

Matter-Wave Metrology as a Complementary Tool for Mass Spectrometry**

Stefan Gerlich, Michael Gring, Hendrik Ulbricht, Klaus Hornberger,* Jens Tüxen, Marcel Mayor,* and Markus Arndt*

Mass spectroscopy is a powerful tool that is routinely used to probe not only mass but also molecular structures and properties. In nearly all practical realizations, mass selection explicitly depends on the availability of molecular ions.^[1] However, many molecules are so weakly bound and most ionization processes so energetic that it cannot be discounted that the ionization process modifies or even destroys the original compound. It is therefore important to develop methods that may assist in identifying the original neutral particle in the gas phase before the act of ionization. A number of characterization techniques can be used for a detailed analysis of a solid or liquid sample. However, if a molecular side chain can be lost during the volatilization process, the unambiguous identification of the flying neutral object remains a nontrivial challenge for conventional mass spectroscopy.^[2]

In such cases, matter-wave diffraction is an interesting, complementary tool. The de Broglie wavelength λ of a molecule [Eq. (1)] is inversely proportional to the molecular mass m and the velocity v , and a far-field diffraction pattern

contains explicit mass information. This idea was successfully utilized for establishing the existence of the weakly bound helium dimer^[3] and it was also extended to hot fullerenes^[4] with de Broglie wavelengths in the range of $\lambda = 2\text{--}5$ pm. For more complex molecules, the wavelength is however often too short and the beam-collimation requirements too tight to be experimentally accessible.

$$\lambda = h/(mv) \quad (1)$$

Quantum coherence of very large molecules may, however, also be explored in a near-field interference process, such as the Talbot–Lau interferometer.^[5,6] A recent extension of this idea, the Kapitza–Dirac–Talbot–Lau (KDTL) interferometer, even promises to be scalable to particles up to 1 000 000 amu.^[7]

Herein, we show how this new interferometer can be employed as a complementary tool for mass spectroscopy where fragmentation might occur in either the source or the ionization process. Our method is based on the fact that the molecular polarizability is often a good indicator of the number of constituents in the molecule. The interference fringe contrast in the KDTL interferometer is sensitive not only to the polarizability-to-mass ratio, which is also determined with classical deflectometers,^[8] but also to the absolute polarizability. It thus allows us to address problems that are not easily accessible to the established methods: one such example is the analysis of a polymer that decays into fragments of nearly identical polarizability-to-mass ratio.

The general principle of the setup has already been described in a previous publication.^[7] As shown in Figure 1, a molecular beam, generated in an effusive cell, is velocity-selected by the confinement to a free-flight parabola in the gravitational field. It is then detected by electron-impact quadrupole mass spectrometry (EI-QMS).

The interferometer entrance is defined by the nanofabricated SiN_x grating G1, with a period of 266 nm and gap openings as small as 100 nm. This is followed by a standing light-wave grating G2, formed by a green laser at 532 nm that is focused to an elliptical waist of 850 × 20 μm² (height × width). Diffraction within each slit of G1 serves to delocalize the molecular center-of-mass wave function over about 1 μm at G2, as required for obtaining multi-slit interference. The standing light wave serves as a phase grating.^[9] Its electric field E [Eq. 2] creates a position-dependent potential W [Eq. 3], which causes a position-dependent phase modulation of the transmitted matter wave. Under our experimental conditions, the molecular phase pattern formed at G2 evolves into a nearly sinusoidal molecular density pattern $S(x)$ in front

[*] Dr. K. Hornberger
Arnold Sommerfeld Center for Theoretical Physics
Ludwig-Maximilians Universität
Theresienstrasse 37, 80333 Munich (Germany)
Fax: (+49) 89-2180-4154
E-mail: klaus.hornberger@physik.lmu.de

J. Tüxen, Prof. M. Mayor
Department of Chemistry
University of Basel
St. Johannisring 19, 4056 Basel (Switzerland)
Fax: (+41) 61-267-1016
E-mail: marcel.mayor@unibas.ch

Prof. M. Mayor
Forschungszentrum Karlsruhe GmbH
Institute for Nanotechnology
P.O. Box 3640, 76021 Karlsruhe (Germany)
Fax: (+49) 7247-82-6368

S. Gerlich, M. Gring, Dr. H. Ulbricht, Prof. M. Arndt
Faculty of Physics
University of Vienna
Boltzmannngasse 5, 1090 Vienna (Austria)
Fax: (+43) 1-4277-9512
E-mail: markus.arndt@univie.ac.at
Homepage: <http://www.quantum.at>
Dr. H. Ulbricht
School of Physics and Astronomy
University of Southampton
Highfield, Southampton SO17 1BJ (United Kingdom)

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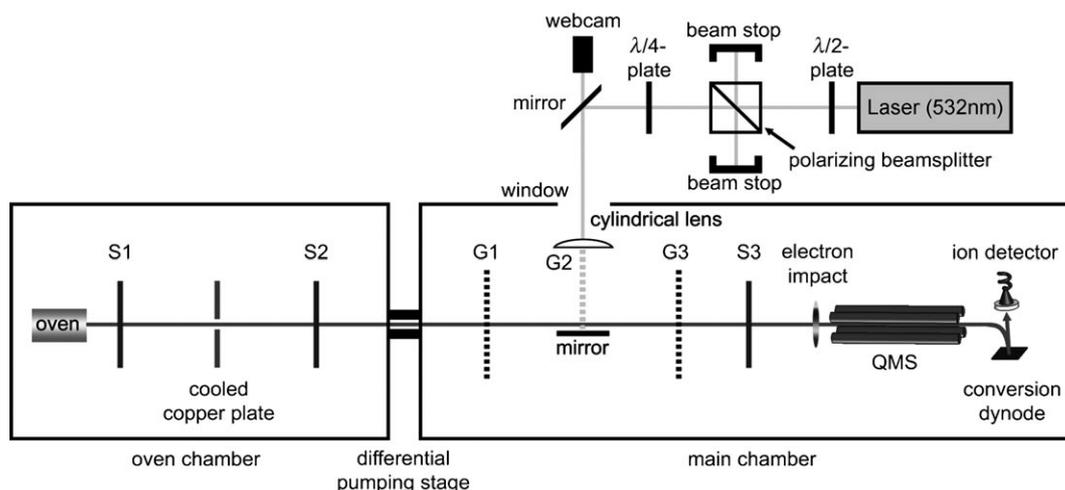


Figure 1. A molecular beam emerges from the sublimation furnace (left). The molecules pass the KDTL interferometer, which consists of one optical (G2) and two mechanical (G1, G3) gratings. The slits S1, S2, and S3 restrict the height of the molecular beam and serve as vibration-free velocity selectors. The molecules are finally ionized by electron impact and counted in a quadrupole mass spectrometer.

of a third grating G3. This is then revealed by scanning the last nanomechanical structure G3 across the molecular density pattern while counting all transmitted molecules in the QMS. The visibility (contrast) V of the interference fringes is determined from the modulation of the transmitted signal according to Equation (4). The absolute value, and even more importantly, the functional form of the interference visibility in dependence of the laser power are governed by the mass and the scalar optical polarizability α_L of the interfering particle.

$$E = E_0 \sin^2(x) \quad (2)$$

$$W = -1/2\alpha_L E^2(x) \quad (3)$$

$$V = (S_{\max} - S_{\min}) / (S_{\max} + S_{\min}) \quad (4)$$

We exploit this fact herein to perform a fragment analysis of the perfluoroalkylated palladium complex **1** ($C_{96}H_{48}Cl_2F_{102}P_2Pd$, CAS No. 343343-17-9, purity 90%), shown in Figure 2, which has been developed as a palladium catalyst for cross-coupling reactions in fluorinated media.^[10,11] The intact molecule has a mass of 3378.5 amu, but quadrupole mass spectroscopy reveals predominantly a compound with a mass of 1601 amu, which corresponds to the mass of the triphenylphosphine ligand **2** ($C_{48}H_{24}F_{51}P$).

KDTL interferometry allows us to answer the question as to whether fragmentation occurs in the source or in the electron impact ionization stage. Our procedure measures the dynamic polarizability α , which differs by a factor of two for the intact molecule and its fragments, whereas α/m remains about the same.

At a wavelength far away from all optical resonances, the dynamic polarizability can be approximated well by the static polarizability. A Hartree–Fock simulation with Gaussian 03W,V6^[12] using the basis set 3–21G results in a static polarizability of 66 \AA^3 for the fluoroalkyl-functionalized triphenylphosphine ligand **2** at 1601 amu. We expect a value

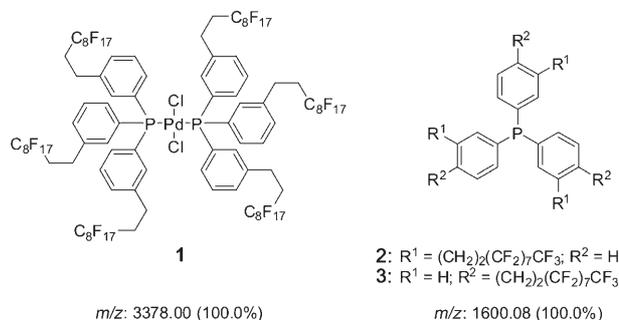


Figure 2. Molecular structure of the palladium complex **1** ($C_{96}H_{48}Cl_2F_{102}P_2Pd$, 3378.5 amu) and of the ligands **2** and **3** ($C_{48}H_{24}F_{51}P$, 1601 amu).

about twice as large for the intact palladium complex **1** at 3379 amu.

An intense molecular beam is typically formed at a temperature of 237°C . About 200 mg of the compound are evaporated in six hours through an orifice of size $0.2 \times 2 \text{ mm}^2$. Figure 3 shows a typical quantum interferogram that was recorded at a mean molecular velocity of 116 ms^{-1} with a width $\Delta v/v$ of 18% (standard deviation).

The quantum wave properties of the palladium complex **1** are of particular interest, owing to its mass of 3379 amu, which is about twice as high as the fluorinated fullerene derivative $C_{60}F_{48}$ (1632 amu), which currently maintains the mass record in matter-wave experiments.^[13] Interference with the triphenylphosphine ligand **2** (1601 amu) would corroborate the existing mark, however with significantly improved contrast. Therefore, a polarizability analysis also serves us to establish whether our high contrast interference pictures confirm or double the earlier mass record.

In contrast to far-field diffraction experiments,^[2] the fringe spacing in Talbot–Lau interferometry is predetermined by the experimental setting, and does not reveal mass information. However, the fringe visibility is a clear indicator for mass and

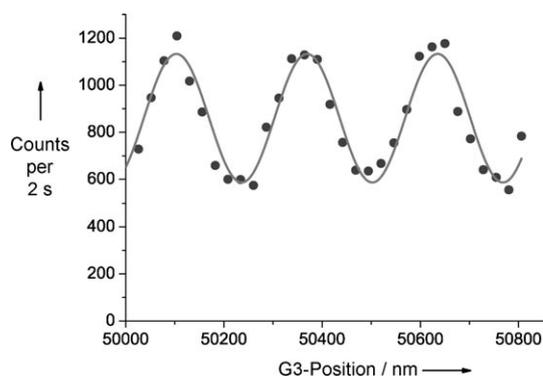


Figure 3. Quantum interferogram of **1** recorded at the mass of 1601 amu.

polarizability, in particular when it is traced as a function of the diffracting laser power P of the second grating G2 (Figure 4).

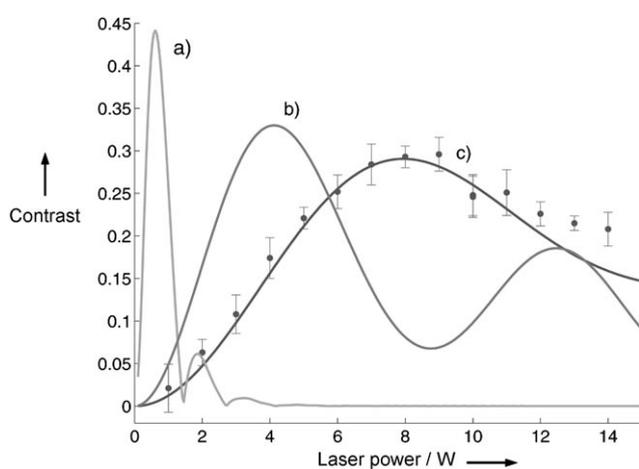


Figure 4. Dependence of the interference fringe contrast (visibility, V) on the diffracting laser power. ● experimental values, a) classical expectation for $m = 1601$ amu and $\alpha = 66 \text{ \AA}^3$, b) theoretical prediction for $m = 3378$ amu and $\alpha = 132 \text{ \AA}^3$, and c) theoretical prediction for $m = 1601$ amu and $\alpha = 66 \text{ \AA}^3$. The good agreement between the quantum expectation (c) and experiment allows a unique assignment of the molecule.

The experimental points are marked as full circles, where each point represents the average of three consecutive measurements. The error bars indicate the standard deviation. In the same figure a classical simulation is shown with Newtonian trajectories of billiard balls in an external potential for the fragment (a). This model clearly fails to describe the experiment. The same holds for a quantum wave model based on the mass and polarizability of the intact particle (b). However, a quantum model based on the mass and polarizability of ligand **2**, a likely fragment of the palladium complex **1**, is in very good agreement with the experimental data (c). This implies that the fragments are already present in the beam before the electron impact

ionization, and it points to fragmentation of **1** during the beam formation.

Two experimental strategies were pursued to confirm the hypothesis of fragmentation of the palladium complex **1** during sublimation. Firstly, we chemically analyzed both the parent palladium complex **1** and the sublimed species which were collected on a cold copper plate in the molecular beam (Figure 1). Extensive washing with hexafluorobenzene delivered the material from the copper plates. Qualitative analyses were performed by ^1H , ^{19}F , and ^{31}P NMR spectroscopy as well as MALDI-ToF mass spectrometry. Whereas the ^{19}F NMR spectra of both samples resemble each other and allowed us only to attest the presence of the $1H,1H,2H,2H$ -tetrahydro-perfluorodecane chains, minor variations in the aromatic region of the ^1H NMR spectrum pointed to the presence of two different compounds. Pronounced differences were observed in the ^{31}P NMR spectra of both samples. Whereas **1** has a ^{31}P NMR signal at $\delta = 20.9$ ppm,^[10] the sample collected from the copper plate has a peak at $\delta = 10.8$ ppm. Thus, the sublimed species creating the molecular wave is not the entire palladium complex **1**, but rather a fragment. Both samples had an additional signal at $\delta = -79.2$ ppm originating from an more easily sublimable impurity. Further analysis of the extract from the copper plate by MALDI-ToF mass spectrometry gave a strong signal at m/z 1618, corresponding to the water adduct of the triphenylphosphine ligand **2**. Thus, chemical analysis further corroborates the hypothesized fragmentation of **1** during sublimation.

To confirm these findings independently, we repeated the interference experiment with triphenylphosphine **3** (CAS No. 325459-92-5, purity 97%) a commercially available structural isomer of **2**. It was detected at its original mass of 1601 amu, under identical ionization conditions and spectrometer settings as used for the initial experiments. As this molecule is a structural isomer of the fragment **2**, it showed the same interference curves and power dependence as observed in the initial experiments with **1** as source material, as expected. We can therefore conclude unambiguously that the molecules fragment already at or before the vaporization and exclude electron impact as being responsible for the observation of the fragments.

In summary, we have demonstrated the analytical capabilities of the KDTL interferometer. The instrument may complement mass spectrometry, as it allows molecular properties of neutral particles to be probed in free flight before possibly being perturbed by ionization. Future work will aim at extending the range of experiments to a larger variety of even more complex molecules and will address a wide range of molecular properties, among them the role of structural or spatial isomers, and electric or magnetic moments.

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