### Supplementary information for "Experimental demonstration of surface selection rules for SERS on flat metallic surfaces"

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#### S.I. SAMPLE PREPARATION AND MEASUREMENT

A gold film (45 nm thickness evaporated on glass with an intermediate 2 nm titanium adhesion layer) was immersed in a  $1\,\mu\text{M}$  Nile Blue (NB) solution in water for  $\sim 30 \,\mathrm{min}$  and then thoroughly washed with ultrapure water and dried. Films prepared with this method achieve a monolayer deposition on the surface (corroborated by independent electrochemical measurements) and present a good overall uniformity of the SERS signal at different positions. The Raman measurements have been carried out in a Jobin-Yvon LabRam spectrometer equipped with an Olympus BX41 microscope and a notch filter for 633 nm laser excitation. Polarisation elements ( $\lambda/2$ -waveplate and polarisers) are used to set the incoming and outgoing polarisation directions. The Au film sample is mounted in a motorised rotation stage (Thorlabs) that allows precise angular scans to be performed. Several points in the sample are measured at each angle, to ensure the results are not influenced by outliers.

#### S.II. ESTIMATION OF THE SERS EF

It is instructive to estimate, at least semiquantitatively, the SERS EF corresponding to our measurements on a flat gold metallic surface. We focus here on the specific example of the spectrum of Fig. 1(b) of the main text. To this end, we first assume that the non-SERS differential Raman cross-section  $(d\sigma/d\Omega)$ of the Raman peaks of NB at 633 nm is of the order of  $\sim 10^{-24}\,{\rm cm^2/sr};$  a typical value for dyes at resonance.<sup>1</sup> Secondly, the number of NB molecules in the spot can be estimated from the expected coverage<sup>2</sup>  $(5.5 \times 10^{-11} \text{ mol/cm}^2)$ . Thirdly, we calibrated the absolute response of our system using a  $\times 50$  (NA=0.5) objective by characterizing its scattering volume as in Ref. 3, and measuring the Raman signal of  $N_2$  (of known Raman differential cross-section<sup>4</sup>) in air. Putting these numbers together, we estimate a SERS enhancement factor of the order of only  $\approx 0.1$  for the spectrum of Fig. 1(b) of the main manuscript. Although a rough estimate, this figure is comparable to the value ( $\approx 0.06$ ) predicted from theory. The remarkable point here is that we can observe a monolayer of molecules on a surface where the Raman signal is actually being quenched, rather than enhanced.



FIG. S1: Angular dependence of the Local Field Intensity Enhancement Factors (LFIEF, see Eqs. S1,S2) for the perpendicular (dashed lines, full symbols) and parallel (solid lines, hollow symbols) components of the electric field, excited with a TE- (triangles) or TM- (squares) polarized plane wave.

### S.III. THEORETICAL PREDICTIONS

#### A. Layout of the problem

The Raman/SERS intensity or enhancement factor can be calculated from the standard theory of SERS<sup>4</sup> and from EM calculations for plane waves incident on a planar multilayer interface.<sup>5</sup> A brief account of the main principles is given in the following. For completeness, calculations were carried out on a layered structure that matches our gold film samples including all intermediate layers (for example, the titanium adhesion layer to the glass substrate). Plane waves with unit electric field amplitude are incident (with angle of incidence  $\theta$  from the normal) from air (n = 1) onto a multilayer composed of:

- a 45 nm thick Au film, whose dielectric function is obtained from a fit of experimental data to a Drude<sup>6,7</sup> model with two critical points<sup>4,8</sup>;
- a 2 nm titanium adhesion layer with dielectric function  $\epsilon = -3.918 + 12.596i$  at 633 nm and  $\epsilon = -4.031 + 13.48i$  at 658 nm (the Raman wavelength for the 590 cm<sup>-1</sup> mode of NB);
- a semi-infinite glass (n = 1.52) medium (the substrate).

Because of the relatively thick Au layer (compared to the skin depth), the results are in fact very similar to those obtained for a simple air/gold interface.



FIG. S2: Angular dependence of the SERS enhancement factors (F, see Eqs. S4,S5) for the 590 cm<sup>-1</sup> NB Raman mode for the four excitation-detection polarizations (TM-TM: squares, TM-TE: circles, TE-TM: up triangles, TE-TE: down triangles), and two different uniaxial Raman tensors: in-plane (hollow symbols, solid lines) and out-of-plane (full symbols, dashed line).

#### B. Preliminary calculations

Calculations of the local electric field in this multilayer structure are performed using the SPlaC codes<sup>9</sup> as detailed in appendix F of Ref. 4. The local electric field  $\mathbf{E}_{\text{Loc}}^{\text{TM}}(\lambda,\theta)$  and  $\mathbf{E}_{\text{Loc}}^{\text{TE}}(\lambda,\theta)$  is calculated at the air/gold interface (on the air side) as a function of wavelength  $\lambda$ and angle  $\theta$  for both TM and TE polarizations. Most of the properties of interest can then be derived from the local field intensity enhancement factors (LFIEFs) corresponding to the perpendicular and parallel components of the field, namely (with P=TM or TE, and  $\mathbf{e}_z$  a unit vector normal to the interface):

 $M_{\perp}^{P} = \left| \mathbf{E}_{\text{Loc}}^{P} \cdot \mathbf{e}_{z} \right|^{2}$ 

and

$$M_{\parallel}^{P} = \left| \mathbf{E}_{\text{Loc}}^{P} \cdot \mathbf{e}_{x} \right|^{2} + \left| \mathbf{E}_{\text{Loc}}^{P} \cdot \mathbf{e}_{y} \right|^{2}$$
(S2)

(S1)

Examples of the angular dependence of these quantities are given in Fig. S1. We note that  $M_{\perp}^{\text{TE}} = 0$  in this problem. We now briefly describe how these relate to the measured SERS intensities.

#### C. Prediction of SERS enhancement factors

For excitation at a given incident polarization  $P_L$ ( $P_L$ =TM or TE), incident angle  $\theta_L$ , incident wavelength  $\lambda_L$ , and for a given Raman polarizability tensor  $\hat{\alpha}$ , the induced Raman dipole is  $\mathbf{p} = \hat{\alpha} \cdot \mathbf{E}_{\text{Loc}}^{P_L}(\lambda_L, \theta_L)$ , and it is the emission of this dipole (modified by the presence of the metal) that we detect as a SERS signal at the Raman-shifted wavelength  $\lambda_R$ . This modified emission



FIG. S3: SERS EF, F, as in Fig. S2, but including the geometrical correction for the excitation shape, i.e.  $F/\cos(\theta_L)$ .

in a given direction  $\theta_R$  can be deduced without further calculations using the optical reciprocity theorem.<sup>4,10,11</sup> If we analyze the emitted light along a given polarization  $P_R$  ( $P_R$ =TM or TE), the SERS enhancement factor can then be expressed as (see Sec. 4.5 of Ref. 4):

$$F^{P_L-P_R} = \left| \mathbf{E}_{\text{Loc}}^{P_R}(\lambda_R, \theta_R) \cdot \hat{\alpha}_N \cdot \mathbf{E}_{\text{Loc}}^{P_L}(\lambda_L, \theta_L) \right|^2.$$
(S3)

where  $\hat{\alpha}_N$  is the normalized Raman polarizability tensor.<sup>3,4,12</sup> Four such SERS EFs can be calculated (and measured) depending on the excitation-detection polarizations, i.e.:  $P_L$  and  $P_R$  being either TM or TE.

For a general  $\hat{\alpha}_N$  this expression can be fairly complicated, so it is interesting to consider a few specific cases:

• For a uniaxial tensor with axis perpendicular to the plane, all tensor components are zero except<sup>12</sup>  $\alpha_{Nzz} = \sqrt{15/4}$ . In this case, we have:

$$F^{P_L-P_R} = \frac{15}{4} M_{\perp}^{P_L}(\lambda_L, \theta_L) M_{\perp}^{P_R}(\lambda_R, \theta_R).$$
(S4)

As a result, we see that  $F^{\text{TE}-\text{TM}} = F^{\text{TM}-\text{TE}} = F^{\text{TE}-\text{TE}} = 0$  in this particular case.

• For a uniaxial tensor with axis parallel to the metallic plane, this axis may take any random orientation inside this plane ( $\alpha_{Nxx} = \sqrt{15/4}$  only is an example, but  $\alpha_{Nyy} = \sqrt{15/4}$  only is another one). Assuming a random in-plane orientation of this axis, we obtain after averaging:

$$F^{P_L-P_R} = \frac{15}{4} \kappa^{P_L-P_R} M_{\parallel}^{P_L}(\lambda_L, \theta_L) M_{\parallel}^{P_R}(\lambda_R, \theta_R), \quad (S5)$$

where  $\kappa^{P_L-P_R}$  results from the averaging process and is 1/5 for TM-TM and TE-TE, but 1/15 for TM-TE and TE-TM.

For our problem of interest here, we may assume in a first approximation that  $\theta_R = \theta_L$  (i.e. backscattering configuration) and take  $\lambda_L = 633 \,\mathrm{nm}$  and  $\lambda_R = 658 \,\mathrm{nm}$  (corresponding to the 590 cm<sup>-1</sup> of NB). The resulting predicted SERS EF for the four polarization configurations, and in the two extreme cases of out-of-plane and in-plane uniaxial tensors, are shown in Fig. S2. It is clear from these predictions that even a small  $\alpha_{zz}$  component in the Raman tensor will strongly dominate the TM-TM signal, but should not contribute to the other three configurations.

# D. Prediction of SERS intensities in the angle-dependent experiments

In order to predict the angular dependence of the SERS signal as measured in the experiments, we are now only lacking two ingredients:

- Firstly, the calculations of the SERS EFs do not take into account the geometrical shape of our incident beam. Thanks to the back-focal plane lens, the beam is to a very good approximation collimated, i.e. it contains only one incident angle  $\theta_L$ . However, the size of the illuminated area on the sample changes with incident angle, and this affects the number of molecules in the beam. It should be noted that the power density felt by these molecules is the same, but there are just more of them contributing to the signal. This introduces an additional geometrical factor  $1/\cos(\theta_L)$  in the measured SERS signal. Predictions including this correction are shown in Fig. S3.
- Secondly, since we use a microscope objective (×20, NA=0.35) to collect the emitted light, we are in reality collecting Raman light over a range of  $\theta_R$  close to  $\theta_L$ . This effect is secondary but can be accounted for by averaging the SERS EF over all possible  $\theta_R$  that fall within the numerical aperture of the objective. This additional correction, although small, was applied to obtain the theoretical results shown in Fig. 2 of the main text, and for the fits of Fig. 3.

# S.IV. EXPERIMENTAL DATA FOR THE 1645 $\rm CM^{-1}$ PEAK OF NILE BLUE

Fig. S4 is the equivalent of Fig. 3 of the main text, but for the  $1645 \text{ cm}^{-1}$  peak of Nile Blue. The results are similar, although the data are subject to more uncertainties because the signal to noise ratio in this region of the spectrum is worse.

#### S.V. INFRARED ABSORPTION AND DFT STUDY OF THE ORIENTATION OF NB ON AU

PM-IRRAS spectra were recorded with a Nicolet 860 FTIR (Thermo- Electron) spectrometer with a resolution



FIG. S4: Same as Fig. 3 of the main paper but for the  $1645\,{\rm cm^{-1}}$  peak of Nile Blue.



FIG. S5: (a) Experimental IR absorption of NB in KBr powder and PM-IRRAS of NB adsorbed on gold. (b) DFT predictions of the IR absorption of NB in the standard case (blue), for PM-IRRAS of NB adsorbed perfectly flat on a surface (green), and same with a small contribution of in-plane components (red). The out-of-plane CH bending modes are clearly visible in PM-IRRAS, indicating a majority of flat molecules.

of  $8 \,\mathrm{cm}^{-1}$  by adding 2000 scans with an optical mirror velocity of 0.474 cm-1/s. The spectrometer was equipped with a commercially available module (Thermo Electron) including a ZnSe photoelastic modulator (PEM) and measurements were performed at an incident angle of 80° under a (partially) dry atmosphere. After reflection on the sample, the incident beam is focused with a ZnSe lens on a MCT-A detector cooled at 77 K. The PEM oscillates at a frequency of 50 kHz and changes the polarization of the incident beam from parallel to perpendicular to the plane of incidence at a frequency of 100 kHz. The polarization-modulated signal is separated from the low frequency signal (between 380 and 3800 Hz) with a 48 kHz high-pass filter (GWC) and then demodulated. The two interferograms are high pass- and low pass-filtered by the spectrometer and simultaneously sampled by the dualchannel electronics. With the PM-IRRAS technique, the output signal is not directly proportional to the IR absorbance, but the quantity  $(R_p - R_s)/(R_p + R_s)$  multiplied by a Bessel function that results from the Fourier transform of the doubly modulated input signal  $(R_p \text{ and } R_s)$ are the reflection coefficients for the p (TM) and s (TE) polarization, respectively). This background Bessel function varies slowly vs the wavenumber within a  $20 \,\mathrm{cm}^{-1}$ range (i.e. the width of an absorption peak). Then, the baseline was subtracted from a spline function of the spectrum excluding the vibrational absorptions. The resulting PM-IRRAS spectrum contains primarily the contribution of out-of-plane components of the IR dipoles.

The experimental PM-IRRAS spectrum of Nile Blue

adsorbed on gold is shown in Fig. S5(a) (red curve) and compared to the bulk IR absorption of NB in KBr (blue curve). The marked difference in the prominent peaks indicate a preferred adsorption geometry. The new peaks appearing in the  $800 \text{ cm}^{-1}$  are in particular attributed to out-of-plane CH bending modes. We conclude that the NB molecules are adsorbed predominantly flat on the gold surface.

This interpretation is further backed up by Density Functional Theory (DFT) calculations of the NB molecule. DFT calculations were performed using the Gaussian DFT package<sup>13</sup> with Becke's 3-parameter hybrid functional<sup>14</sup> and Lee-Yang-Parr<sup>15</sup> non-local electron correlation (commonly abbreviated as B3LYP) with basis set 6-31G(d). A vibrational frequency analysis, which includes IR intensity (I) calculations, was carried out. IR dipoles,  $\mathbf{p}$ , were then derived from the normal mode displacements and the dipole derivatives. A scaling factor of 0.97 was used for the vibrational frequencies. The IR spectrum (blue curve in Fig .S5(b)) was obtained by plotting each mode as a Lorentzian with full width at half maximum of  $20 \,\mathrm{cm}^{-1}$  and integrated intensity *I*. The PM-IRRAS spectrum of NB adsorbed perfectly flat on a surface (green cruve) was obtained by changing the IR intensities to  $I \times |p_z|^2/|\mathbf{p}|^2$ . For the second PM-IRRAS spectrum (red curve), the IR intensities were changed to:  $I \times [0.97|p_z|^2/|\mathbf{p}|^2 + 0.03(|p_x|^2 + |p_y|^2)/|\mathbf{p}|^2]$ , to qualitatively represent a predominantly flat adsorption geometry with small imperfections.

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