Surface enhanced Raman scattering of some nanotechnological material systems: A computational approach

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Abstract. Surface enhanced Raman spectroscopy or scattering, is an old analytical technique having multiple applications, but it still remains with great challenges. The complex physical and chemical processes involved results in difficulties for modelling and experimentation. In this work, numerical results of surface enhanced Raman spectroscopy spectra for some systems of interest in nanoscience and nanotechnology, monochlorobiphenyl isomers, graphene, magnetite and graphene oxide, are presented and discussed. A single gold nanoparticle and a dimer gold nanoparticle were utilized as surface-enhanced Raman spectroscopy substrates. The possibility of predicting structural properties of graphene oxide from comparison between its experimental and simulated Raman spectra is discussed. A relation between the enhancement factor for the G band of graphene oxide and the radius of a spherical nanoparticle dimer of gold, is suggested.

1. Introduction

The Raman effect was theoretically predicted by A Smekal in 1923. It was experimentally discovered by C V Raman and by K S Krishnan in 1928 at the University of Calcutta, and a week earlier by G S Landsberg and L I Mandelstam in Russia [1]. However, it was only in 1960 with the invention of the laser that the Raman effect led to one of the most versatile spectroscopic techniques having applications in diverse fields of nanoscience and nanotechnology. The Raman effect is a spectroscopic process that has a very low probability of occurrence because it has a low effective cross section, and therefore very specialized instrumentation is required for its detection. M. Fleishmann et al in 1974 [2], R Van Duyne and D Jeanmaire in 1976, and MG Albrecht and JA Creighton, in 1977 [3], discovered that, when there are molecules adsorbed on nanostructured surfaces of noble metals, the intensity of the Raman bands could be amplified by factors of the order of 10⁶. The surface enhanced Raman scattering (SERS) effect is then proposed. Thus, a new analytical technique, the SERS spectroscopy was born. Although the physicochemical mechanisms of the SERS effect are complex and remain as a current research topic nowadays, there is a good consensus that it is mainly due to two processes: on the one hand, there is an enhancement due to electromagnetic interaction via local plasmon resonance into the metal nanostructure; on the other hand, there is a mechanism of charge transfer between adsorbed species and the surface atoms of the SERS substrate, so called the chemical mechanism (CM) [4-6]. It is well known that in general, the main responsible for the enhancement of some Raman bands in SERS is the electromagnetic mechanism (EM) [5]. SERS substrates based on bimetallic particles have captured interest of researchers in the last two decades [7] and have recently allowed to low the detection limit up to sense individual molecules [8,9]. In this work, some details on the electromagnetic mechanism for the description of the SERS effect are presented. Computational results of SERS spectra of
monochlorobiphenyl isomers, graphene, magnetite and graphene oxide, are obtained. As SERS substrates, a single gold nanoparticle and a dimer gold nanoparticle were studied. A model which considers the effect of the local field gradient on the molecular polarizability of the species to be studied [10], is utilized. A comparison between the simulated spectrum of graphene oxide and experimental data is carried out. From the analysis of these results, the Raman tensors for graphene oxide were suggested. Finally, an empirical equation relating the enhancement factor to the radius of a dimer nanoparticle for the G band of graphene oxide is proposed.

2. Theory and physical model

A qualitative way of understanding the EM for SERS is illustrated in Figure 1(a). A molecule close to a metal nanoparticle is excited by a plane monochromatic wave of frequency $\omega_0$ at the position $\vec{r}$. If $\omega_0$ matches well the plasmon resonance frequency of the particle, then an enhancement in the incident field $\vec{E}_i(\vec{r}, \omega_0)$, is expected. Hence, the molecule interacts with a net field consisting in the sum of the incident one and the enhanced field so called local or Lorenz-Mie field, $\vec{E}_{LM}(\vec{r}, \omega_0)$. A Raman field of frequency $\omega$, $\vec{E}_{DIP}(\vec{r}, \omega)$, emitted from the molecule, which overlaps the scattered field by the particle, $\vec{E}_{ESC}(\vec{r}, \omega)$, is detected at the position $\vec{r}$. This resulting field is denoted here as $\vec{E}_{LM}(\vec{r}, \omega)$. In other words, $\vec{E}_{LM}(\vec{r}, \omega) = \vec{E}_{DIP}(\vec{r}, \omega) + \vec{E}_{ESC}(\vec{r}, \omega)$. For a single molecule adsorbed on a metal nanoparticle, the SERS enhancement factor (EF) $G_{SERS}$ [5] is defined by Equation (1).

$$G_{SERS} = \left| \frac{\vec{E}_{LM}(\vec{r}, \omega_0)}{\vec{E}_i(\vec{r}, \omega_0)} \right|^2 \left| \frac{\vec{E}_{LM}(\vec{r}, \omega)}{\vec{E}_i(\vec{r}, \omega_0)} \right|^2.$$  

On the right side of Equation (1), the first factor is associated to the incidence enhancement, whereas the second one is associated to the emission enhancement. Physical and chemical properties that affect the EF, among others, are the morphology, the size and the optical properties of the nanoparticle, the optical properties of the surrounding environment, the quantum properties of the molecule, and the frequency of the incident field.

![Figure 1](image1.png)

**Figure 1.** (a) Schematic of the electromagnetic mechanism for SERS and (b) schematic of the dimer model used for the computational results reported in this work.

In general, a uniform resulting field interacting with the molecule $\vec{E}_{LM}(\vec{r}, \omega_0)$ is considered. However, non-uniformities are inherent to this type of complex processes; hence the variation of the field should be considered. Chulhai and Jensen proposed to consider a non-uniformity introducing the gradient of the local field in the induced molecular polarizability [10]. They implemented the model in a tool called SERS Simulator which is free in NanoHub at https://nanohub.org/resources/dsers.

All the results presented in this work were performed using the SERS Simulator tool from NanoHub. SERS by a single spherical nanoparticle and a dimer of nanoparticle were numerically obtained. Gold nanoparticles were considered. In Figure 1(b), the set up for the dimer is depicted. A molecule located at the midpoint of the dimer is excited by a $y$-axis linear-polarized plane monochromatic electromagnetic
wave (EW). The molecule is placed in the xy-plane while the EW travels along the z-axis. In this case, there is a “hot spot” at the position of the molecule [11-13]. Both particles of the dimer have radii $R = 10\text{nm}$ and a separation between them $d = 1\text{nm}$. Both system, molecule-sphere and molecule-dimer are embedded in water whose dielectric constant is 1.77. Because the plasmon resonance of the described nanoparticle system is around $488\text{nm}$ and having into account that a common laser line of $532\text{nm}$ is found in many laboratories, a wavelength of $532\text{nm}$ for the incident field was used. The Chulhai and Jensen formulation consider the Drude model for the dielectric constant of the metal [10]. However, in their work they report only silver nanoparticles. In our work, as said, gold was considered and the respective Drude model constants were obtained from the work by Barchiesi and Grosges [13] using the fitting obtained with the experimental data reported by Palik [14]. In this way, the values of $\omega_p$, $\varepsilon\infty$ and $\gamma$ were 9.09 $\text{eV}$, 6.91 $\text{eV}$ and 1.156 $\text{eV}$, respectively.

3. Simulated results
The normal Raman and SERS spectra for four systems were analyzed: monochlorobiphenyl isomers, graphene, magnetite and graphene oxide. Zhou, et al. [15] used SERS as a tool for the rapid recognition of isomers of monochlorobiphenyls at trace levels. By using Ag nanorods as substrate, they found that the C-C-C in-plane stretching modes in the 1-4, 3-6 and 2-5 directions having Raman shift or wavenumber of 760 cm$^{-1}$ (4-chlorobiphenyl), 680 cm$^{-1}$ (3-chlorobiphenyl) and 460 cm$^{-1}$ (2-chlorobiphenyl), respectively, are the analytical bands for the respective isomer. The simulated results for SERS spectra by using the model described in our work are shown in Figure 2. Increases of three and four orders of magnitude relative to the normal Raman spectrum were respectively obtained for the SERS spectra of the single sphere and the dimer. These results are in agreement with those reported in reference [16] in which the corresponding Raman tensors associated to the vibrational modes were obtained.

![Figure 2](image_url)

**Figure 2.** Raman spectra for an idealized of isomers of monochlorobiphenyls mixing showing only the principal bands. Normal Raman (NR), SERS from a sphere and SERS for a dimer, are shown.

A well-studied iron oxide, magnetite, was analyzed in this work too. Its vibrational structure is composed of three $T_{2g}$ modes, one Raman-silent and others with 193 cm$^{-1}$ and 538 cm$^{-1}$ shifts, respectively; a mode $E_g$ with 306 cm$^{-1}$; and an $A_{1g}$ mode with 668 cm$^{-1}$, the main band [17]. In Figure 3, simulated results for the NR spectra, SERS from a sphere (SS) and SERS from a dimer (SD) of magnetite, are presented. In a linear scale in the intensity axis NR spectrum are not visible, Figure 3(a); However, if the same data are presented in a logarithmic scale, Figure 3(b), considerable differences between the cross-section values in SS and SD spectra as compared to NR spectra, were found.

In Figure 4(a), the NR, SERS from a SS and SERS from a SD spectra of graphene are shown. On a linear scale in the intensity axis Figure 4(a), NR spectra are not visible due to the difference in the order of magnitude. However, if a zoom is done, the three spectra, NR, SS and SD, are observed, as shown in the inset of Figure 4(a). This can be better observed in Figure 4(b) by presenting the data using a logarithmic scale for the intensity. It is important to say, that only two bands, the G band and the 2G band were studied because a perfect graphene sample was considered. It is well known that the D band...
comes from defects in the graphene lattice and therefore, the D band is not present in this case. Other bands like D’, 2D and D+G which depend on the presence of defects, should not appear either. The Raman tensors for the vibrations were obtained from Budde, et al. [18].

Figure 3. (a) NR spectra, SERS from a SS and SERS from a SD of magnetite. By using a linear scale in the intensity axis, NR spectrum are not visible, the same data are presented in (b) using a logarithmic scale.

Figure 4. (a) NR, SERS from a SS and SERS from a SD spectra of graphene. By using a linear scale in the intensity axis, NR spectrum are not visible, the same data are presented in (b) using a logarithmic scale. The inset in (a) allows the visualization of NR, SS and SD.

In Figure 5, the NR spectra of graphene oxide are shown. Similarly, on a linear scale in the intensity axis Figure 5(a), NR spectrum is not visible due to the difference in the order of magnitude. However, the spectra are observed by presenting the data using a logarithmic scale for the intensity, as can be seen in Figure 5(b). All bands, D, G, D’, 2D and D+G, were taken into account and, in order to the simulated spectra and those reported in references [19] and [20] had a good match, a set of Raman tensors was supposed. The bands, their corresponding Raman shift and the utilized tensor components, are presented in Table 1. Because the D band is associated to defects in the graphene lattice, it was assumed that those defects could produce lattice deformation, which could induce an out-of-plane vibration component. It is the reason why a nonzero $\sigma_{zz}$ component was introduced for the D band.

Finally, an analysis on the dependence between $G_{SERS}$ and the radius $R$ of a dimer system was performed. Fixing the distance $d = 1$ nm, $R$ was varied from 5 nm to 60 nm by step of 5 nm. Only the G band was considered in this discussion. In Figure 6 (a), $G_{SERS}$ for three selected values or $R$, are shown. The difference between the $G_{SERS}$ values is evident.
In Figure 6(b), $G_{\text{SERS}}$ as a function of $R$ is presented. The blue rectangles represent the simulated values, and the solid curve the fitting function. The calculated values were fitted by an exponential curve, $G_{\text{SERS}} = y_0 + A_1 e^{\left(-\frac{R}{x_1}\right)}$. The result was the Equation (2).

$$G_{\text{SERS}} = 5397 - 5640 e^{-\left(\frac{R}{11.4}\right)} \quad (2)$$

Being $y_0 = 5347 \pm 51$, $A_1 = -5649 \pm 160$ and $x_1 = 11.4 \text{ nm} \pm 0.6 \text{ nm}$. The commercial software Origin6.1 was employed for the fitting, which allows to be obtaining the reported uncertainties for the parameters. It is clear that $G_{\text{SERS}}$ shown in Equation (2) increases as the particle radius increases. However, a limit value of 5397 is reached as the radius approaches to 60nm. It is important to mention that for $R = 65$ nm and higher values, $G_{\text{SERS}}$ is less than 1% different from that for 60 nm. Hence, the results suggest that particles with radius higher than 60 nm do not generate higher $G_{\text{SERS}}$ values.

To the best of our knowledge, it is the first time that the Chulhai and Jensen model is used to obtain SERS numerical spectra of monochlorobiphenyl isomers graphene, graphene oxide and magnetite.

It is convenient to note that, when the distance between the nanoparticles and their dimensions are of the order of atomic lengths, non-locality effects may appear that can modify the way in which the light is concentrated. In this case, models that account for these effects should be considered. Dimensions of 5nm for the radii of the nanoparticles and separations between them of the order of 1nm could be within a limit situation. In this case, comparative studies with non-locality models should be performed.

![Figure 5](image)

**Figure 5.** (a) NR spectra, SERS from a SS and SERS from a SD of graphene oxide. By using a linear scale in the intensity axis, NR spectrum are not visible, the same data are presented in (b) using a logarithmic scale.

| Band | Raman shift (cm$^{-1}$) | $\sigma_{xx}$ | $\sigma_{yy}$ | $\sigma_{zz}$ |
|------|------------------------|--------------|--------------|--------------|
| D    | 1358                   | 0.15         | 0.15         | 0.10         |
| G    | 1570                   | 0.45         | 0.45         | 0.00         |
| D'   | 1608                   | 0.50         | 0.50         | 0.00         |
| 2D   | 2775                   | -0.25        | -0.25        | 0.00         |
| D+G  | 2948                   | 0.15         | -0.15        | 0.00         |
4. Conclusions

Numerical results for SERS spectra of monochlorobiphenyl isomers, graphene, magnetite and graphene oxide, were reported and discussed. A single spherical gold nanoparticle and a dimer gold nanoparticle were used as SERS substrates. The adsorbed species were placed at the midpoint of the dimer, which is a hot point for local plasmon resonance. Raman cross sections of the order of $10^4$ were obtained. The simulated results could be of great help in order to complement experimental studies. An empirical equation relating the enhancement factor with the radius of the dimer for the G band of graphene oxide was proposed. Other materials for SERS substrates as cooper and platinum, among others, should be explored. Experimental studies are needed in order to contrast the simulations and advance in the chemical sensors designing.

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