Deliverable D2-5:
Optical depletion gratings

Description of the deliverable

Report on working principles of pulsed optical depletion gratings for complex molecules / nanoparticles. This objective relates closely to *Objective 4.2: Quantum diffraction at a pulsed photo-depletion grating.* Deliverable D2-1 contains the concepts, D4.2. describes the experimental results.

Work performed and achievements

Our earlier and ongoing efforts in developing the ultimate nanomechanical mask (see D2.1 and D4.1) for quantum diffraction experiments with complex molecules, clusters or nanoparticles has led to the insight that material structures will inevitably entail some particle-wall interaction. This can be an interesting feature in molecule metrology, but it can be a hindrance in high-mass applications, too.

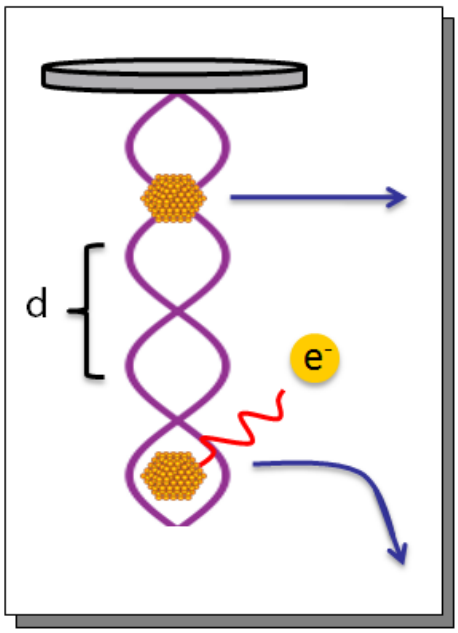

Figure 1: *A photodepletion grating removes particles selectively from the antinodes of a standing light wave. In the OTIMA setup at UNIVIE this is done with a 157 nm standing light wave which may induce 1-photon or 2-photion ionization of the clusters.[1]*

In order to avoid all material boundaries we have been working with optical gratings in different settings. Already earlier we explored the use of phase gratings for diffraction[2] and Kapitza-Dirac-Talbot-Lau (KDTLI) interferometry [3], which also led to the first demonstration of quantum interference in the mass range beyond 10,000 amu [4]. The KDTLI concept relies, however, still on mechanical gratings for preparing the initial coherence and for sampling the final interferogram. At ultrahigh masses (beyond 10^6 amu) this is believed to impose significant constraints – for geometrical

reasons when the particles grow to dimensions comparable with the grating openings and because the induced dipole potential (vdW) may bind the particles to the grating when they should pass.

It is therefore important to establish tools that can serve as absorptive masks without introducing van der Waals forces. Optical absorption gratings turn out to fill this gap in an ideal way.

Standing waves of laser light can have a very high reproducibility and periodicity. They can be controlled in situ and as a function of time. They can be pulsed and interact with all particles in the same volume at the same time in the same manner. Interferometers with pulsed absorptive gratings eliminate a number of dispersive phase shifts which are believed to limit high-mass and ultrahigh-mass quantum interference.

Our most recent realization of the Optical Time-Domain Ionizing Matter-Wave Interferometer (OTIMA) [1] is a perfect example of a sophisticated combination of photodepletion gratings: Three laser pulses emitted by three 157 nm fluorine excimer lasers can be used to cause single-photon ionization in certain organic clusters, here tested with clusters of anthracene molecules. In the anti-nodes of the standing light wave the analyte object is ionized while it can pass the grating nodes without any loss.

However, even optical ionization gratings imprint a spatially periodic phase onto the transmitted de Broglie wave. The interaction between the electric laser light field E and the particle's optical polarizability $\alpha_{157\mathrm{nm}}$ (here at $\lambda = 157$ nm) induces a phase shift $\Delta\phi \propto \alpha_{157\mathrm{nm}} E^2 \tau$, with τ the interaction time. The total fringe pattern then depends on the ratio of photoionization (generally photo-*depletion*) cross section to optical polarizability, in practice on the β-parameter: $\beta \propto \alpha_{opt}/\lambda\, \sigma_{ion}$.

Single-photon ionization gratings have been successfully employed in the OTIMA setup at UNIVIE and have led to the first quantum interference with clusters of organic molecules [1] – down to de Broglie wavelengths as tiny as 200 fm. This demonstrates the power of the concept, which shall be extrapolated to higher particle mass and other types of depletion gratings, too. Given the work function of metal clusters and many pure dielectric nanoparticles, 1-photon ionization is expected to be universally applicable to a very large class of nanoparticles.

The feasibility of 2-photon absorption gratings

At first, one might think that photodepletion gratings need to be realized on the single-photon level and that the quantum interference contrast would be reduced if two or more photons were required for the depletion process. This reasoning is based on the assumption that photon absorption in a laser beam follows a Poissonian distribution. If two photons are needed to induce the desired phenomenon, it may occur that only a single photon is absorbed. This would not trigger the depletion process but still impart a 1-photon momentum kick, which shifts the interferogram.

However, if this recoil is well-defined and coherent and if phase scrambling by spontaneous reemission processes is avoided one can identify settings under which high-contrast quantum interference fringes are still expected.

Photodepletion gratings have recently been theoretically studied by UDE with regard to single and two-photon ionization. The results are very promising as they show that quantum interference is also to be expected in the OTIMA setup under realistic conditions for two-photon absorption/ionization. Interestingly, even incomplete knowledge of the transition probabilities and excited state life times is no major obstacle in the assessment of whether a given molecular species is suitable for 2-photon depletion gratings. The molecular transmission through a single depletion grating yields all the required information to predict the success of the interferometer experiment.

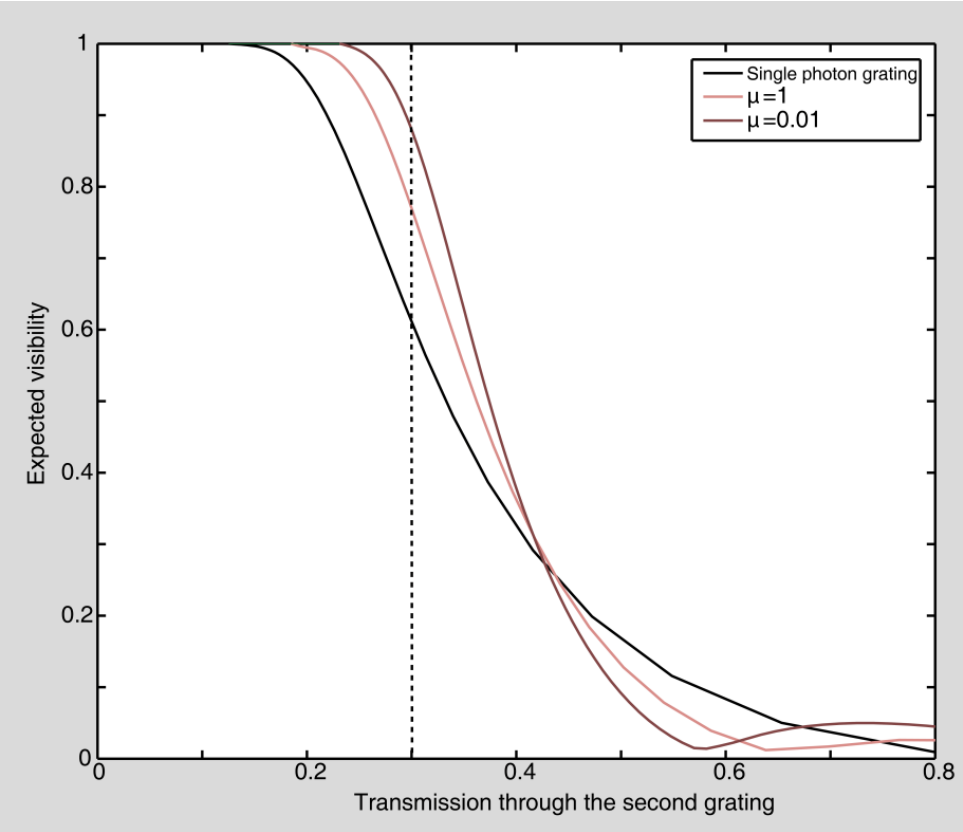

Figure 2: *Simulated interference contrast as a function of the transmission through the diffraction gratings in the OTIMA experiment. Single photon gratings (black curve) versus two-photon depletion gratings, both analyzed at even Talbot order. Incomplete knowledge of molecular properties such as the excited state lifetime, absorption cross section and polarizability represents no major obstacle since these properties only slightly affect the expected transmission vs. visibility curve. This is illustrated here by varying the lifetime of the excited state from being equal to the grating pulse length (μ=1) to one hundredth thereof (μ=0.01).*

Since it may be challenging to find a molecule for the demonstration of a pure 2-photon ionization grating in OTIMA (as the experiment is based on the use of 157 nm light in the gratings and the

detection), far-field diffraction on a single grating formed with a 266 nm laser seems more feasible. In combination with single molecule fluorescence detection, a strongly UV absorbing dye molecule such as Nile Red represents an ideal test molecule.

The role of grating imperfections

A photodepletion grating can only be as good as the optics that forms the standing light wave. In practice, present-day technology allows fabrication of VUV mirrors with a reflectivity of 96% at $\lambda = 157$ nm. In consequence, every standing light wave is superposed by a running wave component which contributes to the photodepletion and phase shift, independent of the particle position. The relevance of this contribution is described in D4.2.

Photo-cleavage of covalently bond molecules

The concept of photodepletion is not limited to ionization. Any process that transfers a particle from a detected to an undetected state serves this purpose. We are interested in any measurement-induced grating which restricts the possible particle positions to a well-defined periodic transmission comb [5].

This may be implemented by other photoactivated processes such as for instance photofragmentation – which alters the cluster mass spectrum – or photoisomerization which modifies the population of internal states. Fragmentation gratings have been seen in OTIMA interferometry of HFB, most recently. Isomerization gratings shall be studied in far-field diffraction in the next evaluation period.

In order to obtain better control over the dissociation path ways the group of Marcel Mayor synthesized a tailored perfluoralkyl-functionalized compound, with 1-4 dedicated cleavage sites. Volatilization and cleavage experiments with these compounds are under way and shall be reported in the next evaluation.

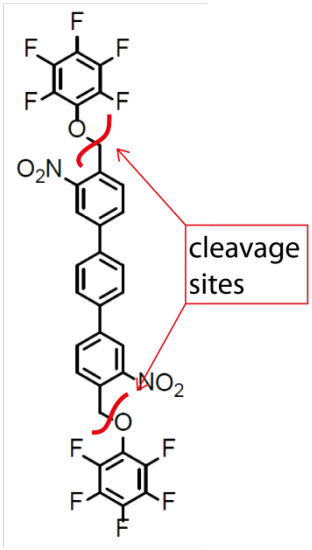

Figure 1: *Chain molecule with two equal cleavage sites. Cleavage of benzylic alcohols para to a nitro group is well described in literature and can be observed by irradiation with UV-light.*

In order to obtain better control over the dissociation path ways the group of Marcel Mayor at UNIBAS synthesized a **tailored compound** with dedicated cleavage sites as shown in Figure 3. First volatilization experiments with these tailored molecules still led to unstable molecular beams but new synthesis, sublimation and cleavage experiments with these compounds are under way and shall be reported in the next evaluation period.

The groups at UNIBAS and UNIVIE are also further exploring the synthesis, volatilization and ionization of complex tailor-made organic and inorganic compounds for high-mass quantum interferometry. Good progress has been made recently [6] and this work is still being continued to increasingly more massive particles.

Photo-dissociation of weakly bound clusters

In contrast to *photo-cleavage gratings* which address specific bonds in covalently bound molecules, *photodissociation gratings* deposite enough energy per molecule to dissociate weakly bound van der Waals clusters on the time scale of several nanoseconds. Figure 4 illustrates two examples of energy minimized conformations of hexafluorobenzene and anthracene pentamers. Once these structures are heated to beyond 100 K they fly appart before the particles have a chance to reach the detector.

Whenever a 7.9 eV photon is absorbed the chances for rapid interconversion in these clusters is very high and the heat capacity is so small that the internal temperature is estimated to rise to beyond 3000 K, even if we start from a rather coarse assumption that each internal degree of freedom $(3N-3)$ achieves a new thermal equilibrium and stores on average $E_n = kT/2$. This is expected to to blast the cluster apart with a high probability unless the compound relaxes its energy radiatively and unless a second photon is absorbed before the onset of fragmentation. In that case ionization of the intact sample may still prevail.

Although it is difficult to clearly distinguish experimentally between one or the other process – in the diffraction gratings both lead to depletion and the remnants leave the beam and can no longer be analyzed – single beam experiments allow distilling the difference between 1-photon and 2-photon processes. This is currently being evaluated at UNIVIE.

Conclusion

Photodepletion gratings have been analyzed theoretically by UDE with regard to two examples that are of particular interest for the experiments, i.e. 1-photon ionization and 2-photon ionization gratings. Both have been successfully documented experimentally at UNIVIE, as documented in D4.2. **The deliverable can therefore be counted as successfully accomplished.**

Outlook

Research on advanced photodepletion gratings will continue as it promises to open quantum coherence experiments also to molecules and clusters which are not photoionizable.

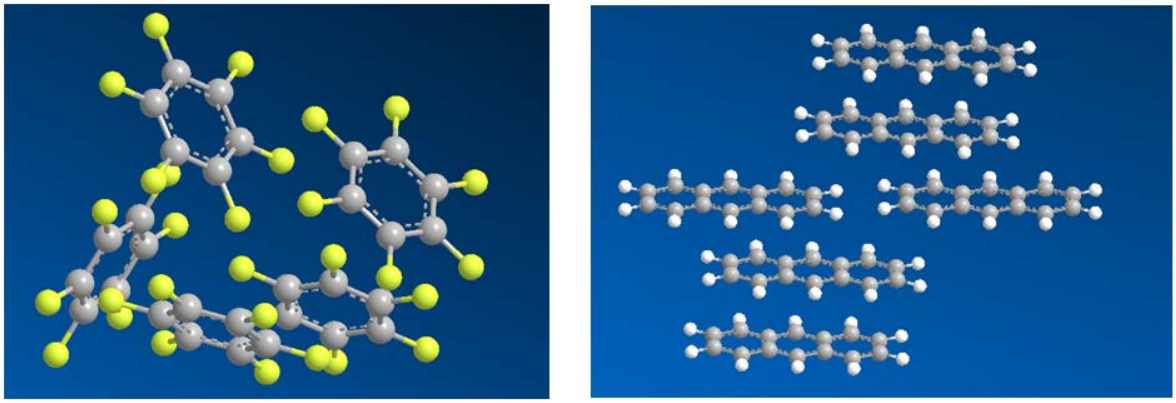

Figure 1: *Clusters of Hexafluorobenzene (left: HFB 5) and anthracene (right: Ac 5). Even soft heating to beyond 100 K suffices to destroy these clusters. Fragmentation gratings are therefore a realistic depletion alternative to ionization gratings. In contrast to the ionization probability which increases with increasing cluster size, as the ionization energy decreases, fragmentation is strongly temperature dependent. Since the heat capacity increases with increasing cluster size the fragmentation probability is expected to decrease with higher cluster number.*

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