

Imaging theory of structured pump-probe microscopy

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Abstract: With sub-micron spatial resolution and femtosecond temporal resolution, pump probe microscopy provides a powerful spectroscopic probe of complex electronic environments in bulk and nanoscale materials. However, the electronic structure of many materials systems are governed by compositional and morphological heterogeneities on length scales that lie below the diffraction limit. We have recently demonstrated Structured Pump Probe Microscopy (SPPM), which employs a patterned pump excitation field to provide spectroscopic interrogation of sub-diffraction limited sample volumes. Herein, we develop the imaging theory of SPPM in two dimensions to accompany the previously published experimental methodology. We show that regardless of pump and probe wavelengths, a nearly two-fold reduction in spectroscopic probe volume can be achieved. We also examine the limitations of the approach, with a detailed discussion of ringing in the point spread function that can reduce imaging performance.

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OCIS codes: (180.4315) Nonlinear microscopy; (110.2990) Image formation theory; (100.6740) Superresolution; (110.4850) Optical transfer functions; (300.6500) Time resolved spectroscopy.

References and links

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1. Introduction

The electronic structure of complex materials systems is often altered by a variety of localized defects, i.e. compositional and morphological variation, point defects, and grain boundaries [1]. Pump-probe and related nonlinear microscopies, which provide both high spatial and temporal resolution, are important tools for understanding how such heterogeneities impact bulk and nanoscale material functionalities, particularly for non-equilibrium processes like photogeneration, charge separation, carrier transport, and recombination [2–4]. To enable more precise structure-function correlations in complex materials systems, extensive technique development efforts have been directed toward surpassing the diffraction limit [5–12]. Recently, we have experimentally demonstrated structured pump probe microscopy (SPPM) [13], which enables both label-free imaging and ultrafast spectroscopic characterization of sub-diffraction limited sample volumes without employing saturation effects or other highly nonlinear interactions. Here, we comprehensively describe the imaging theory of SPPM, exploring spectral parameters and limitations of the approach to broaden the utility of the technique.

The resolution limit of optical systems is often characterized by the full width at half maximum (fwhm) of the point spread function (PSF), which is restricted by the Abbe limit [14]:

$$fwhm_{\min} = \frac{\lambda}{2NA} \quad (1)$$

In Eq. (1), λ is the wavelength of the imaging light, NA is the numerical aperture of the objective, and $fwhm_{\min}$ is the characteristic dimension of the optical system PSF. The conjugate space counterpart of the PSF is the coherent optical transfer function (OTF). The OTF acts as a low-pass filter, attenuating the high (spatial) frequency information of the imaged object that lies outside the passband. This reduction in transmitted high frequency information reduces the spatial resolution of the object image.

SPPM is theoretically related to Structured Illumination Microscopy (SIM), a fluorescence imaging technique that utilizes a structured excitation field to improve spatial resolution [15–18]. We have adapted the SIM approach to pump probe microscopy by implementing a structured pump excitation field along with a diffraction-limited probe field. Structuring the excitation field expands the optical system's OTF, and improves spatial resolution by nearly a factor of two.

The remainder of this manuscript is organized as follows. In Section 2, we briefly discuss the experimental apparatus to connect the main theoretical body to practical implementation. Section 3 develops the imaging theory of both diffraction-limited (DL) and structured pump-probe approaches. In Sections 4 and 5, we describe the conjugate space reconstruction procedure used to achieve sub-diffraction limited imaging and transient kinetics. In Section 6, we discuss the results of our modeling including improvements in resolution, wavelength dependence, and ringing artifacts that can limit imaging performance.

2. Experimental

While a more detailed discussion of the relevant experimental factors can be found elsewhere [13], a condensed schematic of the experimental apparatus utilized for 2D SPPM is shown in Fig. 1. The key requirement to implement SPPM is sample photoexcitation by a structured pump field. To achieve the structured field, four diffraction orders from a grating are overlapped at the sample position to create an interference fringe pattern with a well-defined spatial phase. While the interference pattern can be produced with actuator-mounted diffraction gratings placed at the image plane of the microscope objective [15], computer-controlled two-dimensional spatial light modulators (SLMs) are facile and accessible alternatives, particularly with the advent of low-cost digital micromirror devices [13]. The probe pulse is focused to a diffraction limited spot at the sample plane, and the sample is raster scanned with a piezoelectric translation stage. The schematic in panel A shows a reflection-type detection geometry, however transmission detection is also possible with a second objective placed behind the sample.

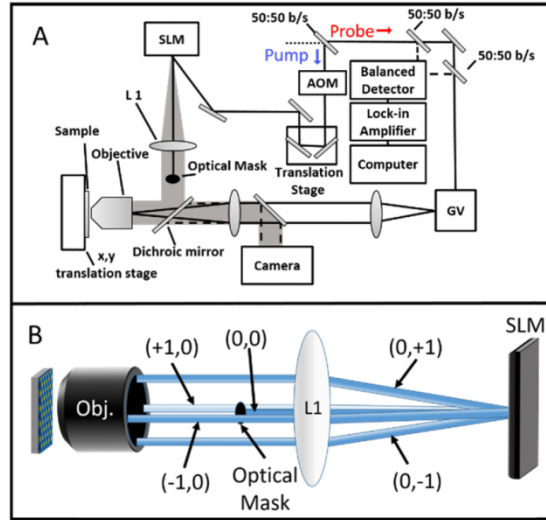


Fig. 1. (A) Experimental schematic of two-dimensional SPPM. The dotted line represents the input pulse train derived from a suitable ultrafast laser source. After a beamsplitter, the probe pulse is directed to a set of Galvanometer (GV) mirrors and coupled through a 4-f lens system onto the back aperture of the objective. The GV mirrors provide a reliable method for spatially overlapping the pump and probe pulses. The pump path is directed through an acousto-optic modulator (AOM), a translating delay stage, and toward an SLM, which is programmed to display a two dimensional grating pattern. The four 1st order diffractions are collected by a collimating lens (L1) in such a way that they are incident at the far outer edges of the objective aperture. (B) An expanded view of the optics needed to create a structured pump excitation field. The 5 diffraction orders from the SLM are labeled in the (x, y) directions where a value of one denotes the 1st order diffraction of the respective axes. The (0,0) diffraction order is blocked with a mask.

3. Imaging theory

3.1 Diffraction limited imaging

In time-resolved pump-probe microscopy, an image is formed by recording the position-dependent, transient sample response after photoexcitation with a coherent, pulsed light source. The pump-probe image (I_N) can be described by:

$$I_N(r) = o(r) \otimes (E(r) \otimes h(r)) \quad (2)$$

where the object function ($o(r)$) contains both the spatial position and the third-order nonlinear response of the sample, $E(r)$ is the electric field, and the imaging system PSF is given by $h(r)$. In pump-probe microscopy, the effective field $(E \otimes h)_{eff}$ is described by Eq. (3):

$$(E \otimes h)_{eff} = |E_1(r) \otimes h_1|^2 \cdot |E_2(r) \otimes h_2|^2 \quad (3)$$

where E_1 and E_2 are the pump and probe electric fields, each convolved with their respective PSFs (h_1, h_2) [18,19]. Substitution of Eq. (3) into Eq. (2) yields the DL pump-probe image (I_{DL}):

$$\begin{aligned} I_{DL} &= o(r) \otimes |E_1(r) \otimes h_1|^2 \cdot |E_2(r) \otimes h_2|^2 \\ &= o(r) \otimes (\delta(r) \otimes h_1)^2 \cdot (\delta(r) \otimes h_2)^2 \\ &= o(r) \otimes (h_1^2 \cdot h_2^2) \end{aligned} \quad (4)$$

In the second line of Eq. (4), the delta functions describe the pump and probe fields, overlapped at the same position in the image plane. The Fourier Transform (FT) of Eq. (4) yields the conjugate-space representation of the DL image, where we use capital letters and tildes to distinguish conjugate-space terms:

$$\tilde{I}_{DL}(k) = \tilde{O}(k) \cdot [\tilde{H}_1(k) \otimes \tilde{H}_1(k) \otimes \tilde{H}_2(k) \otimes \tilde{H}_2(k)] \quad (5)$$

In Eq. (5), $\tilde{O}(k)$ is the complete image spectrum, and the H_n are coherent OTFs for the pump ($n = 1$) and probe ($n = 2$). A coherent OTF acts as an ideal pass-band filter which transmits low frequency information unaltered and completely attenuates any information that lies outside the passband [20]. As illustrated in Fig. 2, the effective OTF, which resembles a Gaussian function for the DL imaging case, is formed from the triple convolution of the H_n . In DL pump-probe imaging, spatial resolution of the image, $\tilde{I}_{DL}(r)$, (the inverse Fourier transform of $\tilde{I}_{DL}(k)$) is determined by the extent to which the effective OTF attenuates high-frequency object information.

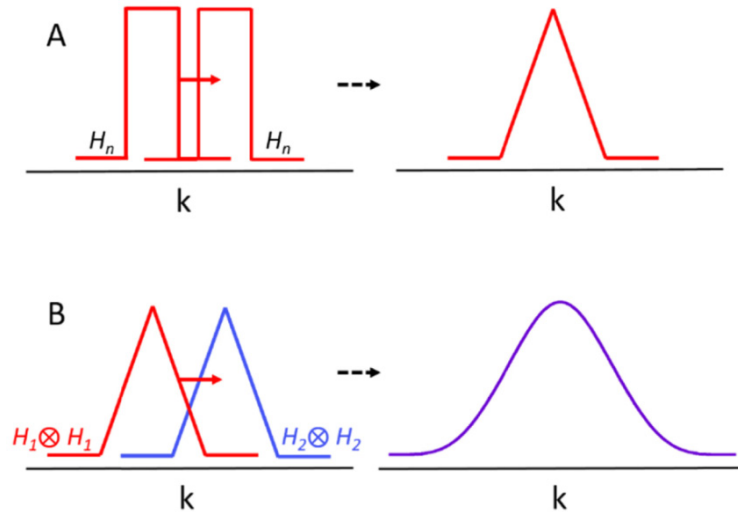


Fig. 2. One-dimensional illustration of four component convolution in Eq. (5). (A) Coherent OTFs H_n are convolved, producing a triangle function for both pump ($n = 1$) and probe ($n = 2$). (B) Convolution of the pump and probe OTFs produced in step 1 resulting in the diffraction-limited effective OTF.

3.2 Structured imaging

In contrast to the diffraction limited case, SPPM utilizes a structured pump electric field comprised of two perpendicularly propagating sinusoidal fields:

$$E_1(r) = \exp(ik^x r + \varphi^x) + \exp(-ik^x r - \varphi^x) + \exp(ik^y r + \varphi^y) + \exp(-ik^y r - \varphi^y) \quad (6)$$

while the probe field remains diffraction limited. In Eq. (6), k^x and k^y determine the period and the φ^x and φ^y the phase of the fringe pattern along the x and y image axes. The structured pump field associated with SPPM is illustrated in Fig. 3. Panels A and B show the two sinusoidally-modulated fields produced by the interference of two counter-propagating ± 1 diffraction orders in the y and x axes, respectively. When all four diffraction orders interfere at the sample plane, they produce the two-dimensional sinusoidally-modulated field shown in panel C of Fig. 3. The FT of the 2D excitation field is shown in panel D; it consists of nine distinct (spatial) frequency components of varying relative amplitudes. The component centered at the origin has a relative amplitude of 1, while the four components (green) located at $(+k^x, \pm k^y)$ and $(-k^x, \pm k^y)$ have relative amplitudes of 0.5, and the four components (yellow) located at $\pm 2k^x$ and $\pm 2k^y$ have relative amplitudes of 0.25.

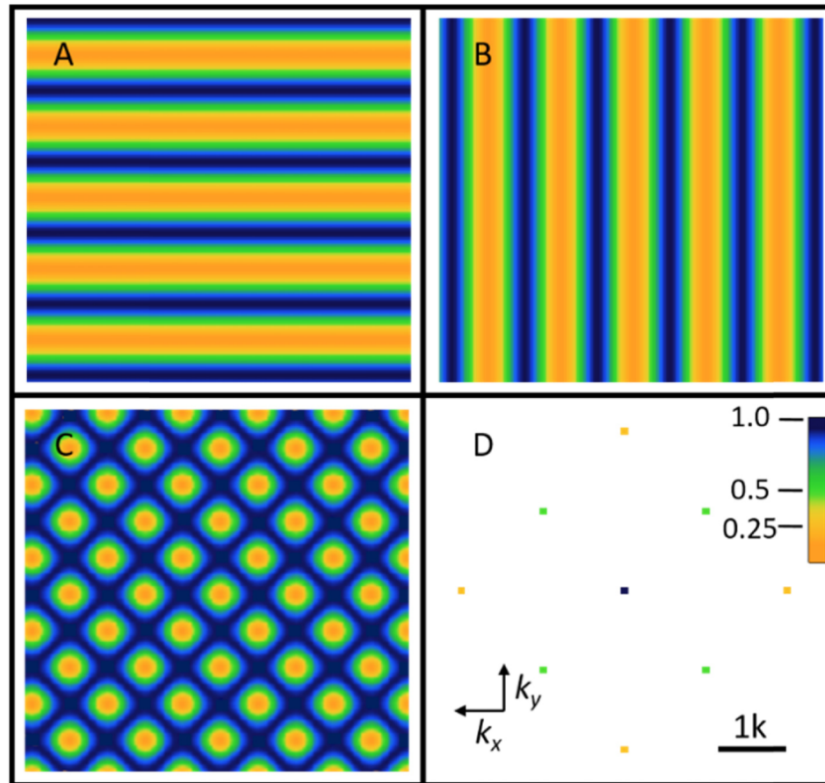


Fig. 3. The structured excitation field employed in SPPM. (A, B) Sinusoidal fields propagating along the y - and x - axes, respectively, formed by the interference of two ± 1 st order diffractions. (C) Two-dimensional excitation field produced from the mutual interference of all four diffraction orders. (D) Fourier Transform of the 2D excitation field in panel C showing the nine shifted delta functions in the k_x - k_y plane. The amplitude of each component is normalized to the component centered at k_0 .

Substitution of the structured pump field (Eq. (6)) into Eq. (3) and Eq. (2) results in the structured pump probe image (I_{Str}):

$$\begin{aligned} I_{Str}(r; \varphi^x, \varphi^y) &= o(r) \otimes \left| \frac{\exp(ik^x r + \varphi^x) + \exp(-ik^x r - \varphi^x)}{\exp(ik^y r + \varphi^y) + \exp(-ik^y r - \varphi^y)} \right|^2 \cdot (\delta(r) \otimes h_2)^2 \\ &= o(r) \otimes \left| \frac{\exp(ik^x r + \varphi^x) + \exp(-ik^x r - \varphi^x)}{\exp(ik^y r + \varphi^y) + \exp(-ik^y r - \varphi^y)} \right|^2 \cdot h_2^2 \end{aligned} \quad (7)$$

In Eq. (7), the pump PSFs vanish due to the necessary condition that the frequency components of the pump field are allowed to pass through the optical system ($k^{x,y}$ must lie within $\tilde{H}_1$). Expanding Eq. (7), performing the FT, and convolving the nine components with the effective probe OTF ($\tilde{H}_2' = \tilde{H}_2 \otimes \tilde{H}_2$) we obtain the conjugate space representation of the structured image:

$$\begin{aligned} \tilde{I}_{Str}(k; \varphi^x, \varphi^y) &= \tilde{O}(k) \cdot \left[\begin{aligned} &(\tilde{H}_2'(k))_1 \\ &+ \left(\frac{1}{2} \tilde{H}_2'(k + k^x + k^y) e^{-i\varphi^x - i\varphi^y} \right)_2 \\ &+ \left(\frac{1}{2} \tilde{H}_2'(k - k^x - k^y) e^{+i\varphi^x + i\varphi^y} \right)_3 \\ &+ \left(\frac{1}{2} \tilde{H}_2'(k + k^x - k^y) e^{-i\varphi^x + i\varphi^y} \right)_4 \\ &+ \left(\frac{1}{2} \tilde{H}_2'(k - k^x + k^y) e^{+i\varphi^x - i\varphi^y} \right)_5 \\ &+ \left(\frac{1}{4} \tilde{H}_2'(k - 2k^y) e^{+i2\varphi^y} \right)_6 + \left(\frac{1}{4} \tilde{H}_2'(k + 2k^y) e^{-i2\varphi^y} \right)_7 \\ &+ \left(\frac{1}{4} \tilde{H}_2'(k - 2k^x) e^{+i2\varphi^x} \right)_8 + \left(\frac{1}{4} \tilde{H}_2'(k + 2k^x) e^{-i2\varphi^x} \right)_9 \end{aligned} \right] \quad (8) \\ &= \sum_{n=1}^9 a_n \tilde{Y}_n \exp[\Phi_n] \end{aligned}$$

In the first line of Eq. (8), it can be seen that the structured pump-probe image is comprised of nine components, each shifted to one of nine different positions in conjugate space. In the second line we adopt a compact notation that expresses the image as a sum over the nine terms, $\tilde{Y}_n$. The a_n and Φ_n are the corresponding set of index-dependent amplitude and phase shifts, respectively.

4. SPPM image reconstruction

We now turn to reconstructing an image with improved spatial resolution from a series of phase-shifted structured images, $I_{Str}(r)$. We first note that an ideal conjugate image with an expanded effective OTF can be written in a similar form as Eq. (8):

$$\begin{aligned}
 \tilde{I}_{ideal}(k) &= \tilde{O}(k) \cdot \begin{bmatrix} \tilde{H}_2'(k) \\ +\tilde{H}_2'(k+k^x+k^y) \\ +\tilde{H}_2'(k-k^x-k^y) \\ +\tilde{H}_2'(k+k^x-k^y) \\ +\tilde{H}_2'(k-k^x+k^y) \\ +\tilde{H}_2'(k-2k^y)+\tilde{H}_2'(k+2k^y) \\ +\tilde{H}_2'(k-2k^x)+\tilde{H}_2'(k+2k^x) \end{bmatrix} \\
 &= \sum_{n=1}^9 \tilde{Y}_n
 \end{aligned} \tag{9}$$

Comparison of Eq. (8) and Eq. (9) shows that the ideal conjugate image ($\tilde{I}_{ideal}(k)$) differs from the structured conjugate image ($\tilde{I}_{Str}(k; \varphi^x, \varphi^y)$) only by the relative amplitude and phase shift of each component, $\tilde{Y}_n$. It is therefore possible to reconstruct the ideal enhanced-resolution image by solving for each of the nine components present in $\tilde{I}_{Str}(k; \varphi^x, \varphi^y)$. To do so, nine structured images ($I_{Str}^m(r)$, $m = 1-9$) are collected, each with a uniquely phase shifted 2D pump excitation field. The FT of the nine images are arranged into a nine component vector ($\tilde{I}_V$):

$$\tilde{I}_V = \begin{pmatrix} \tilde{I}_{Str}^1(k) & \tilde{I}_{Str}^2(k) & \cdots & \tilde{I}_{Str}^9(k) \end{pmatrix} \tag{10}$$

We then construct a 9x9 matrix (AP), which relates the amplitudes (a_n^m) and unique phase shifts (Φ_n^m), corresponding to each element of the nine structured images:

$$AP = \begin{pmatrix} a_1^1 \exp(\Phi_1^1) & \cdots & a_9^1 \exp(\Phi_9^1) \\ \vdots & \ddots & \vdots \\ a_1^9 \exp(\Phi_1^9) & \cdots & a_9^9 \exp(\Phi_9^9) \end{pmatrix} \tag{11}$$

The phase shifts (φ_x, φ_y)^m are chosen so that AP is nonsingular. We then solve for the 9 components, $\tilde{Y}_n$:

$$AP^{-1} \cdot \tilde{I}_V = \begin{pmatrix} \tilde{Y}_1 & \tilde{Y}_2 & \cdots & \tilde{Y}_9 \end{pmatrix} \tag{12}$$

which when summed, yield $\tilde{I}_{ideal}(k)$ (Eq. (9)). As a final step, the conjugate image is normalized by the effective OTF:

$$OTF_{SPPM} = \begin{bmatrix} \tilde{H}_2'(k) \\ +\tilde{H}_2'(k+k^x+k^y) \\ +\tilde{H}_2'(k-k^x-k^y) \\ +\tilde{H}_2'(k+k^x-k^y) \\ +\tilde{H}_2'(k-k^x+k^y) \\ +\tilde{H}_2'(k-2k^y) \\ +\tilde{H}_2'(k+2k^y) \\ +\tilde{H}_2'(k-2k^x) \\ +\tilde{H}_2'(k+2k^x) \end{bmatrix} \quad (13)$$

Figure 4 shows a comparison of the DL, SPPM (Eq. (13)), and final normalized OTFs. The additional high frequency information encompassed by the normalized (solid black) and raw (black dashed) SPPM OTFs over the DL case (purple dots) is especially apparent at spatial frequencies greater than $\pm 2k^x$.

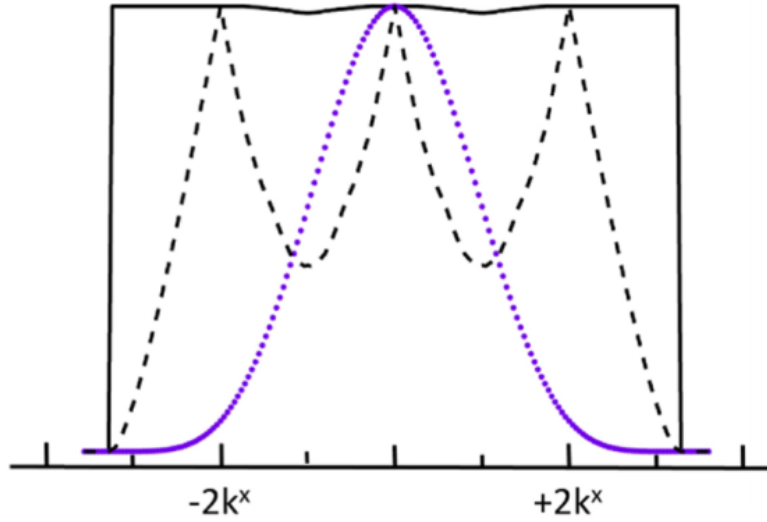


Fig. 4. Comparison of SPPM and DL OTF profiles along the k_x axes. The diffraction-limited effective OTF (purple dots) is given by the triple convolution in Eq. (5). The effective SPPM OTF before normalization is shown as a black dashed line. The normalized effective OTF is shown by the solid black line.

The final SPPM image (I_{SPPM}), which contains additional high frequency information passed by the modified OTF, is obtained by Inverse FT of the summed, normalized $\tilde{Y}_n$:

$$I_{SPPM}(r) = \text{Re} \left[FT^{-1} \left\{ \left(\sum_n \tilde{Y}_n \right) \div OTF_{SPPM} \right\} \right] \quad (14)$$

5. Time-resolved SPPM

Analogously to the imaging modality, SPPM can also be utilized to collect time-resolved kinetics from a sub-diffraction limited probe volume [13]. For such a measurement, nine phase-dependent kinetics traces are collected. These traces, which measure the decay of the sample response as a function of the pump-probe delay, Δt , are arranged into a vector equivalent to the image vector of Eq. (10):

$$\tilde{K}_v = (\tilde{K}_{Str}^1 \ \tilde{K}_{Str}^2 \ \cdots \ \tilde{K}_{Str}^9) \quad (15)$$

As before, the nine kinetics traces are collected with unique phase shifts of the pump field and a diffraction-limited probe field. Reconstruction of the kinetics data then follows the process described in Eqs. (11)-(14) with $\tilde{K}_v$ replacing $\tilde{I}_v$. Within this context, SPPM kinetics traces can be understood as a one-pixel image, collected at a series of pump-probe delays, Δt . Because the effective interrogation volume of the resultant kinetics is reduced with respect to the DL case, observables from neighboring sample domains can be more effectively deconvolved, providing a far-field approach for interrogating excited state dynamics of sub-wavelength material domains.

6. Results and discussion

6.1 Imaging

Pump-probe measurements require two distinct laser pulses, separated by a well-defined delay, (pump and probe) to interact with the sample. Because the center wavelength of the pump and probe pulses will vary depending on the spectral response of the studied system and the photophysical process of interest, the width of the effective PSF will also necessarily vary. To understand how changes in pump and probe wavelength affect the effective PSF of SPPM, we compare the DL and SPPM imaging linewidths of a single delta function (Black profile in Fig. 5(a)) while varying both pump and probe wavelengths between 400 and 800 nm. Note that for these and all subsequent results in this manuscript, we have imposed a coordinate system that reproduces the imaging performance of our experimental apparatus with a 0.90 NA objective [13]. We also assume monochromatic excitation fields. While ultrashort laser pulses used in pump-probe microscopy do have finite spectral bandwidth, the difference in spatial resolution between broadband and single wavelength fields is not expected to be significant [21]. Panel A of Fig. 5 shows examples of SPPM and DL PSFs with 400 nm pump and 540 nm probe wavelengths. For this combination of wavelengths, the PSF of SPPM has a fwhm (97 nm) that is 1.86-fold narrower than the DL case (180 nm). In Panel B, we show the ratio of the SPPM and DL PSFs plotted versus the pump wavelength for a series of probe wavelengths. Overall, the SPPM PSF is narrowed by a factor of 1.69 to 1.92 over that achievable with DL imaging, suggesting significant improvements in spatial resolution can be achieved, regardless of pump or probe wavelengths. While the localization enhancement achieved by SPPM generally improves as the probe wavelength is decreased, the effective PSF narrowing is dependent on both the fringe spacing of the pump field and the width of the convolved probe OTFs. Shorter excitation wavelengths can support larger shifts in conjugate space of the of the image components ($\tilde{Y}_n$), in principle providing access to higher frequency information in the image spectrum. However, if the effective probe OTF ($\tilde{H}_s$) is narrower than the spacing of the pump-field components, significant ringing is introduced into the reconstructed image and the PSF width can increase. Based on the 0.90 NA objective we modeled, the narrowest full width at half maximum (fwhm) is achieved with pump and probe wavelengths both equal to 400 nm. At these wavelengths, the SPPM PSF fwhm is 87 nm while the DL PSF fwhm is 165 nm.

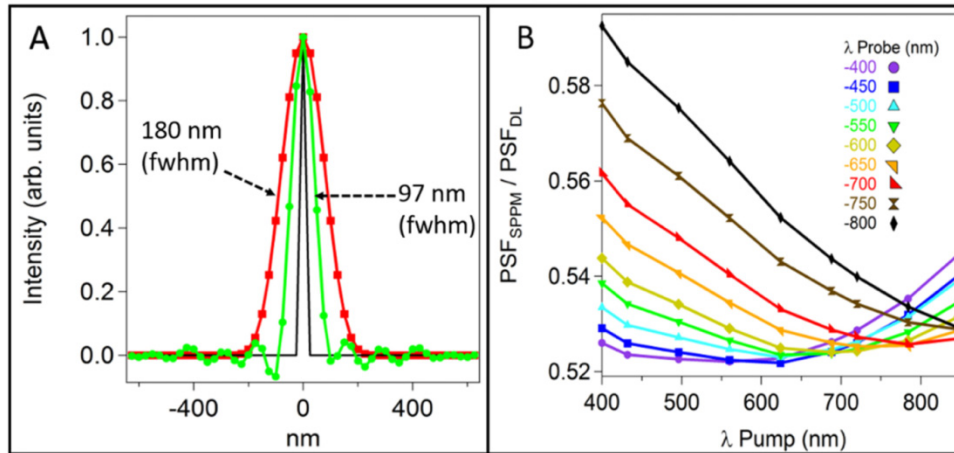


Fig. 5. (A) Profile comparison of the SPPM (green circles, 97 nm fwhm) and DL (red squares, 180 nm fwhm) effective PSFs with 400 nm pump and 540nm probe wavelengths. The black profile is the profile of the delta function used to determine the PSF of the imaging model. (B) Wavelength dependence of SPPM localization enhancement represented by the ratio of the SPPM PSF to the DL PSF at varying excitation and probe wavelengths through the visible spectrum.

We next modeled the improvement in imaging performance by comparing DL and SPPM images of a modified 1951 USAF target shown in panel A of Fig. 6. The target was modified to include the group of four smallest elements oriented at 45° to study directional anisotropy in imaging performance (see below). Target imaging was modeled at two sets of pump and probe wavelengths, with a pump/probe wavelength ratio of 0.8.

Panels B and C of Fig. 6 show the image produced with DL and SPPM models, respectively, with 432 nm pump and 540 nm probe wavelengths. In contrast to DL imaging, the SPPM image in panel C clearly resolves even the smallest components on the target. Panel D compares the profiles from DL and SPPM methods to the ideal target profile along the red-dashed line in magnified subsection of panel A. Along this profile the spatial period of the target elements (~ 237 nm) is approximately a factor of two shorter than the structured pump fringe pattern period (~ 450 nm). Panels E, F show equivalent images when 784 nm pump and 980 nm probe wavelengths are utilized for both the DL and SPPM models. Again, the profiles in panel G are taken from the location indicated by the red-dashed line in Panel A. In this case, while neither DL or SPPM resolves the features as they are nearly a factor of three below the diffraction limit, the SPPM approach does improve the contrast of the group relative to background and produces relatively little image distortion.

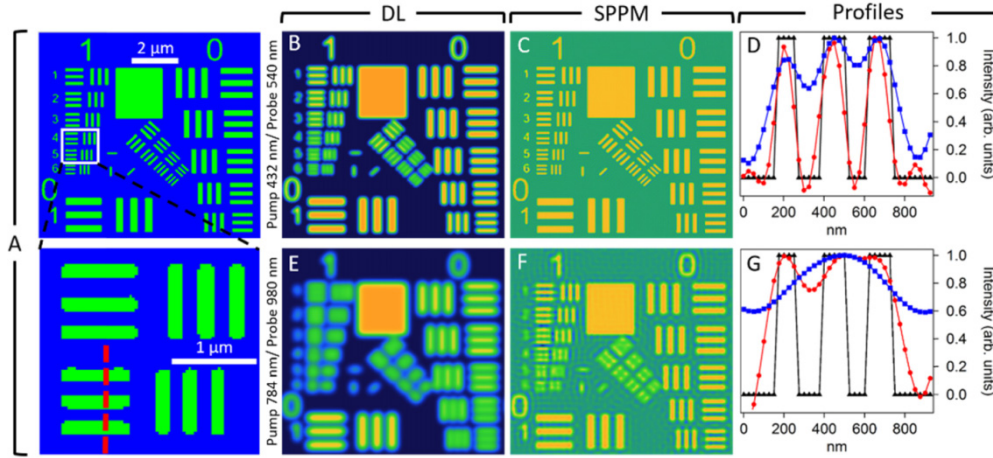


Fig. 6. Comparison of DL and SPPM imaging capabilities. (A) Shows the simulated test target (top) with a magnified region (bottom) designated by the white square. The remaining panels (B-G) are arranged so that the top and bottom rows correspond to the modeled wavelengths (labeled to the left of panels B and E). The three separate columns of panels B-G show DL (B, E), SPPM (C, F) imaging models and profile comparisons (D, G). Profile comparison are from location indicated by the red dashed line in the magnified region of panel A. The black (triangles) trace represents the original object while the blue (squares) and red (circles) traces are the DL and the SPPM models, respectively.

Although the width of the SPPM PSF is nearly half that of DL imaging regardless of pump and probe wavelength, imaging performance along the diagonal is reduced relative to along the x or y axes. This anisotropy stems from the shape of the SPPM OTF. Panel D in Fig. 3 shows that along the k_x and k_y axes, image components ($\tilde{Y}_n$) are shifted to $\pm 2k^x$ and $\pm 2k^y$, however the diagonal components are only shifted away from the center by $\pm\sqrt{2}k^{xy}$. Because the components are not shifted as far, the effective OTF is narrowed along the diagonal, resulting in lower image resolution. These effects are illustrated in Fig. 7, where panel A shows the target described in Fig. 6 imaged with the SPPM model at 560 nm pump and 800 nm probe wavelengths, and panel B shows the associated two-dimensional SPPM PSF.

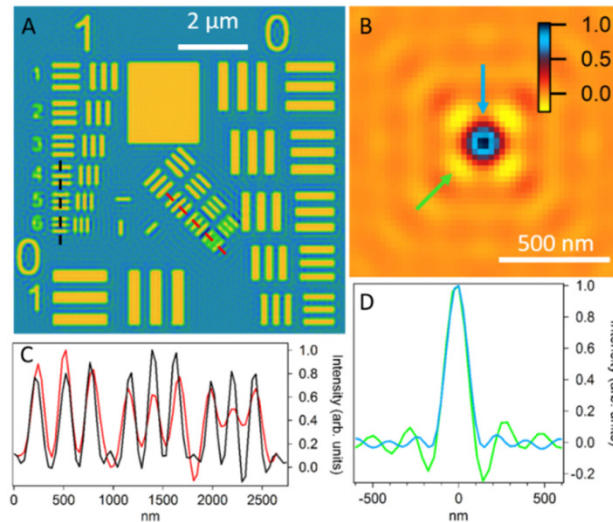


Fig. 7. Evaluation of the vertical and diagonal features of the SPPM OTF. (A) The object described in panel A of Fig. 6 imaged using the SPPM model (560 nm pump, 800 nm probe). (B) The resulting PSF generated by the SPPM model. (C) The black and red traces correspond to the red and black dashed lines in panel A. The nine components are identical in the original image. However, the nine components that produce the red trace in panel C have been rotated 45° . (D) Profile comparison of the SPPM PSF along directions of the blue and green arrows in panel B.

Panel D illustrates that while the narrowing of the SPPM OTF along the diagonal does not significantly change the width of the PSF, it does increase the magnitude of ringing present. Such ringing can significantly impact imaging performance as highlighted in panel C. Here, profiles collected from the red and black dashed lines on panel A are compared. The nine components profiled by the red trace are identical to the nine components corresponding to the black trace but are rotated 45° . For the smallest group of three, the decrease in spatial resolution is especially clear, illustrating the importance of mitigating PSF ringing for both imaging and spectroscopic applications.

6.2 Sub-diffraction limited spectroscopy

While SPPM can be employed exclusively for enhanced resolution imaging, it also provides the ability to perform ultrafast spectroscopy of sub-diffraction limited sample volumes [13]. Figure 8 models the time-resolved capabilities of SPPM as described in Section 5. Here, we compared the decay kinetics recovered using DL and SPPM approaches from two single-pixel features (black profiles), one with a single exponential lifetime of 100 ps and the other with a longer lifetime of 200 ps. The left column of Fig. 8(a)-8(c) shows $\Delta t = 0$ ps images while the right column shows the time-dependent kinetics obtained with DL (Panel A) and SPPM (panels B, C) models. In panel A, it can be seen that the DL approach does not resolve the two features and consequently recovers decay kinetics that are an average of the short and long lived components. Panel B shows that the SPPM model spatially distinguishes the two objects and recovers decay dynamics that accurately reflect the distinct lifetimes of the objects. When the two objects are spaced more closely (panel C, 125 nm) so that they are no longer resolved with SPPM, the recovered kinetics reflect an average of the fast and slow components as in the DL case.

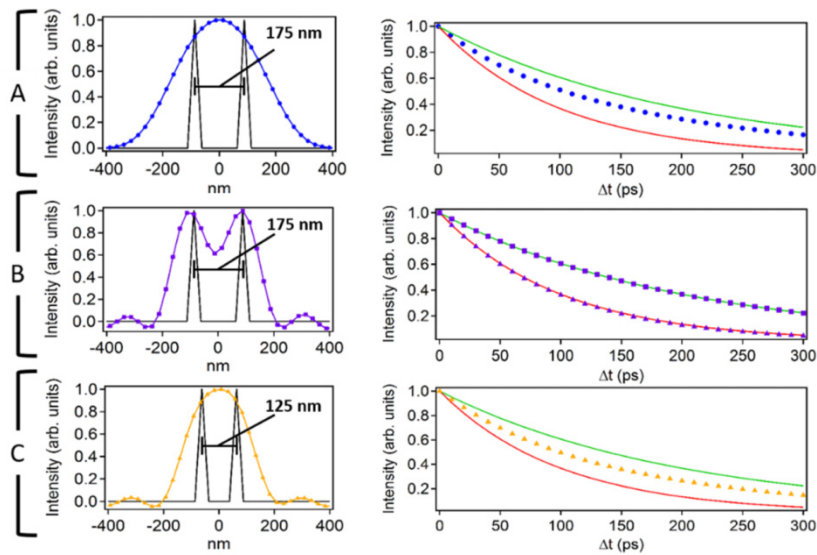


Fig. 8. Comparison of $\Delta t = 0$ ps images (*left*) and time-resolved kinetics (*right*) of modeled single pixel features using DL and SPPM approaches. Simulated pump wavelength is 560 nm and probe wavelength is 800 nm. The amplitude of the feature located to the left of the origin decays with a single exponential lifetime of 100 ps (red, solid line), whereas the feature to the right decays with a lifetime of 200 ps (green, solid line). (A) DL decay kinetics (blue circles) reflect an average of the fast and slow components with an object spacing of 175 nm. (B) The SPPM model recovers the distinct kinetics of the two objects (purple squares and triangles) when separated by 175 nm. (C) If the objects are unresolvable with SPPM, the recovered kinetics (orange triangles) reflect the average of fast and slow decays. For all panels, the kinetics are collected at the peak location(s) of the lineshape at $\Delta t = 0$ ps.

7. Summary

With SPPM we have demonstrated a route for achieving far-field, label-free super resolution spectroscopies. We have provided the theoretical basis for achieving increased resolution and examined several limitations of the approach. While the structured excitation field and diffraction limited probe field utilized in SPPM produces a nearly 2-fold enhancement over the diffraction limit, further improvements will require additional approaches. Possible routes toward far-field spatial resolution far below 100 nm include utilizing higher-order nonlinear processes such as two photon absorption (TPA) or by implementing total internal reflection (TIR) geometries. Our hope is that sub-diffraction limited spectroscopies like SPPM will continue to enhance understanding of complex materials systems by distinguishing the contributions of nanoscale heterogeneities and improving characterization of emergent functionality.

Funding

Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences of the U.S. Department of Energy (DOE) (DE-SC0014128).