Tip-enhanced Stokes and anti-Stokes Raman scattering in defect-enriched carbon films

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Abstract. Anti-Stokes Raman scattering is one of the mechanisms that lie behind an optical refrigeration due to release of photons with greater energy than of incoming photons. To achieve a cooling regime the enhancement of anti-Stokes scattering is necessary, since spontaneous Stokes scattering dominates over anti-Stokes scattering under normal conditions. Here, we investigate the opportunity of enhancement of spontaneous anti-Stokes Raman scattering in defect-enriched carbon film by means of localized plasmon resonances. In our simulations, incoherence of Raman scattering results in excess of anti-Stokes intensity over Stokes one. However, when the field is localized within the phonon coherence volume (coherent regime), the anti-Stokes intensity is lower compared to Stokes one. The provided analysis shows that plasmon-enhanced anti-Stokes Raman scattering can be achieved in highly-defective carbon films. The results are beneficial for Raman-based temperature measurements on the nanoscale.

1. Introduction

The control over the state of a quantum object, monitoring its temperature, amplification and analysis of its optical response are of important in photonics [1]. In particular, light can be used to maintain a certain local temperature using the effects of photo-induced heating and laser cooling of solids. One of the optical cooling methods is the anti-Stokes Raman scattering (ARS) [2]. When photons inelastically scatter in solid, either a creation (Stokes) of a phonon or an annihilation (anti-Stokes) of a phonon generally possible [3]. However, Stokes scattering usually dominates over anti-Stokes scattering at room temperatures due to the fact that the equilibrium population of vibrational states and phonons obey the Bose-Einstein statistics. Existing methods for inverting Stokes to anti-Stokes intensities ratio use various intrinsic and optical resonances to increase the anti-Stokes scattering cross section [2] or suppress Stokes scattering [4].

This work is devoted to a theoretical study of the possibilities of enhancing ARS in carbon films. Generally, carbon films serve as protective coatings. In addition, carbon materials are biocompatible and can be chemically functionalized by various organics. Impurities and structural defects can activate forbidden Raman lines. Moreover, moderate values of the wavenumbers of the most active lines in the Raman spectrum (\textgreater 1000 cm\textsuperscript{-1}) favor the use of sufficiently wide plasmon resonances in nanoparticles to enhance ARS. Graphene oxide with a thickness of 10 nm is considered as the carbon film. The optical parameters of graphene oxide fragments functionalized with hydroxyl groups were obtained from calculations based on...
density functional theory (DFT). Our results are beneficial in nanoscale thermometry, design of optoelectronic devices and functionalized cooling coatings.

2. The model of carbon thin film
The system under consideration consists of a homogeneous graphene oxide layer, on the surface of which functional hydroxyl groups are located, and an elongated gold nanoparticle, which plays the role of an optical nanoantenna. The nanocoating is located on the substrate; however, for the sake of computational simplicity, we take the dielectric constant of the substrate to be equal to that of the carbon coating. Due to the anisotropy of graphene oxide, the nanoantenna should be positioned obliquely to the surface in order to excite in-plane vibrations[5]. In this work, we assume the tip’s tilt angle of the nanoparticle is 45 degrees.

In order to determine the scattered field $\mathbf{E}(\mathbf{r}, \omega)$ at the frequency of the incident light at different points of the carbon layer, one can use the approach based on dyadic Green’s function (see for details [6]). Due to the relatively large refractive index of graphene oxide [7], it is necessary to calculate the near-field interaction of the nanoparticle and the carbon layer. Elementary dipoles represent both the optical nanoantenna and the Raman-active carbon layer in the model. However, in contrast to the discrete-dipole approximation, the nanoantenna is replaced in this work with a single point dipole located at the actual tip’s curvature center and that has the polarizability of a gold nanospheroid when the nanoantenna interacts with incident light. In turn, the nanoantenna follows the quasistatic theory of images for a polarizable sphere during the near-field induction from carbon film [8]. The local electric field $\mathbf{E}(\mathbf{r}_n)$ at the point $\mathbf{r}_n$ in this model is written as:

$$\mathbf{E}(\mathbf{r}_n) = \mathbf{E}_0(\mathbf{r}_n) + \sum \mathbf{G}(\mathbf{r}_n, \mathbf{r}_0) \hat{\alpha}_p \mathbf{E}_0(\mathbf{r}_0) + \sum z \mathbf{G}(\mathbf{r}_n, \mathbf{r}_z) \hat{M}_{\text{im}}(z, \mathbf{r}_0) \mathbf{R}_{\text{sub}} \hat{\alpha}_p \mathbf{E}_0(\mathbf{r}_0), \quad (1)$$

where $\mathbf{E}_0$ is the incident field, $\hat{\alpha}_p$ is the polarizability of the nanoparticle at the point $\mathbf{r}_0$, $\mathbf{G}$ is the dyadic Green’s function, $\mathbf{R}_{\text{sub}}$ is the quasi-static reflection tensor, $\hat{M}_{\text{im}}$ is the dressed (generalized) propagator of the problem of the image dipoles induction in the sphere-substrate system. The latter differs from bare propagator $\hat{M}_0$ found in [8] by the account of the self-interaction of image dipoles through the near-field reflection of dipoles [6]. One can find the dressed propagator solving the Dyson type integral equation.

One of the remarkable properties of graphene oxide is low absorption in the presence of resonant electronic transitions in the visible spectrum, which are observable in ellipsometric experiments [7]. By selecting functional groups and their surface coverage, it is possible to further enhance ARS. For resonant Raman scattering, the polarizability tensor can be estimated by the formula [9]:

$$\alpha_{R \rho \sigma}^{sf} = \frac{1}{\hbar} \sum_r \frac{(M_\rho)_{fr}(M_\sigma)_{rs} - \omega - i\Gamma_r}{\omega_{rf} + \omega + i\Gamma_r} + \frac{(M_\sigma)_{fr}(M_\rho)_{rs} - \omega - i\Gamma_r}{\omega_{rf} + \omega + i\Gamma_r}, \quad (2)$$

where the subscripts “s”, “r” and “f” denote the initial state, the intermediate states and the final state, respectively, $M$ are the transition dipole moment matrix elements, $\Gamma$ is the width of the excited level. Note that in this approach, we neglect the effects of electron-phonon coupling.

For the simulation, the transition energies and level widths were taken from the experimental work [7]. When the fraction of coverage of the surface of the graphene sheet with hydroxy groups is 50-75 percent, the transition energy lies in the range 1.8-2.6 eV. Moreover, due to the anisotropy of graphene oxide, the parameters of resonance transitions do not coincide for different components of the Raman tensor. This allows us to speak about the selective electronic enhancement of Raman bands depending on the type of vibration symmetry. It should be noted
that in equation (2) the matrix elements of the dipole operator are calculated in an unperturbed basis; therefore, they can be obtained from DFT-calculations. For the sake of simplicity we considered a graphene fragment with only hydroxyl groups and static polarizabilities were obtained at the B3LYP-D3/def2-TZVP level. The principal axes of the inertia tensor determine the orientation of the molecule. The obtained Raman tensors are then used to find the elementary dipole moments at the Stokes and anti-Stokes frequencies. Since functional groups have an arbitrary orientation, each dipole moment takes arbitrary rotation angles in space.

3. Results and discussion

Using equation (1) one can find the total gain tensor \( \hat{F} = \frac{\mathbf{E}\mathbf{E}^*}{|\mathbf{E}_0|^2} \) at the incident frequency. Averaging the trace of its squared tensor over all elementary dipoles gives the mean enhancement factor of the field intensity \( |f_e|^2 = \frac{1}{N} \sum_n |\mathbf{E}(\mathbf{r}_n)|^2 / |\mathbf{E}_0|^2 \). In a similar way, the gain tensor \( \hat{F}(\mathbf{r}_n, \omega_k) \) is found for each point \( \mathbf{r}_n \) at which an elementary Raman-active dipole is located for each either Stokes or anti-Stokes shifted frequencies \( \omega_k \). According to the reciprocity theorem, the Hermitian-conjugate gain tensor \( \hat{F}^\dagger(\mathbf{r}_n, \omega_k) \) will describe the field propagation back to the nanoantenna and near-field induction at the Raman-shifted frequency. Both the material dispersion parameters of the carbon layer and the nanoparticle parameters and geometry substantially affect the plasmon resonance. It is possible to tune them to achieve the plasmon resonance band covering the anti-Stokes side of the Raman spectrum. Figure (1) shows an example of such a selection. It is seen that the anti-Stokes lines experience a greater amplification averaged over all dipoles, and the enhancement factor exceeds the Stokes-anti-Stokes intensities ratio \( I_S/I_{aS} \) for the given wavenumbers at room temperature (~300 K).

The resulting Raman activity of the vibration mode taking into account the partial coherence of the dipole moment oscillations at the shifted frequency, is equal to:

\[
S(\omega_k) = \int \int \hat{F}(\mathbf{r}_n, \omega_k) \mathbf{p}(\mathbf{r}_n, \omega_k) \mathbf{p}^\dagger(\mathbf{r}_m, \omega_k) \hat{F}^\dagger(\mathbf{r}_m, \omega_k) g(|\mathbf{r}_n - \mathbf{r}_m|) d\mathbf{r}_n d\mathbf{r}_m. \tag{3}
\]

Here \( g(|\mathbf{r}_n - \mathbf{r}_m|) \) is the correlation function of phonon vibrations at the Raman-shifted frequency. Typically, spontaneous Raman scattering is considered to be an incoherent process. In various carbon materials, the phonon coherence length is tens of nanometers, which is comparable to the localization of the near field. In this regard, a coherent spontaneous Raman scattering regime becomes possible [10]. Figure (2) shows the results of the simulation for both fully coherent and incoherent enhanced Raman scattering. Applying the mean phonon number statistics gives the Raman intensities \( I(\omega_k) = A(\omega_k^4/\Omega_k)S(\omega_k)/e^{-\langle N \rangle/k_BT} - 1 \), in which the Raman shift of k-th
vibration $\Omega$ is assumed to be positive for the anti-Stokes scattering and negative for the Stokes scattering. It is worth to note that the Raman coherence gives a greater enhancement to the Stokes side of the spectrum compared to the anti-Stokes side due to the longer wavelength of light, i.e. better phase-matching of the dipoles. The absence of the $G$ band (1600 cm$^{-1}$) in the anti-Stokes spectrum is associated with the rather narrow plasmon resonance band (Fig.1).

4. Conclusion
In summary, we have performed the simple analysis of tip-enhanced Raman intensities at the Stokes and the anti-Stokes frequencies. Our simulations demonstrate that in order to anti-Stokes intensity surpassed the Stokes intensity the coherence volume of a phonon should be much less than field localization. In that case, the destructive interference of secondary waves on the Raman-shifted frequency from the sources distributed over the carbon surface is suppressed. As shown, the plasmon resonances are promising to enhance anti-Stokes radiation. These findings can substantially improve measurements of both the phonon coherence volume and the local temperature in solid films using tip-enhanced Raman spectroscopy.

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