Figure 3 Contingency map. Every laser shot is recorded in this plot according to the number of electrons measured in the left (channel A) and the right (channel B) arm of the electron spectrometer. In the colour code, the pixel colours represent the number of laser shots with electron numbers given by the coordinates of the pixel. The signature of the absolute phase is an anticorrelation in the number of electrons recorded with the left and the right detector. In the contingency map they appear as features inclined at −45°.

The absolute phase is an anticorrelation in the number of electrons recorded with the left and the right detector. In the contingency map they appear as features inclined at −45°. Shown here (main figure) is a typical measurement with krypton atoms for circular laser polarization, a pulse duration of 6 fs, and an intensity of 5x10^13 W cm⁻². The data were taken over 200,000 laser shots, corresponding to a measuring time of 200 s. On average, each laser shot led to the recording of approximately 5 electrons in each arm of the spectrometer. Inset, the corresponding measurement for slightly longer pulses, showing no indication of anticorrelation.

expected because of the inevitable laser pulse fluctuations, as described above. In the light of this, the anticorrelation observed is a rather strong effect.

This is, to our knowledge, the first unambiguous measurement of an effect stemming from the absolute phase of an ultrashort pulse, and we believe that the method presented here is important for its potential applications. These include detailed investigations of the influence of the absolute phase on strong-field ionization. The close relationship of ATI and coherent soft-X-ray generation (high-harmonic generation) will also make such investigations instrumental in understanding absolute-phase effects in high-harmonic generation. One way to investigate ATI in detail is to measure the strength of the anticorrelation as a function of the photoelectron's kinetic energy, the laser intensity, and so on. The strength of the anticorrelation can also serve as a measure of the pulse duration, which is useful because such measurements become increasingly difficult for shorter and shorter pulses when conventional methods are used. Finally, with suitable refinements, our stereo ATI apparatus could be used to measure the absolute phase. The measured value could then be used to interpret other experiments, such as the generation of coherent soft X-rays, generation of isolated attosecond laser pulses, or coherent control of chemical reactions.
light sources (free-electron lasers) these ‘photon sieves’ offer new opportunities for high-resolution X-ray microscopy and spectroscopy in physical and life sciences.

A variety of optical devices have been developed to focus X-ray radiation, ranging from X-ray mirrors to concentrators in the form of tapered capillaries, compound refractive lenses and Fresnel zone plates. The most severe limitation in using refracting optics for focusing electromagnetic radiation arises from absorption. The visible spectral region has a large number of optical materials available for fabricating lenses. At shorter wavelengths all solids are strongly absorbing until the hard X-ray region (10–50 keV). Recently, compound refractive lenses for use with hard X-rays have been fabricated—consisting of tens or hundreds of small holes, or hollow spheres, arranged in arrays to achieve focusing in one or two dimensions. In the vacuum ultraviolet (VUV) and extreme ultraviolet (XUV) regime (10–1 keV) strong absorption rules out this technique but Fresnel zone plates provide an effective solution. Nevertheless, improvements are desirable in three areas: (1) overcoming the limitation in the spatial resolution given by the width of the zone-plate outermost zone; (2) elimination of unwanted diffraction orders; (3) reduction of the scattered intensity arising from the edge of the finite-sized zone plate.

Here we demonstrate that an appropriate distribution of pinholes over the Fresnel zones (a photon sieve) can be used to focus soft X-rays effectively. In contrast to conventional zone-plate optics, a sharpening of the focal spot combined with an effective suppression of higher orders and finite-size effects is achieved by exploiting variations in pinhole diameter and pinhole distribution to optimize the optical performance.

In the standard optical configuration shown in Fig. 1, a photon sieve with a quasi-random distribution of transmissive pinholes (white) replaces a comparable conventional zone plate which consists of transmissive (grey) and opaque (black) rings. Designing a photon sieve with a given smallest pinhole diameter \( d_{\text{min}} \) is simple. We consider point-to-point focusing of a source at finite distance \( p \) from a photon sieve to a focus at distance \( q \). For simplicity, the source and image are on the optical axis (in general, however, photon sieves can be constructed where the source or image point, or both, are off-axis). To obtain a distinct first-order focus, the pinholes have to be positioned such that the optical path length from the source via the centre of the pinholes to the focal point is an integral number of wavelengths \( \lambda \). Consequently, the pinholes have to be centred at distances \( r_n \) from the optical axis given by:

\[
\sqrt{r_n^2 + p^2} = \sqrt{r_n^2 + q^2} = p + q + n\lambda
\]

where \( \lambda \) is the wavelength of the radiation and \( n \) a positive integer. By choosing random numbers for \( n \) and \( \varphi (0 < \varphi \leq 2\pi) \), an uncorrelated distribution of pinholes with centres at \( (r_n, \varphi) \) can be generated. A useful feature of our diffraction optics is that aberrations can be corrected by modifying both the positions of the pinholes and their distribution.

Next we discuss how to choose the diameters of the pinholes. The trivial case is for pinholes of diameter \( d < w \) centred on a white (constructive interference) zone of width \( w \) (Fig. 2a). Light from all parts of the pinhole interferes constructively at the focus. Pinholes with diameters larger than the width of the underlying zone can also be used (Fig. 2b). Such holes transmit contributions that partially compensate—indicated by the black and white areas. As long as the white areas dominate there is a net positive contribution to the focus. If the black contributions were to predominate (Fig. 2c) the pinhole just needs to be centred on a black zone (Fig. 2d) instead of a white zone (Fig. 2c) to produce again a positive contribution to the focus.

We calculate the light amplitude at \( P \) (see Fig. 1) using Fresnel–Kirchhoff diffraction theory

\[
E(P) = -\frac{iA}{2\lambda} \int \frac{e^{i(l+i)\varphi}}{rs} (\cos \theta_i + \cos \theta_s) dS
\]

where \( A \) is the amplitude at unit distance from the source and the integral is performed over the pinholes.

Calculated contributions to the focal amplitude of a single pinhole as a function of \( dw \) are plotted in Fig. 2. Contributions from the white (constructive) and black (destructive) parts are calculated separately. Considering first only the white regions, we observe for small pinhole diameters \( d < w \) a quadratic increase of constructive contributions to the focal amplitude until the pinhole diameter equals the width \( w \) of the underlying transmissive Fresnel zone (A in Fig. 2). For larger \( d \) the white area in the \( y \) direction increases essentially linearly (see arrows in B in Fig. 2 inset), but for \( d > 3w \) the increase is nominally quadratic because the white area also

![Figure 1](https://example.com/figure1.png)

**Figure 1** Diagram showing point-to-point imaging with a diffractive optical element. The details are described in the text.

![Figure 2](https://example.com/figure2.png)

**Figure 2** Examples of photon sieve pinholes together with the underlying zone-plate geometry and the contributions of a single pinhole to the focal amplitude. Constructive and destructive interference contributions from ‘white’ and ‘black’ areas inside the pinhole are plotted as solid and dashed grey curves, respectively. The total amplitude at the focus from a single pinhole of diameter \( d \) centred on a transmissive zone (A, B, C) of width \( w \) is given by the solid black curve; the total contribution to the amplitude at the focus from a pinhole centred on an opaque zone (D) is given by the dotted black curve.
increases in the $x$ direction (C in Fig. 2). The constructive contribution to the focal amplitude is indicated by the solid grey curve.

Competing with the increasing constructive contribution (white areas) is an increase of destructive contributions (black areas within the pinhole) as indicated by the dashed grey curve in Fig. 2. For $d < w$ this contribution is zero; it then increases quadratically up to $d = 3w$, linearly to $d = 5w$, and so on.

The resulting oscillating total contribution to the focal amplitude is given by the solid black curve. Constructive and destructive contributions compensate at $d/w$ values of about 2.4, 4.4, 6.4, and so on. The largest focal amplitudes from a single pinhole are for pinhole diameters $d$ of about 1.5w, 3.5w, 5.5w, and so on (corresponding to 1st, 3rd, 5th, ... order of diffraction at the focus). The sign of the focal amplitude is reversed when pinholes are centred on opaque zones instead of transmissive zones, so pinholes with diameters around 3.5w, 7.5w, and so on, should be centred on an opaque zone to give positive contributions to the focal amplitude (D in Fig. 2). Combining pinholes corresponding to different maxima allows mixed-order photon sieves to be constructed in analogy with composite zone plates which also use combined orders of diffraction.

The ultimate spatial resolution $\Delta x$ of a conventional zone plate is limited by the width $w_{\text{min}}$ of the outermost zone: $\Delta x \approx w_{\text{min}}$ (first order of diffraction); when working in higher orders of diffraction $m$ (odd) smaller spots ($\sim 1/m$) with reduced intensity ($\sim 1/m^2$) can also be achieved. For a photon sieve, however, even in the first order of diffraction the spatial resolution can be smaller than the smallest pinhole diameter $d_{\text{min}}$. In fact, it is limited by the width of the outermost zone of the underlying zone plate geometry. This effective smallest width $w_{\text{eff}}$ depends on the maximum $d/w$ ratio employed:

$$\Delta x \approx w_{\text{eff}} = d_{\text{min}}/\langle d/w \rangle_{\text{max}}$$

Calculated spot sizes for a zone plate (dotted curves) and photon sieves (solid and dashed curves) are shown in Fig. 3a. For all three diffractive optical elements the smallest structure size is 30 nm.

Focal spot sizes (full-width at half-maximum, FWHM) are 32 nm for the zone plate (in first order) and 18 nm and 6 nm for the photon sieves with $(d/w)_{\text{max}} = 2.4$ (in first order) and $(d/w)_{\text{max}} = 7.5$ (in 1st + 3rd + 5th + 7th order), respectively. The highest spatial resolution achievable with photon sieves is limited by the accuracy in positioning the centre of a pinhole on the corresponding zone. With today’s fabrication procedures an accuracy of 2 nm can be achieved, which is sufficient to place 30 nm pinholes on a 6 nm effective zone.

It should be noted that to achieve a potentially better spatial resolution of mixed-order photon sieves or composite zone plates a bandwidth of the light source $\Delta \lambda / \lambda < 10^{-4}$ is required. Photon sieves with pinhole diameters $d < 2.4w$, however, which already increase the spatial resolution to $\Delta x = d_{\text{min}}/2.4$ exclusively employ first-order diffraction and do not need a high degree of monochromaticity.

In addition to the principal focus, zone plates also produce ring-shaped secondary maxima that decrease the signal-to-noise ratio and blur the images. This phenomenon is analogous to the production of side bands in a digital filter with a rectangular transmission window. Optimized window functions are routinely used in digital filtering. By adapting this concept, we have implemented a Weber-type transmission window by modulating the pinhole density on each ring of the photon sieve. In this way, as shown in Fig. 3a, we can achieve a substantial suppression of the secondary maxima. A similar concept (for example, adjusting the mark-to-space ratio) could be implemented for zone plates.

Higher-order diffraction occurs when the diffractive optical element has the appropriate symmetry. The higher (odd) orders along the optical axis of a Fresnel zone plate are well known (Fig. 3b, dotted line). With a photon sieve (Fig. 3b, solid line) such higher-order contributions can be efficiently reduced by the random distribution of the pinholes on each zone.

A direct comparison of focal intensities of photon sieves and zone plates is difficult because of the possibility of using higher-order diffraction and transmission windows, for example. To give a basic idea, we compare first-order diffractive optics of equal diameter. A zone plate has a transmission of 50% whereas a photon sieve
transmits only 15–20% of the incident light. The intensity scales as the square of the area, so the first-order diffraction intensity is lower than that of a zone plate of equal diameter by a factor of 10. However, despite this lower intensity, experimentation with photon sieves is possible on acceptable timescales with present-day synchrotron light sources.

For an experimental verification of the above results we have constructed a photon sieve and a zone plate with a minimum structure size of 100 μm working in the optical region at 632.8 nm wavelength (He–Ne laser). The diffraction optics depicted in Fig. 4a and b were printed with 4,000 lines on 35-mm slides. The transmission windows used are plotted in Fig. 4c and d. The smallest structure sizes in both cases are 100 μm (λ = 632.8 nm (He–Ne laser), p = 20 μm, q = 1 μm).

Figure 4 Optical prototypes for a photon sieve and a zone plate together with experimental and calculated intensity distributions. a, Photon sieve (5,646 pinholes, (d/w)max = 4) with Weber-type transmission window (c). b, Zone plate with rectangular transmission window (d). The smallest structure sizes in both cases are 100 μm.

Photon sieves can be produced using techniques similar to those for making zone plates. The limitations of conventional zone plates can be overcome by using pinholes with varying diameters instead of concentric rings as the basic diffracting elements. This generalization enables the development of a new class of diffractive optical elements with additional design parameters that can result in unprecedented focusing of electromagnetic radiation to spot sizes well below the dimensions of the smallest diffracting structure. The development of fourth-generation synchrotron light sources (free-electron lasers) that deliver transversally coherent radiation in the soft X-ray regime in combination with photon sieves will provide a wealth of new opportunities in X-ray microscopy, spectroscopy and lithography. Photon sieves for use at the Hamburg Free-Electron Laser facility (HASYLAB)/DESY synchrotrons are being developed.

Received 30 May; accepted 4 September 2001.

We designed a short 12 uncapped, single-walled nanotube 13.4 Å long with a diameter of 8.1 Å, and simulated for 66 ns the dynamics of this nanotube solvated in a water reservoir. Despite its strongly hydrophobic character, the initially empty central channel of the nanotube is rapidly filled by water from the surrounding reservoir, and remains occupied by about five water molecules during the entire 66 ns (Fig. 1a). These water molecules form a hydro-bonded chain (Fig. 1c). The number of water molecules, $N$, fluctuates between 2 and 7, with $N = 2$ occurring only once in 66 ns (Figs 1a and 2a). The radial and axial density profiles of the water in the nanotube show considerable structure and density depletion at the nanotube openings (Figs 1a and 2a).

Water molecules entering the nanotube lose on average two out of four hydrogen bonds. Only a fraction of the lost energy ($\sim 10\text{ kcal mol}^{-1}$) can be recovered through van der Waals interactions with the carbon atoms of the nanotube ($\sim 4\text{ kcal mol}^{-1}$), while electrostatic interactions with water molecules beyond the nanotube wall are found to be negligible. Considering this loss of hydrogen bonding, and the weak attraction of water to the nanotube carbon atoms, with a Lennard–Jones well depth of only about 0.114 kcal mol$^{-1}$, this persistent hydration of the nanotube interior seems surprising, but is consistent with the experimentally inferred adsorption of water onto nanotubes$^{12}$. Further support comes from recent simulations$^{14}$ showing that a potassium iodide melt would be sucked into carbon nanotubes to form nano-crystallites, despite favourable solvation in the surrounding liquid.

The water occupancy of the channel is determined by the local excess chemical potential, $\mu_{\text{ex}}$, defined as the negative free energy of removing a water molecule from the channel. This free energy is dominated not by how strongly bound a water molecule is on average, but by how populated weakly bound states are (see Methods, equation (2)). The average binding

![Figure 1](image-url)