Measurement of the Surface-Enhanced Coherent Anti-Stokes Raman Scattering (SECARS) Due to the 1574 cm^{-1} Surface-Enhanced Raman Scattering (SERS) Mode of Benzenethiol Using Low-Power (<20 mW) CW Diode Lasers

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The surface-enhanced coherent anti-Stokes Raman scattering (SECARS) from a self-assembled monolayer (SAM) of benzenethiol on a silver-coated surface-enhanced Raman scattering (SERS) substrate has been measured for the 1574 cm^{-1} SERS mode. A value of 9.6 ± 1.7 × 10^{-14} W was determined for the resonant component of the SECARS signal using 17.8 mW of 784.9 nm pump laser power and 7.1 mW of 895.5 nm Stokes laser power; the pump and Stokes lasers were polarized parallel to each other but perpendicular to the grooves of the diffraction grating in the spectrometer. The measured value of resonant component of the SECARS signal is in agreement with the calculated value of 9.3 × 10^{-14} W using the measured value of 8.7 ± 0.5 cm^{-1} for the SERS linewidth Γ (full width at half-maximum) and the value of 5.7 ± 1.4 × 10^{-7} for the product of the Raman cross section σ_{SERS} and the surface concentration N_s of the benzenethiol SAM. The *xxxx* component of the resonant part of the third-order nonlinear optical susceptibility $|3\chi^{(3)R}_{xxxx}|$ for the 1574 cm^{-1} SERS mode has been determined to be 4.3 ± 1.1 × 10^{-5} cm·g^{-1}·s^2. The SERS enhancement factor for the 1574 cm^{-1} mode was determined to be 3.6 ± 0.9 × 10^7 using the value of 1.8 × 10^{15} molecules/cm^2 for N_s.

Index Headings: **Surface-enhanced Raman scattering; SERS; Surface-enhanced coherent anti-Stokes Raman scattering; SECARS.**

INTRODUCTION

Coherent anti-Stokes Raman scattering (CARS) was first observed by Terhune.[1] A more detailed account of CARS was reported by Maker and Terhune.[2] CARS is a four-wave mixing process, which involves third-order optical nonlinearity $\chi^{(3)}$. Two pump photons are annihilated, resulting in the creation of a coherent Stokes Raman photon and a coherent anti-Stokes Raman photon. The generation of coherent Stokes Raman and anti-Stokes Raman photons are referred to as coherent Stokes Raman scattering (CSRS) and coherent anti-Stokes Raman scattering (CARS). Plane metal (silver) surface CARS due to the 992 cm^{-1} mode of benzene was reported by Chen et al.[3] in 1979. Nanostructured metal surface-enhanced CARS (SECARS) was proposed by Chew et al.[4] in 1984. The observation of SECARS due to the 992 cm^{-1} mode of benzene molecules on silver nanoparticles (NPs) was reported by Liang et al.[5] in 1994 using the 458, 501, 511, and 521 nm pump laser excitation with 8 ns pulses. Ichimura et al.[6] reported in 2003 the observation of SECARS from the 1329 cm^{-1} mode of adenine molecules attached to a single gold NP using 785.4 nm pump laser excitation. SECARS of pyridine on silver NPs has been reported by Namboodiri et al.[7] More recently, SECARS spectra of benzenethiol and nitrobenzenethiol on commercially available SERS substrates (Mesophotonics Ltd., Hampshire, UK) were reported by Stew et al. using pulsed Ti:Sapphire lasers.[8] Abnormal anti-Stokes Raman emission has been reported by Baibarac et al.[9] as a single-beam CARS in $LiNbO_3$ and CdS powder resulting from the mixing of the pump light with the Stokes component of the Raman scattered light. There are several other important articles on CARS.[10–12]

In this paper, we report the measurement of the SECARS signal due to the 1574 cm^{-1} SERS mode of a self-assembled monolayer (SAM) of benzenethiol on a silver film over nanospheres (AgFON)[13,14] surface-enhanced Raman scattering (SERS) substrate using low power (<20 mW) continuous wave (CW) diode lasers for the 784.9 nm pump and 895.6 nm Stokes beams. This paper includes a quantitative comparison of the measured value of the resonant component of the SECARS signal with that computed using the measured values of the SERS line width Γ and that of the product of the SERS cross section σ_{SERS} and the surface concentration N_s of benzenethiol molecules in the SAM. The measured value of the SECARS signal is found to be consistent with its calculated value. The SECARS may have potential for the detection of trace amounts of contaminants.

EXPERIMENTAL

The AgFON SERS substrate was fabricated at Northwestern University using SiO_2 nanospheres and 200 nm thick Ag film following the procedure described previously.[15] A benzenethiol SAM was deposited on the SERS substrate following the procedure reported earlier.[16] A schematic of the optical setup is shown in Fig. 1, which includes a Raman spectrometer (RS), a pump laser (PL), a Stokes laser (SL), half-wave plates (HWPs) for setting the polarization of the pump and Stokes lasers, a 785 nm short-wave-pass beam splitter (BS1) for reflecting the pump laser beam and transmitting the SECARS beam, a 795 nm short-wave-pass beam splitter (BS2) for combining the pump and Stokes laser beams, a lens (L1) for focusing the pump and Stokes laser beams upon the SERS substrate as well as for the collection and collimation of the SECARS beam, short-wave-pass filters (SWPFs) to block the pump light from entering the Raman spectrometer, and a lens (L2) for focusing

Received 4 May 2012; accepted 19 September 2012.
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DOI: 10.1366/12-06714

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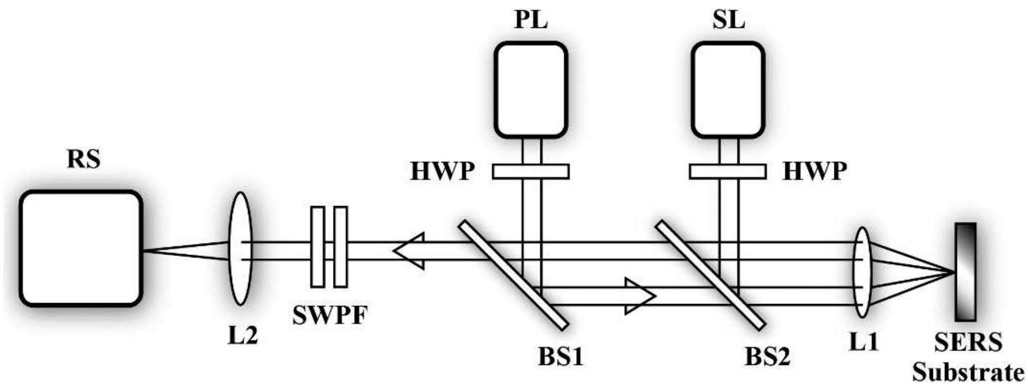

FIG. 1. Schematic of the optical setup for the measurement of the SECARS signal from a self-assembled monolayer (SAM) of benzenethiol on a surface-enhanced Raman scattering (SERS) substrate.

the SECARS beam upon the entrance slit of the Raman spectrometer.

The Raman spectrometer is the Princeton Instruments model SP-2556 (Princeton Instruments, Trenton, NJ), which is equipped with the Princeton Instruments CCD camera model PIXIS 100BR. The grating in the spectrometer has 1200 grooves/mm. The blaze wavelength of the grating is 750 nm. The resolution (full width at half-maximum) of the Raman spectrometer was determined to be 2.0 $\pm$ 0.1 cm^{-1} for the 784.9 nm pump laser beam using 80 μm entrance slitwidth.

The pump laser is a 784.9 nm, 1400 mW CW single-mode (both transverse and longitudinal), linearly polarized Sacher Lasertechnik diode laser model SYS-420-0785-1400 (Sacher Lasertechnic, Marburg, Germany/Buena Park, CA). The Stokes laser is a tunable (870–940 nm), 30 mW CW single-mode, linearly polarized Sacher Lasertechnik diode laser model TEC-500-0920-030. The half-wave plates are achromatic for the 700 1000 nm spectral range, Edmund Optics part number 46-561 (Edmund Optics, Barrington, NJ). The beamsplitter BS1 has reflectance $R > 95\%$ for the 784.9 nm pump laser and transmittance $T > 90\%$ for the 685–780 nm spectral range. The beamsplitter BS2 has transmittance $T > 90\%$ for the 687–787 nm spectral range and $R > 90\%$ for the 795–940 nm spectral range. The L1 lens is a 12 mm diameter, 20 mm effective focal length (EFL), near-infrared (NIR) achromat Edmund Optics part number 45-792. The L2 lens is a 25 mm diameter, 40 mm EFL, NIR achromat Edmund Optics part number 45-801. The short-wave-pass filters are 25 mm diameter Semrock part number SP01-785RU-25 (Semrock, Rochester, NY) with $T > 97\%$ for the 400–774 nm spectral range. The diameter of the focused pump and Stokes laser beam spots was determined to be 40 $\pm$ 5 μm by measuring laser power transmitted through 20 and 30 μm diameter pinholes.

THEORETICAL

The maximum value of the resonant component of the SECARS signal (erg/s) is given by[17]

$$P^R_{SECARS} = \left(\frac{c^2 \nu_{SECARS} \sigma_{SERS} N_s}{4\pi^2 h \nu^4_{SERS} \Gamma}\right)^2 \left(\frac{P_P}{A_P}\right)^2 P_S \qquad (1)$$

where c (cm/s) is the speed of light in vacuum, ν_{SECARS} (Hz) is the frequency of the SECARS signal, σ_{SERS} (cm^2/molecule) is the SERS cross section, N_s (molecules/cm^2) is the surface concentration of benzenethiol SAM, h (erg·s) is the Planck's constant, ν_{SERS} (Hz) is the frequency of the Stokes component of the SERS signal, Γ (Hz) is the SERS line width (full width at half-maximum), P_P (erg/s) is the pump laser power incident upon the SERS substrate, A_P (cm^2) is the area of the pump and Stokes laser beams spot on the SERS substrate, and P_S (erg/s) is the Stokes laser power incident upon the SERS substrate. For given values of P_P, A_P, and P_S, the value of P^R_{SECARS} may be computed from Eq. (1) using the values of $\sigma_{SERS,}$ N_s, Γ, c, ν_{SECARS}, and ν_{SERS}.

RESULTS AND DISCUSSION

The SECARS data were obtained with the pump laser operating at a fixed wavelength of 784.91 nm, which corresponds to the value of 12 740 cm^{-1} for ν_P. The Stokes laser wavelength was set to 895.54 nm, corresponding to ν_{SERS} of 11 166 cm^{-1} for 1574 cm^{-1} SERS mode for the on-resonance data. The Stokes laser wavelength was set to 896.53 nm, corresponding to 11 154 cm^{-1} for the off-resonance data. Figure 2 shows the on-resonance, off-resonance, and pump only spectra obtained using 1.0 s integration time, 17.8 mW of pump laser power, and 7.1 mW of Stokes laser power incident upon the SERS substrate.

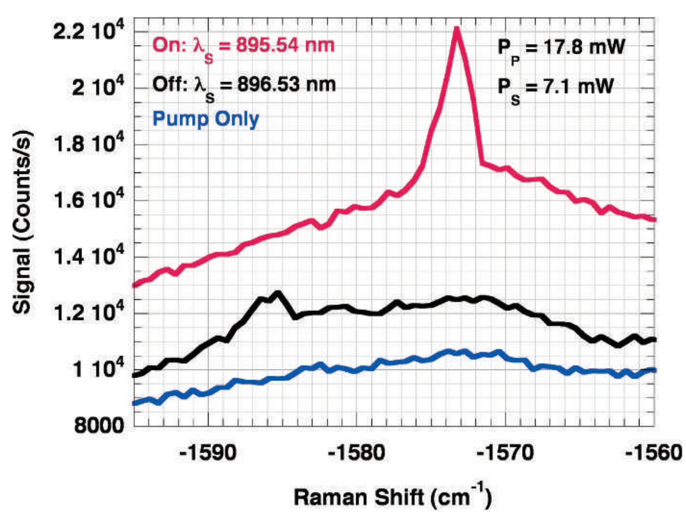

FIG. 2. On-resonance, off-resonance, and pump only spectra for the 1574 cm^{-1} SERS mode obtained using 1.0 s integration time, 17.8 mW of pump laser power, and 7.1 mW of Stokes laser power incident upon the SERS substrate.

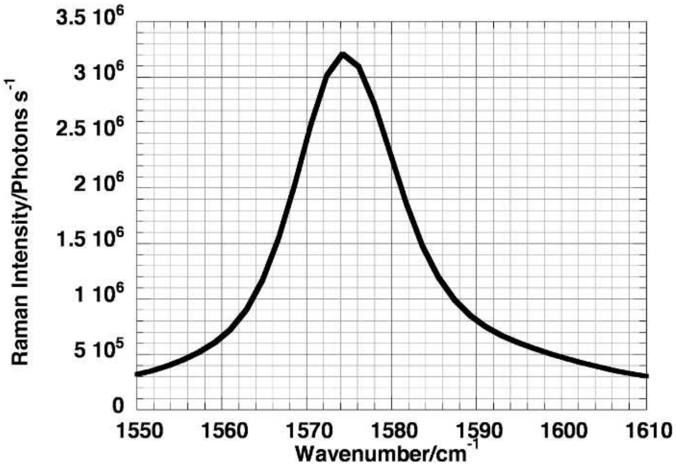

FIG. 3. SERS spectrum for the 1574 cm^{-1} mode of benzenethiol SAM obtained using 0.5 mW of 784.9 nm pump laser power and 0.25 s integration time.

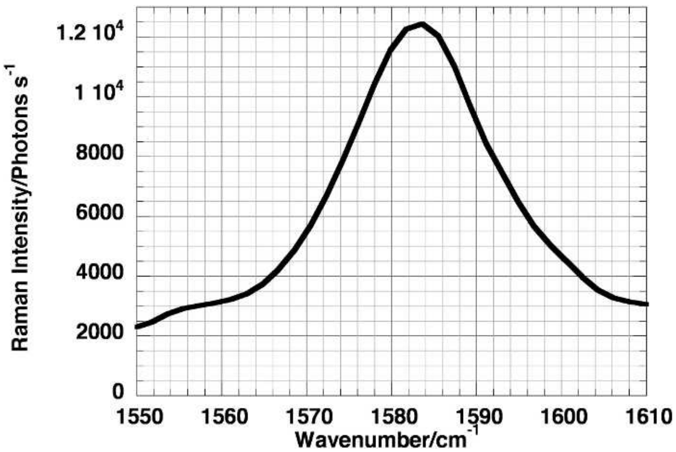

FIG. 4. Raman spectrum for the 1584 cm^{-1} mode of neat benzenethiol in a 0.5 mm cell obtained using 1.0 mW of 784.9 nm pump laser power and 1.0 s integration time.

We note that the on-resonance spectrum shows a SECARS component superimposed on a background for the 1574 cm^{-1} mode; the linewidth (full width at half-maximum) is 2.5 ± 0.2 cm^{-1} at 698.6 nm, which is limited by the resolution of the Raman spectrometer (2.0 ± 0.1 cm^{-1} at 785 nm). The off-resonance spectrum shows the SECARS component for the 1586 cm^{-1} mode, which is approximately an order of magnitude weaker than the 1574 cm^{-1} mode, because the SERS cross section for the 1586 cm^{-1} mode is about 1/3 of that for the 1574 cm^{-1} mode.[15]

Our claim for the observation of the SECARS signal is based on the following arguments: (1) The linewidth of the SECARS signal should be equal to/or less than the sum of the linewidths of the pump and Stokes lasers, which are about 1 MHz for the CW diode lasers used in this work. The observed linewidth of the SECARS signal (2.5 ± 0.2 cm^{-1}) is limited by the resolution of the Raman spectrometer (2.0 ± 0.1 cm^{-1}), which is consistent with the expected result; (2) Divergence of the SECARS signal/beam should be similar to that of the pump laser beam. The divergence of the SECARS beam was determined by placing an aperture in front of the lens L2, which is used to focus the scattered light on the slit of the Raman spectrometer. The maximum intensity of the SECARS signal was obtained for an aperture diameter of ~2.7 mm, which is comparable to the diameters of the pump and Stokes laser beams incident upon the lens L1; (3) The measured value of the SECARS signal is found to be in good agreement with its computed value, as shown later in this section.

The value of the counts per second integrated over the −1577.3 to −1570.4 cm^{-1} spectral region in Fig. 2 is 2.3 ± 0.1×10^4 counts per second for the resonant component of the SECARS signal. The reflectance of the SERS substrate was measured to be 19.5 ± 1.0% at 698.6 nm, which corresponds to the wavelength of the SECARS signal for the 1574 cm^{-1} mode. The combined transmittance of L1, BS2, BS1, SWPFs, and L2 is estimated to be 72 ± 4% at 698.6 nm. Therefore, only 14 ± 2% of the SECARS photons generated by the benzenethiol SAM are incident upon the Raman spectrometer. The throughput of the Raman spectrometer was estimated to be 52 ± 3% at 698.6 nm using the values for the reflectance of the mirrors, reflectance of the diffraction grating, and the transmittance of the vacuum window on the camera. The quantum efficiency of the CCD camera is 91 ± 1% at 698.6 nm. Therefore, it requires an input of 2.1 ± 0.2 photons at the entrance slit of the spectrometer to produce a signal output of one count. Therefore, the measured value of the resonant component of the SECARS signal is 3.4 ± 0.6×10^5 photons/s, which corresponds to 9.6 ± 1.7×10^{-14} W or 9.6 ± 1.7×10^{-7} erg/s using the value of 2.84×10^{-19} J for the energy of a SECARS photon.

In order to calculate the value of the resonant component of SECARS from Eq. (1), we need a value of the product of σ_{SERS} and N_s, which is determined as follows. Figure 3 shows the SERS spectrum for the 1574 cm^{-1} mode obtained with a low-resolution (~15 cm^{-1}) Raman spectrometer DeltaNu model Advantage 785 (DeltaNu, Laramie, WY) using 0.5 mW of 784.9 nm pump laser power and 0.25 s integration time.

The value of the integrated (1550–1600 cm^{-1}) SERS photon flux F_{SERS} in Fig. 3 is 2.6 ± 0.4×10^7 photons/s after subtracting the contribution due to the background. The value of $\sigma_{SERS}N_s$ is determined from

$$\sigma_{SERS}N_s = \left(\frac{h\nu_P}{\eta_c P_P}\right)F_{SERS} \quad (2)$$

where η_c is the collection efficiency given by

$$\eta_c = \frac{d^2}{16f^2} \quad (3)$$

where d is the diameter and f is the focal length of the collimating lens. Using the values of 12.0 mm and 20 mm for d and f, respectively, Eq. 3 yields a value of 2.25×10^{-2} for η_c. Using the values of 3.822×10^{14} Hz for ν_P, 2.25×10^{-2} for η_c, 5.0 ± 0.2×10^3 erg/s for P_P corresponding to 0.50 ± 0.02 mW, and 2.6 ± 0.4×10^7 for F_{SERS}, Eq. 2 yields a value of 5.9 ± 1.2×10^{-7} for $\sigma_{SERS}N_s$.

Figure 4 shows the Raman spectrum for the 1584 cm^{-1} of neat benzenethiol in a 0.5 mm cell using 1.0 mW of 784.9 nm pump power and 1.0 s integration time. The value of the integrated (1560–1610 cm^{-1}) Raman photon flux F_R is 1.04 ± 0.15×10^5 photons/s after subtracting the contribution due to the background.

The value of $\sigma_{SERS}N_s$ is given by

$$\sigma_{SERS}N_s = \left(\frac{\sigma_{RS}NL}{n^2}\right)\left(\frac{P_P^{RS}}{P_P^{SERS}}\right)\left(\frac{F_{SERS}}{F_{RS}}\right) \quad (4)$$

where σ_{RS} (cm^2/molecule) is the Raman cross section of neat benzenethiol, N is the molecular concentration (cm^{-3}) of neat benzenethiol, L (cm) is the length of the benzenethiol cell along the direction of the pump laser, P_P^{SERS} is the pump laser power incident upon the benzenethiol SAM, and P_P^{RS} is the pump laser power incident upon the neat benzenethiol sample. Substituting the value of $8.9 \pm 1.8\times10^{-30}$ cm^2/molecule for σ_{RS},[16] 5.9×10^{21} molecules/cm^3 for N, 0.05 cm for L, 1.56 for n,[18] 1.00 ± 0.04 mW for P_P^{RS}, 0.50 ± 0.02 mW for P_P^{SERS}, $2.6 \pm 0.0.4\times10^7$ photons/s for F_{SERS}, and $1.04 \pm 0.15\times10^5$ photons/s for F_{RS}, Eq. 4 yields a value of $5.5 \pm 1.4\times10^{-7}$ for $\sigma_{SERS}N_s$, which is in agreement with the value of $5.9 \pm 1.2\times10^{-7}$ obtained from Eq. 2. Thus, the average value of $\sigma_{SERS}N_s$ is $5.7 \pm 1.4\times10^{-7}$.

Using the value of $1.8\times10^{15}/cm^2$ for N_s,[16] we obtain a value of 3.2×10^{-22} cm^2/molecule for σ_{SERS}. The value of the Raman cross section σ_{RS} for neat benzenethiol was determined to be 8.9×10^{-30} cm^2/molecule.[16] This yields a value of 3.6×10^7 for the SERS enhancement factor EF.

Substituting the values of 4.294×10^{14} Hz for ν_{SECARS}, 5.7×10^{-7} for $\sigma_{SERS}N_s$, 3.349×10^{14} Hz for ν_{SERS}, and 2.61×10^{11} Hz for Γ, 1.78×10^5 erg/s for P_P corresponding to 17.8 mW, 1.26×10^{-5} cm^2 for A_P, and 7.1×10^4 erg/s for P_S corresponding to 7.1 mW, Eq. 1 yields a value of 9.3×10^{-7} erg/s for P_{SECARS}^R, which is in agreement with the measured value of $9.6 \pm 1.7\times10^{-7}$ erg/s. The *xxxx* component of the resonant part of $\chi^{(3)}$ is given by

$$|3\chi_{xxxx}^{(3)R}| = \frac{c^4\sigma_{SERS}N_s}{32\pi^5 h\nu_{SERS}^4\Gamma L} \quad (5)$$

where L is the thickness of the benzenethiol SAM; we assume a value of 0.5 nm for L. Using the measured values of 5.7×10^{-7} for $\sigma_{SERS}N_s$ and 2.61×10^{11} for Γ, Eq. 5 yields a value of $4.3 \pm 1.1\times10^{-5}$ $cm \cdot g^{-1} \cdot s^2$ for $|3\chi_{xxxx}^{(3)R}|$. The corresponding value of $|3\chi_{xxxx}^{(3)R}|$ for the 1584 cm^{-1} Raman mode of neat benzenethiol should be $1.2 \pm 0.3\times10^{-12}$ $cm \cdot g^{-1} \cdot s^2$, as reduced by 3.6×10^7, the value of the SERS EF. The deduced value of $1.2 \pm 0.3\times10^{-12}$ $cm \cdot g^{-1} \cdot s^2$ for $|3\chi_{xxxx}^{(3)R}|$ for the 1584 cm^{-1} Raman mode of neat benzenethiol, because of its larger linewidth, should be less than the measured value of $2.8 \pm 0.3\times10^{-12}$ $cm \cdot g^{-1} \cdot s^2$ for the 1002 cm^{-1} mode.[19]

SUMMARY

We have measured the value of the resonant component of the SECARS signal for the 1574 cm^{-1} SERS mode of benzenethiol SAM. The measured value of the resonant SECARS signal is found to be consistent with that calculated using the measured values of $5.7 \pm 1.4\times10^{-7}$ for $\sigma_{SERS}N_s$ and 8.7 ± 0.5 cm^{-1} for Γ.

ACKNOWLEDGMENTS

We thank Dr. T.Y Fan, Dr. B. Saar, Dr. J. Parkhill, and Prof. A. Aspuru-Guzik for their comments regarding this work and Russell Goodman for depositing benzenethiol SAM on the SERS substrate. The MIT Lincoln Laboratory portion of this work was sponsored by the Defense Advanced Research Projects Agency under Air Force Contract FA8721-05-C-0002. Opinions, interpretation, and recommendations are those of the authors, and do not necessarily represent the view of the United States Government.

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