Coherent anti-Stokes Raman scattering on single-walled carbon nanotube thin films excited through surface plasmons

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We report experimental data that indicate an anti-Stokes Raman emission, reminiscent of coherent anti-Stokes Raman scattering. It originates from a wave mixing process between the incident laser light ($\omega_0$) and Stokes Raman light ($\omega_s$) generated by a surface enhanced Raman scattering (SERS) mechanism. The variation of anti-Stokes SERS spectra of single-walled carbon nanotubes, copper phthalocyanine, and poly(bithiophene) as a function of the film thickness, the laser excitation intensity, and the numerical aperture of the microscopic objective used for collecting the scattered light demonstrate the described phenomenon.

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I. INTRODUCTION

Field enhancement effects in close proximity to nanometric metallic structures play an important role in generating various surface optical phenomena such as surface enhanced Raman scattering,1,2 enhanced infrared absorption,3,4 stimulated Raman scattering,4 second-harmonic generation,5 and two-photon-excited fluorescence.6 Such effects are strongly dependent on the surface morphology and the polarization properties of the exciting radiation. They appear as a combination of the electrostatic lightening rod effect, invoked by sharp structures on rough Au surfaces and localized surface plasmons (SPs) excitation that is sensitively dependent on the excitation wavelength.7 For a rough surface having a columnar structure of mean diameter much smaller than the wavelength of the exciting radiation, the enhanced fields, consisting of evanescent components, are strongly confined to the tip end.5 The enhanced fields interact locally with adsorbed molecules and generate optical signals that are detected in the far field. Surface enhanced Raman scattering (SERS) is such a signal.

SERS spectra show the fundamental characteristics of spontaneous Raman scattering: (i) an identical absolute value of the frequency of the corresponding anti-Stokes–Stokes pair lines; (ii) an anti-Stokes–Stokes intensity ratio ($I_{ss}/I_s$) described by the Maxwell-Bolzmann law; (iii) the same depolarization ratio $\rho$ for each pair of Stokes and anti-Stokes lines$^9$ ($\rho$ is the ratio between the intensity of the light scattered perpendicular to the incident polarization and that scattered parallel to it). These features can considerably change and an anti-Stokes radiation often appears almost as intense as the Stokes radiation. This has been explained as resulting from a nonthermal overpopulation of higher vibration states produced by the large photon density of the excitation light combined with the enhancement of the Raman cross section. For this, as a distinctive characteristic, a quadratic dependence of the surface enhanced anti-Stokes Raman scattering intensity on the incident laser power was found.$^{10}$

Recently, it has been reported that on tight-focusing two excitation fields on molecules attached to a nanometric gold structure can result in coherent anti-Stokes Raman scattering (CARS) signals.$^{11–13}$ These data, considered in the more general frame of CARS microscopy,$^{14–17}$ seem promising as a method to acquire new chemical and physical information on molecules having a nanoscale spatial distribution. Theoretical considerations on local-field enhancement of CARS in nanocomposite materials was also recently reported.$^{18}$

CARS is a four-wave mixing process in which the anti-Stokes light ($\omega_{ss}$) results from the parametric coupling of incident laser light ($\omega_0$), Stokes light ($\omega_s$; $\omega_s < \omega_0$), and a probe light ($\omega_p$).$^{19}$ When the frequency difference ($\omega_p - \omega_s$) coincides with the frequency of a Raman active mode ($\Omega_R$), an anti-Stokes Raman signal is resonantly generated at the frequency $\omega_{ss}(\omega_s = \omega_0 - \omega_s + \omega_p = \omega_0 + \Omega_R)$. In general, every CARS experiment appears as a degenerate four-wave mixing process. If $\omega_p = \omega_0$, the mixing process reduces to an energy transfer between the two pump waves. In the plane-wave approximation and for a nonabsorbing medium, the CARS intensity depends nonlinearly on the incident pump intensity $I_i$:

$$I_{CARS} \propto N_A \omega_{ss} d^2 |\chi^{(3)} |^2 |I_i|^2 \times I_s \text{sinc}^2(|\Delta k| \times d/2),$$  \hspace{1cm} (1)

where $\chi^{(3)}$ is the third order nonlinear dielectric susceptibility, $d$ is the sample slab thickness, $\Delta k$ the phase mismatch $[\Delta k = k_m - (2k_p - k_s)]$, and $k_m$, $k_s$, and $k_p$ are the wave vectors of the anti-Stokes, Stokes, and pump light, respectively. In Eq. (1) $\text{sinc}(x)$ means $\sin(x)/x$ and $N_A$ is the numerical aperture of the collecting lens. The generation of the CARS signal needs to fulfill the phase-matching condition $|\Delta k| \times d \ll \pi$ that reflects the coherent nature of the process.$^{19}$ It is important to notice that for a very thin film, $d \ll \lambda$, the phase-matching condition is satisfied in both the forward and backward directions. Equation (1) indicates that for exact phase matching ($\Delta k = 0$), when the term $\text{sinc}(|\Delta k| \times d/2)$ is equal to unity, the signal must increase as $d^2$. The
phase-matching requirement can be fulfilled in a collinear and a noncollinear geometry of the propagating beams. For condensed media, the small dispersion of refractive index makes $\Delta k \approx 0$, even over small paths, so that the phase-matching condition is fulfilled if the beams cross under an angle $\theta$. Focusing the input beams onto the sample, an increased intensity and an optimal overlap of the beam waist are obtained. For tightly focused beams, the requirement of phase matching relaxes, being no longer sensitive to the Raman shift and so a CARS spectrum can be observed without changing the alignment. The essential result of these considerations is that under focused beams, the maximum CARS emission takes place at an angle $\theta_{\text{opt}}$ larger than the Stokes angle $\theta_S$.

CARS intensity depends on the third-order nonlinear dielectric susceptibility,

$$\chi^{(3)} = \chi_R + \chi_{NR}$$

which is the sum of the resonant Raman part $\chi_R$ contributed by the closed vibration resonance $\Omega_R$ of the particular molecular species and a slowly varying nonresonant part $\chi_{NR}$, due to electronic resonances, independent of the Raman shift. As in a regular Raman effect that enhances when the incident or scattered frequencies match the energy corresponding to an electronically allowed transition, the CARS intensity increases when the energies of pumping beams are close to an electronic absorption. In this case, due to the different polarization properties of the resonant electronic portion of the $\chi^{(3)}$, the CARS emission will be characterized by a different polarization compared to conventional Stokes Raman emission.

In these circumstances one can raise the question of whether the intense anti-Stokes emission can originate from a CARS-type process or not. Below, we demonstrate such an origin. In the following, using SERS microscopy we demonstrate that an abnormal intense anti-Stokes Raman emission, reminiscent of Coherent anti-Stokes Raman scattering (CARS) resulting from the mixing of the incident laser light and Stokes Raman scattered light generated by a SERS mechanism, can be observed in any material whenever the energy of the exciting light coincides with the energy of an electronically allowed transition. Our attention was focused on the anti-Stokes Raman spectra on single-walled carbon nanotubes (SWNTs), copper phthalocyanine (CuPc) and poly(bithiophene) (PBTh).

SWNTs are as a rolled up graphene sheet into a seamless cylinder, with both ends capped with hemispheres made of hexagonal and pentagonal carbon rings. Theoretical calculations have predicted that the electronic properties of SWNTs depend on the tube diameter $d$ and on the helicity of the hexagonal carbon ring alignment on the nanotube surface, defined by the chiral angle $\theta$. These calculations for the one-dimensional (1D) electronic structure of SWNTs show that about 1/3 of the nanotubes are metallic and 2/3 are semiconducting. Both the tube diameter $d$ and the chiral angle $\theta$ depend on the $n$ and $m$ integers, which denote the number of unit vectors $a_1$ and $a_2$ in the hexagonal lattice of graphite:

$$a_{c-e} = 1.42 \, \text{Å}$$

is the nearest-neighbor C-C distance. Single-walled nanotubes are metallic if $n-m=3k$, $k=1,2,3,...$, and semiconducting otherwise. A slight variation in these parameters causes a shift from a metallic to a semiconducting state. Whatever the synthesis method, microscopic studies have revealed that nanotubes form bundles of 20–100 individual tubes aligned in a two-dimensional crystal packing arrangement over essentially their entire lengths. The 1D electronic density of states shows sharp singularities. When the photon energy matches the energy separation between an occupied peak in the electron density of states and an empty one, the strong optical absorption gives rise to exceptionally high intensities for the resonant Raman effect.

Raman spectroscopy is one of the widest used techniques for characterizing and understanding of properties of the carbon tubes. Raman scattering spectra obtained under various excitation wavelengths give rise to resonance Raman spectra, displaying specific changes in frequency, line shape, and intensity. It is worth noting that such modifications are observed in the 150–200-cm$^{-1}$ range, due to bands associated with the radial breathing modes (RBMs) whose frequencies are inversely proportional to the tube diameter. In the interval from 1100 to 1700 cm$^{-1}$ two bands are found: a broad one in the range of 1500–1600 cm$^{-1}$, named “G” band, associated with the tangential stretching modes (TMs), and another, referred to as the “D” band which is not intrinsically related to the nanotube structure, being also present in the Raman spectrum of graphitic materials. The D band is indicative of disorder induced in graphitic lattices or defects in nanotubes. A distinguishing feature of the G band is an asymmetric component with a maximum at $\sim 1540$ cm$^{-1}$ that appears at laser excitation energies of 1.7–2.2 eV. This band fits a Breit-Wigner-Fano (BWF) profile, indicating electron-phonon type interactions and corresponds to the resonant excitation of metallic nanotubes. Investigations of confocal Raman microscopy combined with atomic-force microscopy (AFM) and transmission electron microscopy (TEM) have demonstrated that the BWF line is strongly enhanced in bundles of SWNTs due to the excitation of plasmon modes resulting from the internanotube electrostatic interactions.

In Raman studies on SWNTs, much attention has been paid to an unusual anti-Stokes Raman effect distinguished by an abnormal intensity, sometimes increasing with the vibrational wave number, large differences in line profiles in Stokes and anti-Stokes sides, and some discrepancies between the Stokes and anti-Stokes frequencies. High values of the anti-Stokes/Stokes intensity ratio ($I_{\text{as}}/I_{\text{s}}$) and different lines shapes of the G band are the most distinguishing features in the anti-Stokes Raman spectra of SWNTs. The asymmetry of the Stokes and anti-Stokes spectra was generally interpreted as resulting from a double resonant Raman scattering effect produced by the excitation of different $(n,m)$ nanotubes with the incident and Stokes scattered photons.

$$d(n,m) = 3^{1/2}a_{c-e}(m^2 + mn + n^2)^{1/2}/\pi;$$

$$\theta = \tan^{-1}\left[\frac{3^{1/2}m(m+2n)}{n}\right].$$
II. EXPERIMENT

SERS spectra were recorded at room temperature in air, in a backscattering geometry, using a Jobin Yvon T64000 Raman-spectrophotometer. Single mode argon and krypton ion lasers operating at 514.5 and 676.4 nm, respectively, were used as excitation light sources. A Bruker FT Raman S/100 spectrophotometer was used to record spectra excited at 1064 nm. Both equipments were endowed with a microscope allowing the laser light to be focused to a dot on the sample with micrometer accuracy. Perturbing effects due to sample inhomogeneities, temperatures, and different local thicknesses were prevented by measuring Stokes and anti-Stokes pair spectra in the same conditions. In all these experiments we used films 30–100 nm thick deposited on a SERS active support. SWNTs films were obtained by evaporating a solvent (toluene) from a uniformly distributed emulsion of nanotubes on rough Au substrates. The mean thicknesses of the measured films was estimated by taking into account the concentration of the nanotubes in the emulsion, the substrate area, and adopting the value of 1.7 g cm\(^{-3}\) for the nanotubes’ density. CuPc and poly(bithiophene) films were prepared by thermal sublimation and electrochemical synthesis, respectively. For SWNTs and CuPc SERS active Au substrates, with a mean roughness of about 30–100 nm, were prepared by the vacuum evaporation with a deposition rate of approximately 1 nm/sec at a pressure <10\(^{-5}\) torr, with the atomic beam at constant grazing incidence (\(\beta\text{in} = 85^\circ\)) on the microscope slide used as target support. The decrease of the incidence angle \(\beta\text{in}\) of the atomic beam reduces the roughness of the metallic film which, in turn, determines an important decrease of the intensity of SERS spectra.

Poly(bithiophene) (PBTh) films, of about 60 nm thickness, were electrochemically prepared by cyclic voltammetry in a three-electrode cell containing a solution of 0.05 M 2, 2′-bithiophene and 0.1 M tetrabutylammonium tetrafluoroborate (TBABF\(_4\)) in acetonitrile (CH\(_3\)CN). The working electrode was a roughened mechanically Au plate and a spiral Pt wire was used as counter electrode. The reference electrode is Ag/AgCl. The PBTh film was obtained on the working electrode by cycling between −500 and +1500 mV versus Ag/AgCl at sweep rate of 1000 mV s\(^{-1}\). The electrochemical synthesis were carried out using a potentiosstat-galvanostat-type Princeton Applied Research (PAR), model 173, equipped with a digital coulometer, a PAR pulse generator, model 175 and a Philips-type X-Y recorder.

III. RESULTS AND DISCUSSIONS

Earlier studies on conducting polymers and carbon nanotubes deposited on Au or Ag substrates with an average roughness of approximately 50 nm, have shown significant variations of the SERS spectra as a function of sample film thickness.\(^{33,34}\) The changes observed in Raman spectra were related to the different weights of the two basic mechanisms involved in SERS generation: (i) electromagnetic, resulting from the resonant excitation of the surface plasmons and (ii) chemical, mainly due to charge transfer processes between the metallic substrate and adsorbed molecules. Because the surface chemical reactions involve only few molecular layers and the penetration depth of the surface electromagnetic evanescent wave (SEEW) associated with the SPs is much larger (≈12 nm metal and ≈95 nm in air), the selection of the film thickness is an important parameter in SERS studies. We have shown previously that the enhancement of the Raman signal through SPs can still be observed on films with a thickness up to 150 nm.\(^{30,41}\)

Once these details were established, a first challenge was to demonstrate that the intensity of the anti-Stokes emission is strongly enhanced if the wavelength of the excitation light coincides with an electronically allowed transition. According to Eq. (2) such a resonance is depicted by the contribution of two terms, \(\chi_R\) and \(\chiNR\) and the weight of each one in the final value of \(\chi^{(3)}\) is modified changing the wavelength of the exciting light.

In Fig. 1 are shown SERS spectra of SWNTs films of about 30 nm thickness recorded at different excitation wavelengths and in particular at the resonant excitation of semi-conducting (\(\lambda_{exc} = 1064\) nm) and metallic nanotubes (\(\lambda_{exc} = 676.4\) nm). In the interval 100–200 cm\(^{-1}\), one finds Raman bands associated with the radial breathing modes (RBMs) whose peak positions are very sensitive to the excitation. Thus, for a nanotube assigned \((n,m)\), a resonant Raman effect is observable when the exciting photon energy matches the energy separation between an occupied level in the electron density of state and an empty one.\(^{33,34}\) This requirement is accomplished in Fig. 1 for \(\lambda_{exc} = 676.4\) and 1064 nm. The resonance is marked by an intense radial band whose position, in agreement with the relation \(\nu(cm\text{-}^{-1}) = 223.75/d(nm)\),\(^{25}\) indicates nanotubes of about 1.35 nm diameter. As a distinctive fact, an abnormal anti-Stokes emission, extended over whole spectral range, is detected at \(\lambda_{exc} = 676.4\) and 514.5 nm. At \(\lambda_{exc} = 1064\) nm, excepting the radial bands, the anti-Stokes spectrum is practically the Stokes spectrum transformed by the Maxwell-Boltzmann law:

\[
I_{as}/I_s = [(\omega_0 - \Omega)/(\omega_0 + \Omega)]^4 \exp(-h\omega_0/kT),
\]

where \(\omega_0\), \(\Omega\), \(h\), \(k\), and \(T\) are the excitation frequency, Raman phonon frequency, the Planck constant, the Boltzmann constant, and temperature, respectively. The abnormal anti-Stokes Raman effect was measured by the ratio \(I_{as}/I_s\) at \(\lambda_{exc} = 676.4\), 514.5, and 1064 nm for the G band. We found values of 0.5, 0.02, and \(2 \times 10^{-5}\), respectively. In the latest case, the measured anti-Stokes emission was very close to that resulted by calculation using Eq. (4). Another fact to be noticed is that the abnormal anti-Stokes emission is equally observed over whole spectrum when the excitation is tuned at \(\lambda_{exc} = 676.4\), and 514.5 nm, whereas it concerns only the Raman bands associated to RBM at \(\lambda_{exc} = 1064\) nm. According to Eq. (3), this result suggests that in the first two cases, the appearance of the anti-Stokes Raman spectrum has to be related with the slowly varying nonresonant \(\chi_R\) term.

It is generally admitted that the radial band associated to specific \((n,m)\) nanotube discloses two components, one associated with the isolated tubes and the other, upshifted by \(\approx 14\) cm\(^{-1}\) associated with the bundled tubes.\(^{24}\) In Fig. 2,
these bands are peaked at 164 and 178 cm\(^{-1}\) on one hand and 176 and 190 cm\(^{-1}\) on the other hand for the excitation wavelengths 1064 and 676.4 nm, respectively. The relative intensity of these bands can be varied by an intense ultrasonic homogenization of the solution used for the film preparation, indicating a different dispersion degree of nanotubes. As was previously shown,\(^{42}\) these bands vary oppositely in the anti-Stokes side. In the Stokes branch, one observes that increasing the thickness of the SWNTs film leads to the decrease of both bands, reflecting a less efficient SERS effect. In comparison with the anti-Stokes spectrum calculated with the Maxwell-Boltzmann law, one finds systematically that the radial mode component associated with the bundled nanotubes is more intense and increases with the film thickness while the component associated with the isolated tubes is always weaker. This particular behavior suggests that the SERS mechanism is less efficient in the anti-Stokes side of the Raman spectrum and that the contribution of the \(\chi_4\) term...

FIG. 1. Stokes and anti-Stokes SERS spectra on SWNTs films of different thicknesses (\(h_1 < h_2 < h_3\), i.e., about 30, 60, and 120 nm) recorded through a microscope objective of 0.55 numerical aperture under excitation wavelengths of 676.4, 514.5, and 1064 nm. The \(I_{as}/I_S\) ratio was estimated for the G band and films of about 60 nm thickness. Au was used as metallic SERS support.
Coherent anti-Stokes Raman scattering on SWNTs: Stark shift effects and frequency dependence

Concerns only the radial mode component of isolated nanotubes. Outside the resonance domain of a specific \((n,m)\) nanotube, such as in the \(\lambda_{\text{exc}}=514.5\text{ nm}\) conditions, Fig. 2 shows that the particular behavior of the two components of radial bands is no longer observed.

The contribution of \(\chi_B\) term, independent of the Raman shift, is activated when the energy of laser excitation light coincides with the energy of an electronically allowed transition. Accordingly, the intensity of anti-Stokes Raman spectrum will vary with the absorption strength of the exciting light. Such a dependence is evidenced in Figs. 1a and 1b by the change of the excitation light from 676.4 nm, when the metallic nanotubes are resonantly excited to 514.5 nm when the resonance is less accomplished. The same variation of the intensity of anti-Stokes Raman emission, extended over whole spectral range, which results from the contribution of the \(\chi_B\) term, is observed also in Figs. 3 and 4 for CuPc and poly(bithiophene), respectively, when the excitation is done at 676.4 nm which corresponds to an electronic transition in both materials.

Following Eq. (2), another challenge was to demonstrate that the intensity of emission in the Stokes and anti-Stokes branches increased differently with the film thickness—linearly for the former and quadratically for the latter. In the case of SWNTs, such a variation is observed especially in the bands located in the 1200–1700 cm\(^{-1}\) Raman range. Figure 1 shows the Stokes and anti-Stokes SERS spectra recorded on films of different thicknesses, \(h_1<h_2<h_3\), around mean values of 30, 60, and 120 nm, which are suitable to generate a SERS emission by the electromagnetic enhancement mechanism. In general the approximation of the thickness of a SWNTs film is a difficult task. Observations by scanning electron microscopy (SEM) on the sample used reveal clusters containing isolated and bundled nanotubes spread over the sample surface that modify the local reflectivity of the Au substrate. A stronger or weaker reflection indicates a thinner or a thicker film, respectively. This aspect was exploited to establish that the measurements really were made on different local spots of various thicknesses. We think that such an estimation is precise enough and reproducible, with an error limit up to 10%. We present, as an example, the band marked with the asterisk in Fig. 1(b), which is a “parasite line” arising from the laser discharge tube. This line is reflected back by the sample and is observed in the Raman spectrum at 113 cm\(^{-1}\) having a varying intensity depending on different local thicknesses of the SWNTs film.

As mentioned above, the typical intensity variations of Stokes SERS spectra as a function of film thickness is illustrated in the Figs. 1(a) and 1(b). According to our expectations, when the excitation of Raman transitions is achieved by SPs, the intensity of scattered light depends on the efficiency of energy transfer from the surface electromagnetic evanescent wave (SEEW), associated with SPs, to the film deposited on the rough metallic support. As a result of the matching between the penetration depth of the SEEW and the film thickness, the intensity of a SERS Raman spectrum must vary inversely with the film thickness; i.e., it is higher on thin films and weaker on thick films. A priori, a variation like this must be equally observed in all Raman bands both in the Stokes and anti-Stokes branches. Figure 1 shows that, regardless of the excitation wavelength used, this is clearly only satisfied in the Stokes branch. In the anti-Stokes side, with the exception of the radial bands observed under resonant excitation (\(\lambda_{\text{exc}}=676.4\text{ nm}\)), the intensity of the Raman signal increases almost quadratically with the sample film thickness. A result like this, anticipated by Eq. (1), strongly suggests a CARS-like emission. Unfortunately, this statement is rather qualitative, since an exact evaluation of the local film thickness, using real measurements, was not possible. Assuming that a CARS process had developed on a thin film deposited on a metallic SERS support, the same dependence must also be observed on other materials. The expectation is confirmed by Fig. 5 where a similar variation of the intensity of anti-Stokes Raman spectrum as a function of sample thickness is demonstrated for CuPc films.
TM vibrations modes vary differently with film thickness when excitation is performed at 676.4 and 514.5 nm, i.e., inside and outside of the metallic resonance window of nanotubes.\textsuperscript{35,36} Assuming that each anti-Stokes line appears as a sum of two contributions, one resulting from the Maxwell-Boltzmann law and the other from a wave mixing process associated to the relative weight of the two terms, $\chi_R$ and $\chi_{NR}$ involved in the third-order nonlinear dielectric susceptibility, the final intensity of the line reflects the most weighted contribution. Because the intensity of anti-Stokes lines, derived from the Maxwell-Boltzmann law, decreases exponentially towards high frequencies, its contribution becomes negligible in the overall intensity of the D and TM bands that are quite far from the laser excitation line. If in the value of $\chi^{(3)}$ one finds only the contribution of $\chi_{NR}$, then the variations of intensity reflect only the film thicknesses and, in accordance with Figs. 1(a) and 1(b), are in the same sense regardless of the wavelength of the excitation light used. This is indeed what is observed in Figs. 1(a) and (b).

Outside the resonant excitation of a specific $(n, m)$ nanotube, i.e., at $\lambda_{exc} = 514.5$ nm, two light scattering processes become observable: CARS, operating in the anti-Stokes branch, is characterized by a quadratic increase of the Raman lines intensity with the film thickness and SERS, operating in the Stokes branch, for which the highest intensity is observed on the thinnest films. The latter reveals an optimal matching between the film thickness and the penetration depth of SEEW associated to the SPs.

Another convincing argument for a presumed CARS emission results from exploring the variation of intensity of

FIG. 3. SERS spectra of CuPc film (=60 nm thickness) deposited on rough Au support recorded through a microscope objective of 0.55 numerical aperture under laser excitation of 676.4 and 514.5 nm. The former excitation wavelength coincides with an electronic absorption band of CuPc. The dotted curves are the calculated Maxwell-Boltzmann replicas of the measured Stokes Raman spectra. On the top figure, for clarity, the calculated spectrum was multiplied by 10.

FIG. 4. SERS spectra on poly(bithiophene) film (=60 nm thickness) deposited electrochemically on rough Au support a recorded through a microscope objective of 0.55 numerical aperture under laser excitation of 676.4 and 1064 nm.
FIG. 5. Stokes and anti-Stokes SERS spectra, at $\lambda_{exc} = 676.4$ nm, on copper phthalocyanine films of different thicknesses ($h_1 < h_2 < h_3$) deposited on Au as metallic support.

FIG. 6. Anti-Stokes (full symbols) and Stokes (open symbols) Raman intensity plotted as a function of laser intensity ($\lambda_{exc} = 676.4$ nm). Spectra were recorded on films of SWNT (a) squares and up triangles, and CuPc (b) circle, films deposited on rough Au substrate. $h_1$ and $h_3$ notice spectra recorded on films of different thicknesses i.e., $h_1 < h_3$). (b) shows for the $h_3$ samples a quadratic dependence of the ratio $I_{aS}/I_S$ on incident laser intensity.
the anti-Stokes lines with the exciting laser power. Experimental data presented in Fig. 6 display the variation as a function of laser intensity of the Raman bands at 1595 cm\(^{-1}\) (G band) in the Stokes (open symbols) and anti-Stokes (full symbols) branches. Data were obtained under varying laser intensities prior to focusing on the sample, between 25 and 100 mW (676.4 nm) and 25 and 300 mW (514.5 nm). Notice that no permanent thermal transformation of SWNTs was observed during blank experiment under identical irradiation conditions. Figures 6a and 6b show an anti-Stokes signal that increases nonlinearly with the intensity of the excitation radiation. At first sight, this is not surprising—such a nonlinear variation of the anti-Stokes Raman lines on the incident light power was reported for crystal violet and rhodamine 6G adsorbed on colloidal silver. It was explained as resulting from an overpopulation of the first excited vibration state by a spontaneous SERS effect.\(^{10}\) However, Figs. 5a and 5b discloses something different; the slopes of the fitted lines in a log-log plot of the dependence of anti-Stokes and Stokes emission on laser incident intensity also depend on the film thickness. Measurements performed in the spectra series of \(h_1, h_2, h_3\) always reveal that the anti-Stokes component is characterized by a more abrupt slope in comparison with the Stokes emission, their values being \(\approx 2\) and \(\approx 1\) in the spectrum \(h_1\) and \(>2\) and \(>1\) in the spectrum \(h_3\), respectively. These different slopes are not surprising if one supposes that the anti-Stokes Raman emission results from a CARS-like process in which the incident laser light mixes with the Stokes Raman scattered light generated in the sample. Together, these two contributions result in the appearance of a more complicated dependence on the incident light power. In this case, according to Eq. (1), the CARS-like emission must reveal a double dependence on the components (\(\omega_i\) and (\(\omega_s\)), the latter increasing also with the incident laser light intensity. Therefore, in Fig. 6(c), a \(I_{\text{AS}}/I_S\) plot as a function of the incident power is a stronger indication of a quadratic dependence. Similar to the results shown in Fig. 1, where the CARS emission appears to be more related to the thicker samples, Fig. 6 shows that the quadratic variation of the anti-Stokes Raman line intensity with the incident laser intensity is observed mainly in the spectrum \(h_3\), i.e., on the thicker film. Finally, these data reveal that the anti-Stokes emission originates from two different processes, a SERS one in thin films of few nanometers and a CARS one in thick films in the tens of nanometers range.

The fact that this intense anti-Stokes emission appears under tight focusing of the excitation light is very reminiscent of CARS microscopy. As is well known in that field, the interaction volume of the two beams, (\(\omega_i\)) and (\(\omega_s\)), depends on the focusing parameters and on the geometric configuration in which the requirement of phase matching is achieved. In our case, when the CARS emission is detected in the backward direction it is hard to presume that inside the focusing volume a collinear phase-matching geometry can be achieved. In the parametric coupling of incident laser light (\(\omega_i\)) and Stokes light (\(\omega_s\)) the latter is generated by a SERS mechanism in molecules situated in the proximity of the tip end of the roughness. This light, emitted in all directions,
mixes with the incident laser light elsewhere in the focusing volume so that a plausible phase-matching geometry might be a planar box-wave shaped configuration or a nonplanar scheme\textsuperscript{20,21} that results in a spatial separation of the anti-Stokes Raman signal from the input laser beam. In accordance with Eq. (1) such a property will be noticed by a dependence of the CARS intensity on the numerical aperture (NA) of the microscope objective used for detection. Such a dependence is quite well illustrated in Fig. 7. Maintaining the same location on a SWNTs film and using microscope objectives of different numerical apertures, 0.95, 0.55, and 0.25, we obtained the spectra displayed in Fig. 7. Figures 7(a) and 7(b) show spectra recorded on films of different thicknesses, thin ($h_1$) and thick ($h_3$), respectively. In the Stokes side, where the spontaneous Raman process is dominant, the intensity of Raman measured emission over the full $2\pi$ radians of a hemisphere depends on the collection efficiency of the scattered photons so that it increases monotonically with NA. In the anti-Stokes branch, the detection of the Raman signal was possible only with a microscope objective of high NA, 0.95 or 0.55. Figure 7(b) discloses also a double dependence of the anti-Stokes Raman intensity on film thickness and numerical aperture. The former is related to the fact that the generation of a CARS signal needs fulfillment of the phase-matching condition and that in a box-wave shaped geometry a greater interaction volume is needed. The latter dependence is related to the CARS emission which no longer emerges uniformly from the sample, in a hemisphere of $2\pi$ radians, being concentrated in a $60^\circ$–$80^\circ$ angular gateway.

Finally, another experimental fact, shown in Fig. 8, which can be added as an argument for a CARS process concerns the value of the polarization ratio in the anti-Stokes side that is always greater in comparison with that measured for a spontaneous Stokes Raman emission. This is due to the different polarization properties of the electronic and resonant portion of the $\chi^{(3)}$ which induces in the CARS emission a different polarization ratio in comparison with the conventional spontaneous Stokes Raman scattering.\textsuperscript{19,22,45}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig8.png}
\caption{Polarized SERS spectra at $\lambda_{exc.} = 676.4$ nm of CuPc (a) and SWNTs (b) films of approximately 60 nm thickness deposited on rough Au support. In (c) is shown $I_{VH}/I_{V}$ for Stokes and anti-Stokes spectra of CuPc (full and open squares) and SWNTs (full and open triangle), respectively. Dotted lines represent the linear fit of the $I_{VH}/I_{V}$ ratio.}
\end{figure}
Although the quantum description of a CARS process generated in a thin film of nanometric thickness deposited on a metallic SERS active support is a very difficult task, the qualitative observations collected from our experiments present a significant finding in the field of nonlinear spectroscopy. We demonstrate that under tight-focusing of the excitation light, a CARS emission resulting from a wave mixing process between the incident laser light ($\omega_i$) and Stokes Raman light ($\omega_s$) generated by a SERS mechanism is produced. Although the effect was observed on different materials, the signal intensity and film thickness; CARS emission:

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