

Population Pumping of Excited Vibrational States by Spontaneous Surface-Enhanced Raman Scattering

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We observed significant transfer of ground state population to the first excited vibrational state by spontaneous surface-enhanced Raman scattering (SERS) which can be explained by unexpectedly large SERS cross sections. Evidence for this pumping includes (i) anti-Stokes to Stokes ratios which exceed those expected from a Boltzmann distribution, (ii) a quadratic dependence of the anti-Stokes signal on the excitation intensity, whereas the Stokes signal remains linearly dependent, and (iii) a component of $\nu = 1$ to $\nu = 2$ Raman transitions in the SERS Stokes signals.

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New methods of exciting coherent and incoherent molecular vibrations are of growing interest as a prerequisite for studying phase and energy vibrational relaxation processes [1], as well as for creating chemical pathways which may not occur under normal excitation conditions [2]. Current methods of populating vibrational states include IR absorption using intense far IR laser light [1,3], stimulated Raman processes [1,2], and stimulated emission pumping [4].

The extremely small cross sections of spontaneous Raman scattering preclude its use for pumping vibrational states. However, this situation is dramatically altered for surface-enhanced Raman scattering (SERS). Surface-enhancement factors on the order of 10^{10} or larger [5,6] increase the effective Raman cross sections from a range of 10^{-31} – 10^{-29} to about 10^{-20} cm^2 , suggesting that SERS can be a valuable tool for pumping vibrational states and performing vibrational pump-probe experiments on adsorbed molecules [7].

In this Letter we show that SERS can significantly populate the first excited vibrational states of molecules adsorbed on the surface of colloidal metal particles, even under cw conditions at relatively low excitation intensities. We studied near infrared excited surface-enhanced Stokes and anti-Stokes Raman scattering of crystal violet (CV) and rhodamine 6G (R6G) adsorbed on colloidal silver in aqueous solution. Samples were prepared in the same way as described previously [8,9] to achieve optimal conditions for SERS at near IR excitation.

SERS spectra were measured from a 100 μl droplet of the colloidal sample solution placed on a glass microscope slide. A microscope attachment was used for excitation and for collecting the scattered light. The water immersion microscope objective was brought into direct contact with the droplet. Raman spectra were excited by means of an argon-ion laser pumped cw Ti:sapphire laser operating at 830 nm with a power of 10 to 150 mW at the sample. The scattered light was dispersed using a Chromex spectrograph with a deep depletion charge coupled device detector. This experimental geometry provides efficient

signal acquisition, due to both a large collection angle and total overlap of excitation and collection volumes, as well as relatively high excitation intensities, between 4×10^{23} and 5×10^{24} photons/ cm^2 s.

Figures 1(a) and 1(b) show Stokes and anti-Stokes SERS spectra of CV and R6G measured at 150 mW excitation power. The Stokes-SERS spectra agree with those previously reported [5,6,8,9]. For purpose of display, Stokes and anti-Stokes spectra are normalized to the 1174 cm^{-1} band for CV and the 610 cm^{-1} band for R6G.

The anti-Stokes to Stokes SERS signal ratios, $P_a^{\text{SERS}}/P_s^{\text{SERS}}$, for various SERS bands of CV and R6G (Raman shifts ν_m) were normalized to the anti-Stokes to Stokes signal ratios for a "normal" (non-surface-enhanced) Raman experiment (RS) measured under the same conditions and at the same temperature:

$$K(\nu_m) = \frac{P_a^{\text{SERS}}(\nu_m)/P_s^{\text{SERS}}(\nu_m)}{P_a^{\text{RS}}(\nu_m)/P_s^{\text{RS}}(\nu_m)}. \quad (1)$$

By using this normalization potential errors due to system response were excluded, and thus $K(\nu_m)$ directly describes the measured deviations of the anti-Stokes to Stokes SERS signal ratios from a Boltzmann population. To establish the expected Boltzmann values of $P_a^{\text{RS}}/P_s^{\text{RS}}$ at the appropriate Raman shifts, we measured the signal ratios of the anti-Stokes to Stokes Raman bands of benzene in a non-SERS experiment using the same apparatus and interpolated between the benzene peaks. The resulting experimental values for $K(\nu_m)$ for the different Raman bands of CV and R6G measured at 150 mW excitation power are indicated by crosses in Figs. 2(a) and 2(b), respectively. As can be seen, values of $K(\nu_m)$ between 3 and 80 are observed.

A simple theoretical estimate for $K(\nu_m)$ can be derived from the rate equation describing the population or depopulation of the first excited vibrational level by SERS Stokes and anti-Stokes transitions [7]. In the steady state, and assuming that $\sigma^{\text{SERS}}(\nu_m)\tau_1(\nu_m)n_L \ll 1$ (weak

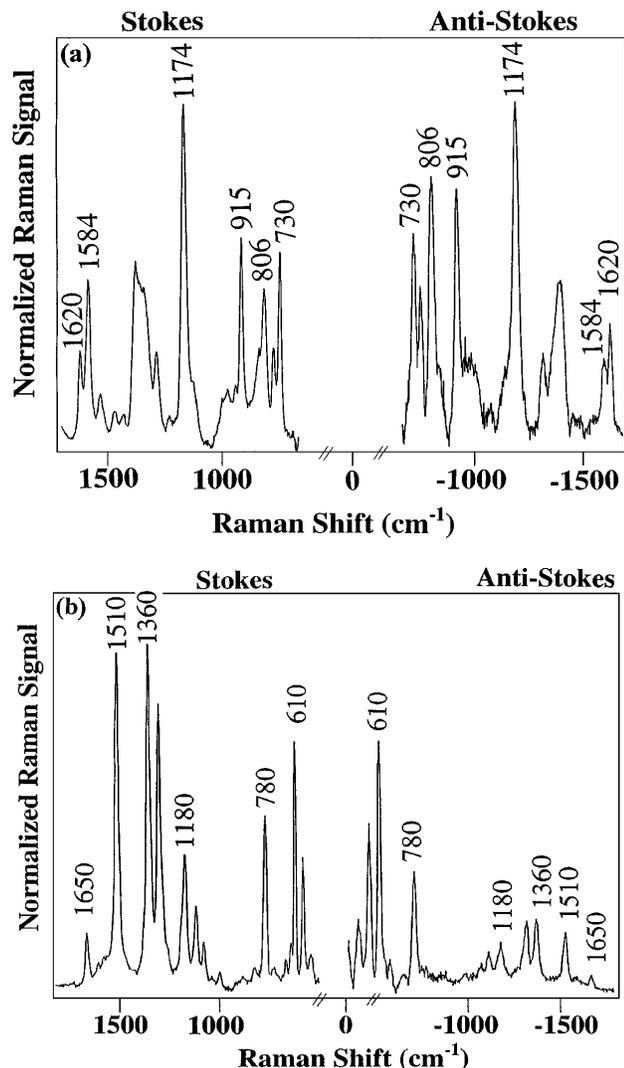


FIG. 1. SERS Stokes and anti-Stokes spectrum of (a) crystal violet and (b) rhodamine 6G.

saturation), $K(\nu_m)$ can be expressed as

$$K(\nu_m) = \sigma^{\text{SERS}}(\nu_m)\tau_1(\nu_m)e^{h\nu_m/kT}n_L + 1, \quad (2)$$

where σ^{SERS} is the effective SERS cross section, τ_1 the lifetime of the first excited vibrational state, and n_L the photon flux density of the excitation laser beam. The first term on the right hand side of Eq. (2) is proportional to the population of the first excited vibrational state in excess of the Boltzmann population at temperature T . For normal Raman scattering $\sigma^{\text{RS}}(\nu_m)\tau_1(\nu_m)$ is on the order of $10^{-40} \text{ cm}^2 \text{ s}$. At a sample temperature of 300 K the exponential term is in the range 10^2 – 10^3 , so in order to account for the large $K(\nu_m)$ values we obtained in our experiments for laser intensities of about 10^5 W/cm^2 , the product $\sigma^{\text{SERS}}(\nu_m)\tau_1(\nu_m)$ must be on the order of $10^{-27} \text{ cm}^2 \text{ s}$.

The curves labeled *C* in Fig. 2 show the estimated $K(\nu_m)$ values versus Raman shift predicted by Eq. (2) by setting n_L to the experimental values

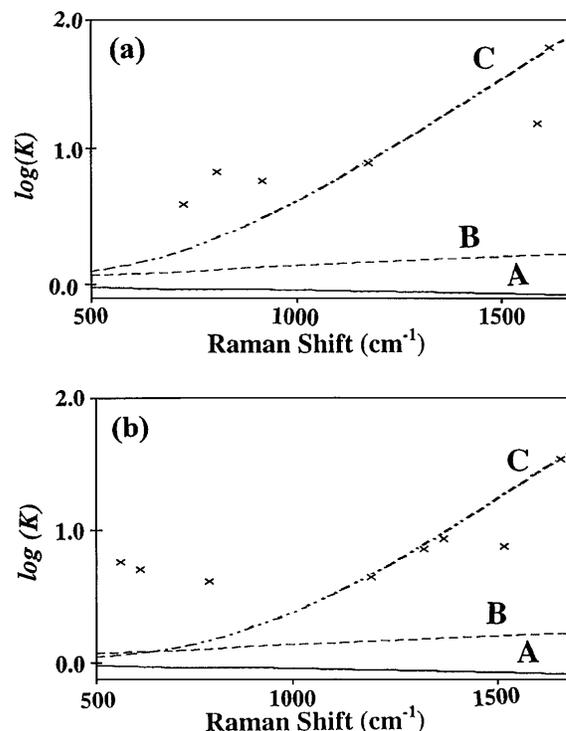


FIG. 2. Experimental $K(\nu_m)$ values (crosses) at 150 mW excitation power for CV (a) and R6G (b) vs Raman shifts and estimated $K(\nu_m)$ values (curves *C*) (see text). Curves *A*: ratios of the electromagnetic SERS enhancement factors for anti-Stokes and Stokes scattering [7], curves *B*: anti-Stokes to Stokes ratios for an increased sample temperature (330 K) [10].

of $5 \times 10^{24} \text{ photons/cm}^2 \text{ s}$ and $\sigma^{\text{SERS}}(\nu_m)\tau_1(\nu_m)$ to a constant value for each dye, $3 \times 10^{-27} \text{ cm}^2 \text{ s}$ for R6G and $6 \times 10^{-27} \text{ cm}^2 \text{ s}$ for CV, which fit the experimental $K(\nu_m)$ values for 1174 and 1180 cm^{-1} for CV and R6G, respectively. The estimated $K(\nu_m)$ curves include corrections for different electromagnetic SERS enhancement factors for Stokes and anti-Stokes scattering as described by curves *A* [7].

The curves labeled *B* show the anti-Stokes to Stokes ratios predicted [10] for an increased SERS sample temperature of 330 K compared to the normal ratio for the reference sample at 300 K. There was no evidence of heating effects in our SERS samples. However, even if the local temperature of the colloidal silver particles in the focus of the laser beam had increased to 375 K, the second term on the right hand side of the expression for $K(\nu_m)$ in [10] would only change from 1 to values between 1.5 and 4 for the different SERS bands. Thus, the observed $K(\nu_m)$ values cannot be attributed to sample heating.

The qualitative agreement of curves *C* with the experimental data supports the explanation that spontaneous SERS pumping is responsible for the large $K(\nu_m)$ values we observe. However, some of the data points deviate from the predictions. Deviations are not surprising because the theoretical estimate of curves *C* neglects

features such as variations in the Raman cross sections and energy relaxation behavior for different molecular vibrations, as well as Stokes pumping to the second excited vibrational state. The measured deviations may reflect the relative lifetimes and the SERS cross sections of the particular vibrational modes compared to the fitting mode. The higher $K(\nu_m)$ values measured mainly for the low frequency modes could be the result of intramolecular energy relaxation, which would give rise to longer effective lifetimes of the lower molecular vibrational levels.

Accepting the product $\sigma^{\text{SERS}}(\nu_m)\tau_1(\nu_m)$ to be on the order of $10^{-27} \text{ cm}^2\text{s}$, which explains the observed pumping rates to the excited vibrational states, and assuming a lifetime of the vibrational excited state on the order of 10 ps [11,12], the surface-enhanced Raman cross sections must be on the order of 10^{-16} cm^2 . Such a cross section exceeds all previous estimates of SERS cross sections or SERS enhancement factors [5,6]. These estimates were based on the assumption that nearly all molecules in the SERS sample contribute in a similar way to the measured SERS signal, resulting in a relatively "small" average cross section per molecule. In the present case, in order to make the large cross sections consistent with the level of the observed SERS Stokes signal, we must draw the conclusion that the number of molecules which are involved in the SERS process is extremely small. By comparing the SERS-Stokes signal with the non-SERS Raman scattering signal of pure benzene measured under the same experimental conditions, we roughly estimate that the dye molecules participating in the SERS process are $10^{-13}M$ to $10^{-12}M$ concentration. This means that only 0.01% of the molecules in the sample contribute to the observed SERS signal.

Pumping of vibrational levels by a surface-enhanced Stokes process in the weakly saturating intensity regime [$\exp(h\nu_m/kT) \leq \sigma^{\text{SERS}}(\nu_m)\tau_1(\nu_m)n_L \ll 1$], as in our experiments, gives rise to a quadratic dependence of the anti-Stokes power P_a on the excitation intensity, whereas the Stokes power P_s remains linearly dependent [7]:

$$P_a \approx (N_0 e^{-h\nu_m/kT} + N_0 \sigma^{\text{SERS}} \tau_1 n_L) \sigma^{\text{SERS}} n_L, \quad (3a)$$

$$P_s \approx N_0 \sigma^{\text{SERS}} n_L, \quad (3b)$$

where N_0 is the number of molecules in the vibrational ground state interacting with the laser beam and n_L is the laser intensity. The data of Fig. 3 show the plots of the anti-Stokes and Stokes SERS signals versus excitation intensity. The lines indicate quadratic and linear fits to the respective data, displaying the predicted dependence. Plots displaying such dependence can be obtained for every Raman line of both molecules. Analysis of either peak areas or heights gives the same results.

Appreciably populating the first excited vibrational state permits the observation of $\nu = 1$ to $\nu = 2$ Stokes scattering as well. We extracted the Raman spectrum of the $\nu = 1$ to $\nu = 2$ transitions from SERS Stokes spectra measured at excitation intensities

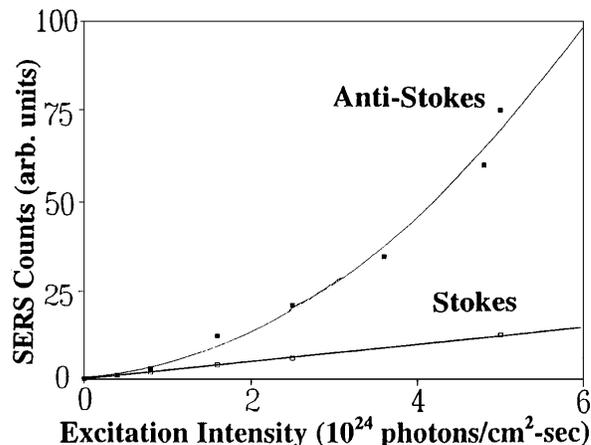


FIG. 3. Anti-Stokes and Stokes SERS signals vs excitation intensity for the 1174 cm^{-1} Raman band of CV.

high enough to give clearly increased anti-Stokes to Stokes ratios. By subtracting a low excitation intensity ($4 \times 10^{23} \text{ photons/cm}^2\text{s}$) SERS spectrum (traces A and C in Fig. 4) from a spectrum measured at higher laser intensity ($5 \times 10^{24} \text{ photons/cm}^2\text{s}$) and taking into account the factor of 12 due to the ratio of the excitation intensities of the two spectra, a residual spectrum appears, as shown by traces B and D in Fig. 4. The Raman bands in the Stokes difference spectrum are shifted between 3 and 8 cm^{-1} to lower wave numbers compared with the low-power spectrum, and it is reasonable to attribute spectrum B to $\nu = 1$ to $\nu = 2$ vibrational transitions. The frequency shifts observed between the $\nu = 0$ to $\nu = 1$ (spectrum A) and $\nu = 1$ to $\nu = 2$ vibrational transitions are proportional to the absolute Raman shifts of the vibrational modes, and they provide direct information about the anharmonicity of the electronic ground state potentials. The anti-Stokes difference spectrum (trace D) shows no spectral shifts, as expected, indicating that the anti-Stokes scattering is restricted to $\nu = 1$ to $\nu = 0$ vibrational transitions. A contribution from the $\nu = 2$ to $\nu = 1$ anti-Stokes transition is not expected

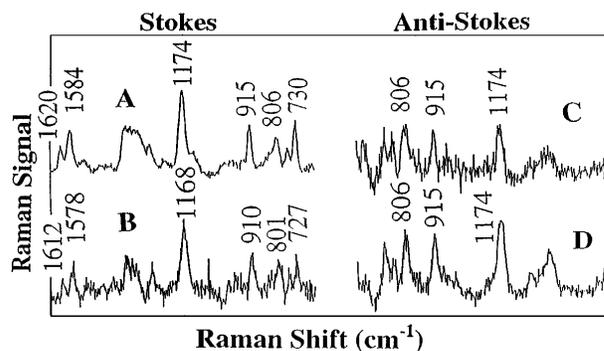


FIG. 4. Low-excitation intensity Stokes (A) and anti-Stokes (C) SERS spectrum of CV and intensity-normalized difference spectrum between high- and low-excitation intensity Stokes (B) and anti-Stokes (D) SERS.

at excitation intensities employed in these experiments [7]. The appearance of the spectrum D provides further evidence of the nonlinear dependence of the anti-Stokes power on the excitation intensity.

We did not observe a threshold intensity for the appearance of a nonlinear dependence of the anti-Stokes signal, nor for the appearance of deviations from $K(\nu_m) = 1$. This, as well as the linear dependence of the Stokes scattering signal on the excitation intensity, provides evidence that the observed vibrational pumping is the result of spontaneous Raman scattering and that stimulated Raman scattering does not contribute to the observed population transfer. This is reasonable because, despite the extremely large Raman cross section, the stimulated Raman gain remains small due to the small number of scattering molecules participating in the process.

In summary, we have shown that spontaneous surface-enhanced Raman scattering can transfer significant population to the first excited vibrational states. Our experimental results using cw excitation at a relatively low power level suggest a simple way to pump a "system" in order to populate high-lying vibrational levels using pulsed excitation lasers at higher intensities. It should be noted that system means that small fraction of molecules that are subject to the extremely large SERS enhancement or, in other words, the system has a very low density. Consequently, the method of probing the population of such a system must be extremely sensitive. As we have shown, spontaneous surface-enhanced anti-Stokes Raman scattering meets this requirement. In this way, SERS pumping using pulsed excitation and time resolved anti-Stokes SERS probing could provide a method to study vibrational energy relaxation of adsorbed molecules. The large effective SERS cross sections also present interesting possibilities for coherently driven Raman experiments [2] and for generating large coherent vibrational amplitudes of adsorbed molecules.

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