I. INTRODUCTION

Porphyrs and their derivatives are widely used and well-investigated objects in physics and chemistry. They are of interest because of their numerous potential applications from molecular electronics, over sensors, information storage elements, to medical agents. Our own research initially focused on the question of whether these biodyes could also reveal their quantum mechanical wave nature in spite of their structural complexity. This question was answered positively in a recent experiment. The present study reverses the question and asks what we can learn about molecular properties by using a near-field matter-wave interferometer.

For this purpose, we first analyze in Sec. II the thermal characteristics of two porphyrin derivatives and show that they possess a sufficiently high vapor pressure for our subsequent interferometry experiments. We discuss the possible influence of internal molecular properties on the external de Broglie interference in Sec. III and then compare experimental Talbot-Lau interference patterns for H$_2$TPP and Fe(TPP)Cl in Sec. IV. These two derivatives differ only slightly in their internal structure and de Broglie wavelength but are distinguished by the absence and presence of a permanent electric dipole moment. By exposing these molecules to an external field gradient—inside the same matter-wave interferometer—we can determine their scalar electric polarizabilities with good precision and also discuss the influence of the electric dipole moment (Sec. IV). We compare our measurements and density functional theory (DFT) calculations in Sec. V, taking into account the thermal evolution of the molecules at 650 K.

II. MOLECULAR SUBLIMATION ENTHALPIES

In order to determine the sublimation properties of the porphyrs, a resistively heated furnace generates an effusive molecular beam of temperature dependent flux. The molecules are detected using electron impact ionization quadrupole mass spectrometry (EI-QMS) in a differentially pumped vacuum chamber. The pressure in the source chamber varies with the furnace temperature, but it always remains in the low $10^{-6}$ mbar region. In the detection chamber, the pressure is kept below $5 \times 10^{-8}$ mbar.

The sublimation enthalpy $\Delta H_{\text{sub}}(T)$ can then be measured by observing the molecular beam intensity $I$ as a function of the source temperature $T$, assuming that the enthalpy is constant over the interval of interest.

The QMS signal at the mass of the singly charged ion is then continuously recorded, while the source temperature is ramped at a rate of 1.5 K/min. In Fig. 1 we show the resulting Arrhenius plots for meso-tetraphenylporphyrin (H$_2$TPP) for tetraphenylporphyrin-iron(III) chloride (Fe(TPP)Cl), as well as for a fragment that we discuss below. The Clausius-Clapeyron relation,

$$\ln(I) = \text{const} - \frac{\Delta H_{\text{sub}}}{RT},$$

then allows us to determine the sublimation enthalpy from the slope of a linear fit to the data (Fig. 1).
It is conspicuous that these data are not described by a single line, as one might expect from Eq. (1). As already discussed earlier, the use of the Clausius-Clapeyron equation is restricted to either the molecular or the hydrodynamic flow regime at low and high source temperatures and densities, respectively. In Fig. 1 we find that for a given molecule the slopes at both ends of the temperature scale are identical within the experimental uncertainty (see also Table I). Because the ionization efficiency of porphyrins in the QMS is not known, we cannot extract the absolute vapor pressure from our measurement. The published values for the vapor pressure of H2TPP Refs. (10 and 11) are different but both of them lead to a transition to the hydrodynamic flow at around 625 K. There are no published values for the vapor pressure of Fe(TPP)Cl; however, our measurements at 625 K using a quartz balance show similar signals for both molecules. If we assume an equal sticking factor on the quartz this tends to show that the transition occurs in the same temperature range for both molecules. This indicates that the kink at around 600 K in Fig. 1 corresponds to the transition region between the two flow modes.

One uncertainty in the determination of the sublimation enthalpies is associated with the sample temperature, which is known with a relative precision of better than 1 K and an absolute accuracy of better than ±10 K. Another contribution to the total uncertainty is related to the slight nonlinearity of the enthalpy curves, in particular, at the edges of the temperature intervals. Our fits are therefore limited to the intervals marked by the straight lines in Fig. 1. Our sublimation data for H2TPP are in the range of literature values. While we did not find any reference values for Fe(TPP)Cl, it is interesting to note that the literature enthalpy for Fe(TPP)Cl is by a factor of 2 smaller than our value for Fe(TPP).

This is particularly noteworthy since the enthalpies associated with Fe(TPP)Cl at m=704 amu and Fe(TPP) at m=668 amu in our own experiments are nearly identical within the error bars, as shown in Fig. 1 and Table I. This is in agreement with a recent finding of Feil et al. that Fe(TPP)Cl evaporates as an intact molecule but undergoes a strong and well-defined fragmentation upon electron impact ionization when the electron energy rises above 30 eV. The dominance of Fe(TPP) over Fe(TPP)Cl in our experiments, with EI~70 eV, is therefore in good agreement with the expectations. In the following we will therefore assume that the molecules at mass m=668 amu also represent free-flying Fe(TPP)Cl.

III. INTERNAL MOLECULAR PROPERTIES AND de BROGLIE WAVES

Already in our earlier work, we showed that complex molecules may reveal their quantum mechanical wave-particle duality in a near-field interferometer, such as that shown in Fig. 2. These experiments supported the view that porphyrins may be coherently delocalized over more than 2 μm, i.e., thousand times their structural size.

Our present study now uses a similar setup to compare H2TPP and Fe(TPP)Cl, which differ only by two central atoms as shown in Fig. 3. Their polarizability is rather similar, but while H2TPP has neither an electron magnetic moment nor an electric dipole moment in its ground state, we calculate D=2.7 D for Fe(TPP)Cl (see Sec. V).

We therefore first investigate the possible role of these internal properties for de Broglie (center-of-mass) interference in the presence of material diffraction gratings, in which the molecules pass gold slits as narrow as 450 nm and as thin as 500 nm.

For pointlike objects without any internal properties, matter-wave interferometry is only determined by the momentum p=mv, which is related to the de Broglie wavelength through λ=ℏ/mv. In addition to that, earlier experiments showed that, in particular, the scalar polarizability can be rather relevant for quantum interferometry. A conservative interaction potential V(r) between the polarizable molecule and the grating wall causes a wave dephasing.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Formula</th>
<th>Mass (amu)</th>
<th>ΔH_{sub} (kJ/mol)</th>
<th>T range (K)</th>
<th>Max. signal (kcounts/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2TPP</td>
<td>C44H30N4</td>
<td>614</td>
<td>160±3</td>
<td>618–665</td>
<td>1000</td>
</tr>
<tr>
<td>Fe(TPP)Cl</td>
<td>C44H28ClFeN4</td>
<td>704</td>
<td>203±15</td>
<td>631–647</td>
<td>120</td>
</tr>
<tr>
<td>Fe(TPP)Cl</td>
<td>C44H28ClFeN4</td>
<td>704</td>
<td>196±7</td>
<td>561–592</td>
<td>16</td>
</tr>
<tr>
<td>Fe(TPP)Cl-frgm.</td>
<td>C44H28FeN4</td>
<td>668</td>
<td>205±8</td>
<td>621–652</td>
<td>1300</td>
</tr>
<tr>
<td>Fe(TPP)Cl-frgm.</td>
<td>C44H28FeN4</td>
<td>668</td>
<td>203±4</td>
<td>557–600</td>
<td>60</td>
</tr>
</tbody>
</table>
The molecule-wall interaction often turns out to be an undesired effect in quantum interferometry. The added phase \( \Delta \phi \) depends on the transition time \( \tau \). For molecular beams of finite velocity spread, phase averaging may then strongly modify and also reduce the observed interference fringe visibility.\(^{15}\)

In traversing a grating slit, the molecular center-of-mass wave function \( \psi(r) \) acquires a phase

\[
\Delta \phi = -\frac{i}{\hbar} \int_0^\tau V(r)dt.
\]

Depending on the distance between the molecule and the grating wall, \( r \), the attractive interaction \( V \) is best described by the van der Waals potential at short distances,

\[
V_{vdW} = -C_d/r^3,
\]

the Casimir-Polder approximation at long distances,

\[
V_{CP} = -\frac{C_4}{r^4} = -\frac{3\hbar c}{32\pi^2\varepsilon_0 r^4} \alpha,
\]

or a more elaborate transition formula valid for all distances.\(^{15}\)

Typically the transition between \( V_{vdW} \) and \( V_{CP} \) occurs already at several tens of nanometers away from the surface, and it is therefore justified to use the Casimir-Polder approximation for the description of our experiments. This molecule-wall interaction is associated with the particle’s polarizability and quantum fluctuations of the molecular dipole moment.\(^{16}\)

For polar molecules with a permanent electric dipole moment \( D \), we also have to consider the interaction with its own mirror image in the grating wall. If we neglect their rapid rotation at high temperature—which tends to reduce the mutual attraction—the maximum interaction potential reads\(^{16}\)

\[
V_{DD} = -\frac{D^2}{4\pi\varepsilon_0 (2r)^3}.
\]

In order to assess the relative importance of these effects, we choose Systeme International units and assume a polarizability of \( \alpha=(4\pi\varepsilon_0)(100 \text{ Å}^3) \), an electric dipole moment of \( D = 2.7 \text{ D} = 8.9 \times 10^{-30} \text{ C m} \), and an average molecule-wall distance of \( r = 200 \text{ nm} \). The Casimir-Polder energy then amounts to \( V_{CP} = 1.5 \text{ neV} \), whereas the dipole-dipole potential reaches only \( V_{DD} = 0.07 \text{ neV} \). With regard to matter-wave interferometry and in the absence of any external electric fields, the influence of the molecular polarizability should therefore be clearly dominant.

**IV. INTERFEROMETRIC MEASUREMENT OF THE MOLECULAR POLARIZABILITY**

Because of its high sensitivity to external perturbations, a matter-wave interferometer may also serve for precisely determining \( \alpha \). It is important to explore this possibility, since the knowledge of biomolecular polarizabilities may also reveal information on molecular conformations, from small polyperptides\(^{17}\) up to genuine macromolecules, such as DNA.\(^{18}\)

For biomolecules, \( \alpha \) is often determined using optical light scattering and refractive index measurements\(^{19,20}\) in solvents or on substrates. This always includes an interaction with a local environment, which can be avoided when working with isolated particles in molecular beams. Classical Stark deflectometry of free beams in an inhomogeneous external electric field has therefore become a very useful tool for the determination of molecular polarizabilities.\(^{21,22}\)

Our Talbot-Lau deflectometer (TLD), shown in Fig. 2, now combines a near-field matter-wave interferometer of the Talbot-Lau type\(^{13}\) with a pair of electrodes. The electrodes generate a constant electric force field in the transverse direction to the molecular beam to deflect the interference pat-
terms in proportion to \( \alpha \). The TLD is capable of operating with a rather wide molecular beam and has a high throughput and at the same time a high spatial resolution. Thanks to the nanostructured diffraction gratings, it may resolve molecular beam shifts even down to \( \Delta s \sim 10 \text{ nm} \).

The principles of Talbot-Lau interferometry\(^{13,23}\) and its application to metrology have already been explained before.\(^{24}\) In brief, the basic principles are as follows: The porphyrins are sublimated and emerge with a typical de Broglie wavelength of \( \lambda_{\text{dB}} \sim 5 \text{ pm} \). The longitudinal (spectral) coherence length \( l_c \sim \lambda^2/\Delta \lambda \) is determined by the velocity selection, \( \Delta \lambda/\lambda = \Delta v/v \sim 15\% \), and thus amounts to about 30 pm in the porphyrin experiments. The transverse coherence covers only a few tens of nanometers in width when the molecules encounter the first grating. But according to the van Cittert–Zernike theorem,\(^{25}\) each of the many narrow and parallel slits of the first grating localizes the molecular position so well that the corresponding momentum uncertainty suffices to delocalize each single-molecule wave function coherently over at least two neighboring slits of the second grating, 38.5 cm downstream of the first grating. Diffraction at this second nanostructure then creates an interference fringe pattern, again 38.5 cm further downstream, which is sampled by help of a third mask of identical period. This third grating is translated in the \( x \) direction by a low vibration, UHV compatible piezo translation stage with solid state hinges. In order to minimize vibrations, the whole setup is sitting on an optical table and the turbo pumps are mechanically decoupled from the vacuum chamber by using damping bellows. Additionally, to minimize thermal drifts, the three gratings are mounted on a single steel bar connected to the chamber by only 12 contact points with less than 1 mm\(^2\) contact area for each point. Typical molecular interferograms are shown in Fig. 4.

The Talbot-Lau interferometer is now complemented by two electrodes which create a constant force field \( F_z = \alpha (E V) E_z\), perpendicular to both the directions of the molecular beam and the grating slits (Fig. 2). The experimental geometry is chosen such that an applied voltage of 5 kV will yield \( F_z/\alpha = (3.84\pm0.02) \times 10^{13} \text{ V}^2\text{ m}^{-3} \), which varies by not more than 1% over the entire cross section of the porphyrin beam.

The interaction between the external electric field and the polarizability then leads to an interference fringe shift

\[
\Delta \phi_z = \frac{\alpha}{m} \left( \frac{d}{2} + K \right),
\]

where \( m \) is the molecular mass, \( v_y \) is the longitudinal beam velocity, and \( d = (4.73\pm0.1) \text{ cm} \) and \( K = (27\pm1) \text{ cm} \) are the characteristic dimensions of our TLD, as indicated in Fig. 2.

All interference experiments are done using the same source and detector as in the sublimation studies. However, the final flux in the deflection experiments is smaller because of the longer flight path, the filtering by three gratings—required for coherence preparation, diffraction, and detection—and the velocity selection. The Fe(TPP)Cl measurements were therefore recorded on the clearly identified mass peak at 668 amu, which showed a much stronger signal than the parent peak.

We first select a given velocity band (for details see Ref. 13), namely, \( \bar{v} = 222 \text{ m/s}, \Delta v/v = 22\% \) for H\(_2\)TPP and \( \bar{v} = 180 \text{ m/s}, \Delta v/v = 16\% \) for Fe(TPP)Cl. Each interference curve is then recorded by shifting the third grating in steps of several 10 nm and by measuring the number of passing molecules at each of these steps. We vary the deflection voltage \( U \) for each grating position, within the interval of 0–15 kV for H\(_2\)TPP and between \( U = 0 \) and 13 kV for Fe(TPP)Cl.

Two typical interference curves—with and without applied deflection voltage—are shown in Fig. 4 for both H\(_2\)TPP and Fe(TPP)Cl. The data are fitted by the expected sinusoidal fringe shape, and they also include a linear term to take into account an overall decrease of the signal with time.

The curves show a slightly larger period than expected. The stretching factor is, however, consistent with the known thermal drift of about 2–3 nm/min, which has already been observed in earlier experiments in this machine. The influence of this drift on the polarizability measurements is strongly reduced by recording the curve shift for all deflection voltages in a row before moving the grating to the next step of the interference curve.

In Fig. 5 we plot the observed interference fringe shift as a function of the applied voltage. A quadratic fit to these data then yields the experimental polarizability, according to Eq. (6). The results are presented in Table II together with the theoretical values that we compute in Sec. V.

The error bar on \( \alpha \) includes the uncertainties of the electric deflection field, the velocity distribution, the geometrical factors \( (L,d,K) \), as well as the isotopic mass distribution. It turns out that the electric field and the experimental geometry are still the main factors in the present setup and amount to a systematic error of \( \Delta \alpha/\alpha \sim 6\% \). The other errors are
related to the accuracy of the high voltage measurement (0.5%), the knowledge of the mean velocity (1%), and the fit to the interference fringe visibility (3%).

The interference contrast also depends on the spread of the velocity distribution. Slow molecules will acquire a larger deflection than fast ones. Therefore, a broad velocity distribution causes a dephasing which reduces the contrast at high voltages. We therefore limit the maximum voltage to $U = 15$ kV, where the fringe shift can still be read reliably.

In Fig. 6 we show the clear influence of this voltage dependent dephasing on the fringe visibility for both H$_2$TPP and Fe(TPP)Cl. The decay behavior is obviously different. The polarizabilities of both species are measured and computed to be nearly identical. However, the velocity distributions in both experiments were different. The velocity spread of Fe(TPP)Cl was somewhat smaller (16%) than that of H$_2$TPP (22%), and Fe(TPP)Cl was also 25% slower than the lighter porphyrin derivative. The quadratic dependence of the fringe shift with $v_y$ explains already most of the observed difference.

At the prevailing temperature of 650 K, all molecules are in highly excited rotational states and enter the interferometer with a randomly oriented principal rotation axis. Depending on the internal molecular temperature, the force of the electric field gradient on the dipole moments may therefore broaden the molecular beam in both horizontal directions and thus blur the interference pattern additionally. But better resolved velocities are required (and possible) in the future to allow a distinction of the different effects related to the dipole moment and the polarizability from the reduction of the interference contrast.

### V. FINITE TEMPERATURE AB INITIO POLARIZABILITY CALCULATIONS

In general the molecular polarizability may strongly vary with the molecular conformation, as has been shown, in particular, for polypeptides. It is therefore important to compute the structural form and corresponding polarizability of the porphyrins for realistic temperatures in our experiments.

We have carried out Car-Parrinello molecular dynamics simulations$^{26-28}$ of H$_2$TPP at 650 K in an orthorhombic periodic unit cell of size $22 \times 22 \times 18$ Å$^3$ using a time step of 4 a.u. and a fictitious electron mass of 400 a.u. The electronic structure was described by density functional theory using the PBE exchange-correlation functional$^{29}$ with a plane-wave basis set truncated at 25 Ry in conjunction with Vanderbilt ultrasoft pseudopotentials. The temperature was controlled using a Nosé-Hoover chain thermostat$^{31-33}$ for each degree of freedom.

For ten structures picked at random from the trajectory (one every 0.5 ps), the polarizability was calculated using two different protocols. Using the variational density functional perturbation theory approach$^{34,35}$ implemented in the CPMD package,$^{26}$ the polarizability tensor was calculated in a large periodic box of size $24 \times 24 \times 20$ Å$^3$.

In order to be able to exploit this feature of CPMD, we switched to the BLYP functional$^{36,37}$ norm-conserving pseudopotentials of the Troullier-Martins type$^{38}$ and a plane-wave cutoff of 70 Ry. The resulting thermally averaged polarizability is $(117.5 \pm 2.5)$ Å$^3$. In a second series of calculations, the thermally averaged polarizability was computed to be $(112.4 \pm 2.4)$ Å$^3$ with the GAUSSIAN package$^{39}$ using the

### TABLE II. Comparison of experimental and computed polarizability values.

The experimental uncertainties include statistical and systematic uncertainties, respectively. The theoretical polarizabilities were calculated by ab initio methods as described in the text. For H$_2$TPP we give a thermal average of the polarizability, corresponding to a temperature of 650 K, and the standard deviation between various thermally accessible molecular configurations.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Formula</th>
<th>Mass (amu)</th>
<th>$\alpha_{exp}$(Å$^3$)</th>
<th>$\alpha_{calc}$(Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$TPP</td>
<td>C$<em>{44}$H$</em>{28}$N$_4$</td>
<td>614</td>
<td>105±4±6</td>
<td>112.4±2.4</td>
</tr>
<tr>
<td>Fe(TPP)Cl</td>
<td>C$<em>{46}$H$</em>{26}$ClFeN$_4$</td>
<td>704</td>
<td>102±9±6</td>
<td>113.4</td>
</tr>
</tbody>
</table>

FIG. 5. Interference fringe shift as a function of voltage for (a) H$_2$TPP and (b) Fe(TPP)Cl. The experimental data are shown as full circles. The error bars represent the statistical uncertainty of fits to interference curves, such as shown in Fig. 4. The solid lines represent a quadratic fit to the data weighted by the uncertainty bars.

FIG. 6. Reduction of the interference fringe visibility as a function of the applied deflection voltage. At finite spread of the longitudinal velocity $\Delta v_y = 10\% - 20\%$, the interaction between the polarizability and the external field gradient leads to a spreading of the interferograms, according to Eq. (6), and therefore to a reduced fringe contrast. H$_2$TPP (full circles) shows a weaker dephasing than Fe(TPP)Cl (full triangles) mainly because of its higher initial velocity. The solid lines represent a quadratic and a linear fit to guide the eyes.
same ten structures, the same functional (BLYP), and the 6-31+G* basis set. It is interesting to note that for the optimized structure we obtain a value of 116.5 Å³ with CPMD and 111.4 Å³ with GAUSSIAN.

We conclude that the effect of thermal fluctuations on the polarizability is comparatively minor, even at such elevated temperatures. We therefore calculated only the polarizability of an optimized structure for the case of Fe(TPP)Cl. For the geometry optimization, we used spin-unrestricted DFT, assuming a multiplicity of 6, with the BLYP functional and the 6-31G* basis set. The polarizability was computed using the 6-31+G* basis set yielding a value of 113.4 Å³. This calculation also predicts the dipole moment of Fe(TPP)Cl to be 2.7 D, while it vanishes for H₂TPP.

VI. CONCLUSION

We have successfully used near-field Talbot-Lau interferometry for determining the scalar polarizability of two porphyrin derivatives for the first time. Our experimental results are in good agreement with our ab initio calculations. The experimental accuracy is presently limited to a few percent, given by the finite knowledge of the electric field distribution and the molecular velocity distribution.

Earlier experiments using far-field Mach-Zehnder interferometry reached even an accuracy of better than one permille for the polarizability of neutral sodium atoms. But such an instrument is not scalable to large masses and small de Broglie wavelengths.

In contrast to that, the Talbot-Lau deflectometer presented here has the advantage of being scalable to higher masses while preserving a high transmission and high spatial resolution. The accuracy can be improved in future experiments: Calibrating the field and all geometric factors with atoms of known polarizability, such as cesium, sodium, or lithium, will improve the field values to better than 1%.

The velocity resolution can also be improved by more than a factor of 10 in the future, for instance, by changing from effusive beams for small biomolecules to pulsed laser desorption and pulsed photoionization detection as typically used for larger polypeptides. Since the molecular velocity enters quadratically into the molecular beam shift, the increased resolution of Δν/ν < 1% will be very important in future experiments, in particular, for discriminating the effects of polarizability from that of the static permanent electric dipole moment. At such a high ν resolution, nonpolar molecules are expected to show a flat curve in a visibility-versus-voltage diagram, whereas polar molecules would still show a loss of interference contrast. Improving Δν also has the additional advantage that higher deflection voltages can still be used and larger shifts may be reached. Future improved experiments with an absolute accuracy of 1% will thus be important for validating competing numerical models for complex molecular systems.

ACKNOWLEDGMENTS

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