

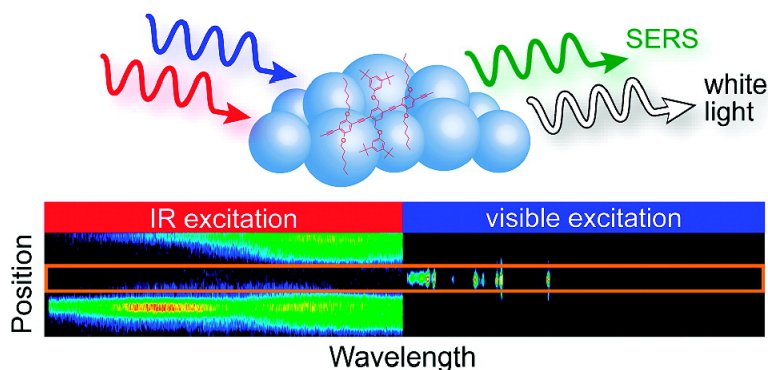
Communication

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## Spatial Anticorrelation between Nonlinear White-Light Generation and Single Molecule Surface-Enhanced Raman Scattering

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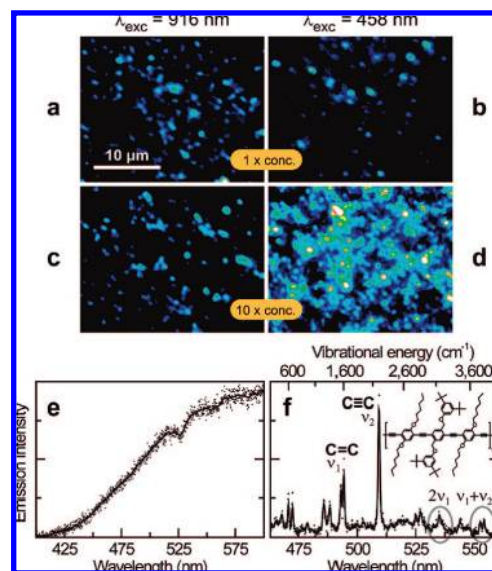
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One of the most exciting avenues of plasmonics,<sup>1</sup> the exploitation of collective electron oscillations in a metal to manipulate local optical fields, is the potential to amplify the light-matter interaction such that Raman scattering from a molecule becomes as probable as direct absorption. Such surface-enhanced Raman scattering (SERS)<sup>2</sup> of single molecules<sup>3–6</sup> requires a huge amplification of the effective cross section of Raman scattering by up to 14 orders of magnitude. The problem with single molecule SERS (SM-SERS) arises from the circumstance that it is often not only the desired signal of the analyte which is amplified:<sup>7</sup> signatures of contaminants,<sup>7</sup> temporal fluctuations,<sup>5,6</sup> and broad background emission<sup>3,6,8</sup> limit the method. We recently demonstrated that a few simple measures can greatly facilitate SM-SERS: working under vacuum and at cryogenic temperatures (5 K), as well as using rigid analyte molecules with well-defined vibronic modes, such as conjugated polymers.<sup>4</sup>

SM-SERS is often affected by a broad background,<sup>3</sup> which has been attributed to stimulated scattering or fluorescence of metal clusters.<sup>6,8,9</sup> A localized plasmonic excitation can also lead to enhanced nonlinear optical responses due to the local field increase. In this contribution we show that SM-SERS preferentially occurs at spatial positions on the nanoparticle substrate that do not exhibit nonlinear luminescence under two-photon excitation, suggesting that broad backgrounds seen in SERS may not be intrinsic effects.

Following the procedures for SM-SERS in ref 10 we used fractal silver films grown on glass by the Tollens silver mirror reaction. Fractal metal films are known to exhibit a variety of nonlinear optical effects such as second-harmonic generation and white-light (WL) generation at plasmonic hot spots.<sup>11</sup> The relation between these enhancement effects and the actual SERS phenomenon is, however, not immediately obvious. To investigate the link between localized WL generation and SERS we deposited the analyte conjugated polymer [poly(phenylene-ethynylene-butadiynylene), inset of Figure 1f] at a concentration of  $\sim 10^{-10}$  mol/L in toluene on the Tollens substrates by spin coating. This process leads to a spatial separation of molecules larger than the resolution limit of our microscope. The samples were mounted under vacuum ( $10^{-7}$  mbar) in a liquid helium coldfinger cryostat at 5 K, and the light emission was collected using a microscope objective in a wide-field imaging configuration. The same sample area could be alternately imaged with radiation from an Ar<sup>+</sup> laser (457.9 nm,  $\sim 250$  W/cm<sup>2</sup>) and a pulsed Ti:Sapphire laser (916 nm,  $\sim 350$  W/cm<sup>2</sup>, 80 MHz, 140 fs pulse length). Both lasers were linearly polarized in the same plane. The Ar<sup>+</sup> laser line overlaps the electronic transition of the polymer so that resonance SERS (SERRS) occasionally occurs simultaneously with single molecule photoluminescence (PL) from the same analyte molecule, allowing an unambiguous identification of SM-SERS.<sup>4</sup>

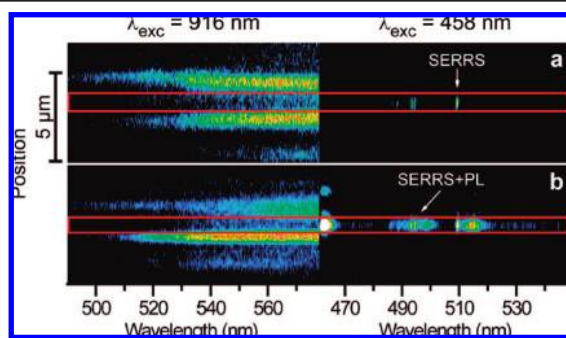
Figure 1 compares the same sample region under 458 nm continuous wave (CW) and 916 nm pulsed excitation for two



**Figure 1.** Microscope images of the silver nanoparticle substrates covered with a SM sample of the conjugated polymer used and excited at different wavelengths at 5 K. The intensity scale for all images is constant. (a,c) Excitation with femtosecond pulses at 916 nm reveals spots corresponding to broadband emission (spectrum shown in panel e). (b,d) Excitation with a CW laser in resonance with the molecule at 458 nm can lead to single molecule resonance Raman scattering (spectrum displayed in panel f), and fluorescence.<sup>4</sup> Raising the analyte concentration 10 $\times$  does not affect the white-light hot spot density (a vs c), whereas it dramatically increases the signal under CW excitation (b vs d).<sup>12</sup>

different analyte concentrations. Under excitation at 916 nm, Figure 1a displays irregularly distributed, isolated diffraction-limited WL spots. The corresponding emission spectra of the spots are extremely broad (panel e) and virtually independent of the infrared excitation wavelength. The origin of WL generation has been debated widely in the literature, but has mainly been considered under (linear) one-photon excitation.<sup>8c,9c</sup> Our preliminary results suggest that the nature of hot spots responsible for one-photon and two-photon (i.e., exhibiting a quadratic intensity dependence<sup>12</sup>) WL (2WL) generation differs as these two phenomena occur at different spatial locations and do not agree spectrally (2WL is broader). However, as 2WL (a nonlinear optical process arising from local field enhancement) occurs at spatially discrete positions, it is readily assigned to field-enhancement hot spots.

The same sample position, under illumination at a wavelength in resonance with the electronic transition of the analyte polymer, exhibits fewer spots (panel b). As we discussed previously,<sup>4</sup> the spots observed under this condition correspond either to Raman scattering, PL, joint Raman and PL, or one-photon WL generation (note that the latter process typically requires higher powers). A SM-SERRS spectrum is shown in panel f, which clearly displays



**Figure 2.** Spectral analysis of the samples from Figure 1, showing spatial anticorrelation between white-light generation and single molecule SERRS. The same sample region is probed under one-photon (right panels) and two-photon (left panels) excitation. 2WL emission is drastically reduced at locations of strong SERRS. SERRS can either appear on its own (a) or in combination with simultaneous PL from the same analyte molecule (b).

the characteristic bands corresponding to the double (labeled  $\nu_1$ ) and triple (labeled  $\nu_2$ ) carbon–carbon bonds, along with the first order harmonics  $2\nu_1$  and  $\nu_1 + \nu_2$ . Upon raising the analyte concentration 10-fold the 2WL hot spot density is unchanged (panel c). In contrast, under one-photon excitation, the overall emission increases  $\sim 10\times$  as the image acquires more PL background from molecules which are in resonance with the laser but do not have a nearby SERS hot spot to couple to (panel d).<sup>12</sup> Now, the key question is how the SERRS hot spots (panel b) and the 2WL hot spots (panel a) are related.

Figure 2 shows two examples of a comparison of the same region of a SM-SERRS sample under different excitation conditions. The light emission of a thin vertical stripe of the image is spectrally resolved in an imaging spectrograph: while the spatial information of the image in  $x$ -direction is lost, the  $y$ -axis corresponds to the spatial  $y$ -coordinate on the substrate. The left-hand side shows the 2WL emission, and the right-hand panels display the emission under blue CW excitation. On the right, the images show spatially discrete SM-SERRS signals. Remarkably, SM-SERRS is observed precisely at positions on the substrate where 2WL generation does not occur or is significantly reduced. Of the 113 single molecules studied, such a clear anticorrelation, a spatial disruption of 2WL in favor of SERRS, was observed in 68% of all cases. Discriminating between situations where only SERRS is observed (panel a) or simultaneous SERRS and PL occurs (panel b) does not alter this anticorrelation ratio. The same experiment was performed on a further 107 single molecules for 950 nm pulsed excitation.<sup>12</sup> Even when the SERRS wavelength is not half the 2WL generation wavelength, the anticorrelation remains similar at 72%. No correlation exists between 2WL and PL.

The frequent occurrence of an anticorrelation between SERRS and 2WL generation is not due to the analyte molecules quenching the WL hot spot emission. If this were the case, the  $10\times$  higher concentration in Figure 1c would lead to fewer WL spots compared to Figure 1a, which is not observed.<sup>12</sup> We conclude that, at least in a majority of cases, different types of hot spots are responsible for SERRS and 2WL. In 32% of the cases we identified 2WL and SERRS signals at the same position. We attribute this observation to the limited spatial resolution of our experimental setup ( $\sim 800$  nm). Close-lying but nevertheless distinct SERRS and WL hot spots cannot be resolved. Reducing the hot spot density should raise the degree of anticorrelation.

In most cases, SERS occurs from positions on the substrate that do not exhibit 2WL generation (Figure 2). This suggests that hot

spots responsible for 2WL emission will not also give rise to SERS-type field enhancement. Whereas one-photon WL is considered a signature of nonmetallic, fluorescent aggregates of a few silver atoms<sup>9</sup> which are not directly related to the extraordinary plasmonic field enhancements of the substrates, two-photon excitation necessitates strong local field enhancement.

Because of concerns about background and stability, SM-SERS does not always receive the attention it merits. Indeed, background emission under one-photon excitation has previously been found to be correlated directly with the observed SERS intensity.<sup>6a–c,8d</sup> Our results suggest that nonlinear WL emission is neither intrinsic to SERS nor a necessary outcome of the vast plasmonic field enhancements responsible for SERS. A key problem in SM-SERS is the need to spatially combine one single molecule with one single hot spot. Two-photon WL generation provides facile prescreening to identify substrates of poor SM-SERS performance. Background-free SERRS, as shown in Figure 1f, is preferentially observed from positions on the substrate which are mute under high intensity infrared excitation.

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**Supporting Information Available:** Analysis of spot densities in Figure 1; spatial correlation measurements under 950 nm excitation; power dependence of 2WL generation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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