Mass Spectrometry

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The Wave Property of Heavy Molecules—Its Use in Mass Spectrometry

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Atoms, molecules, or whole solid-state bodies are not as rigid as many believe. Their quantum mechanical description as oscillators is not just a mathematical tool—it actually reflects physical reality. An impressive manifestation is the fact that a copper surface, when encircled by a ring (corral) of 48 iron atoms, clearly shows wave properties (Figure 1).[1]

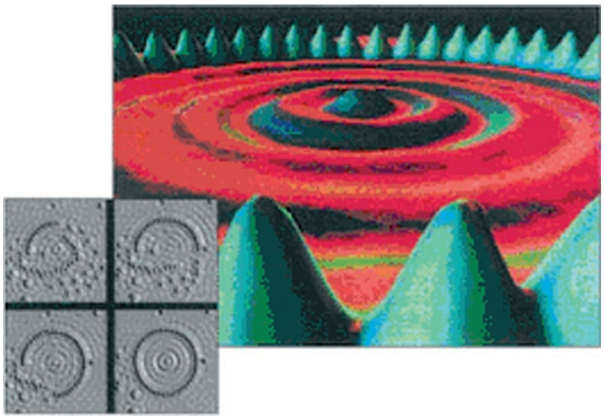

Figure 1. The wave properties of matter. A ring (quantum corral) of 48 iron atoms is built with a nanocantilever on a copper(111) surface, which reveals clear wave properties. The black and white images were obtained by a scanning tunnel microscope. The color picture is a graphical representation of this wave behavior. Reproduced from Ref. [1].

Wave properties have not only been found for atoms, but also, for example, for C_{60} fullerenes in a type of double-slit experiment.[2,3] Surprisingly, this property is not just a quantum mechanical curiosity, but has found a quite practical application in the mass spectrometric analysis of a perfluoroalkylated palladium complex.[4] The use of the wave properties of molecules is particularly useful when only fragments of a given molecule, but not the intact molecule, are found in the mass spectrum. In conventional mass spectrometry it is often not clear whether the fragmentation has occurred during preparation of the molecular beam or at a later stage, for example, after mass determination, when the molecule is ionized for subsequent detection in an ion counter.

The (de Broglie) wavelength of any object with mass m is given by Equation (1), where h is the Planck constant and v and m its velocity and mass, respectively. A consequence of the de Broglie wave property is that atoms or molecules can be diffracted when they pass through a grating. In practice it is difficult to generate such a grating, since typical de Broglie wavelengths of heavy molecules are in the picometer range.

$$\lambda = h/(v\,m) \qquad (1)$$

There is, however, a way round this dilemma: near-field diffraction. This property is achieved in the Talbot–Lau interferometer (TLI), which consists essentially of a combination of three identical gratings. In such a near-field interferometer, grating constants of a few hundred nanometres (here 266 nm) can be used to measure de Broglie wave properties in the picometer range. Such an interferometer can be positioned in a molecular beam to reveal the wave properties of the corresponding molecules. However, the range of de Broglie wavelengths which can be measured with a set of three micromachined gratings is very narrow.

A modification is required: the second grating is not a micromachined one but a grating of light made by generating a standing light wave with a period of 266 nm by using a laser with a working wavelength of 532 nm. The standing wave represents a periodic potential which acts as a diffraction grating on polarizable molecules. The underlying physics is called the Kapitza–Dirac effect; thus, the full name of the whole system is a Kapitza-Dirac-Talbot-Lau interferometer.[5] The light grating imposes a phase shift $\Phi_{\max}$ on the de Broglie matter wave [Eq. (2); α_L: polarizability of the molecules, P: power of the laser which generates the light grating, v_z: velocity of the molecules through the interferometer]. Knowledge of the value of $\Phi_{\max}$ would give information on the molecular properties α_L and v_z, both of which are related to the molecular weight. Unfortunately, the phase $\Phi_{\max}$ cannot be measured directly. It can, however, similar as in phase-contrast microscopy, be converted into an intensity fluctuation which varies periodically with the distance L between the second (the one made of light) and the third (micromachined) grating. The signal intensity S follows a quite complex law (the phase-space theory of the Talbot–Lau

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interferometer). In the not too rare cases where the absorption is weak, this law can be simplified to Equation (3).

$$\Phi_{\max} \approx \alpha_L P/v_z \tag{2}$$

$$S \approx (1-\Phi_{\max} \sin L) J_2(P) \tag{3}$$

Here, J_2 is a Bessel function. In contrast to far-field diffraction experiments,[6] the fringe spacing in Talbot–Lau interferometry, which is, essentially the wavelength L of the sinus, is predetermined by the experimental setting and does not reveal information on the mass of the molecule. However, the fringe visibility (contrast), calculated from the minima and maxima of the sinus function through $(S_{\max}-S_{\min})/(S_{\max}+S_{\min})$ gives information regarding the mass and polarizability. The visibility can be determined from a plot of S versus L (Figure 2, top). A subsequent plot of visibility versus the power of the laser for grating G2, (Figure 2, bottom) gives the desired information on the molecule.

This approach has been used in the study reported in Ref. [4] to analyze the perfluoroalkylated palladium complex [$PdC_{96}H_{48}Cl_2F_{102}P_2$] (3378.5 amu). The top part of Figure 2 shows the sinusoidal dependence of the visibility on the position of the mechanical grating G3. The bottom part of Figure 2 gives the theoretical dependence of the visibility on the laser power of the light grating G2 for three cases: a) classical calculation assuming that the molecules are hard balls with $m = 1600$ amu and $\alpha_L = 66$ Å^3; b) calculation using the phase-space theory of the Talbot–Lau interferometer for 3378.5 amu and $\alpha_L = 132$ A^3. Neither calculation fits the experimental data. In contrast, a good fit is obtained with 1601 amu and $\alpha_L = 66$ A^3, curve c). The mass corresponds to {$C_{48}H_{24}F_{51}P$}, a fragment of the original molecule. This mass of 1601 amu has also been observed by conventional mass spectrometry, but in this case it could not be determined where in the experiment the fragmentation occurred. In the matter-wave mass spectrometer it is clear that the molecule is fragmented early in the preparation of the molecular beam, before it enters the interferometer and not during ionization after passing through the mass separator.

This study is exciting for two reasons: First it extends the analytical power of mass spectrometry. The second reason is that it brings the wave property of matter, which for many may still appear to be rather in the realm of philosophy, very close to true application in chemistry. A commercial (de Broglie) matter-wave mass spectrometer is now readily conceivable.

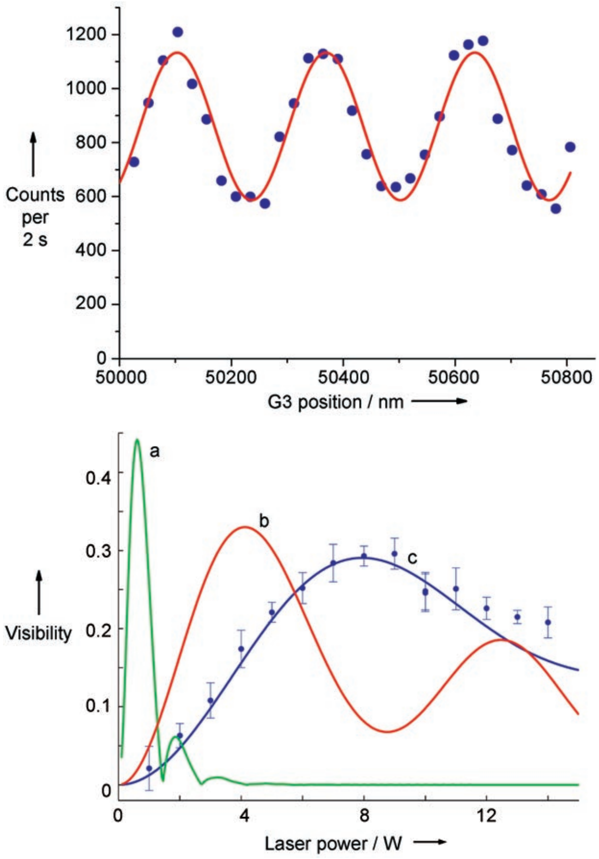

Figure 2. Top: Intensity S (count rate) as a function of the distance L between gratings G2 and G3 of the three-grating interferometer. The axis for the G3 position spans only 800 nm. The visibility can be determined from the minima and maxima. Bottom: Visibility as a function of the power P of the laser for grating G2. Curve (a), which treats the molecules as hard balls, is far from experimental reality. Only curve (c), calculated for $C_{48}H_{24}F_{51}P$ as a de Broglie wave, fits the experimental data.

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[1] D. Eigler, IBM http://www.almaden.ibm.com/vis/stm/stm.htm. Print version: R. F. Service, *Science* **2000**, *290*, 1524–1531. Original paper: M. F. Crommie, C. P. Lutz, D. M. Eigler, *Science* **1993**, *262*, 218–220.

[2] M. Arndt, O. Nairz, J. Vos-Andrae, C. Keller, G. van de Zouw, A. Zeilinger, *Nature* **1999**, *401*, 680.

[3] K. O. Greulich, *Angew. Chem.* **2000**, *112*, 4412–4414; *Angew. Chem. Int. Ed.* **2000**, *39*, 4242–4244.

[4] S. Gerlich, M. Gring, H. Ulbricht, K. Hornberger, J. Tüxen, M. Mayor, M. Arndt, *Angew. Chem.* **2008**, *120*, 6290–6293; *Angew. Chem. Int. Ed.* **2008**, *47*, 6195–6198.

[5] S. Gerlich, L. Hackermüller, K. Hornberger, A. Stibor, H. Ulbricht, M. Gring, F. Goldfarb, T. Savas, M. Müri, M. Mayor, M. Arndt, *Nat. Phys.* **2007**, *3*, 711–715.

[6] R. Antoine, P. Dugourd, D. Rayane, E. Benichou, M. Broyer, F. Chandezon, C. Guet, *J. Chem. Phys.* **1999**, *110*, 9771–9772.