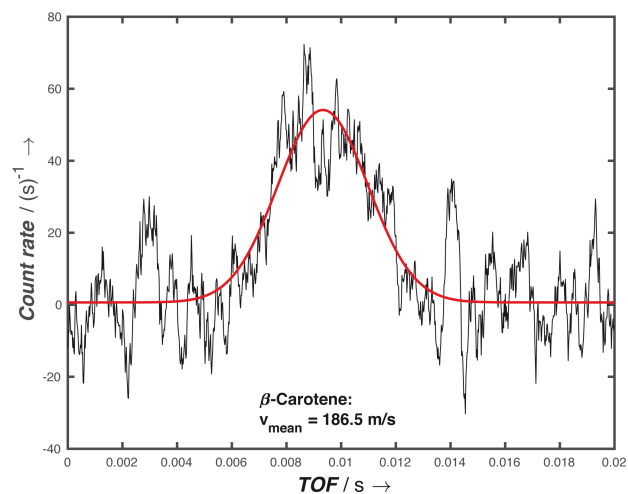
The velocity measurement with the pseudorandom chopper showed a most probable velocity of around 200 m/s with a spread of about 45% (full width at half maximum) for all three vitamins leading to de Broglie wavelengths between 3 pm and 6 pm according to the molecule's mass and velocity. Figure 5.4 shows the time-of-flight distribution for the three vitamins.

We did the calibration of the setup for the metrology measurements with the fullerene  $C_{60}$ , as its properties are well known.  $C_{60}$  has an optical polarizability  $\sigma_{opt}$  of  $87 \times 10^{-30} \text{ m}^3$  [54] and an electric susceptibility  $\chi$  of  $90 \times 10^{-30} \text{ m}^3$  [6]. Interference of a molecule with known optical polarizability allows the determination of the effective vertical waist  $w_y$  of the diffraction grating. This is possible, because the phase shift of the molecule's center-of-mass wave function in the grating depends on both the molecule's optical polarizability as well as on the intensity of the diffraction grating as expressed in equation 2.18, whereas according to equation 2.19 the intensity in turn depends on the vertical waist of the standing light wave. For the calibration of the diffraction grating's vertical waist we recorded a curve of the visibility's dependence on the laser power with  $C_{60}$ .

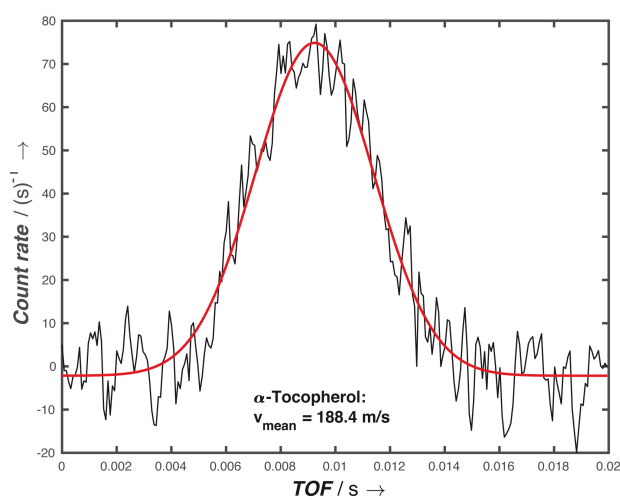
Furthermore, we also determined the electrode's  $K$ -factor for the deflectometry measurements. This factor describes the electrode's geometry as well as its position relative to the molecular beam and the interferometer. We determined the electrode's  $K$ -factor with deflection measurements with  $C_{60}$ , since its electrical susceptibility is well known. It is noteworthy, that the visibility obtained in these experiments was lower than theoretically expected due to imperfect alignment of the machine. Therefore we normalized the visibility with the expected values of  $C_{60}$  as well.

In addition to the experiments, Armin Shayegi simulated the molecular properties of the vitamins with a combined approach using Molecular Dynamics calculation (MD) and Density Functional Theory (DFT) to compare the results of the experiment with the ones of the simulation. MD is a semi-classical simulation method based on Newtonian mechanics to calculate the evolution of a particle's motion in a force field defined by a potential function. The potential can either be a classical one or a quantum mechanical potential. For simulations with the latter the computational costs are much higher and thus, the former is preferable if the results are satisfying.

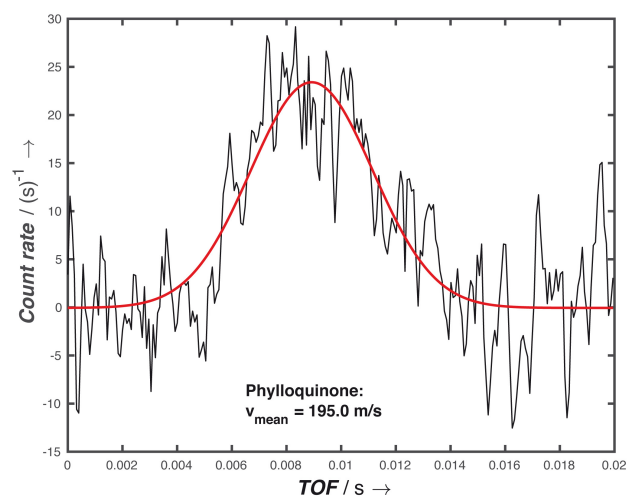
In our case, the vibrational motion of the molecules at the respective oven temperatures of about 450 K was calculated using a classical force field (CHARMM – Chemistry at HARvard Macromolecular Mechanics [12]) over 100 ns in time steps of 1 fs. For comparison, the motion was also simulated with a quantum mechanical approach (Ab Initio MD using the PBE0/3-21G model [2]) including electron behaviour like formation and fragmentation of covalent bonds.



(a)  $\beta$ -carotene



(b)  $\alpha$ -tocopherol



(c) phylloquinone

Figure 5.4: Time-of-flight (TOF) distribution of  $\beta$ -carotene (a),  $\alpha$ -tocopherol (b) and phylloquinone (c) within the molecular beam. From the TOF distribution we can calculate the mean velocity, since we know the length of the molecular path. However, the calculated mean velocity strongly depends on the calibration of the chopper disc, i.e. the exact position of the disc.

A short evolution over 50 ps showed that for our oven temperature the approximation using a classic potential is accurate enough. The molecular structure of the vitamins was extracted from the MD simulation in steps of 2 ns to subsequently compute their static and optical polarizabilities at the light grating's wavelength of 532 nm as well as their electric dipole moments and susceptibilities using two different models of DFT [101]. DFT is based on quantum mechanics and uses functionals of the spatially dependent electron density to model the electronic structure of many-body-systems.

The results of the experimental studies of these vitamins as well as the theory and the simulations were published in [68].

### 5.1.1 Optical polarizability

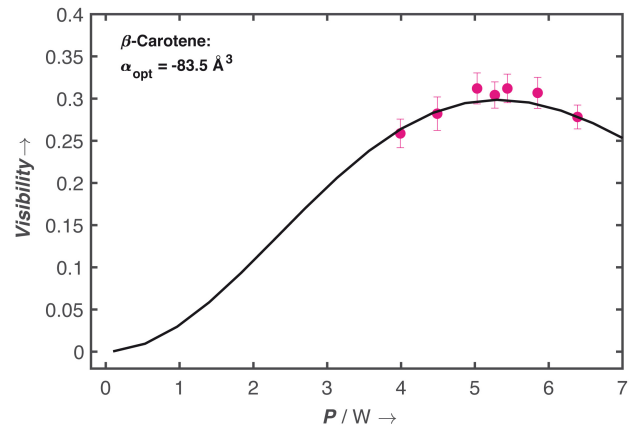
We can extract the vitamin's optical polarizability  $\sigma_{opt}$  from interference scans at different light grating intensities, since the visibility depends on the phase shift of the vitamin's center-of-mass wave function according to equation 2.22 and the phase shift again depends linearly on both the intensity  $I(P)$  of the light grating and the optical polarizability according to equation 2.21. To change the light grating's intensity we rotate the  $\lambda/2$  plate as mentioned in chapter 2.2.2.2.

By fitting the visibility as a function of laser power, one can determine the optical polarizability of a particle. Figure 5.5 shows this function for all three vitamins, while table 5.1 lists the results for the molecules' polarizabilities.

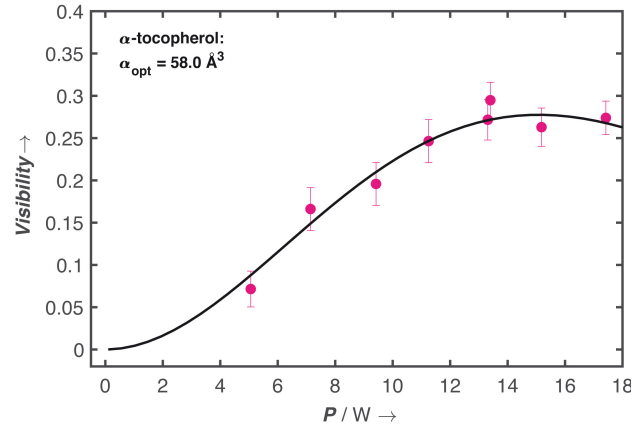
According to equation 2.21 the phase shift in the light grating's antinodes grows linearly with increasing laser power. Concurrently, the number of absorbed photons in the standing light wave also grows with increasing laser power as described in equation 2.25. Since absorption is an additional beam splitting mechanism as mentioned in chapter 2.1.6, it usually leads to a decreasing visibility of the interference pattern, although maxima of the visibility recur at higher laser powers. This happens if the phase shifts due to the absorption of more photons is large enough to shift the molecule's center-of-mass wave function over an entire period [54].

While the horizontal position of the visibility's maxima in the graph of figure 5.5 depends on the laser's vertical waist, the height of the maxima depends on the molecule's absorption cross section  $\sigma_{abs}$ , in principle allowing for the extraction of that quantity from the power-versus-visibility curve as well. [100]

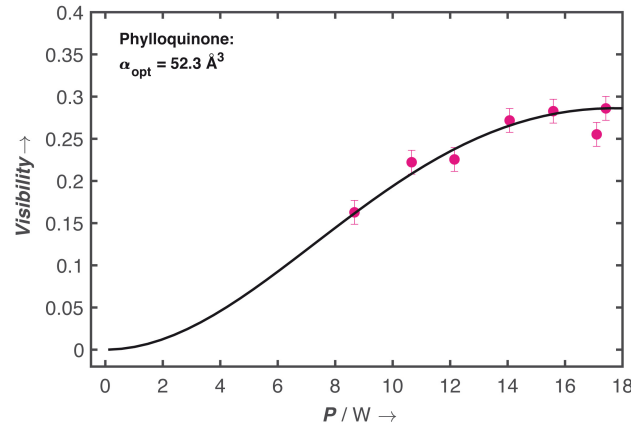




(a)  $\beta$ -carotene



(b)  $\alpha$ -tocopherol



(c) phyloquinone

Figure 5.5: Visibility as a function of the light gratings laser power for  $\beta$ -carotene (a),  $\alpha$ -tocopherol (b) and phyloquinone (c). From the fitting curves to the recorded data points we obtain the optical polarizability  $\alpha_{opt}$  of these molecules. The values for the optical polarizability within the plots result from the fitting curve. However, the model depends on the velocity distribution in the molecular beams, since it determines the interaction time with the light grating laser, as well as on the vertical light grating laser's waist. Both of these factors come with errors and thus, the actual accuracy is lower than calculated from the curves. For  $\alpha$ -tocopherol and phyloquinone the vertical laser waist  $w_y$  was  $920 \mu\text{m}$ , while for  $\beta$ -carotene it was only  $440 \mu\text{m}$ . Thus, for the latter molecule the intensity of the light grating was almost twice as high as for the other ones.

| Vitamin                                        | $\beta$ -carotene | $\alpha$ -tocopherol | phylloquinone |
|------------------------------------------------|-------------------|----------------------|---------------|
| Temperature [K]                                | $460 \pm 5$       | $400 \pm 5$          | $450 \pm 5$   |
| Mass [amu]                                     | 536.9             | 430.7                | 450.7         |
| $\alpha_{opt}$ [ $\text{\AA}^3$ ] (CAM-B3LYP)  | $-152 \pm 11$     | $56 \pm 1$           | $62 \pm 1$    |
| $\alpha_{opt}$ [ $\text{\AA}^3$ ] (PBE0)       | $-107 \pm 4$      | $56 \pm 1$           | $61 \pm 1$    |
| $\alpha_{opt}$ [ $\text{\AA}^3$ ] (Experiment) | $-83 \pm 10$      | $58 \pm 5$           | $52 \pm 7$    |

Table 5.1: Optical polarizabilities of vitamins. The first two rows give the results of the two different calculations, the third row shows the experimental result. The values for  $\alpha_{opt}$  convert to SI by multiplying them with  $4\pi\epsilon_0$ .

The experimental results for the optical polarizability  $\alpha_{opt}$  are in good agreement with the theoretical calculation for this property using MD and DFT. However, the uncertainties of the experimental result are one order of magnitude higher than for the theoretical calculation. We estimated these uncertainties by testing the robustness of our model, i.e. varying all factors contributing to the result such as mean velocity of the molecular beam, the vertical laser waist of the standing light wave and the chopper calibration.

### 5.1.2 Electrical susceptibility and electrical dipole moment

If molecules are exposed to a external static electric field, their degree of polarization is the molecule's electric susceptibility  $\chi$  depending on the molecule's static polarizability  $\alpha_{stat}$  as well as on the thermal average of its squared electric dipole moment  $\langle\mu^2\rangle$ . The electric susceptibility at a certain temperature  $T$  is described by the van Vleck relation [46]

$$\chi = \alpha_{stat} + \frac{\langle\mu^2\rangle}{3k_B T} \quad (5.1)$$

with  $k_B$  being the Boltzmann constant. The polarization density  $\mathbf{P} = N\mathbf{d}$  for  $N$  particles per unit volume, with  $\mathbf{d}$  being the molecule's total dipole moment, depends on the molecule's electric susceptibility  $\chi$  and on the applied external electric field  $\mathbf{E}$ . The polarization density  $\mathbf{P}$  for non-polar molecules, i.e. molecules without a permanent dipole moment reads as

$$\mathbf{P} = \epsilon_0\chi\mathbf{E} \quad (5.2)$$

Due to the external static electric field, a deflecting force  $\mathbf{F}$  acts on the particle. In the case of particles with a permanent electric dipole moment contributing to  $\mathbf{d}$  this force is given by

$$\mathbf{F}_{perm} = -(\mathbf{d}\nabla)\mathbf{E} \quad (5.3)$$

Here, the deflection force depends on the gradient of the static electric field and the particle's relative orientation within the field. The random orientation of the particles' dipole moments in a molecular beam leads to a broadening of the interference fringes and thus a reduction of the interference contrast, if a static external electric field is applied [29]. If a dipole moment is induced for a particle with a non-permanent dipole moment, the force acting on the particle in an external electric field is

$$\mathbf{F}_{ind} = -\frac{1}{2} \cdot \alpha_{stat}(\mathbf{E}\nabla)\mathbf{E} \quad (5.4)$$

and depends on the particle's static polarizability  $\alpha_{stat}$  and on the electric field itself as well as on its gradient. Due to this "double-dependence", the force increases quadratically with increasing field strength.

In the KDTLI, an electrode consisting of two wedge-shaped poles mounted close to the diffraction grating yields the static external electric field. This electrode provides a homogeneous transverse force on a beam of molecules without a permanent dipole moment. The homogeneous force is necessary for quantum-interference assisted metrology, since otherwise phase averaging would destroy the interference contrast [94].

The transverse homogeneous force created by the electrode shifts the interference fringes of a beam of neutral particles with a non-permanent dipole moment by

$$\Delta x = K \cdot \frac{\chi}{m} \cdot \frac{\mathbf{E}\nabla\mathbf{E}}{v^2} \quad (5.5)$$

compared to the interference fringes obtained without the external electric field. Here,  $K$  is the geometrical factor of the electrode and  $m$  the particle's mass. In our experimental setup we achieve a spatial resolution of these shifts in the order of 10 nm. On the one hand, the achieved resolution depends on the step-size of the piezo motor which we move the third grating with. On the other hand, it also depends on the obtained visibility, since for a better interference

contrast, i.e. fringes with steeper slopes, it is easier to determine the position of the maxima with high accuracy. In any case, the spatial resolution of the shifts which we achieve offers an increase up to three orders of magnitude compared to classical deflection experiments which have a spatial resolution in the range of a few  $\mu\text{m}$  [50]. However, since the molecules are hot, they change their properties and increase the signal-to-noise ratio. This reduces the actual resolution of the measurement.

In the experiment we measure the relative fringe shift of the molecular beam by recording two interference scans at the same time – one for a reference voltage and another for the deflection voltage. We achieve this by changing the electrode voltage between those two at each scanning position of the third grating and counting the arriving molecules. Figure 5.6 shows the shifts of the interference fringes in dependence of the applied voltage.

In theory, it would be possible to simply make two scans one after the other with the different voltages, but with the approach of performing both scans simultaneously we avoid drifts during the measurements which would not allow for a reliable comparison of the two scans.

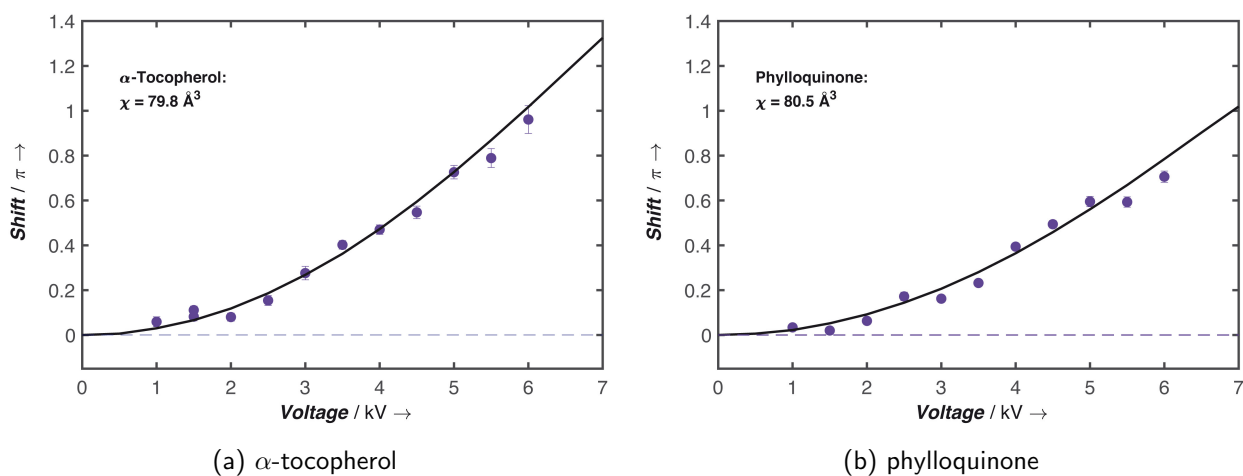


Figure 5.6: Shift of the interference pattern as a function of the applied voltage for  $\alpha$ -tocopherol (a) and phylloquinone (b). From the relative shift of the fringes at different deflection voltages we can extract the molecular susceptibility  $\chi$ . The values given in the plots are just the results of the fit. However, their accuracy is not reliable as such, since they depend on a few factors like the velocity distribution within the molecular beam (and thus, the calibration of the chopper) and the calibration factor  $K$  of the electrode, which are defective. A small change in these factors can have a huge effect on the result already. Therefore, we calculated the error of the result by testing the robustness of our fit.

In principle, we could extract the particle's permanent dipole moment from the voltage-dependence of the interference contrast. However, here the velocity spread within the molecular beam as well as the temperature-dependent alignment of the particle's dipole moment to the external field play a role which is not yet included in the model. Nevertheless, figure 5.7 shows such curves from which the extraction of this property would basically be possible.

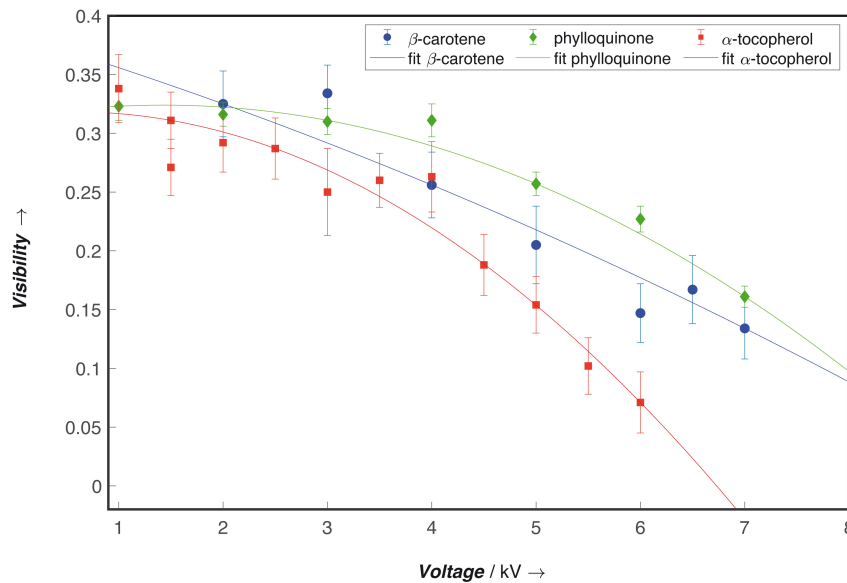


Figure 5.7: Visibility as a function of the applied voltage for  $\beta$ -carotene (blue dots),  $\alpha$ -tocopherol (green diamonds) and phyloquinone (red squares) with the error bars giving the  $1\sigma$  confidence of the achieved interference contrast. In principle, it is possible to extract the molecule's permanent dipole moment from the fitted curves. The modelling for this extraction is not included in our calculation yet however. Thus, in this case the fits serve only as a guide for better orientation within the plot.

Table 5.2 shows the results for the vitamin's thermally induced dipole moments  $\mu$ , the static polarizability  $\alpha_{stat}$  and the total susceptibility  $\chi$ . The values for the first two properties result from the simulations mentioned above, since only the susceptibility can be measured directly in the experiment. The first two lines of each property show the results of the DFT calculations using two different simulation models and thus, two different functionals for the calculation for comparability reasons. For the total susceptibility the experimental results are listed in the third line. The uncertainties of the simulations were determined by the influence of the standard deviations of the contributing factors.

Similar to the optical polarizabilities mentioned in chapter 5.1.1 we estimated the uncertainties for the experimental results of the electrical susceptibility  $\chi$  by testing their robustness against the deviation of the contributing factors like the electrode's calibration factor  $K$  and the velocity distribution of the molecular beam and thus, the interaction time with the applied electric field. The experimental results differ slightly from the calculated ones, but are still in good agreement with each other.

| <b>Vitamin</b>                                 | <b><math>\beta</math>-carotene</b> | <b><math>\alpha</math>-tocopherol</b> | <b>phylloquinone</b> |
|------------------------------------------------|------------------------------------|---------------------------------------|----------------------|
| Temperature [K]                                | $460 \pm 5$                        | $400 \pm 5$                           | $450 \pm 5$          |
| Mass [amu]                                     | 536.9                              | 430.7                                 | 450.7                |
| $\mu$ [D] (CAM-B3LYP)                          | $1.3 \pm 0.1$                      | $1.8 \pm 0.1$                         | $1.1 \pm 0.1$        |
| $\mu$ [D] (PBE0)                               | $1.3 \pm 0.1$                      | $1.8 \pm 0.1$                         | $1.1 \pm 0.1$        |
| $\alpha_{stat}$ [ $\text{\AA}^3$ ] (CAM-B3LYP) | $211 \pm 4$                        | $54 \pm 1$                            | $58 \pm 1$           |
| $\alpha_{stat}$ [ $\text{\AA}^3$ ] (PBE0)      | $229 \pm 3$                        | $54 \pm 1$                            | $59 \pm 1$           |
| $\chi$ [ $\text{\AA}^3$ ] (CAM-B3LYP)          | $229 \pm 4$                        | $78 \pm 3$                            | $65 \pm 1$           |
| $\chi$ [ $\text{\AA}^3$ ] (PBE0)               | $240 \pm 3$                        | $78 \pm 3$                            | $66 \pm 1$           |
| $\chi$ [ $\text{\AA}^3$ ] (Experiment)         | n.a.                               | $80 \pm 8$                            | $80 \pm 10$          |

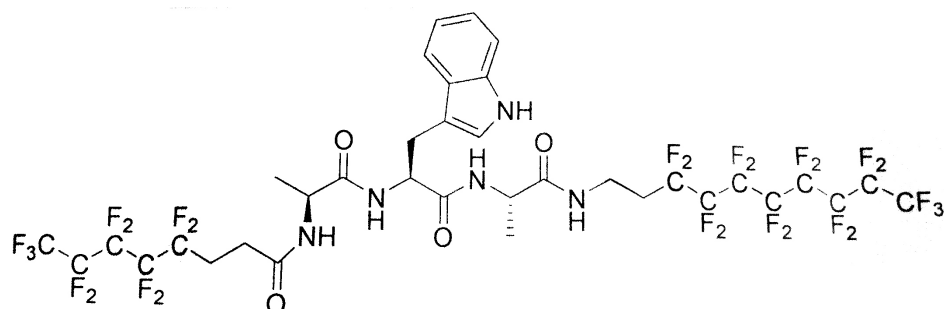
Table 5.2: Thermally induced dipole moment  $\mu$ , static polarizability  $\alpha_{stat}$  and total susceptibility  $\chi$  of vitamins. The first two rows show the results of the two different calculations, the third row shows the experimental result. The values (except temperature) convert to SI by multiplying them with  $4\pi\epsilon_0$ .

## 5.2 Interference with Tripeptides

While vitamins are essential for the proper function of every organism's metabolism, peptides are even more important for life, since proteins – the building blocks of life – are made up of polypeptide chains. Peptides consist of amino acids. If ten or more amino acids form a peptide, it is defined as a polypeptide [70, p. 1359].

The electronic properties of the peptides influence the protein folding mechanisms and thus, are interesting objects of investigation in the gas phase. However, peptides are even more thermally fragile than vitamins which makes it rather difficult to transfer them into the gas phase without fragmentation.

In order to do so with an effusive source, the peptides have to be chemically modified. The chemists of Marcel Mayor's group of the University of Basel therefore synthesized polypeptide chains with fluorinated side groups with lower vapor pressure to perform quantum interference experiments within our setup. At the KDTLI we did so with the tripeptide JSC122/159 with a mass of 1115 amu, which consists of three amino acids and fluorinated chains at both ends. Thus, it is in fact not a polypeptide yet, but still rather massive for a biological molecule to do interference experiments with. Figure 5.8 shows the chemical structure of the tripeptide alanine-tryptophan-alanine.



The working temperature for the tripeptide was between 543 K and 557 K. Within this temperature range the molecules formed a sufficiently stable beam which allowed us to record an interferogram with a visibility of about 19 % at a laser power of 11 W and a integration time of 2 s.

Figure 5.9 shows the recorded interferogram. It is the first demonstration of quantum interference with a peptide. However, the signal only lasted for about half an hour which was too short for further experiments like the ones we did with the vitamins. This could be solved either with more material or probably with another source like the new oven described in chapter 4, since, on the one hand, the heating time is shorter and, on the other hand, the alignment process is shorter as well, which saves material for the measurement itself.

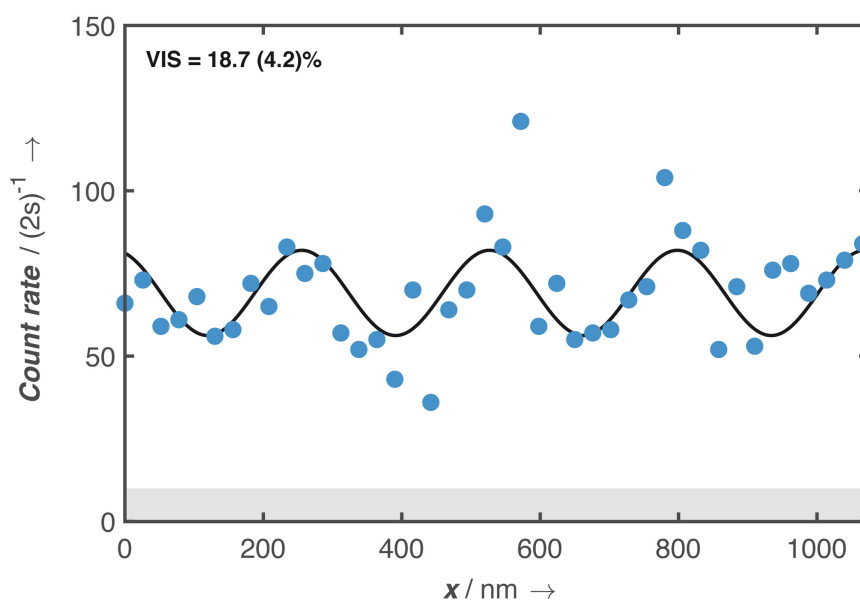


Figure 5.9: Interferogram of the tailor-made tripeptide JSC122/159. This plot shows the first interference contrast for a peptide ever. We achieved a visibility of  $18.7 \pm 4.2\%$ , even though the mean signal for the measurement was only  $40\text{s}^{-1}$  with a dark rate of  $5\text{s}^{-1}$  indicated by the gray area at the bottom of the plot. This also explains why the interference contrast is rather fuzzy compared to the ones of the vitamins.



## 6 Conclusion and outlook

The various experiments performed with the KDTLI showed that a near-field interferometer using a Talbot-Lau setup offers a promising method for the investigation of molecular properties with high resolution and thus, accuracy. However, all these experiments demand a careful alignment in order to achieve accurate results. Additionally, the source and the detection scheme can limit the variety of particles suitable for the interferometer.

On the one hand, the new oven helps to overcome limits in the launch of particles with an effusive source due to its fast response and heating process. It not only allows for the launch of more thermolabile molecules, but also for successful experiments with more expensive and tailor-made particles, since it is less material consuming due to the easier adjustment of the beam relative to the interferometer and less fragmentation during the heating process. Still, it is an effusive source, which in general is not suitable for all kinds of particles.

On the other hand, the setup of the interferometer itself limits the possible mass range of particles due to their de Broglie wavelength, which decreases with increasing mass. Thus, our group built a new and advanced interferometer based on the principles of the KDTLI.

The Long-baseline Universal Matter wave Interferometer (LUMI) is a much longer interferometer than the KDTLI. The distance between the gratings is about 1 m, which allows for interference with more massive particles. Furthermore, the possibility of exchanging the source type as well as the detection scheme makes LUMI suitable for a wider range of particles. Additionally, the diffraction grating is interchangeable between a material one and a standing light wave. The interchangeability of sources, detection methods and grating types makes LUMI more universal compared to the KDTLI.

The successful metrology measurements of vitamins with the KDTLI motivate further experiments with other vitamins – and biomolecules in general – at LUMI. Next to deflectometry by an electric field, the implementation of a magnet allows for magnetic deflectometry measurements at LUMI as well. This reveals the magnet properties of the particles by measuring again the shifts of the

interference fringes in an external magnetic field. Recently, our group successfully demonstrated the quantum-assisted diamagnetic deflection of anthracene and adamantane [36]. Furthermore, due to the interchangeability of the diffraction grating, electric deflection of particles is possible with improved uncertainties [34].

Aside from metrology, the promising results of the first interference experiments with a tripeptide led to further measurements with this molecule at LUMI. Next to mere interference, our group also performed electric deflection measurements with the tripeptide revealing the electric properties of this particle [82]. These results motivate for quantum interference experiments with even larger biomolecules such as polypeptides, proteins or yet strains of RNA.

# Bibliography

- [1] Fatemeh Abyar and Hossein Farrokhpour. "Ionization energies and photoelectron spectra of fat-soluble vitamins in the gas phase: a theoretical study". In: *RSC Advances* 4.68 (2014), pp. 35975–35987. DOI: 10.1039/c4ra05271d.
- [2] Carlo Adamo and Vincenzo Barone. "Toward reliable density functional methods without adjustable parameters: The PBE0 model". In: *The Journal of Chemical Physics* 110.13 (1999), pp. 6158–6170. DOI: 10.1063/1.478522.
- [3] Markus Arndt and Klaus Hornberger. "Testing the limits of quantum mechanical superpositions". In: *Nature Physics* 10.4 (2014), pp. 271–277. DOI: 10.1038/nphys2863.
- [4] Markus Arndt et al. "Wave-particle duality of C60 molecules". In: *Nature* 401.6754 (1999), pp. 680–682. DOI: 10.1038/44348.
- [5] Peter Asenbaum et al. "Phase Shift in an Atom Interferometer due to Spacetime Curvature across its Wave Function". In: *Physical Review Letters* 118.18 (2017). DOI: 10.1103/physrevlett.118.183602.
- [6] Martin Berninger et al. "Polarizability measurements of a molecule via a near-field matter-wave interferometer". In: *Physical Review A* 76 (2007), p. 013607. DOI: 10.1103/PhysRevA.76.013607.
- [7] Johannes Bischoff. "Computer control and data acquisition for the Kapitza-Dirac-Talbot-Lau interferometer". MA thesis. University of Vienna, 2018.
- [8] Kai Bongs et al. "Taking atom interferometric quantum sensors from the laboratory to real-world applications". In: *Nature Reviews Physics* 1.12 (2019), pp. 731–739. DOI: 10.1038/s42254-019-0117-4.
- [9] William Henry Bragg. "The Reflection of X-Rays by Crystals". In: *Proceedings of the Royal Society of London. Series A* 88.605 (1913), pp. 428–438. DOI: 10.1098/rspa.1913.0040.

- [10] Markus Brezger Björn Arndt and Anton Zeilinger. "Concepts for near-field interferometers with large molecules". In: *Journal of Optics B: Quantum and Semiclassical Optics* 5.2 (2003). DOI: 10.1088/1464-4266/5/2/362.
- [11] Louis De Broglie. "Waves and Quanta". In: *Nature* 112.2815 (1923), p. 540. DOI: 10.1038/112540a0.
- [12] Bernard R Brooks et al. "CHARMM: a program for macromolecular energy, minimization, and dynamics calculations". In: *Journal of computational chemistry* 4.2 (1983), pp. 187–217.
- [13] Rüdiger Brühl et al. "Diffraction of Neutral Helium Clusters: Evidence for Magic Numbers". In: *Physical Review Letters* 92.18 (2004). DOI: 10.1103/physrevlett.92.185301.
- [14] O. Carnal and J. Mlynek. "Young's double-slit experiment with atoms: A simple atom interferometer". In: *Physical Review Letters* 66.21 (1991), pp. 2689–2692. DOI: 10.1103/physrevlett.66.2689.
- [15] William B. Case et al. "Realization of optical carpets in the Talbot and Talbot-Lau configurations". In: *Optics Express* 17.23 (2009), pp. 20966–20974. DOI: 10.1364/oe.17.020966.
- [16] The QFlag - Quantum Flagship Coordination and Support Action. *The future is Quantum*. URL: <https://qt.eu/> (visited on 03/18/2021).
- [17] J. P. Cotter et al. "Coherence in the presence of absorption and heating in a molecule interferometer". In: *Nature Communications* 6.1 (2015). DOI: 10.1038/ncomms8336.
- [18] Alexander D. Cronin, Jörg Schmiedmayer, and David E. Pritchard. "Optics and interferometry with atoms and molecules". In: *Reviews of Modern Physics* 81.3 (2009), pp. 1051–1129. DOI: 10.1103/revmodphys.81.1051.
- [19] C. J. Davisson. "The Diffraction of Electrons by a Crystal of Nickel". In: *Bell System Technical Journal* 7.1 (1928), pp. 90–105. DOI: 10.1002/j.1538-7305.1928.tb00342.x.
- [20] M. Debiossac et al. "Tailored photocleavable peptides: fragmentation and neutralization pathways in high vacuum". In: *Physical Chemistry Chemical Physics* 20.16 (2018), pp. 11412–11417. DOI: 10.1039/c8cp01058g.

- [21] Wolfgang Demtröder. *Experimentalphysik 2: Elektrizität und Optik*. Springer Berlin Heidelberg, 2009.
- [22] Nadine Dörre et al. "Photofragmentation Beam Splitters for Matter-Wave Interferometry". In: *Physical Review Letters* 113.23 (2014). DOI: 10.1103/physrevlett.113.233001.
- [23] Nadine Dörre et al. "Refined model for Talbot-Lau matter-wave optics with pulsed photodepletion gratings". In: *Journal of the Optical Society of America B* 32.1 (2014). DOI: 10.1364/josab.32.000114.
- [24] Héloïse Dossmann et al. "Vacuum Ultraviolet Photoionization Study of Gas Phase Vitamins A and B1 Using Aerosol Thermodesorption and Synchrotron Radiation". In: *The Journal of Physical Chemistry A* 118.47 (2014), pp. 11185–11192. DOI: 10.1021/jp507050y.
- [25] Louis Dunoyer. "Sur la réalisation d'un rayonnement matériel d'origine purement thermique. Cinétique expérimentale". In: *Le Radium* 8.4 (1911), pp. 142–146. DOI: 10.1051/radium:0191100804014201.
- [26] Sandra Eibenberger. "Quantum interference experiments with complex organic molecules". PhD thesis. University of Vienna, 2015.
- [27] Sandra Eibenberger, Ugur Sezer, and Markus Arndt. *Matter-wave physics with nanoparticles and biomolecules*. Mar. 2017. URL: <https://arxiv.org/abs/1703.02129>.
- [28] Sandra Eibenberger et al. "Absolute Absorption Cross Sections from Photon Recoil in a Matter-Wave Interferometer". In: *Physical Review Letters* 112.25 (2014). DOI: 10.1103/physrevlett.112.250402.
- [29] Sandra Eibenberger et al. "Electric moments in molecule interferometry". In: *New Journal of Physics* 13.4 (2011), p. 043033. DOI: 10.1088/1367-2630/13/4/043033.
- [30] Sandra Eibenberger et al. "Matter-wave interference of particles selected from a molecular library with masses exceeding 10.000 amu". In: *Physical Chemistry Chemical Physics* 15.35 (2013), p. 14696. DOI: 10.1039/c3cp51500a.
- [31] Albert Einstein and Leopold Infeld. *The evolution of physics: the growth of ideas from the early concepts to relativity and quants*. Cambridge Univ. Press, 1938.
- [32] Immanuel Estermann and Otto Stern. "Beugung von Molekularstrahlen". In: *Zeitschrift für Physik* 61 (1930).

- [33] U. Even et al. "Cooling of large molecules below 1 K and He clusters formation". In: *The Journal of Chemical Physics* 112.18 (2000). DOI: 10.1063/1.481405.
- [34] Yaakov Y. Fein et al. "Improved accuracy fullerene polarizability measurements in a long-baseline matter-wave interferometer". In: *Physical Review Research* 1.3 (2019). DOI: 10.1103/physrevresearch.1.033158.
- [35] Yaakov Y. Fein et al. "Quantum superposition of molecules beyond 25 kDa". In: *Nature Physics* 15.12 (2019), pp. 1242–1245. DOI: 10.1038/s41567-019-0663-9.
- [36] Yaakov Y. Fein et al. "Quantum-assisted diamagnetic deflection of molecules". In: *Physical Chemistry Chemical Physics* 22.25 (2020), pp. 14036–14041. DOI: 10.1039/d0cp02211j.
- [37] Valerie Gabelica. *Nucleic acids in the gas phase*. Springer-Verlag Berlin, 2014. DOI: 10.1007/978-3-642-54842-0.
- [38] Remi Geiger et al. "High-accuracy inertial measurements with cold-atom sensors". In: *AVS Quantum Science* 2.2 (2020). DOI: 10.1116/5.0009093.
- [39] R. Geiger et al. "Detecting inertial effects with airborne matter-wave interferometry". In: *Nature Communications* 2.1 (2011). DOI: 10.1038/ncomms1479.
- [40] Walther Gerlach and Otto Stern. "Der experimentelle nachweis der richtungsquantelung im magnetfeld". In: *Zeitschrift für Physik* 9.1 (1922), pp. 349–352.
- [41] Stefan Gerlich. "Interferometry and Metrology with Macromolecules". PhD thesis. University of Vienna, 2011.
- [42] Stefan Gerlich et al. "A Kapitza-Dirac-Talbot-Lau interferometer for highly polarizable molecules". In: *Nature Physics* 3.10 (2007), pp. 711–715. DOI: 10.1038/nphys701.
- [43] P Geyer et al. "Perspectives for quantum interference with biomolecules and biomolecular clusters". In: *Physica Scripta* 91.6 (2016). DOI: 10.1088/0031-8949/91/6/063007.
- [44] Phillip L. Gould, George A. Ruff, and David E. Pritchard. "Diffraction of atoms by light: The near-resonant Kapitza-Dirac effect". In: *Physical Review Letters* 56.8 (1986), pp. 827–830. DOI: 10.1103/physrevlett.56.827.
- [45] Jeferson Gross et al. "A Plant Locus Essential for Phylloquinone (Vitamin K1) Biosynthesis Originated from a Fusion of Four Eubacterial Genes". In: *Journal of Biological Chemistry* 281.25 (2006), pp. 17189–17196. DOI: 10.1074/jbc.m601754200.

- [46] Van Vleck J. H. *The theory of electric and magnetic susceptibilities*. Oxford University Press, 1966.
- [47] P. Hamilton et al. "Atom-interferometry constraints on dark energy". In: *Science* 349.6250 (2015), pp. 849–851. DOI: 10.1126/science.aaa8883.
- [48] Philipp Haslinger et al. "A universal matter-wave interferometer with optical ionization gratings in the time domain". In: *Nature Physics* 9.3 (2013), pp. 144–148. DOI: 10.1038/nphys2542.
- [49] Eugene Hecht. *Optics*. Addison Wesley, 2002.
- [50] Sven Heiles and Schafer Rolf. *Dielectric Properties of Isolated Clusters Beam Deflection Studies*. Springer Netherlands, 2014.
- [51] V. L. Hirschy and J. P. Aldridge. "A Cross Correlation Chopper for Molecular Beam Modulation". In: *Review of Scientific Instruments* 42.3 (1971), pp. 381–383. DOI: 10.1063/1.1685100.
- [52] Klaus Hornberger et al. "Collisional Decoherence Observed in Matter Wave Interferometry". In: *Physical Review Letters* 90.16 (2003). DOI: 10.1103/physrevlett.90.160401.
- [53] Klaus Hornberger et al. "Colloquium: Quantum interference of clusters and molecules". In: *Reviews of Modern Physics* 84.1 (Aug. 2012), pp. 157–173. DOI: 10.1103/revmodphys.84.157.
- [54] Klaus Hornberger et al. "Theory and experimental verification of Kapitza-Dirac-Talbot-Lau interferometry". In: *New Journal of Physics* 11.4 (2009), p. 043032. DOI: 10.1088/1367-2630/11/4/043032.
- [55] Momentive Performance Materials Inc. *Heaters and Heater Assemblies*. URL: <https://www.momentive.com/en-us/categories/ceramics/heaters-and-heater-assemblies> (visited on 05/18/2020).
- [56] Corning Incorporated. *Macor - Machinable Glass Ceramic For Industrial Applications*. 2012. URL: <https://www.corning.com/media/worldwide/csm/documents/71759a443535431395eb34ebead091cb.pdf> (visited on 05/18/2020).
- [57] Martin F. Jarrold. "Peptides And Proteins In The Vapor Phase". In: *Annual Review of Physical Chemistry* 51.1 (2000), pp. 179–207. DOI: 10.1146/annurev.physchem.51.1.179.

- [58] Claus Jönsson. "Elektroneninterferenzen an mehreren künstlich hergestellten Feinspalten". In: *Zeitschrift für Physik* 161.4 (1961), pp. 454–474. DOI: 10.1007/bf01342460.
- [59] Thomas Juffmann et al. "Real-time single-molecule imaging of quantum interference". In: *Nature Nanotechnology* 7.5 (2012), pp. 297–300. DOI: 10.1038/nnano.2012.34.
- [60] Peter L. Kapitza and Paul A. M. Dirac. "The reflection of electrons from standing light waves". In: *Mathematical Proceedings of the Cambridge Philosophical Society* 29.2 (1933), pp. 297–300. DOI: 10.1017/s0305004100011105.
- [61] M. A. Kasevich and Guglielmo M. Tino. *Atom interferometry*. Vol. 188. IOS Press, 2014.
- [62] D. W. Keith et al. "Diffraction of Atoms by a Transmission Grating". In: *Physical Review Letters* 61.14 (1988), pp. 1580–1583. DOI: 10.1103/physrevlett.61.1580.
- [63] Filip Kialka et al. "Concepts for long-baseline high-mass matter-wave interferometry". In: *Physica Scripta* 94.3 (2019), p. 034001. DOI: 10.1088/1402-4896/aaf243.
- [64] Christian Knobloch et al. "On the role of the electric dipole moment in the diffraction of biomolecules at nanomechanical gratings". In: *Fortschritte der Physik* 65.6-8 (2016). DOI: 10.1002/prop.201600025.
- [65] T. Kovachy et al. "Quantum superposition at the half-metre scale". In: *Nature* 528.7583 (2015), pp. 530–533. DOI: 10.1038/nature16155.
- [66] Ernst Lau. "Beugungserscheinungen an Doppelrastern". In: *Annalen der Physik* 437.7-8 (1948), pp. 417–423. DOI: 10.1002/andp.19484370709.
- [67] Lukas Mairhofer. "Quantum-interference assisted Metrology with complex Biomolecules". PhD thesis. University of Vienna, 2017.
- [68] Lukas Mairhofer et al. "Quantum-Assisted Metrology of Neutral Vitamins in the Gas Phase". In: *Angewandte Chemie International Edition* 56.36 (2017), pp. 10947–10951. DOI: 10.1002/anie.201704916.
- [69] Peter Martin et al. "Bragg scattering of atoms from a standing light wave". In: *Physical Review Letters* 60.6 (1988), pp. 515–518. DOI: 10.1103/physrevlett.60.515.
- [70] G. Moss, P. Smith, and D. Tavernier. "Glossary of class names of organic compounds and reactivity intermediates based on structure (IUPAC Recommendations 1995)". In: *Pure and Applied Chemistry - PURE APPL CHEM* 67 (Aug. 1995), pp. 1307–1375. DOI: 10.1351/pac199567081307.



- [71] Olaf Nairz et al. "Diffraction of Complex Molecules by Structures Made of Light". In: *Physical Review Letters* 87.16 (2001). DOI: 10.1103/physrevlett.87.160401.
- [72] Stefan Nimmrichter and Klaus Hornberger. "Theory of near-field matter-wave interference beyond the eikonal approximation". In: *Phys. Rev. A* 78 (2 2008), p. 023612. DOI: 10.1103/PhysRevA.78.023612.
- [73] Richard H. Parker et al. "Measurement of the fine-structure constant as a test of the Standard Model". In: *Science* 360.6385 (Apr. 2018), pp. 191–195. DOI: 10.1126/science.aap7706.
- [74] Hans Pauly. *Atom, Molecule, and Cluster Beams: Basic Theory, Production and Detection of Thermal Energy Beams*. Springer, 2000.
- [75] Isabel Peña et al. "Disentangling the Puzzle of Hydrogen Bonding in Vitamin C". In: *The Journal of Physical Chemistry Letters* 4.1 (2012), pp. 65–69. DOI: 10.1021/jz301947g.
- [76] Arkadij Popovic. "Mass Spectrometric Investigation of Fullerenes. II. Determination of the Electron Impact Cross-section of C60 and C70". In: *Rapid Communications in Mass Spectrometry* 10.12 (1996), pp. 1433–1438.
- [77] H. Rauch, W. Treimer, and U. Bonse. "Test of a single crystal neutron interferometer". In: *Physics Letters A* 47.5 (1974), pp. 369–371. DOI: 10.1016/0375-9601(74)90132-7.
- [78] Jonas Rodewald et al. "Isotope-selective high-order interferometry with large organic molecules in free fall". In: *New Journal of Physics* 20.3 (2018). DOI: 10.1088/1367-2630/aaade2.
- [79] Marion Romirer. "Untersuchung von Sublimation und Fragmentationsverhalten biologisch relevanter Moleküle als Vorbereitung für die Materiewellen-Interferometrie". Bachelor Thesis. University of Vienna, 2015.
- [80] G. Rosi et al. "Quantum test of the equivalence principle for atoms in coherent superposition of internal energy states". In: *Nature Communications* 8.1 (2017). DOI: 10.1038/ncomms15529.
- [81] D. Savoie et al. "Interleaved Atom Interferometry for High Sensitivity Inertial Measurements". In: *2019 Joint Conference of the IEEE International Frequency Control Symposium and European Frequency and Time Forum (EFTF/IFC)* (2019). DOI: 10.1109/fcs.2019.8856073.

- [82] Jonas Schätti et al. "Matter-wave interference and deflection of tripeptides decorated with fluorinated alkyl chains". In: *Journal of Mass Spectrometry* 55.6 (2020). DOI: 10.1002/jms.4514.
- [83] Jonas Schätti et al. "Neutralization of insulin by photocleavage under high vacuum". In: *Chemical Communications* 55.83 (2019). DOI: 10.1039/c9cc05712a.
- [84] Jean-Pierre Schermann. *Spectroscopy and modelling of biomolecular building blocks*. Elsevier, 2008.
- [85] Wolfgang P. Schleich et al. "Quantum technology: from research to application". In: *Applied Physics B* 122.5 (2016), pp. 1–31. DOI: 10.1007/s00340-016-6353-8.
- [86] D. Schlippert et al. "Quantum Test of the Universality of Free Fall". In: *Physical Review Letters* 112.20 (2014). DOI: 10.1103/physrevlett.112.203002.
- [87] W. Schöllkopf and J. P. Toennies. "Nondestructive Mass Selection of Small van der Waals Clusters". In: *Science* 266.5189 (1994), pp. 1345–1348. DOI: 10.1126/science.266.5189.1345.
- [88] Ugur Sezer et al. "Laser-Induced Acoustic Desorption of Natural and Functionalized Biochromophores". In: *Analytical Chemistry* 87.11 (2015), pp. 5614–5619. DOI: 10.1021/acs.analchem.5b00601.
- [89] Ugur Sezer et al. "Selective photodissociation of tailored molecular tags as a tool for quantum optics". In: *Beilstein Journal of Nanotechnology* 8 (2017), pp. 325–333. DOI: 10.3762/bjnano.8.35.
- [90] A. Shayeghi et al. "Matter-wave interference of a native polypeptide". In: *Nature Communications* 11.1 (2020). DOI: 10.1038/s41467-020-15280-2.
- [91] Fujio Shimizu, Kazuko Shimizu, and Hiroshi Takuma. "Double-slit interference with ultracold metastable neon atoms". In: *Physical Review A* 46.1 (1992). DOI: 10.1103/physreva.46.r17.
- [92] Extrel Core Mass Spectrometers. *Axial molecular beam ionizer manual*. 2004.
- [93] Extrel Core Mass Spectrometers. *Product Note GP-110F*. 2009.
- [94] Andre Stefanov, Martin Berninger, and Markus Arndt. "A novel design for electric field deflectometry on extended molecular beams". In: *Measurement Science and Technology* 19.5 (2008), p. 055801. DOI: 10.1088/0957-0233/19/5/055801.

- [95] Otto Stern. "Eine direkte Messung der thermischen Molekulargeschwindigkeit". In: *Zeitschrift für Physik* 2.1 (1920), pp. 49–56.
- [96] William Henry Fox Talbot. "LXXVI. Facts relating to optical science. No. IV". In: *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* 9.56 (1836), pp. 401–407. DOI: 10.1080/14786443608649032.
- [97] George Paget Thomson. "Experiments on the Diffraction of Cathode Rays". In: *Proceedings of the Royal Society of London. Series A* 117.7 (1928), pp. 600–609. DOI: 10.1098/rspa.1928.0022.
- [98] N.K. Verma. *Physics for Engineers*. PHI Learning Pvt. Ltd., 2017.
- [99] Dietrich A. Volmer, Luana R.b.c. Mendes, and Caroline S. Stokes. "Analysis of vitamin D metabolic markers by mass spectrometry: Current techniques, limitations of the 'gold standard' method, and anticipated future directions". In: *Mass Spectrometry Reviews* 34.1 (2013), pp. 2–23. DOI: 10.1002/mas.21408.
- [100] Kai Walter. "Coherence and Decoherence in High-mass Matter-wave Interferometry". PhD thesis. University of Duisburg-Essen, 2016.
- [101] Takeshi Yanai, David P Tew, and Nicholas C Handy. "A new hybrid exchange-correlation functional using the Coulomb-attenuating method (CAM-B3LYP)". In: *Chemical Physics Letters* 393.1-3 (2004), pp. 51–57. DOI: 10.1016/j.cplett.2004.06.011.
- [102] Anton Zeilinger et al. "Single- and double-slit diffraction of neutrons". In: *Reviews of Modern Physics* 60.4 (1988), pp. 1067–1073. DOI: 10.1103/revmodphys.60.1067.