Supplementary Material on:

"Optical spectroscopy of functionalized gold nanoparticles assemblies as a function of the surface coverage"

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I. Fresnel factors contribution to the SFG/DFG intensity

In order to calculate the contribution of the Fresnel factors to the SFG/DFG intensity I_{FG} of the Thiophenol/AuNps/Si(100) interface within the 3-layer effective-medium model (Figure 1 of the Main text), we have to consider the following general equation **[1]**:

$$I_{FG}(\omega_{IR}) = \frac{8\pi^3\omega_{FG}^2 \sec^2\theta_{FG}}{c^3 n_1(\omega_{FG}) n_1(\omega_{IR}) n_1(\omega_{vis})} \left|\chi_{eff}^{(2)}\right|^2 I_{IR} I_{vis} \qquad (1)$$

where I_{IR} and I_{Vis} are the intensities of the incident IR and visible laser beams, respectively; ω_{IR}, ω_{vis} and ω_{FG} the IR, visible and sum/difference frequencies of the three laser beams involved in the nonlinear process; θ_{IR}, θ_{vis} and θ_{FG} the angles of incidence of the incoming and outgoing beams; $n_1(\omega)$ the refractive index of the upper medium at frequency ω; $\chi_{eff}^{(2)}$ the effective nonlinear second order susceptibility of the probed interface, which includes Fresnel contributions and microscopic local-field corrections to the molecular nonlinear second order susceptibilities $\chi_{ijk}^{(2)}$. The $\chi_{eff}^{(2)}$ third rank complex tensor can be expressed in ppp polarisation combination as:

$$\begin{aligned}\chi_{eff,ppp}^{(2)} = & -F_x(\omega_{FG})F_x(\omega_{vis})F_z(\omega_{IR})\cos\theta_{FG}\cos\theta_{vis}\sin\theta_{IR}\chi_{xxz}^{(2)} \\ & -F_x(\omega_{FG})F_z(\omega_{vis})F_x(\omega_{IR})\cos\theta_{FG}\sin\theta_{vis}\cos\theta_{IR}\chi_{xzx}^{(2)} \\ & +F_z(\omega_{FG})F_x(\omega_{vis})F_x(\omega_{IR})\sin\theta_{FG}\cos\theta_{vis}\cos\theta_{IR}\chi_{zxx}^{(2)} \\ & +F_z(\omega_{FG})F_z(\omega_{vis})F_z(\omega_{IR})\sin\theta_{FG}\sin\theta_{vis}\sin\theta_{IR}\chi_{zzz}^{(2)}\end{aligned} \qquad (2)$$

The Fresnel factors F_i (i=x,y,z) describe the surface reflectivity and we calculate them in a three-layer model: Air/AuNps/Silicon, with respective refractive indices n_1, n* and n_2, as depicted in Figure 1 of the Main text. In principle, the silane monolayer and the thiophenol submonolayer do not affect significantly the sample reflectivity in the probed spectral range with respect to the Si substrate or AuNps layer, which contributions largely dominate in our samples. For an isotropic surface, the explicit complex contribution of the Fresnel factors can be calculated as **[1]**:

$$F_x(\omega) = \frac{2n_1(\omega)\cos\theta_2}{n_1(\omega)\cos\theta_2+n_2(\omega)\cos\theta_1}$$
$$F_y(\omega) = \frac{2n_1(\omega)\cos\theta_1}{n_1(\omega)\cos\theta_1+n_2(\omega)\cos\theta_2} \qquad (3)$$
$$F_z(\omega) = \frac{2n_2(\omega)\cos\theta_1}{n_1(\omega)\cos\theta_2+n_2(\omega)\cos\theta_1}\left(\frac{n_1(\omega)}{n^*(\omega)}\right)^2$$

θ_1 and θ_2 refer to the angles of incidence of the ω-frequency beam in media 1 and 2, knowing that $n_1(\omega)\sin\theta_1 = n_2(\omega)\sin\theta_2$. F_i should be calculated for each optical frequency contributing to the FG process, i.e. for $\omega=\omega_{IR}$, ω_{vis}, ω_{SFG} and ω_{DFG}. Index of air is taken as unity and, for the n_2 refractive index of silicon, we used a double exponential fit of the literature data **[2]**. The difficulty lies in the derivation of an expression for the refractive index of the AuNp layer (n*) in the desired spectral ranges. To address this point, we have to evaluate the dielectric constant $\varepsilon^*=(n^*)^2$ either by considering the Maxwell-Garnett (MG) or the Bruggeman (BM) model, the choice depending on the low or high AuNps surface coverage deduced by AFM.

In the MG formalism **[3]**, the composite layer is constituted by a host matrix (ε_h) with spherical inclusions (ε_1,ε_2,…) of volume fractions v_i (i=1,2,…). In this case, from the general expression

$$\frac{\varepsilon^*-\varepsilon_h}{\varepsilon^*+2\varepsilon_h} = v_1\frac{\varepsilon_1-\varepsilon_h}{\varepsilon_1+2\varepsilon_h} + v_2\frac{\varepsilon_2-\varepsilon_h}{\varepsilon_2+2\varepsilon_h} + \cdots \qquad (4)$$

and by considering a layer of AuNps embedded in a host matrix (air in our case, with ε_h=1)

$$\varepsilon^* = \varepsilon_h\frac{1+2rv_{Au}}{1-rv_{Au}}, r = \frac{\varepsilon_{Au}-\varepsilon_h}{\varepsilon_{Au}+2\varepsilon_h} \qquad (5)$$

$v_1=v_{Au}$ is the volume ratio of the space occupied by the AuNps with respect to the total volume of the layer. We consider an analytical expression of the gold dielectric constant ε_{Au} in the visible range **[4]** and its value at ~3055 cm^{-1} for the IR range **[2]**.

In the BM formalism **[3]**, the matrix host is considered as the composite layer ($\varepsilon_h=\varepsilon^*$) so that each of its component is regarded as an inclusion. Therefore, we have

$$0 = v_1\frac{\varepsilon_1-\varepsilon_h}{\varepsilon_1+2\varepsilon_h} + v_2\frac{\varepsilon_2-\varepsilon_h}{\varepsilon_2+2\varepsilon_h} + \cdots \qquad (6)$$

For a composite layer of AuNps (ε_1, v_1) and air (ε_2=1), it gives

$$v_1\frac{\varepsilon_1-\varepsilon^*}{\varepsilon_1+2\varepsilon^*} = v_2\frac{\varepsilon^*-1}{1+2\varepsilon^*}, \text{ with } v_1+v_2=1 \qquad (7)$$

In these conditions, we have a second order polynomial to solve ε*:

$$\varepsilon^* = \frac{-b \pm \sqrt{\Delta}}{4} \qquad (8)$$

Where $\Delta = b^2 + 8\varepsilon_1\varepsilon_2$ and $b = v_2\,[\varepsilon_1 - 2\varepsilon_2] + v_1\,[\varepsilon_2 - 2\varepsilon_1]$. The sign of the root is chosen as the same of the imaginary part of Δ. From these calculations, we can therefore deduce $\chi^{(2)}_{eff}$ developed above in equation (2) and written in short notation including the angular projections:

$$\chi^{(2)}_{eff,ppp} = -F_{xxz}\chi^{(2)}_{xxz} - F_{xzx}\chi^{(2)}_{xzx} + F_{zxx}\chi^{(2)}_{zxx} + F_{zzz}\chi^{(2)}_{zzz} \quad (9)$$

As in our case, we are interested by the molecular amplitude contribution a_{zzz}, we have to normalize our data by each Fresnel factor contribution. After calculation, it is shown that only F_{zzz} (Table 2 of the Main text) is significant because the other factors (F_{xxz}, F_{xzx}, F_{zxx}) are at least 3 orders of magnitude below whether MG or BM models and, as a consequence, they are neglected. Therefore, only the evolution of $\chi^{(2)}_{zzz}$ is considered in the Main text and we can simply deduce a_{zzz} (Table 2 of the Main text) from the following relation

$$a_{zzz} = \frac{a_0}{F_{zzz}} \qquad (10)$$

where a_0 (Table 1 of the Main text) is the thiophenol molecular amplitude deduced from the data fitting procedure as explained in the Main text.

II. On the origin of the thiophenol vibration mode at 3057 cm^{-1}

From the abundant literature on the subject, the origin of the vibration mode at 3057 cm^{-1} is generally cited as "the stretching vibration mode of the CH groups of the phenyl ring", which lacks of accuracy. One of the first publications on the origin of the vibrational assignment of Infared and Raman spectra of thiophenol (benzenethiol) relates to a paper of D. W. Scott **[5]**. The bands of interest are reported in Table S1. Without adsorption of the molecules, we name it "Free-thiophenol" (C_6H_5SH).

Table S1: Free-Thiophenol vibration modes in the 3000 cm^{-1} spectral range from reference [5]

Mode (C_{2v} geometry)	Geometry Class	Frequency (cm^{-1})	IR	Raman
13	A1 (fundamental)	3037	-	4
7b	B1 (fundamental)	3048	-	12
2	**A1 (fundamental)**	**3056**	**-**	**10**
20b	B1 (fundamental)	3086	Strong	-
20a	A1 (fundamental)	3150	-	2

The best match for the "free-thiophenol" vibration mode is the well-known mode 2, which is Infrared active in liquid phase and therefore difficulty observed in SERS on silver benzenethiolates **[6]**. Theoretically, none of these vibration modes is SFG/DFG active because they are not simultaneously Infrared and Raman active. Nevertheless, upon adsorption on metal surfaces as in our experiments, these exclusion rules are lifted and nonlinear vibrational spectroscopy apply as shown by our experimental measurements performed in the Main paper (Figure 4). Upon adsorption on metallic surface, it depends on the nature of the atoms at play (Gold, Silver, Copper, Platinum) and the subsequent frequency shift it implies. In other words, the exact position of these vibration modes will depend on the SH group substituent because the anchoring process is achieved through the covalent S-Metal chemical bond. In this way, we developed DFT calculations based including either the SH group or a gold atom instead of the H atom of the thiol for comparison (See reference **[7]** and its Electronic Supplementary Information for the complete description of the method developed within the Gaussian 09 package). The results are reported in Table S2 and S3 for the SH and S-Au bonds, respectively.

Table S2: Free-Thiophenol vibration modes in the 3000 cm^{-1} spectral range from DFT

Mode (C_{2v} geometry)	Frequency (cm^{-1})	Corrected Frequency (cm^{-1}) (by 0.96)	Corrected Frequency (cm^{-1}) (by 0.97)	IR	Raman
13	3161.755	3035.3	3066.9	4.09	10.17
7b	3166.1613	3039.5	3071.2	0.02	100.49
7a	**3176.4196**	**3049.4**	**3081.1**	**5.64**	**124.7**
20b	**3181.4918**	**3054.2**	**3086**	**24.01**	**18.30**
20a	**3193.4849**	**3065.7**	**3097.7**	**11.27**	**301.52**

It is clear that the "Free-thiophenol" DFT calculations do not fit well with the SFG/DFG experimental results whatever the correction set to the frequency. By considering the position and the IR and Raman activities, only the 7a, 20b and 20a modes could eventually match with the experimental results. If we

now take into account the gold atom to be more realistic, we consider the "Bounded-thiophenol" (C_6H_5SAu) and the DFT results are reported in Table S3.

Table S3: Bounded-Thiophenol vibration modes in the 3000 cm^{-1} spectral range from DFT

Mode (close to C_{2v} geometry)	Frequency (cm^{-1})	Corrected Frequency (cm^{-1}) (by 0.96)	Corrected Frequency (cm^{-1}) (by 0.97)	IR	Raman
"13"	3164.112	3037.5	3069.2	0.55	40.9
"7b"	3172.9144	3046	3077.7	8.62	131.3
"20a"	**3185.1379**	**3057.7**	**3098.6**	**14.04**	**153**
"20b"	3193.2022	3065.5	3097.4	10.20	5.5
"2"	**3196.8407**	**3069**	**3100.9**	**9.45**	**248.75**

From our SFG/DFG results combined with the FTIR measurements, the "20a" mode seems to have the best match in frequency (corr. 0.96) and with strong IR and Raman activities. Nevertheless, the "2" mode has the highest Raman activity. This is why it pleads in favour of a combination of the "2" and "20a" vibration modes as the dominant contributions to our spectroscopic measurements. In fact, advanced DFT calculations of the Infrared and Raman activities of thiophenol adsorbed on small gold clusters are coherent with our assumptions **[8]**.

References

[1] X. Zhuang, P. B. Miranda, D. Kim and Y. R. Shen, *Phys. Rev. B*, 1999, 59, 12632.

[2] E. D. Palik, in *Handbook of Optical Constants of Solids*, Academic, New York, 1985.

[3] D. E. Aspnes, J. B. Theeten and F. Hottier, *Phys. Rev. B*, 1979, 20, 3292.

[4] P. G. Etchegoin, E. C. Le Ru and M. Meyer, *J. Chem. Phys.*, 2006, 125, 164705.

[5] D. W. Scott, J. P. McCullough; W. N. Hubbard, J. F. Messerly, I. A. Hossenlopp, F. R. Row, G. Waddington, *J. Am. Chem. Soc.*, 1956, 78.

[6] T. H. Joo, M. S. Kim, K. Kim, *J. Raman Spectrosc.*, 1987, 18, 57.

[7] C. Humbert, O. Pluchery, E. Lacaze, A. Tadjeddine, B. Busson, *PCCP*, 2012, 14, 280.

[8] C. G. T. Feugmo, V. Liegeois, *ChemPhysChem*, 2013, 1633.