# Investigation of non-linear optical effects at conjugated polymer/silver interface by surface plasmon resonance and surface enhanced Raman scattering

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## Abstract

SERS experiments performed at 1064 nm with quasi-monomolecular layers of polycarbazolyldiacetylene (polyDCHD-HS: 1,6-bis-(3,6-dihexadecyl-*N*-carbazolyl)-2,4-hexadiyne) spun on silver-coated plates suggest that the very large value of the intensity dependent refractive index measured in such samples and at the same wavelength by surface plasmon spectroscopy (SPS) tests is related to the nanostructured surface of the silver films, that provides an electromagnetic mechanism for the enhancement of the non-linearity through local field effects at optical frequencies far from the plasmon resonance of the metal.
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## 1. Introduction

Considerable effort is currently being made in the synthesis and characterization of novel $\chi^{(3)}$ polymers. In particular, a PDA of recent synthesis, the polycarbazolyldiacetylene (polyDCHD-HS: 1,6-bis-(3,6-dihexadecyl-*N*-carbazolyl)-2,4-hexadiyne), exhibited high solubility in common organic solvents and made possible the fabrication of optical waveguides by means of spin coating. The good processability of this material stimulated the study of its linear and non-linear optical properties [1,2]. A surprisingly large off-resonance intensity-dependent refractive index was observed by using surface plasmon spectroscopy (SPS) with quasi-monomolecular layers deposited on silver. At 1064 nm and with ps pulses, the intensity-dependent refractive index observed in 10–200 nm-thick polymer layers on silver corresponded to an effective $\chi^{(3)}$ of the order of $10^{-17}$ m$^2$/V$^2$ or more, which is one of the largest ever observed with organic materials [3]. This result, which was not in agreement with other non-linear tests [1,2], suggested a surface enhanced Raman scattering (SERS) investigation of analogous samples, at the same wavelength, in order to elucidate the origin of this anomalous non-linearity, which might be related either to chemical interactions at metal/polymer interface, or to a local-field-induced electromagnetic enhancement [4].

## 2. Experimental tests and discussion

The details of the experimental setup and of the data processing procedure adopted to evaluate the intensity-dependent refractive index of thin polyDCHD-HS films (10–200 nm) spun on silver-coated glass plates are reported elsewhere [3]. Such experiments, which were based on the SPS method, were performed by using *p*-polarized light from a Nd:YAG mode-locked laser ($\lambda = 1064$ nm, 27 ps FWHM pulses, 10 Hz repetition rate) at average intensity levels between 18 and 170 MW/cm$^2$. Within this intensity regime, the results obtained with different films could be fitted by assuming a third-order non-linearity with saturation [3]:

$$\Delta n_{\mathrm{R}} = \frac{n_{2\mathrm{R}} I}{1 + I/I_{\mathrm{S}}}; \qquad \Delta n_I = \frac{n_{2I} I}{1 + (I/I_{\mathrm{S}})^2} \qquad (1)$$

where $\Delta n_{\mathrm{R},I}$ represent the increase of the complex index of refraction, and the complex non-linear index of refraction $n_2 = (n_{2\mathrm{R}} + i n_{2I})$ and the saturating intensity $I_{\mathrm{S}}$ are the unknown parameters. To account for the observed bleaching effect of the imaginary part, represented by the existence of

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Table 1
Non-linear refractive indices for two samples of PDCHD-HS on silver
(from [3])

| PolyDCHD-HS thickness (nm) | Ag thickness (nm) | $n_{2R}$ (m²/W) | $n_{2I}$ (m²/W) | $I_S$ (W/m²) |
|---|---|---|---|---|
| 43 | 33 | $-1.3 \times 10^{-14}$ | $1.7 \times 10^{-14}$ | 60 |
| 157 | 41 | $-1.3 \times 10^{-15}$ | $1.1 \times 10^{-15}$ | 40 |

a maximum in the non-linear absorption, a higher order saturating behavior had to be assumed. Table 1 summarizes the results obtained in [3] with two polyDCHD-HS films. The experimental errors were of the order of 20–30%. In both cases, the magnitude of the non-linearity was very large for an off-resonant process. At first glance, these results could be explained by a heat transfer from the metal to the polymer layer. However, according to the SPS experiments reported in [5], and on the basis of our specific tests described in [3], we could reasonably exclude both a significant thermal contribution to the non-linear behavior of the polymer layer and a temperature-induced variation of the dielectric constant of the metal.

An AFM analysis of the same metal/polymer structures used for the SPS tests showed, in particular, that the silver layers exhibited a nanostructured surface having a roughness of the order of 5–10 nm rms and consisting of silver isles with an average diameter of 70 nm [4]. This surface morphology suggested a different explanation of the SPS results, related to anomalous field fluctuations. These giant fluctuations were predicted for semi-continuous films consisting of metal granules randomly distributed on an insulating substrate [6]. These fluctuations persist, although with lower values, also in the case of metal/dielectric fill-

ing factors close to one and for wavelengths far from the plasmon resonance of the metal. In these conditions, the molecules, which are in close vicinity to the metal surface, undergo huge magnification of the Raman scattering and of the non-linear properties. In particular, a close relationship between the gain coefficients obtained in the case of Kerr and SERS effects was found experimentally and theoretically justified via electromagnetic calculations [6]. On this basis, we performed SERS experiments with the aim of using the SERS efficiency as a demonstration of the existence of large field fluctuations at metal/polymer interface.

Raman measurements were performed at 1064 nm on thin polyDCHD-HS films spun on Ag-coated glass plates, and on a thick (1400 nm) polyDCHD-HS layer deposited on an uncoated glass plate, to be used as a reference for the bulk Raman response of the polymer. Fig. 1 shows the Raman spectra obtained with 108 and 84 nm-thick polymer films on Ag and with the 1400 nm-thick reference sample. The most intense bands occurred at about 1520 and 2120 cm⁻¹ and correspond to C=C and C≡C stretching modes, respectively, as observed in the reference Raman spectrum. Intensification of the Raman bands is evident for both films deposited on silver. We attributed the enhancement to a purely electromagnetic contribution related to the roughness of the Ag layer. Indeed, no evidence of chemisorption was observed either at 1064 nm, or with other exciting wavelengths [4].

Fig. 2a describes the model that we used to explain the SERS results and provides a sketch of the impinging EM field. In particular, we supposed that the SERS effect was present only in a 7 nm-thick polymer layer in close contact with the metal. With this hypothesis, which was sug-
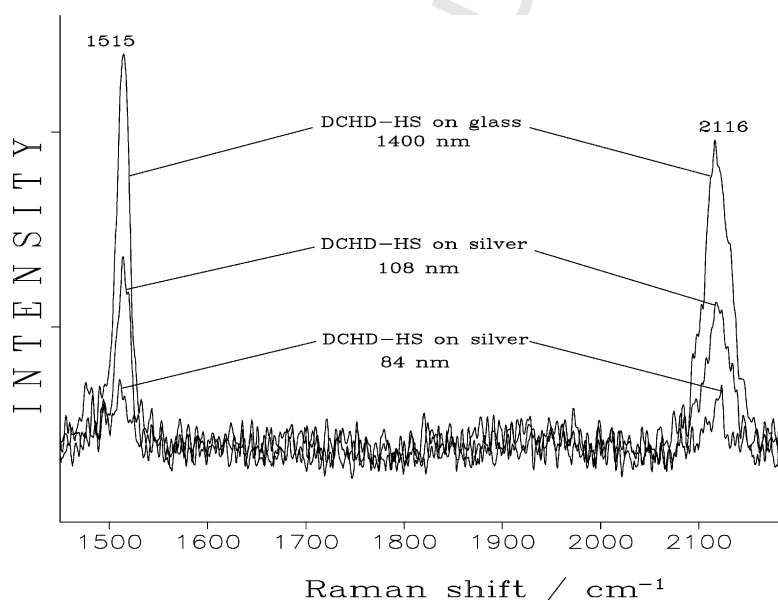


Fig. 1. Raman spectra of 108 and 84 nm-thick polymer layers on Ag and of a 1400 nm-thick polymer layer on a silver-free glass plate. Exciting line: 1064 nm.

**a) Configuration adopted for SERS tests**

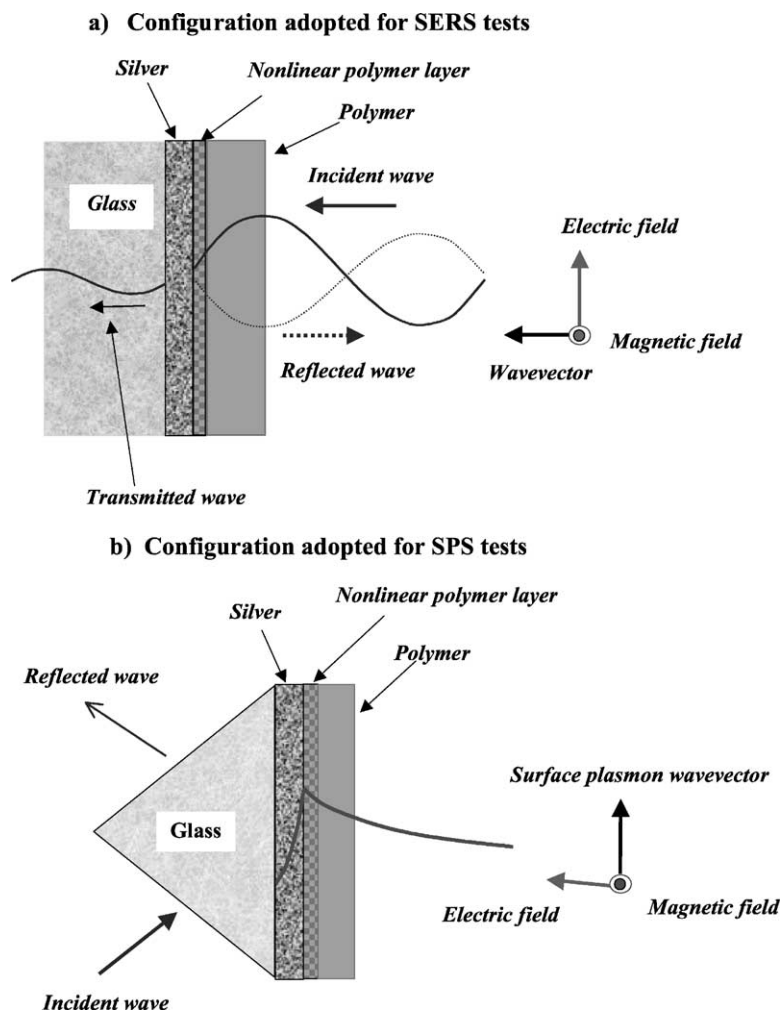**b) Configuration adopted for SPS tests**

Fig. 2. Modeling of (a) SERS and (b) SPS experiments. The shape of the EM fields impinging on the two samples is also sketched.

gested by the AFM investigation of the silver surfaces, we evaluated the enhancement factor $G_{SERS} = I_{SERS}/I_{RS} \approx 6 \times 10^2$. $I_{SERS}$ is the intensity of the Raman scattering from the 7 nm-thick dielectric layer in contact with Ag and $I_{RS}$ the Raman signal from a polymer film having the same thickness, but without silver.

We adopted the previous model also for SPS experiments, in order to get further indications that support our interpretation of the SPS results in terms of giant fluctuations of the local fields. As depicted in Fig. 2b, according to this model, the non-linear effect is significant only in the 7 nm-thick polymer layer, in close contact with the metal, while the contribution to the non-linearity of the remaining film can be neglected. A good agreement with the experimental SPS results was found by assuming an effective susceptibility $|\chi^{(3)}| = 3.5 \times 10^{-16}$ for the thin non-linear layer. Lastly, an evaluation of the enhancement factor $G_{\chi^{(3)}}$ for the non-linearity was obtained by comparing this value of $|\chi^{(3)}|$ with that measured by third harmonic generation (THG) with polyDCHD-HS films on glass ($|\chi^{(3)}| \approx 2.8 \times 10^{-19}$ [1]),

obtaining $G_{\chi^{(3)}} \approx 10^3$. A substantial agreement has to be noted between the values of $G_{\chi^{(3)}}$ and $G_{SERS}$.

## 3. Conclusions

The large intensity-dependent refractive index exhibited at 1064 nm by thin polyDCHD-HS films adhering to silver layers was related to an electromagnetic enhancement promoted by giant fluctuations of the local field, that, as predicted theoretically in [6], can be large, not only in the visible, but also far from the metal plasmon resonance, namely in the near IR. The previous statement was confirmed by SERS tests performed at the same wavelength. A rough modeling of our SPS tests which limited the non-linear contribution of the polymer to a 7 nm-thick layer in close contact with the Ag film could fit well the experiments, giving also a qualitative idea of the factor of enhancement $G$. The values of $G$ obtained for the SPS and the SERS tests resulted in substantial agreement and well in the range of the results published

155 in the case of semi-continuous metal/dielectric composites
156 [6].

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