

Supporting Information

PhotoChemistry at the Surface of Gold Nanoprisms from Surface Enhanced Raman Scattering Blinking

Amine Mezni ^{1,2}, Thameur Dammak ³, Anis Fkiri ¹, Adnen Mlayah ^{2,*}, Younes Abid ³
and Leila Samia Smiri ¹

¹ Unité de recherche Synthèse et Structure de Nanomatériaux UR11ES30, Faculté des Sciences de
Bizerte, Université de Carthage, 7021 Jarzouna, Tunisia

² Centre d'Elaboration de Matériaux et d'Etudes Structurales, CNRS-Université de Toulouse, 29
Rue Jeanne Marvig, 31055 Toulouse, France

³ Laboratoire de Physique Appliquée, Faculté des Sciences, Université de Sfax, BP 802, 3018 Sfax,
Tunisia

Assignment of the Raman Features

Figure S1 shows the Raman spectrum measured on a PVP powder and the spectrum calculated for an isolated PVP molecule using DFT. The measured and calculated Raman intensities and frequencies differ. For instance, the frequencies calculated for the C-H stretching vibration modes are around 3200 cm^{-1} while the corresponding vibrational band in the experimental spectrum is located at 3000 cm^{-1} . The shift between measured and calculated vibrational frequencies is well known and is attributed to the molecular environment (i.e., to inter-molecular interactions).¹ In order to account for the measured vibrational frequencies, a rescaling factor is usually applied to the calculated vibrational spectrum.² In our case, a rescaling factor of 0.925 gives a good agreement between the experimental and the DFT vibrational frequencies (Figure S1). In particular, after rescaling, the stretching vibrations of the C=O bond is identified at 1660 cm^{-1} . It is found around 1700 cm^{-1} in the free PVP molecules surrounding the gold nanoparticles certainly because of the less dense molecular environment in comparison with the compact PVP powder.

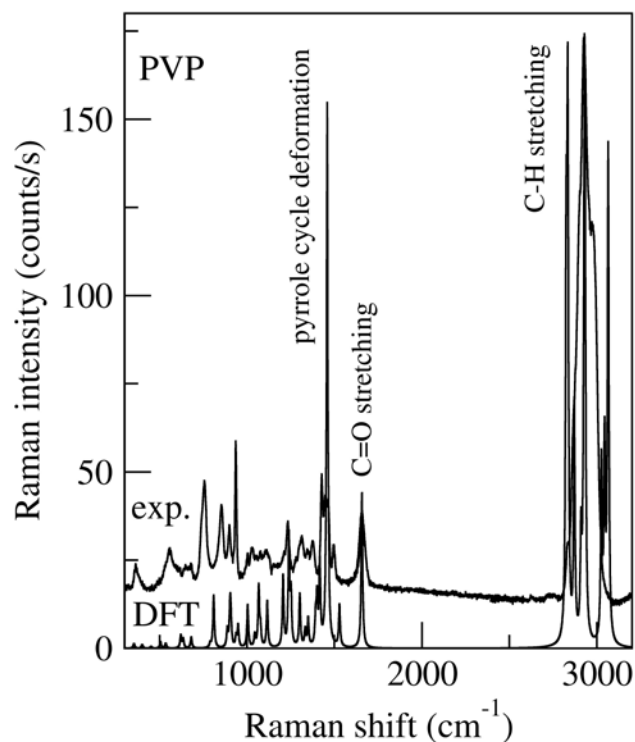


Figure S1 Raman spectra measured on a PVP powder and calculated by the DFT method. The calculated spectrum has been rescaled by a factor 0.925.

Assignment of the Raman-SERS Features of PVP-Au and TREG-Au observed in the 900-1800 cm^{-1} region

Tableau S1. Assignment of the main Raman SERS features based on DFT calculations.

Measured Raman Frequency (cm^{-1})	Assignments
900	CC breathing (TREG)
1023	CC, CH_2 rocking (TREG, PVP)
1080-1150	C-O stretching (TREG)
1296	CH_2 wagging , CN stretching (PVP)
1342	Totally symmetric pyrrole cycle breathing (PVP)
1380	CH bending (TREG)
1450	Deformation of the pyrrole cycle (C-N-C) (PVP)
1494	CN stretching (PVP)
1685-1730	CO stretching (PVP)

Density Functional Theory Calculations

The calculations based on the Density Functional Theory were performed using the Gaussian 03 software package.³ The molecular geometries of the PVP (monomer) and TREG molecules were optimized using the Becke's three-parameter Lee-Yang-Parr exchange-correlation functional (B3LYP) without any symmetry restrictions.^{4,5} For the PVP-Au and TREG-Au systems we have used the combined B3LYP/LANL2DZ basis set.⁶ This method is suitable for systems involving heavy atoms and transition metal atoms. Vibrational frequency calculations were performed for the optimized geometries corresponding to total energy minimum (i.e., no imaginary frequencies). The Raman activity S , generated by Gaussian 03, is converted to a Raman intensity using

$$I(\nu_i) = (\nu_{exc} - \nu_i)^4 S n(\nu_i, T)$$

where ν_{exc} is the laser excitation energy expressed in cm^{-1} , ν_i is the vibrational wavenumber of the i th normal mode and $n(\nu_i, T)$ is the Bose-Einstein population factor. The Raman spectra were plotted using pure Lorentzian lines with a full width at half maximum of 10 cm^{-1} . The visualization of the atoms displacements, for a given vibrational mode, was made using molden software.

The optical properties of a PVP molecule bound to a gold atom have been investigated using Time-Dependent Density Functional Theory (TDDFT). Convergence of the optical absorption spectrum is obtained with 20 lowest energy unoccupied molecular orbitals that contribute to the optical transitions. The optical absorption spectrum was generated using a lorentzian lineshape with 40 nm FWHM for all for transitions.

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Raman movies

File 638nm_nano-object1.mp4 corresponds to Figure 5a,c.

File 638nm_nano-object2.mp4 corresponds to Figure 5b,d.

File 785nm_nano-bjoect3.mp4 corresponds to Figure 10.

File 638nm_nano-object1_withbackground.mp4 is from nano-object1 (Figure 5a,c) but with background included (i.e., without intensity normalization).