

Deliverable D4-1:

Diffraction at thin gratings

Objectives and Description of Tasks

UNIVIE leads work-package WP4. They test quantum diffraction and interference in different experimental settings at **UNIVIE**. This requires a close collaboration with the work packages on nanomaterial synthesis (WP3) and the development and quantum description of novel diffraction elements (WP2).

Description of work done and achievements

Work on thin and ultrathin diffraction gratings included

- Far-field diffraction at 10 nm thick SiN gratings, also under varying angles (tilted gratings)
- Far-field diffraction at thin carbonaceous gratings
- Far-field at thinned SiN gratings (5 nm)
- Far-field diffraction at a naturally grown nanostructure

The goal of this work is to test beam splitters that are universally useful for a large class of particles, which can be made reliably and/or at moderate costs and which will prepare the road for what may be the ultimate material diffraction grating, i.e. a single-layer or bilayer sheets of graphene.

Similar goals pertain to deliverable D4-5 on photodepletion gratings. During the first year, the far-field equipment was assigned to D4-1, while the OTIMA interferometer served the deliverable D4-5.

In most implementations of atom interferometry the beam splitter is made from laser light close to an atomic resonance. This allows refined control over the internal and momentum states. But it also restricts each laser system to one particular atomic or molecular species. Nanomechanical structures are universal in that they act as amplitude filters for the delocalized quantum wave function, to first order largely independent of the internal molecular state.

They have been successfully used in many early experiments on atom [1-3] and molecule interferometry [4-9]. Compared to laser gratings, nanomechanical masks are on the low cost side and even more so if we can achieve diffraction with organically grown masks, such as the nanoporous skeleton of marine algae [10]. The successful demonstration of its use in quantum experiments may enable new technologies for teaching laboratories, too. But they also pose important challenges related to the van der Waals (vdW) interaction between the particles and the grating walls.

The vdW interaction plays a subtle but fundamental role in matter wave interferometry as it entails an effective reduction of the opening fraction of the diffraction element. This effect has often been reported as one of the possible limiting factors for quantum assisted metrology and applications in nanotechnology. A deep understanding and control of vdW potential is thus highly desirable in order to control undesired absorption or dispersion effects.

Name	Material	t (nm)	w (nm)	# of slits	α
G1	SiN	10	46	50	50
G2	SiN	46 +/- 5	46	50	17
G3	SiN	10	79	30	33
G4	SiN	87 +/- 9	57	$\sim 10^4$	10
G5	C	20	58	50	19

Table 1: Specification of the gratings used for the diffraction recordings of Figure 3. We compare 4 gratings in silicon nitride with one carbonaceous grating. The grating thickness t varies between 10 - 90 nm, while the opening is varied between 45 and 80 nm. The number of slits can be used to calculate the total width of the open window, since all gratings have the same period of $d = 100$ nm. The wedge angle α is explained further below, in Fig. 4.

This is the reason, why we have gone through substantial efforts to elucidate the role of molecule-grating interactions, quantitatively, with man-made tailored nanostructures. Different gratings were written at TAU using focused ion beam (FIB) milling of a thin SiN_x membrane (Table 1). All gratings have a nominal periodicity of $d=100$ nm. They are produced with different opening widths w between 45 and 80 nm and a thickness t ranging between 10 and 90 nm.

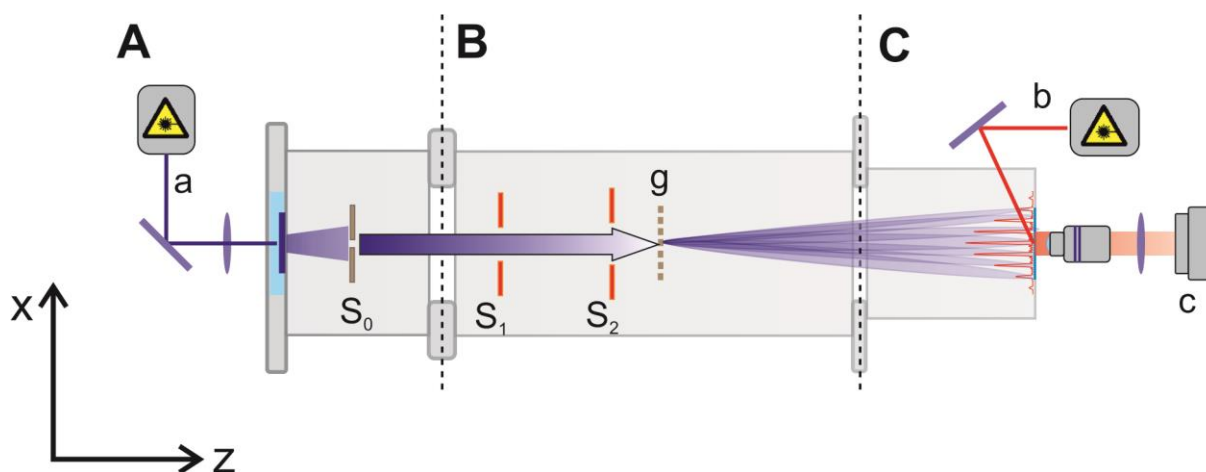


Figure 1: Quantum diffraction of molecules at a nanograting. Preparation chamber A: individual molecules are promoted into the gas phase by laser evaporation. Diffraction chamber B: Quantum diffraction takes place at the grating g . Detector chamber C: Wide-field fluorescence microscopy resolves the molecular diffraction pattern that is collected in high vacuum on a quartz plate.

In our diffraction experiments, the gratings are placed into a molecular beam that is collimated to a few microradians. Launched from a microlaser source the beam has a transverse coherence of several hundred nanometers – wide enough for each molecule to be delocalized across several grating slits. The far-field diffraction patterns are deposited onto a quartz surface and imaged in fluorescence microscopy still under high-vacuum conditions (Fig. 1).

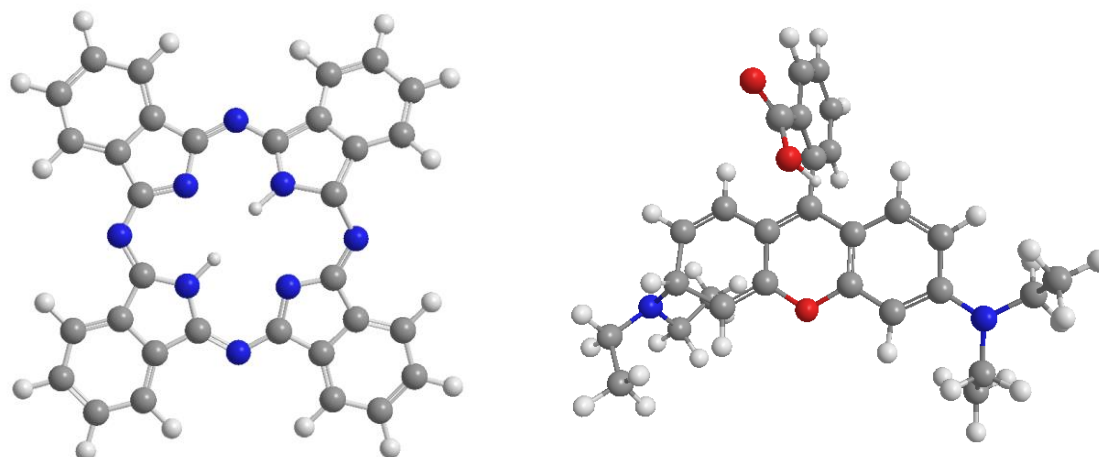


Figure 2: Left: The Phthalocyanine (PcH_2) is a highly anisotropic but non-polar organic molecule which shows intense fluorescence. Right: Rhodamine B (RhB) is an equally efficient fluorophore, which is not only anisotropic but also highly polar. Both molecules are sufficiently stable to be volatilized in a micro laser focus source.

The experiments started with the non-polar phthalocyanine PcH_2 (Fig. 2, left) which yields beautiful high-contrast interference fringes (Fig. 3). The detailed theoretical modeling of the amplitude distribution, however, turned out to be surprisingly challenging. We expected the influence of the van der Waals interaction to be substantially reduced when the grating thickness was reduced by a factor of 20 – from 100 nm eventually down to 5 nm – yet the comparison of the experimental data with a detailed model by Scheel and Fiedler at Rostock University indicates that this assumption is oversimplified for ultrathin gratings. This observation has triggered a detailed refinement of the theoretical description:

For gratings that are only 3-10 times thicker than the diameter of the diffracted molecule it is no longer correct to approximate the transverse van der Waals force, alone. Even using the proximity force approximation (PFA) one has to include the approach and departure towards and from the grating. The simple PFA approach also breaks down as soon as the delocalization of the electrons inside the grating wall needs to be taken into account. This is expected to hold in particular for future studies with graphene membranes.

Our latest models also include the frequency dependent molecular polarizability as well as its anisotropy. This contributes a variability of 100% for a rather oblate rotor like PcH_2 . Interestingly the transit time of each molecule through the grating slit is comparable to typical molecular rotation times. This is a reason to believe that we can no longer assume a full rotational averaging of anisotropic forces. Extra care is going into the modelling of this effect, too.

Grating charges – possibly deposited during the FIB writing process – may also play a role. In order to estimate their role experimentally, we exposed the gratings to electrons emitted by a nearby hot tungsten wire. As this did not incur any substantial changes in the diffraction pattern there is good reason to believe that at least electrons will be removed on a short time scale from the grating surface. Mechanical form factors of the grating, such as wedge shaped edges due to FIB writing and several other contributions have been studied experimentally, using TEM imaging.

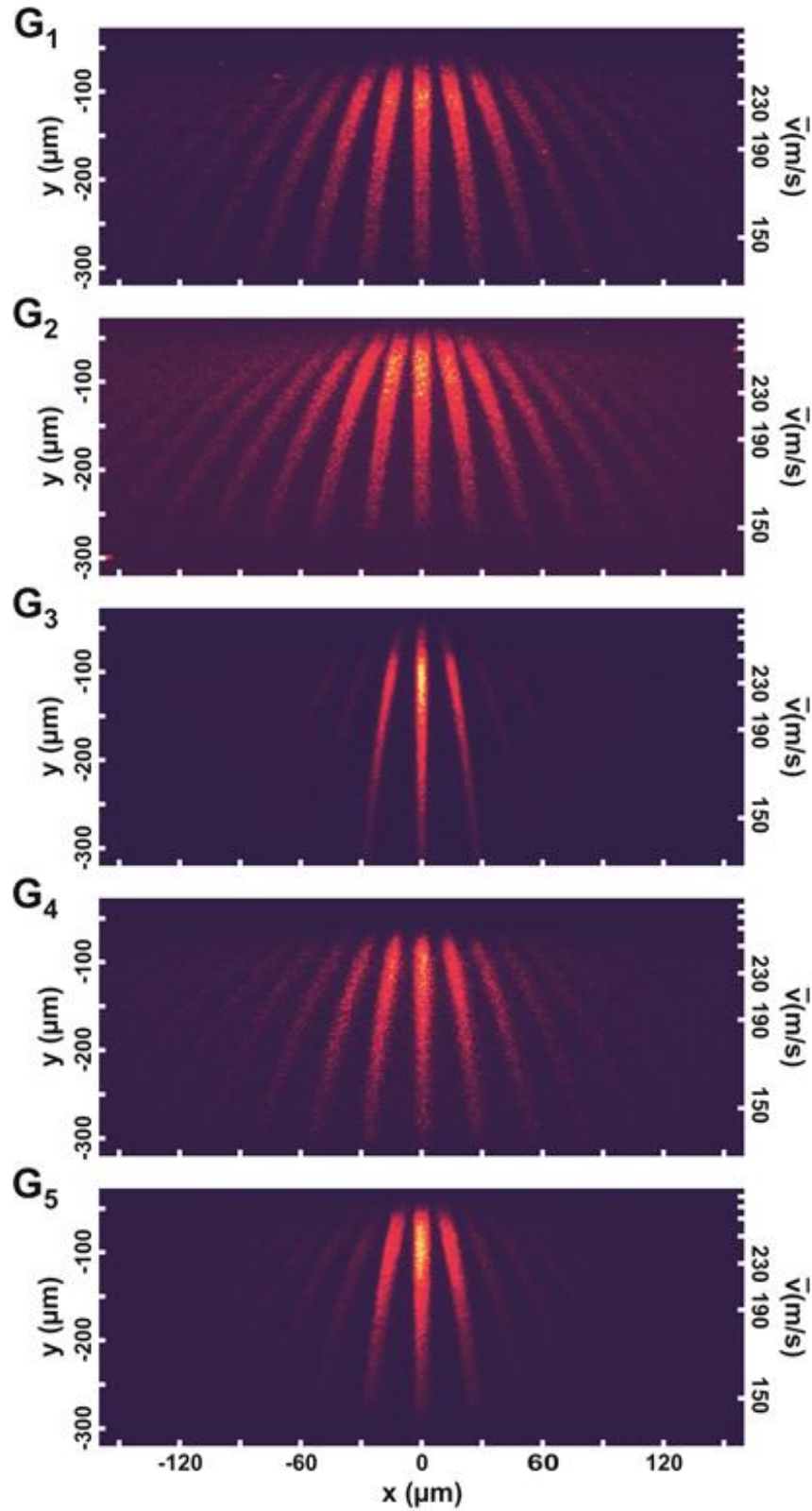


Figure 3: Role of vdW interactions in matter wave interferometry. Quantum diffraction patterns were collected with Pch2 scattered at grating G1-G5 (see Tab. 1) in order to elucidate the role of the grating geometry and van der Waals forces. The widest grating opening leads to the smallest set of interference fringes, as expected but the detailed amplitude distribution is still under review.

Tilted gratings

We have also recorded diffraction images with tilted gratings. As expected, the projected grating period is reduced and the diffraction fringes fan out to larger angles. At the same time the effective interaction distance to the grating walls is reduced while the length is somewhat increased. A systematic comparison of experiment and theory for different diffraction angles resembles a tomographic phase reconstruction and is still underway. Larger angles are in particular interesting for ultrathin gratings in an ultrathin membrane and a dedicated holder, which allows to rotate the grating up to 85 degrees. This could increase the splitting by almost a factor of ten – if the van der Waals forces don't emerge as show stoppers. This is part of ongoing research.

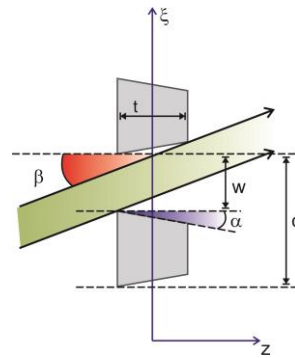


Figure 4: Schematic Illustration of the geometry of a grating with periodicity d and opening width w . Grating bars are characterized by their thickness t and wedge angle α . A rotation of the grating by an angle β corresponds to an effective reduced periodicity $d' = d \cos \beta$.

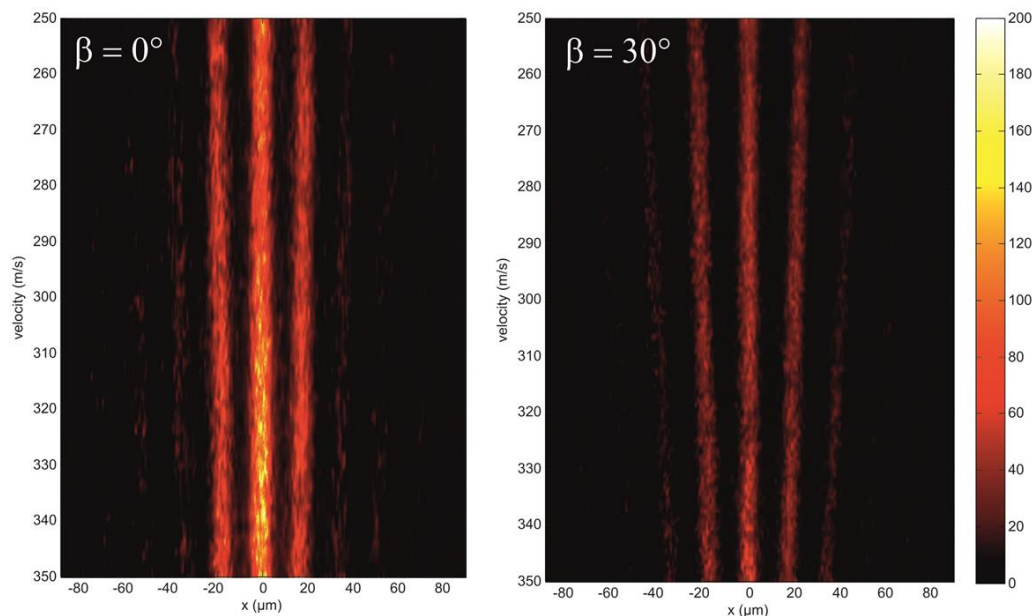


Figure 5: A rotation of the diffraction grating by an angle β results in an effective reduction of its periodicity and in a larger spread of the interference fringes. At the same time the effective exposure of a larger number of slit to the same range of transverse coherence sharpens the fringes because of multi-slit interference. The transmission is effectively reduced as the width of the single slits is also reduced and more molecules pass close by the grating walls.

Diffraction at gratings that were thinned to only 5 nm thickness and under larger angle

In order to minimize the electrostatic dephasing related to vdW interactions between polarizable molecules and the grating bar, a SiN grating with thickness $t=5$ nm and nominal periodicity $d=125$ nm was produced by TAU and tested at the UNIVIE interferometry lab. In order to compensate for the larger periodicity, the grating was rotated by an angle $\beta=60^\circ$ resulting in an effective periodicity $d'=d \cos \beta= 62.5$ nm. The interference fringes illustrated in figure 6 represents the diffraction pattern achieved with the thinnest grating and with the largest rotation angle so far.

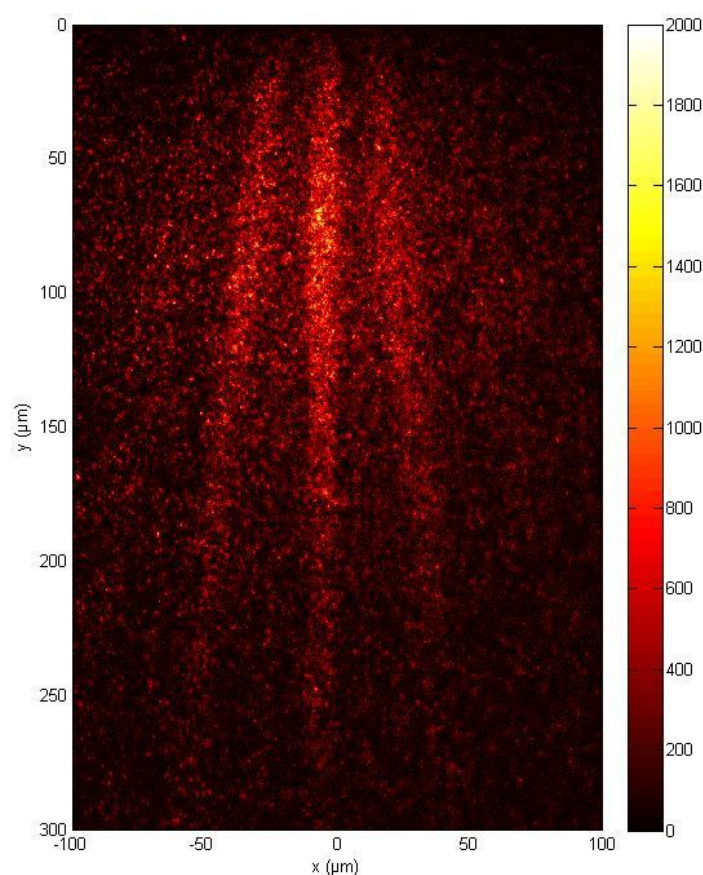


Figure 7: *PcH₂ interference pattern with a thin SiN grating ($t=5$ nm, $d=125$ nm). A rotation of the grating by an angle $\beta=60^\circ$ corresponds to an effective periodicity $d'=62.5$ nm. As expected, the fringes fan out further and become better isolated one from the other. This is a promising perspective also for high mass molecules.*

Quantum diffraction of *non-polar* versus *polar* molecules

High-contrast quantum fringes could be routinely recorded with non-polar Phthalocyanine PcH_2 , whereas the highly polar Rhodamine 6G (Rh6G) and Rhodamine B (RhB) exhibited a strong blurring of the interferograms. The reason for that is still a matter of ongoing research.

One obvious suspicion is related to the observation that a permanent dipole moment must also inevitably lead to stronger interactions with the material grating walls. It surprises, however to see that even for 10 nm wall thickness the effect is still enormous. A direct comparison with diffraction at gratings made of light shall clarify the role of the material gratings in the near future.

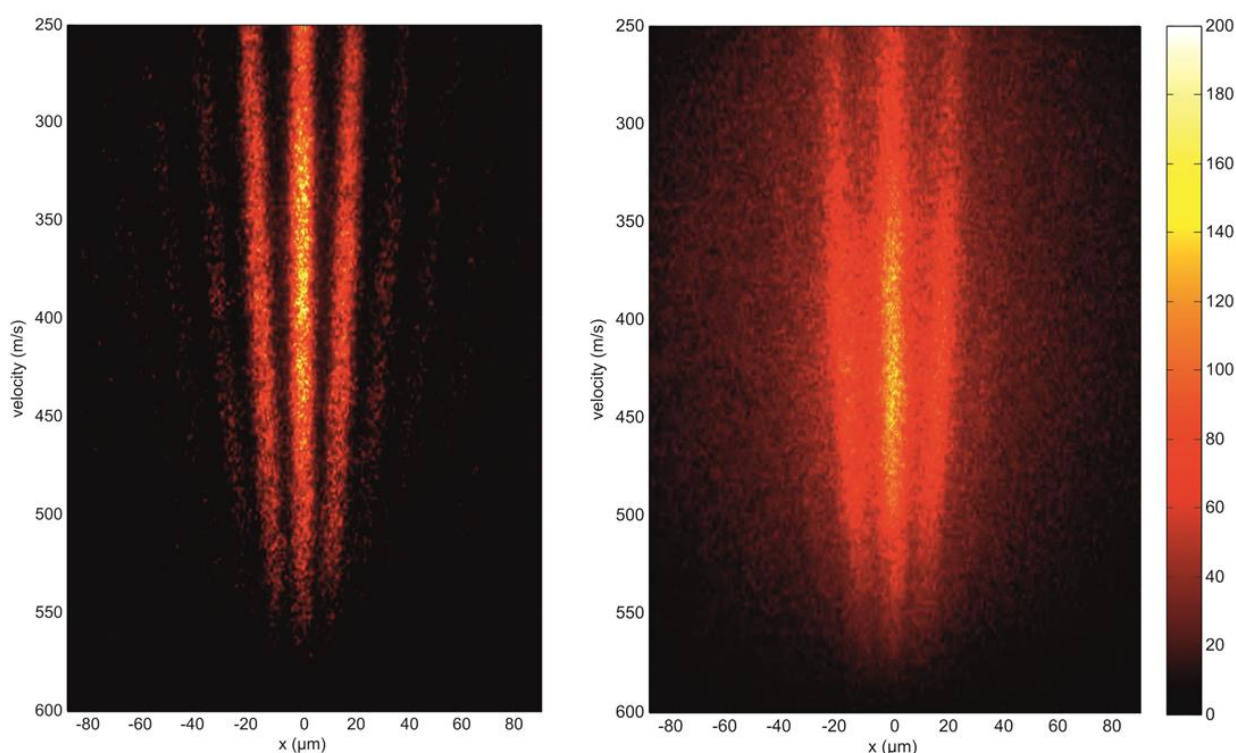


Figure 8: Comparison between PcH_2 (514 u) and Rh6G (479 u). The interference fringes associated with the diffraction of Rh6G (right) appeared more blurred when compared to the PcH_2 pattern (left).

Diffraction of tailor-made perfluoroalkyl functionalized phthalocyanines

With regard to possible extensions of quantum interferometry to higher masses we have also explored the controlled synthesis of perfluoroalkyl functionalized di-porphyrins as well as of the functionalized phthalocyanines PcF_{40} at UNIBAS (see D2.1). The synthesis of these particles was successful (see Fig. 6) but in order for them to be useful in combination with a fluorescence detector they should fly without major decomposition. Electron impact quadrupole mass spectrometry EI-QMS indicated that although the originally material was pure the compounds may not be thermally stable. Mass spectrometry after evaporation shows a substantial contribution of lower mass components as well. It can, however, not be excluded that the decomposition is also triggered by EI-QMS.

Even though this degradation will reduce the overall useful signal, it should not prevent quantum interference from appearing: If the low mass particles emerge at their thermal velocity they should be diffracted to the outer regions of the interferogram, since they have a smaller mass and therefore a longer de Broglie wavelength. If they are split off just after thermal release, they should be even slower and be diffracted even further out. The central two fringes should be rather unaffected by this decomposition.

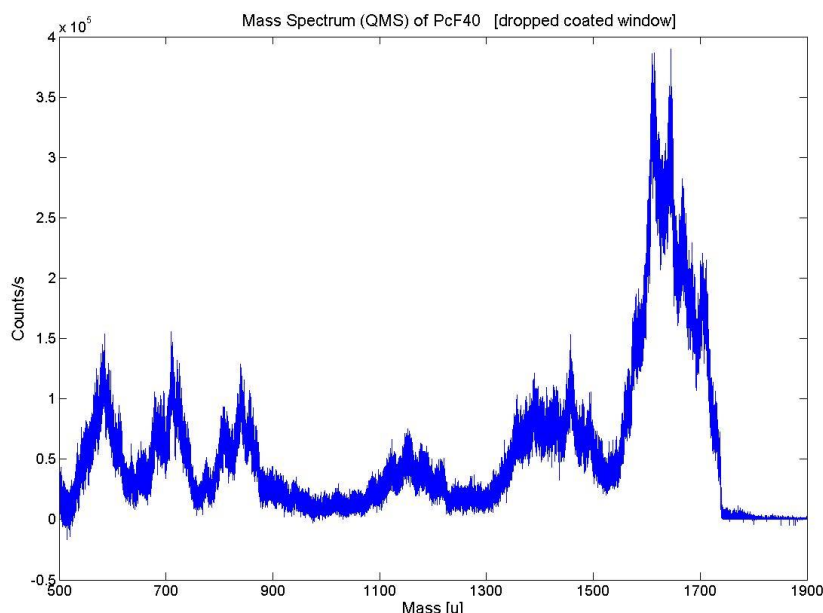


Figure 9: The quadrupole mass spectrum of PcF40 was recorded while the molecules were evaporated in a continuous thermal source. While a principal mass between 1600-1700 amu is clearly dominant, we also see substantial fragmentation.

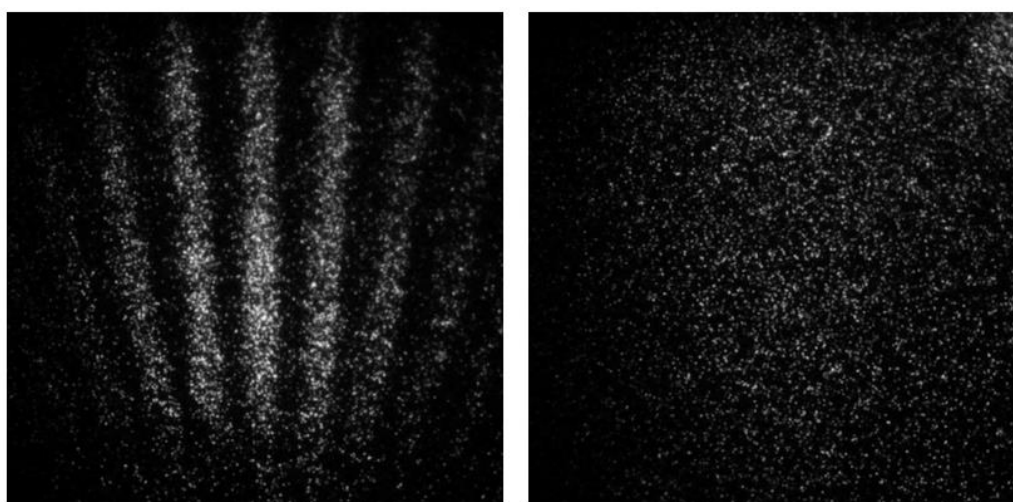


Figure 10: Diffraction of Pch2 (left) and PcF40 (right) under equal conditions. Although one can argue that the lighter masses emerging during fragmentation (see Fig. 9) should not overlay with the central two fringes of the PcF40 the actual diffraction patterns of PcF40 is completely blurred under conditions where Pch2 develops beautiful and high-contrast quantum fringes.

We compared the diffraction of PcH2 and pcF40 at the ultrathin carbon grating G5, with a thickness of $t=20\text{nm}$ and a grating period of $d=100\text{nm}$ (see Tab. 1). No interference was observed for the larger, fluorinated molecule.

To elucidate the surprising absence of fringes we also repeated the experiment with PcF24. Again, the functionalized molecule showed no Interference although the total signal arriving at the screen was comparable to that of PcF40.

Our experiments show that quantum diffraction of PcH2, RhB, Rh6G, TiPcH2 and TPP all worked well under similar settings. The diffraction patterns had low contrast for RhB and Rh6G and they were completely blurred to the level of non-existence for the perfluoralkyl functionalized PcF40

The interpretation of this observation is still open. Among the hypotheses to be checked in follow-up studies we see the following explanations:

- Either the functionalization enhances the surface mobility so much, that even though the molecules arrive as expected they diffuse across several micrometers before the images are recorded. Since the functionalization is made to enhance the volatility of the molecules this is a credible hypothesis. One might suggest to actively trace the molecules with high-speed fluorescence imaging, but the signal-to-noise ratio does not allow to implement this idea on the single molecule level, here.
- Thermally activated dipole moments could play a role in the interaction between the walls of the nanogratings and the floppy molecules. This interpretation is, however, in conflict with the observation that the Rhodamines still show quantum diffraction, in spite of their enormous permanent dipole moments (~ 6 Debye for Rh6G and ~ 19 Debye for RhB). The relevance of this effect will, however, be tested in a near-future experiment with diffraction of these molecules at UV and/or green standing light waves (266 nm, 532 nm). Optical gratings eliminate all effects of real or virtual image charges.

Diffraction at a naturally grown nanostructure

While the increasing refinement of nanotechnology allowed us to work with the thinnest SiN grating that have ever been realized, so far, we also asked ourselves how to realize ultrathin diffraction masks at virtually no costs. We found the answer in marine phytoplankton, in particular the skeleton (frustule) of the alga *amphipleura pellucida* (Fig. 11) [8].

With pore sizes and distances of the order of 200 nm and a wall thickness between 50-100 nm these silicified biologically grown nanostructures are surprisingly stable and ubiquitous. They can be found at the sea shore in great abundance and each nanostructure is worth 5-10 Euros. This is an important first step towards bringing nanophysics and quantum interference to school classes, in the future.

For that reason the publication on this subject received also substantial interest in the scientific community and in the public.

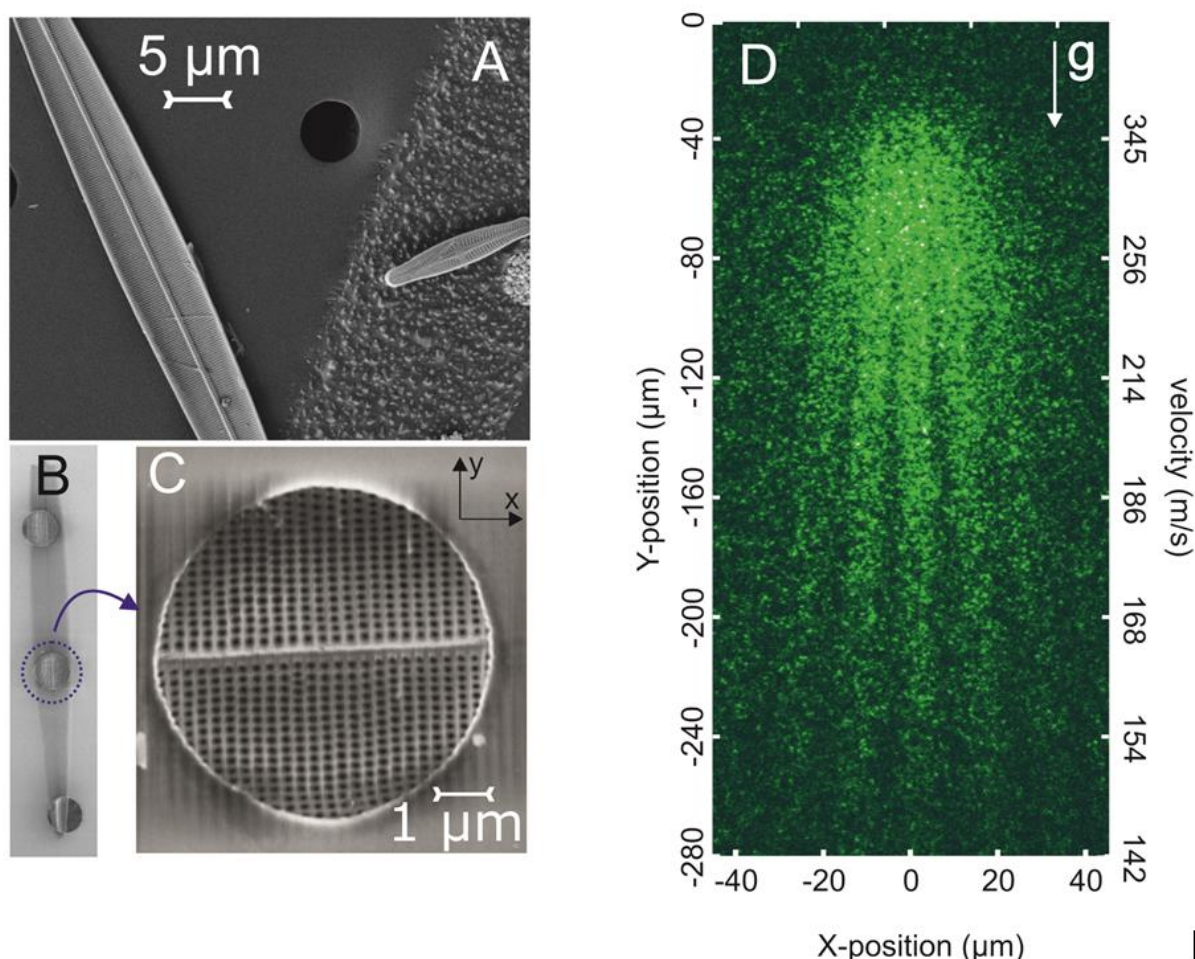


Figure 11: A: Scanning electron micrographs of the skeleton of the alga *amphipleura pellucida*. A magnified image of the sample (panel B – blue circle) reveals a surprising regular 2D-periodic structure (panel C). A 205 nm periodicity with a 122 nm pore opening can be identified along the x-axis. D: coherent diffraction of PCH₂ molecules through the nanoarchitecture of a biologically grown sample.

Conclusions

Diffraction at thin and ultrathin gratings has been achieved and demonstrated with PCH₂, Rhodamine B and Rhodamine 6G at nanostructures made from silicon nitride with a thickness of 100 nm down to 5 nm. Complementary to that we have demonstrated quantum interference behind an ultrathin biologically grown nanostructure.

The deliverable can therefore be counted as successfully completed.

Outlook

Ongoing work is focused on a better understanding of the van der Waals interaction between the molecules and the gratings. Our development efforts will focus on the fabrication of bilayer graphene and the exploration of single-layer graphene gratings which are the content of a future deliverable. Also optical gratings will shift into the focus of interest to further elucidate 1-photon, 2-photon ionization and fragmentation as well as the role of the dipole moments.

References

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