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Widely tuneable scattering-type scanning near-field optical microscopy using pulsed quantum cascade lasers

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We demonstrate the use of a pulsed quantum cascade laser, wavelength tuneable between 6 and 10 μm , with a scattering-type scanning near-field optical microscope (s-SNOM). A simple method for calculating the signal-to-noise ratio (SNR) of the s-SNOM measurement is presented. For pulsed lasers, the SNR is shown to be highly dependent on the degree of synchronization between the laser pulse and the sampling circuitry; in measurements on a gold sample, the SNR is 26 with good synchronization and less than 1 without. Simulations and experimental s-SNOM images, with a resolution of 100 nm, corresponding to $\lambda/80$, and an acquisition time of less than 90 s, are presented as proof of concept. They show the change in the field profile of plasmon-resonant broadband antennas when they are excited with wavelengths of 7.9 and 9.5 μm . © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4832859>]

Scattering-type scanning near-field optical microscopy (s-SNOM) has proven itself to be a valuable tool for non-invasive nanoscale imaging. A wide variety of applications have been demonstrated, ranging from mapping plasmonic resonances to chemical spectroscopy.^{1–8} In an s-SNOM measurement, laser light is focused on to the apex of a very sharp metallic tip (typically of radius ~ 10 nm). Depending on the polarization of this incident light, different sample properties can be measured. If the incident radiation is p-polarised, the probe is sensitive to changes in the dielectric constant of the surface beneath.⁹ If the sample can support localized surface plasmons, s-polarised light can be used to excite the plasmon and measure its field distribution without being sensitive to any changes in chemical contrast, as shown in Figure 1.^{10–17} In both cases, changes in the amplitude and phase of the back-scattered light are measured by an interferometric detection scheme and formed into an image.

If s-SNOM is to be effective in performing nanoscale spectroscopy, its light source should be able to scan through the “chemical fingerprint” region—i.e., mid-infrared (mid-IR) wavelengths spanning approximately a 5 to 10 μm range, where molecular bonds typically have their vibronic absorption peaks. Several groups have recently adapted s-SNOM for use with broadband sources (often referred to as nano-FTIR), where a full mid-IR spectrum is gathered at each pixel,^{18–21} but image acquisition times are long. If single wavelength sources are to be viable for spectroscopy, therefore, they must provide comparable tuneability, so that the wavelength can be altered sufficiently to gather useful chemical information.

The most recently commercialised quantum cascade lasers (QCLs) are ideal candidates for the tuneable approach;

they are compact, turn-key devices that can scan through wavelength ranges of several microns when arranged in an external cavity configuration.^{22,23} However, the majority of the current generation of QCLs operate pulsed, rather than continuous wave (CW). If unaccounted for, this can add a substantial amount of digitization noise to a measurement. Here, we address the digitization issue and implement an s-SNOM based on a tuneable pulsed QCL laser. The technique is tested by imaging the wavelength-dependent localised plasmon electric field distribution of a broadband log-periodic nanoantenna.^{24,25}

A commonly used detection scheme for s-SNOM is the pseudo-heterodyne method (Figure 2).²⁶ Similar to optical heterodyning,¹ it exploits the square law properties of light detectors, to multiply the backscattered light from the probe,

FIG. 1. In s-SNOM measurements of plasmonic samples, s-polarised light is focused onto the sample to excite a plasmon resonance. The tip is a particularly strong scatterer for the out-of-plane component of the plasmon's electric fields. Using this “cross-polarization scheme” to measure just the p-polarised component of the scattered light therefore maps the E_z component of the plasmon resonance.

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FIG. 2. Example of the pseudo-heterodyne detection system, employing a cross-polarization scheme. S-polarised light from a laser is passed through a beam splitter. The illuminating beam is passed to the probe (vibrating at frequency ω) and excites the plasmon modes, the E_z field of which is strongly scattered by the tip. The second path to the vibrating mirror (which oscillates at frequency Ω where $\omega \gg \Omega$) uses a 45° polarizer to create a p-polarised component in the reference beam. After recombination of the two beams at the beamsplitter, this p-polarised reference beam component interferes with the signal beam scattered from the probe. A vertical polarizer is used to ensure that no s-polarised light—which carries no useful signal—can reach the detector.

by a much brighter beam (*the reference beam*). The reference beam is phase modulated at frequency Ω by a vibrating mirror. The backscattered light is also modulated (at frequency ω , where $\omega \gg \Omega$) by oscillating the probe vertically with an amplitude of approximately 30 nm. This backscattered light is made up of two components: *The signal*, I_{sig} , comprising the light that has been modified by the near-field interaction between the tip and the surface, and *the background*, I_{back} —light scattered from the probe and the sample that is unaffected by the interaction between the two. As the height of the oscillating probe increases, the signal strength, I_{sig} , rapidly decreases. This decrease occurs over length scales corresponding to the radius of the probe (typically 10 nm). The background, I_{back} , on the other hand, is only weakly affected by the probe oscillations, as its strength varies over probe height length scales that are much larger, i.e., of the order of the $\lambda \sim 10 \mu\text{m}$ wavelength.

To suppress the effect of the background, I_{back} , on the measurement, therefore, the voltage waveform from the detector is first Fourier transformed. Due to the phase modulation of the reference beam, the Fourier components at the harmonics of the probe oscillation frequency, ω , are split into sidebands separated by the mirror vibration frequency, Ω (Figure 3). As the signal, I_{sig} , is highly sensitive to the probe vibration, the sidebands around the higher harmonics of the probe oscillation frequency contain more of the signal, I_{sig} , relative to the background, I_{back} . The actual harmonic required to suppress the contribution of the background to a negligible level depends on the wavelength. In the mid-infrared, the second harmonic is usually sufficient, whereas in the visible or near-infrared, the third harmonic is typically necessary.²⁷

We use a cross-polarization scheme to image the near-field distribution of plasmon resonant samples without recording the chemical differences of the surface. In this

setup, s-polarised light is used to illuminate the tip and the sample. A simple way to visualise the scattering process is that this light excites the resonant in-plane plasmon modes in the sample, without itself significantly interacting with the probe (which is a very poor antenna to anything but light polarised perpendicularly to the surface). The excited plasmons then have a p-polarised component, which is subsequently scattered strongly by the tip into the far-field. In some cases, the actual scattering process is significantly complicated by the fact that the structure supporting the plasmons can also itself scatter light into the far-field. Whatever the scattering mechanism though, the overall scattering of the probe can be written as

$$E_{\text{out}} = \tau E_{\text{in}}, \quad (1)$$

where the complex scattering coefficient τ has a magnitude s and a phase ϕ . For measurements of plasmon resonant samples, the s-SNOM measured values of s_n and ϕ_n (where n is the measurement harmonic of the probe vibration frequency) correspond to the magnitude and phase of the E_z field of the

FIG. 3. Representation of a pseudo-heterodyne spectrum found by Fourier transforming the detector's voltage waveform. The amplitude and phase changes of the light scattered from the probe, oscillating at frequency ω , are deduced from the relationship between the amplitudes of the odd and even sidebands.

plasmon resonance. The values of s_n and ϕ_n can be inferred from the magnitude of the measured odd and even sidebands in Figure 3 using the following relationships:¹⁴

$$s_n = \sqrt{|c_{n\omega+\Omega}|^2 + |c_{n\omega+2\Omega}|^2}, \quad (2)$$

$$\phi_n = \tan^{-1} \frac{|c_{n\omega+\Omega}|}{|c_{n\omega+2\Omega}|}. \quad (3)$$

For any image taken with an s-SNOM, noise in the measurement will limit its sensitivity. Mechanical vibration, thermal fluctuations, and imperfect electronics all play a role, but for our setup, the biggest contribution arises from fluctuations in the intensity of the illuminating laser. The voltage waveform from a detector illuminated by such a noisy laser can be written as

$$V(t) = x(t) + y(t), \quad (4)$$

where $x(t)$ is the part of the voltage containing the signal (which may be time varying itself) and $y(t)$ is the noise. As s-SNOM measurements take place in the frequency domain, it is necessary to understand how $y(t)$ behaves after having been Fourier transformed. This can be done qualitatively with Parseval's theorem, which states that the total energy contained in a waveform integrated over time is the same as the energy contained in its Fourier components summed over all frequencies. Hence, the larger the variance of $y(t)$, the larger will be its Fourier components, $Y(f)$.

For the frequency range in which s-SNOM measurements are typically made (~ 100 – 1000 kHz), the distribution of the noise power is, to a good approximation, white. This means that the Fourier components of $y(t)$ are equal at all frequencies.

Taking into account Parseval's theorem and the assumption that the noise power is equally spread among all frequencies, it is clear that if the laser intensity noise $y(t)$ is large enough, then its Fourier components, $Y(f)$, can drown out the peaks and sidebands of the pseudo-heterodyne system (Figure 3), especially at the higher harmonics of the probe frequency where the overall signal strength, I_{sig} , is itself lower.

Our experimental setup is based on a union of two commercially available systems: An s-SNOM from Neaspec, Germany (*NeaSNOM*) and a pulsed QCL from Block Engineering, USA (*Lasertune*), the latter modified to accept external triggering of its laser pulses.

When considering a pulsed laser system in conjunction with s-SNOM, one must consider the Nyquist Limit at two different levels. To accurately replicate the laser pulses, the sampling frequency of the analogue-to-digital (ADC) circuitry must be at least twice that of the laser repetition rate f . This repetition rate must, in turn, be more than twice the probe vibration harmonic of interest, to be able to accurately replicate the signal at this frequency. In our system, the bandwidth is limited by the detector (Kolmar Technologies, *Model KLD-0.5-J1-3/10/DC*) at 2.5 MHz, so we chose a laser repetition rate of $f = 625$ kHz and a probe vibration frequency of $\omega \sim 75$ kHz.

In the mid-infrared, measuring at the second harmonic of the probe vibration frequency is sufficient to suppress the

unwanted background scattering, I_{back} , from the probe and sample, corresponding to a measurement frequency of approximately $2\omega \sim 150$ kHz. For this paper, we used gold coated tips from Budget Sensors (*Multi75GB-G*).

Our QCL can be triggered by its own internal clock or via an external signal. The duty cycle of its output—regardless of the triggering mechanism—is limited to a maximum of 5%. We chose to externally trigger the pulses at a frequency of 625 kHz. This means that the ADC sampling circuitry records many samples when the laser is off.

If the sampling and the laser pulses are not well synchronized, it is possible that the sampling will record a rising or falling edge (instead of the peak maximum), resulting in a randomly measured pulse height (Figure 4). The digitization of the detector voltage, therefore, is potentially a major source of “artificial” noise—this noise does not exist physically but is an artefact of the electronic waveform sampling process.

If the laser pulses and the digitization circuitry are properly synchronized, one can be sure that the sampling will fall on a peak maximum. In practice, we achieve this by triggering the laser with an integer multiple of the sampling frequency—in our case 4. This corresponds to a laser repetition rate of 625 kHz with a cycle length of ~ 1600 ns and a lasing period of ~ 80 ns.

Information for s-SNOM measurements is taken in frequency space. The signal-to-noise ratio (SNR) is, therefore, also defined in frequency space, given by

$$\text{SNR} = \frac{s_n}{\sigma}, \quad (5)$$

where s_n is the amplitude measurement at the n th harmonic, as given by Eq. (2) and σ is the standard error of this value. The source of this error is predominantly laser intensity noise. s_n can be replaced with ϕ_n for phase measurements. Conveniently, the standard error for the amplitude and phase measurements of Eqs. (2) and (3) is the same for all the individual sidebands $c_{n\omega+m\Omega}$

FIG. 4. An example of a pulse train measured at the detector when the laser is internally triggered (at 185 kHz) and therefore not synchronized with the ADC sampling circuit. The lack of synchronization between the laser pulses and the sampling leads to a recorded measurement with a very large apparent pulse-to-pulse variation. The inset box shows the detector waveform when the sampling and laser pulses are properly synchronized (at 625 kHz).

$$\sigma_s = \sigma_\phi = \sigma_c. \quad (6)$$

Therefore, if we assume that the noise is white, we can find σ by measuring the noise power at frequencies in between the sideband clusters in Figure 3, and the SNR can be readily calculated.

This principle is demonstrated by the two traces in Figure 5. In the unsynchronized case (b), σ is $\sim 1 \times 10^{-5}$ V. The signal at the second harmonic is clearly considerably smaller than this, and the SNR is therefore < 1 , making imaging impossible. In the synchronized case (a), σ is much smaller, at $\sim 3 \times 10^{-7}$ V, and by combining the sideband heights according to Eq. (2) gives $s_2 \sim 8 \times 10^{-6}$ V, corresponding to an SNR of 26. In both cases, the measurement bandwidth is 153 Hz. σ can be further reduced by decreasing the measurement bandwidth or, equivalently, by increasing the integration time at each pixel. As always, the trade-off for lower noise is a longer image acquisition time.

To demonstrate the ability of the pulsed QCL and s-SNOM to take near-field images over a range of wavelengths, we present pictures of a broadband mid-infrared log-periodic nanoantenna.^{24,25} This sample exhibits plasmonic resonances over a broad range of wavelengths and, as the wavelength is scanned, the electric field distribution across the nanoantenna changes significantly.

FIG. 5. Fourier transform of (a) synchronized and (b) unsynchronized digitized pulse trains for an s-SNOM measurement on a gold substrate using a 6.5 ms signal integration period. The probe vibration frequency is $\omega = 63.5$ kHz and the reference mirror oscillation frequency is $\Omega = 300$ Hz. The first and second harmonic sidebands are clearly visible in the (synchronized) low-noise case, whereas with the laser unsynchronized, they are buried in the extra noise artefacts generated in the digitization process.

Simulation results, generated using finite-difference time-domain (FDTD) commercial software (*Lumerical FDTD Solutions v8.6.0*), were used to compare with the experimental images. A 40 nm thick gold nanoantenna, lying over a 2 nm chromium adhesion layer and a semi-infinite BaF_2 substrate, was discretised with a non-uniform mesh. As a default, the mesh had a volume grid of $7 \text{ nm} \times 7 \text{ nm} \times 5 \text{ nm}$ within the total-field scattered field (TFSF) source volume. However, at the nanoantenna gap, a finer mesh of $4 \text{ nm} \times 4 \text{ nm} \times 5 \text{ nm}$ was used, and in the chromium, the length of the discretization in the z-direction was 0.5 nm.

The incident illumination, generated by the TFSF, is polarized parallel to the teeth of the nanoantenna, and is incident, as in the experiment, at an angle of 60° with respect to the sample normal. The optical properties of gold and chromium are modelled with multi-coefficient functions to fit experimental tabulated data,²⁸ whereas the BaF_2 is assumed to be lossless with a constant refractive index of $n = 1.465$.²⁸ Note that in the simulation, the presence of the s-SNOM probe is not considered. Similar simulation setup parameters, precautions, and convergence analyses to our previous works^{24,25} were carried out to ensure accurate CW information. A 2D field profile monitor was used to record the field distribution at the xy -cross-sectional plane, 20 nm above the gold-air interface.

The resulting images, taken at wavelengths of $\lambda = 7.9$ and $9.5 \mu\text{m}$, are shown in Fig. 6. The pixel resolution was set at 100 nm, corresponding to a value of approximately $\lambda/80$. The acquisition time for each image was less than 90 s. Despite the 180° rotational symmetry of the structures, the field profile itself is not rotationally symmetrical. This is due to retardation effects which occur due to the fact that our setup uses light incident at 60° from the surface normal. As the size of the nanoantenna is comparable to the wavelength, there is a significant shift in the phase of the exciting IR field across it, so the field strength and direction across the sample are not uniform.

In terms of the image quality, the $\lambda = 9.5 \mu\text{m}$ image is superior due to the lower intrinsic pulse-to-pulse intensity variation of the laser at this wavelength. At the position of greatest field enhancement, the SNR is 17 at $\lambda = 9.5 \mu\text{m}$ and 9 at $\lambda = 7.9 \mu\text{m}$.

There is a good qualitative match between the simulation and experiment on the lower half of the antenna; the field profile is similar between the two images at $\lambda = 7.9$ and $\lambda = 9.5 \mu\text{m}$ in the experiment, and this similarity between the two wavelengths is mirrored in the simulations. On the upper half of the antenna—at both wavelengths—there is a better quantitative match. At $\lambda = 9.5 \mu\text{m}$, a “hot spot,” P1, is observed on the outermost left tooth. In the image at $7.9 \mu\text{m}$, this area of high intensity has clearly shifted to the right onto the second tooth from the top, P2, in accordance with the simulations.

In conclusion, we have demonstrated the use of a widely tuneable pulsed QCL for an s-SNOM measurement. This combination of technology is potentially a powerful tool for ultra-high resolution spectroscopy.

QCLs can provide a versatile imaging system, offering high spatial and spectral resolution coupled with a wide wavelength tuning range, fast image acquisition times, and

FIG. 6. (a) AFM, (b) and (c) s-SNOM amplitude images, and (d) and (e) simulation of E_z field at 20 nm above the structure at $\lambda = 7.9 \mu\text{m}$ (left) and $9.5 \mu\text{m}$ (right) for broadband antenna samples. The in-plane direction of the incident light (at 60° to the sample normal) is indicated by the white arrow and its polarization by the red arrow. The pixel size is $100 \times 100 \text{ nm}$ (i.e., $\sim \lambda/80$) and the integration time at each pixel is 13 ms, corresponding to an image acquisition time of less than 90 s. A scale bar showing the relative magnitude of the E_z field is shown in image (d).

simple turn-key operation. Their use with s-SNOM could, therefore, open up fresh regions of the electromagnetic spectrum for nanoscale studies.

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- ¹F. Keilmann and R. Hillenbrand, *Philos. Trans. R. Soc. London, Ser. A* **362**, 787 (2004).
- ²R. Esteban, R. Vogelgesang, J. Dorfmuüller, A. Dmitriev, C. Rockstuhl, C. Etrich, and K. Kern, *Nano Lett.* **8**, 3155 (2008).
- ³A. J. Huber, J. Wittborn, and R. Hillenbrand, *Nanotechnology* **21**, 235702 (2010).
- ⁴R. Hillenbrand and F. Keilmann, *Appl. Phys. B: Lasers Opt.* **73**, 239 (2001).
- ⁵F. Ballout, H. Krassen, I. Kopf, K. Ataka, E. Bruendermann, J. Heberle, and M. Havenith, *Phys. Chem. Chem. Phys.* **13**, 21432 (2011).
- ⁶J. M. Stiegler, A. J. Huber, S. L. Diedenhofen, J. G. Rivas, R. E. Algra, E. P. A. M. Bakkers, and R. Hillenbrand, *Nano Lett.* **10**, 1387 (2010).
- ⁷J. M. Stiegler, Y. Abate, A. Cvitkovic, Y. E. Romanyuk, A. J. Huber, S. R. Leone, and R. Hillenbrand, *Acs Nano* **5**, 6494 (2011).
- ⁸A. J. Huber, A. Ziegler, T. Kock, and R. Hillenbrand, *Nat. Nanotechnol.* **4**, 153 (2009).
- ⁹A. Cvitkovic, N. Ocelic, and R. Hillenbrand, *Opt. Express* **15**, 8550 (2007).
- ¹⁰A. C. Jones, R. L. Olmon, S. E. Skrabalak, B. J. Wiley, Y. N. Xia, and M. B. Raschke, *Nano Lett.* **9**, 2553 (2009).
- ¹¹M. Esslinger, J. Dorfmueller, W. Khunsin, R. Vogelgesang, and K. Kern, *Rev. Sci. Instrum.* **83**, 033704 (2012).
- ¹²J. Chen, P. Albella, Z. Pirzadeh, P. Alonso-González, F. Huth, S. Bonetti, V. Bonanni, J. Åkerman, J. Nogués, P. Vavassori, A. Dmitriev, J. Aizpurua, and R. Hillenbrand, *Small* **7**, 2341 (2011).
- ¹³R. Vogelgesang and A. Dmitriev, *Analyst* **135**, 1175 (2010).
- ¹⁴P. Alonso-Gonzalez, M. Schnell, P. Sarriugarte, H. Sobhani, C. Wu, N. Arju, A. Khanikaev, F. Golmar, P. Albella, L. Arzubia, F. Casanova, L. E. Hueso, P. Nordlander, G. Shvets, and R. Hillenbrand, *Nano Lett.* **11**, 3922 (2011).
- ¹⁵P. Alonso-González, P. Albella, F. Golmar, L. Arzubia, F. Casanova, L. E. Hueso, J. Aizpurua, and R. Hillenbrand, *Opt. Express* **21**, 1270 (2013).
- ¹⁶M. Schnell, A. Garcia-Etxarri, A. J. Huber, K. B. Crozier, A. Borisov, J. Aizpurua, and R. Hillenbrand, *J. Phys. Chem. C* **114**, 7341 (2010).
- ¹⁷J. Dorfmuüller, R. Vogelgesang, R. T. Weitz, C. Rockstuhl, C. Etrich, T. Pertsch, F. Lederer, and K. Kern, *Nano Lett.* **9**, 2372 (2009).
- ¹⁸S. Amarie, T. Ganz, and F. Keilmann, *Opt. Express* **17**, 21794 (2009).
- ¹⁹S. Amarie, P. Zaslansky, Y. Kajihara, E. Griesshaber, W. W. Schmahl, and F. Keilmann, *Beilstein J. Nanotechnol.* **3**, 312 (2012).
- ²⁰F. Huth, A. Govyadinov, S. Amarie, W. Nuansing, F. Keilmann, and R. Hillenbrand, *Nano Lett.* **12**, 3973 (2012).
- ²¹F. Huth, M. Schnell, J. Wittborn, N. Ocelic, and R. Hillenbrand, *Nature Mater.* **10**, 352 (2011).
- ²²J. Faist, F. Capasso, D. L. Sivco, C. Sirtori, A. L. Hutchinson, and A. Y. Cho, *Science* **264**, 553 (1994).
- ²³A. Hugi, R. Maulini, and J. Faist, *Semicond. Sci. Technol.* **25**, 083001 (2010).
- ²⁴M. Navarro-Cia and S. A. Maier, *ACS Nano* **6**, 3537 (2012).
- ²⁵H. Aouani, H. Šípová, M. Rahmani, M. Navarro-Cia, K. Hegnerová, J. Homola, M. Hong, and S. A. Maier, *ACS Nano* **7**, 669 (2013).
- ²⁶N. Ocelic, A. Huber, and R. Hillenbrand, *Appl. Phys. Lett.* **89**, 101124 (2006).
- ²⁷P. G. Gucciardi and G. Bachelier, *J. Appl. Phys.* **99**, 124309 (2006).
- ²⁸E. D. Palik, *Handbook of Optical Constants of Solids: Index* (Academic Press, 1991).